The Role of PM_{2.5} Chemical Composition and Meteorology during High Pollution Periods at a Suburban Background Station in Southern Poland

Barbara Błaszczak*, Natalia Ziola, Barbara Mathews, Krzysztof Klejnowski, Krzysztof Słaby

Institute of Environmental Engineering of the Polish Academy of Sciences, 41-819 Zabrze, Poland

ABSTRACT

This study conducted measurements of PM_{2.5} (particulate matter with a diameter $\leq 2.5 \mu\text{m}$) in Racibórz, Poland, during 2018. Samples were collected daily and analyzed for their chemical composition, specifically, the carbonaceous (elemental and organic carbon) and water-soluble ionic (Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) components. Additionally, the secondary inorganic aerosol (SIA) as well as the secondary and primary organic carbon (SOC and POC, respectively) content was estimated. To identify the causes of elevated PM_{2.5} concentrations, the contributions of these chemical species were further investigated, and the role of meteorological factors was also examined. During the measurement period, PM_{2.5} concentrations exceeding $50 \mu\text{g m}^{-3}$ were recorded on 38 days, and 7 pollution episodes were detected. Such events, however, were observed only in the heating season, when stable meteorological conditions (low air temperatures, weak winds, high relative humidity and lack of precipitation) and increased emissions of PM and its precursors from anthropogenic sources favored the accumulation of pollutants. The PM_{2.5} was dominated by carbonaceous aerosol, especially POC, although the SOC rose significantly during high pollution periods. Furthermore, the fraction of SIA clearly decreased as the concentration of PM_{2.5} increased, and its variability was greatly affected by regional and/or long-range transport events. Our results can help guide the development of effective strategies for reducing air pollution from fine particulate matter. Such control measures are particularly important in Poland, where PM_{2.5} concentrations remain high compared to many European countries.

Keywords: PM_{2.5}; High pollution days; Carbonaceous aerosol; Primary and secondary organic carbon; Secondary inorganic aerosol; Meteorology.

INTRODUCTION

Air pollution is one of the most serious environmental problems of all developed and developing countries (WHO, 2013). Of the various pollutants, particulate matter (PM) affects the environment in the most comprehensive way, due to the diversity of emission sources and formation mechanisms, and the resulting variation in chemical composition and particle size (Hassan and Khoder, 2017). In recent years, particular attention has been paid to PM_{2.5} and PM₁ (particles with an aerodynamic diameter $\leq 2.5 \mu\text{m}$ and $\leq 1.0 \mu\text{m}$, respectively), mainly due to the health effects that they can cause (e.g., Kim *et al.*, 2015). What is more, fine particles are able to persist in the atmosphere for a long time, affect the climate (e.g., Fiore *et al.*, 2015), ecosystems (e.g., Rai, 2016), materials (e.g., Rao *et al.*, 2014) and visibility (e.g., Lin *et al.*, 2014).

The basic components of PM_{2.5} include carbonaceous matter and water-soluble ions. The total carbon (TC) in the aerosol can be divided into elemental carbon (EC), organic carbon (OC) and inorganic (carbonated) carbon (IC/CC), although the latter comes mainly from geological sources and occurs almost exclusively in coarse particles (Mancilla *et al.*, 2015). EC is a primary pollutant emitted during the incomplete combustion of fossil fuels and pyrolysis of biological material during combustion (Jones and Harrison, 2005). In contrast, OC can be emitted directly from emission sources (primary organic carbon [POC]) and/or formed in the atmosphere as a result of gas-particle transformation (secondary organic carbon [SOC]) (Khan *et al.*, 2016). Typically, secondary organic aerosol (SOA) accounts for 20–80% of organic matter in PM_{2.5} and has a large biogenic contribution. However, near urban areas, up to 90% of SOA could be anthropogenic in origin (Mancilla *et al.*, 2015).

In addition to carbonaceous matter, inorganic ions have a dominant share in the total mass of suspended particles and exert a significant impact on the environment. These compounds are an important part of the secondary inorganic aerosol (SIA), especially sulfates (SO_4^{2-}), nitrates (NO_3^-) and ammonium ions (NH_4^+) (Błaszczak *et al.*, 2019). It is

* Corresponding author.

Tel.: +48 322716481; Fax: +48 322717470

E-mail address: barbara.blaszczak@ipis.zabrze.pl

considered that SIA is almost exclusively of anthropogenic origin because its gaseous precursors—mainly sulfur dioxide (SO_2), nitrogen oxides (NO_x) and ammonia (NH_3)—are largely emitted from sources related to human activities. In addition, sources such as coal-fired power plants and residential coal combustion can emit significant amounts of primary sulfates and nitrates into the atmosphere (Dai *et al.*, 2018). The mechanisms of SIA formation include many chemical reactions that largely depend on the characteristics of pre-existing aerosol and gaseous precursors, as well as meteorological conditions (Weijers *et al.*, 2010). Nevertheless, this component largely affects the concentration of fine PM, both in areas far away from significant emission sources and in urban areas (e.g., Błaszczak *et al.*, 2016; Reizer and Juda-Rezler, 2016).

Although the last two decades have brought the improvement of ambient air quality, the problem of exceeding the standards for $\text{PM}_{2.5}$ still remains unresolved in many areas within Europe (Błaszczak *et al.*, 2019). Periods of elevated concentrations of PM and other atmospheric pollutants, also often called “haze episodes,” are of particular concern, because of its adverse effect on public health, visibility and even global climate (Hassan and Khoder, 2017; Wang *et al.*, 2019). Extreme events of ambient $\text{PM}_{2.5}$, in which daily mass concentrations are substantially higher than annual averages, have been reported worldwide (e.g., Juda-Rezler *et al.*, 2011; Heo *et al.*, 2013; Ma *et al.*, 2017). Both observational data and model simulations indicated that local meteorological features along with local source emissions may be the most direct factors resulting in formation and duration time of $\text{PM}_{2.5}$ episodes (Ma *et al.*,

2017). Moreover, there is strong evidence that the regional and long-range transport of air pollutants can contribute significantly during heavy PM pollution (Juda-Rezler *et al.*, 2011; Heo *et al.*, 2013).

Bearing in mind the above considerations, an annual measurement campaign of $\text{PM}_{2.5}$ was carried out at a suburban background site in Racibórz (southern Poland). The main objectives of the present study are to: (1) assess the role of primary and secondary PM components in the occurrence of elevated concentrations of $\text{PM}_{2.5}$ and (2) explore the impacts of meteorological conditions on $\text{PM}_{2.5}$ concentration and chemical composition during high pollution periods.

METHODS

Study Area and Sampling Equipment

The study was conducted at a suburban background site in Racibórz (Fig. 1)—located on the outskirts of the town—at the meteorological station belonging to the Institute of Meteorology and Water Management–National Research Institute (IMWM–NRI). The nearest surroundings of the station (~100 m) are arable fields. National Freeway No. 45 and the nearest dispersed residential buildings are located ~100–250 m east of the station. At a distance of ~2.5 km northeast of the sampling site, the city center is located. The nearest large cities are Opava (~24 km SW) and Ostrava (~25 km S) in the Czech Republic, as well as Rybník (~25 km E), Jastrzębie-Zdrój (~28 km SE) and cities of the Upper Silesian Industrial District (~42 km NE) in Poland. More details about the specificity of measurement station in

Fig. 1. Location of the measurement station in Racibórz.

Racibórz and the region in which it is located (Silesia Province, southern Poland) can be found in Błaszczak *et al.* (2016).

The PM_{2.5} samples were collected using a reference low volume sampler (PNS-15; AtmoService), providing the 2.3 m³ h⁻¹ air flow, which meet the requirements of the PN-EN 12341:2014-07 standard. Samples were accumulated on quartz microfiber filters (diameter: 47 mm, grade: QM-A; Whatman) over 24 hours starting at midnight. Research was performed during the annual measurement period (2018). The results obtained were also averaged in the heating (January–March and October–December) and non-heating (April–September) periods, to capture specific seasonal fluctuations.

Meteorological data were provided by the IMWM-NRI and are summarized in Table 1. According to division of Poland into climate regions (Romer, 1949), Racibórz lies in the climate zone “Moravian Gate,” one of the warmest zones in the country. The local climate is primarily influenced by the terrain and the land use. The relatively strong industrialization and compact development of the city center contribute to the occurrence of specific climatic features such as the “urban heat island” or an increased number of days with low precipitation. The distribution of wind directions in Racibórz is determined by general-circulation conditions with clearly visible topographical modifications. Winds blowing from the NNW, N and NW sectors dominate during the heating period, while SSW and SW sectors prevail during the non-heating one (Table 1).

Analytical Procedures

A total of 330 PM_{2.5} samples collected over 2018—163 and 167 samples in the heating and non-heating season, respectively—were subjected to gravimetric analysis in the laboratory of the Institute of Environmental Engineering, Polish Academy of Sciences (IEE PAS), in Zabrze (Poland). PM_{2.5} concentrations were determined according to the PN-EN 12341:2014-07 standard, using Mettler Toledo AT20 microbalance (resolution: 2 µg). Conditioning, weighing and storage of both non-exposed and exposed filters were conducted in the weighing room at fixed conditions of temperature (20 ± 1 °C) and relative humidity (RH; 50 ± 5%).

Every second sample (153 samples) was passed for chemical composition analyses. A 1.5 cm² fragment was cut from these samples and analyzed for OC and EC content, by means of thermal-optical carbon analyzer with a flame ionization detector (FID) (Model 4L Main Oven Assembly; Sunset Laboratory Inc., USA) using the EUSAAR_2 protocol. The measurement performance was controlled by regular analysis of blank filters and systematic calibration of the apparatus. In addition, certified reference materials (CRMs; RM 8785 and RM 8786; National Institute of Standards and Technology [NIST]) were periodically analyzed—recovery of 90–102% and 98–124% was obtained, respectively, for OC and EC. The total uncertainties in EC and OC measurements are of the order of 5%. The limit of detection (LOD) was 0.17 µg cm⁻² and 0.80 µg cm⁻² respectively for EC and OC.

The content of SOC and POC was calculated according to the methodology proposed in Castro *et al.* (1999)—

Eqs. (1)–(2):

$$\text{POC} = \text{EC} \cdot (\text{OC}/\text{EC})_{\text{pri}} \quad (1)$$

$$\text{SOC} = \text{OC} - \text{POC} \quad (2)$$

where OC and EC represent analytically determined daily concentrations of organic and elemental carbon, respectively, while (OC/EC)_{pri} is the ratio of primary organic carbon to elemental carbon. To determine the value (OC/EC)_{pri}, a graphical approach was used, including the correlation between OC and EC concentrations. Linear regression was performed for 10% of the samples with the lowest OC/EC ratio, because the value of the determination coefficient for this range of data will represent the impact of POC emission sources (Pavuluri *et al.*, 2011).

The remaining filter surface was subject to analysis of water-soluble ions (SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺) using the Dionex ICS-1100 ion chromatographs (Thermo Scientific, USA). The quality of analytical data was assured by using the CRM Fluka products Nos. 89316 and 89886. The method detection limits, expressed in mg L⁻¹, were as follows: 0.073 (NO₃⁻), 0.12 (SO₄²⁻), 0.111 (Cl⁻), 0.027 (NH₄⁺), 0.091 (Na⁺), 0.095 (K⁺), 0.221 (Ca²⁺) and 0.17 (Mg²⁺). The total uncertainties of the measurement ranged from 4.3% (Na⁺) to 11.2% (SO₄²⁻).

The assessment of the SIA contribution in PM_{2.5} mass was made on the basis of analytically determined concentrations of sulfate [SO₄²⁻], nitrate [NO₃⁻] and ammonium ions [NH₄⁺], wherein the share of sulfates was corrected for the share of sulfates associated with sea salt (Sillanpää *et al.*, 2006)—Eqs. (3)–(4):

$$[\text{SIA}] = [\text{nss-SO}_4^{2-}] + [\text{NO}_3^-] + [\text{NH}_4^+] \quad (3)$$

$$[\text{nss-SO}_4^{2-}] = [\text{SO}_4^{2-}] - (0.246 \times [\text{Na}^+]) \quad (4)$$

More details about analytical methodologies used can be found in the earlier publications of the authors (e.g., Rogula-Kozłowska *et al.*, 2014). Before statistical analyses, the measurement results were subjected to preliminary verification by comparing the sum of the concentrations of the analyzed components with the gravimetrically determined concentration of PM_{2.5}. If the total concentration of TC and ions exceeded the PM_{2.5} concentration on a given measurement day, such a sample was not included in the calculations.

RESULTS AND DISCUSSION

Variability of PM_{2.5} Concentrations

During the 2018 year, PM_{2.5} concentrations varied from 5.11 to 129.85 µg m⁻³ with an annual mean of 26.90 µg m⁻³, which was slightly higher than the EU limit value (25 µg m⁻³; Directive 2008/50/EC). The provisions of European law do not set limit values for average daily concentrations of PM_{2.5}. Such standards are provided by the World Health Organization (WHO, 2013) and the United States Environmental Protection Agency (U.S. EPA, 2016)—they are 25 and 35 µg m⁻³, respectively. Considering the annual measurement period,

Table 1. Characteristics of meteorological conditions for the annual measurement period (2018) and divided into the heating and non-heating season.

Parameter	WHOLE PERIOD			HEATING			NON-HEATING		
	Ave ± SD	Min	Max	Ave ± SD	Min	Max	Ave ± SD	Min	Max
T (°C)	10.7 ± 8.8	−11.2 (27 Feb)	26.4 (09 Aug)	3.4 ± 5.9	−11.2 (27 Feb)	17.4 (30 Oct)	17.9 ± 4.1	4.8 (01 Apr)	26.4 (09 Aug)
Pr* (mm)	440.7*	0 (217 days [59.5%])	30.5 (08 Aug)	170.7*	0 (109 days [59.9%])	12.8 (10 Jan)	270.0*	0 (108 days [59.0%])	30.5 (08 Aug)
Ins (h)	2,185.6*	0 (65 days [17.8%])	15.5 (04 Jul)	543.7*	0 (60 days [33.0%])	11 (22 Mar)	1,641.9*	0 (5 days [2.7%])	15.5 (04 Jul)
Vis (m)	17,245.7 ± 9,903.3	1,414.2 (27 Jan)	44,535.7 (09 Dec)	11,655.6 ± 8,791.5	1,414.2 (27 Jan)	44,535.7 (09 Dec)	22,805.3 ± 7,547.1	6,534.9 (14 Sep)	42,824.3 (30 Jun)
WS (m s ^{−1})	3.2 ± 1.4	1 (27 Jan; 15 Sep)	8.9 (24 Sep)	3.4 ± 1.5	1 (27 Jan)	8.6 (24 Oct)	3.0 ± 1.2	1 (16 Sep)	8.9 (24 Sep)
RP (%)	75.1 ± 11.6	49.2 (07 Jun)	98.3 (04 Nov)	81.8 ± 9.1	53.1 (30 Oct)	98.3 (04 Nov)	68.4 ± 9.8	49.2 (07 Jun)	96.1 (14 Sep)
Ps (hPa)	1,017.2 ± 7.3	996.1 (12 Mar)	1,037.1 (17 Nov)	1,017.9 ± 8.9	996.1 (12 Mar)	1,037.1 (17 Nov)	1,016.4 ± 5.2	999.7 (01 Apr)	1,036.3 (26 Sep)
WD									

Designations: Ave ± SD: average ± standard deviation; Min: minimum; Max: maximum; T: temperature; Pr: precipitation; Ins: insolation; Vis: visibility; WS: wind speed; RH: relative humidity; Ps: atmospheric pressure; WD: wind direction.

* Presented as annual sum.

80 exceedances of the U.S. EPA standard were found, which constituted ~24% of the measurement time. The more stringent WHO guideline was exceeded in 113 cases (34% of measuring time).

The histogram of a series of daily $\text{PM}_{2.5}$ concentrations (Fig. 2) revealed a log-normal distribution, which is typical for the concentrations of most atmospheric pollutants (Maciejewska et al., 2015). The most common concentrations were in the range of $15\text{--}20\ \mu\text{g m}^{-3}$ (22.4% of cases) and $10\text{--}15\ \mu\text{g m}^{-3}$ (19.4% of cases); however, they were recorded mainly in the non-heating season (average: $14.74\ \mu\text{g m}^{-3}$). Much worse living conditions for the inhabitants of the analyzed area—in relation to exposure to $\text{PM}_{2.5}$ —occurred in the heating season (average: $39.37\ \mu\text{g m}^{-3}$), similar to many other regions in Europe (Błaszczak et al., 2019). During this period of the year, $\text{PM}_{2.5}$ concentrations were higher than $25\ \mu\text{g m}^{-3}$ for 66% of the measurement time (108 days).

The reason for the observed seasonal differences may be due to several factors. In Poland, the production of electricity and heat is mainly based on the combustion of hard coal and lignite. However, the waste gases emitted from large point sources affect $\text{PM}_{2.5}$ concentrations throughout the whole year. The main factors shaping the levels of $\text{PM}_{2.5}$ concentrations—both in large cities and in rural areas—are municipal sources, which activity increases considerably in the cold season (Rogula-Kozłowska et al., 2014). The impact of meteorological conditions is also significant.

PM_{2.5} vs. Meteorological Parameters: Identification of Pollution Episodes

Numerous scientific studies have proven that meteorological conditions play an important role in the results obtained at every monitoring site (Galindo et al., 2011; Reizer and Juda-Rezler, 2016; Wang et al., 2019). Their impact is particularly evident in the cold season, when low air temperatures, weak winds and the presence of a low inversion layer limit the

dispersion of pollutants, while promoting their local accumulation. Previous experience to identify episodes of high concentrations of pollutants has shown that such situations are associated with a set of meteorological factors, of which the most important are: high atmospheric pressure system, average daily air temperature $< 5^\circ\text{C}$, average daily wind speed $< 3\ \text{m s}^{-1}$, wind direction, average daily relative humidity $> 85\%$ and no atmospheric precipitation (Rogula-Kozłowska et al., 2014).

The variations of daily $\text{PM}_{2.5}$ concentrations and selected meteorological parameters are illustrated in Fig. 3. In this study, an *episode* is defined as a situation with the daily $\text{PM}_{2.5}$ concentration exceeding $50\ \mu\text{g m}^{-3}$ for at least 2–3 consecutive days. In 2018, 38 such exceedances were recorded, but these were often only single days. During the year, a total of 7 $\text{PM}_{2.5}$ episodes were identified (shaded areas), the longest being recorded in February (06–12 Feb) and at the turn of February and March (28 Feb–06 Mar).

The mean values of $\text{PM}_{2.5}$ concentration and meteorological parameters for individual episodes are presented in Table 2. In general, average concentration of $\text{PM}_{2.5}$ during episodes was $85.66\ \mu\text{g m}^{-3}$, more than considering all days (38) with $\text{PM}_{2.5} > 50\ \mu\text{g m}^{-3}$ (average: $76.98\ \mu\text{g m}^{-3}$), and significantly higher than during the heating period. The highest concentrations of $\text{PM}_{2.5}$ were recorded during the long-lasting Episode 4 (average: $97.31\ \mu\text{g m}^{-3}$), when the lowest air temperatures were also observed (average: -6.77°C). The second long episode, Episode 2, had slightly lower concentrations of $\text{PM}_{2.5}$ (average: $89.31\ \mu\text{g m}^{-3}$). During the other episodes, average concentrations of $\text{PM}_{2.5}$ were within the range $\sim 75\text{--}78\ \mu\text{g m}^{-3}$. Apart from the differences in observed meteorological parameters, it was found that all identified $\text{PM}_{2.5}$ episodes caused significant visibility impairment, which can pose a serious threat to transportation, economic production, and people's living.

Fig. 2. Frequency distribution of daily $\text{PM}_{2.5}$ concentrations at suburban background station in Racibórz.

Fig. 3. Time series of daily $\text{PM}_{2.5}$ concentrations and selected meteorological parameters during annual measurement period (2018).

Table 2. Averages of the PM_{2.5} concentrations and selected meteorological parameters during PM_{2.5} episodes against the values obtained for other averaging periods.

Period	PM _{2.5} ($\mu\text{g m}^{-3}$)	T ($^{\circ}\text{C}$)	Pr (mm)	Ins (h)	Vis (m)	WS (m s^{-1})	RH (%)	Ps (hPa)
E1 ($n = 3$)	75.45	−1.47	0.73	1.43	2,715.28	2.49	91.04	1,017.43
E2 ($n = 7$)	89.31	−2.43	0.729	2.44	3,484.30	2.26	85.77	1,017.01
E3 ($n = 3$)	78.11	−3.37	0.000	3.97	4,669.53	2.08	81.96	1,022.24
E4 ($n = 7$)	97.31	−6.77	0.257	5.21	4,583.97	2.36	73.69	1,009.87
E5 ($n = 2$)	76.23	8.10	0.000	6.80	3,187.69	2.00	88.90	1,017.82
E6 ($n = 2$)	76.93	1.90	0.05	0.00	1,918.75	1.73	94.44	1,025.12
E7 ($n = 2$)	76.84	−2.60	0.00	4.85	4,974.38	2.65	80.94	1,031.41
All episodes ($n = 26$)	85.66	−2.47	0.35	3.58	3,799.77	2.26	83.22	1,017.53
All days with PM _{2.5} > 50 $\mu\text{g m}^{-3}$ ($n = 38$)	76.98	−0.58	0.52	3.30	4,835.34	2.23	83.09	1,017.85
Heating season ($n = 163$)	39.37	3.59	0.85	3.27	11,786.5	3.40	81.24	1,017.30
Whole period ($n = 330$)	26.90	10.86	1.07	6.19	17,496.87	3.19	74.57	1,016.69

E: episode; n : number of samples; T: temperature; Pr: precipitation; Ins: insolation; Vis: visibility; WS: wind speed; RH: relative humidity; Ps: atmospheric pressure.

Concentrations and Contributions of PM_{2.5} Components during High Pollution Days

Average values of the concentrations of PM_{2.5} and its chemical compounds during high pollution days are shown in Table 3, against the data for other averaging periods. Since chemical composition analyses were performed every other day, all days on which PM_{2.5} concentration exceeded 50 $\mu\text{g m}^{-3}$ were taken into account, without selection of PM_{2.5} episodes.

The carbonaceous matter was the dominant component of PM_{2.5} and during days with the highest PM_{2.5} concentrations it represented on average more than half (~52%) of PM_{2.5} mass. The concentrations of TC, EC and OC in such days were on average 36.91, 4.79 and 32.12 $\mu\text{g m}^{-3}$, respectively, and these values were significantly higher compared to those for normal days. The average EC share in PM_{2.5} during days with PM_{2.5} > 50 $\mu\text{g m}^{-3}$ (~7%) was slightly lower than in the entire heating season (~8%). Thus, the high share of TC in PM_{2.5} in high pollution days could be attributed to the high share of OC, which was on average ~45%. Clear dominance of OC over EC was confirmed by significantly higher OC/EC ratios in such periods (average: 7.20). The reason for the observed differences was probably condensation of gas phase semi-volatile organic species due to lower temperature combined with frequent events of air stagnation (Khan *et al.*, 2016; Ma *et al.*, 2017). The average SOC concentration in high pollution days amounted to 14.59 $\mu\text{g m}^{-3}$, and it was ~5 times higher in comparison with the normal days in the heating season. Despite this, POC (average: 17.53 $\mu\text{g m}^{-3}$) remained dominant component of OC, suggesting the impact of local sources, which can emit significant amounts of primary organic matter (Błaszczak *et al.*, 2016).

The periods of high PM_{2.5} concentration were characterized by a large disproportion between the content of carbonaceous matter and water-soluble ions. Although the total concentration of all ions in such periods (average: 21.94 $\mu\text{g m}^{-3}$) was significantly higher compared to those for normal days, the share of ions in PM_{2.5} decreased with the increase in the pollution level. Among all the ionic species determined in

the present study, nss-SO_4^{2-} , NO_3^- and NH_4^+ remained dominant ions during high pollution periods, with average concentrations of 5.54, 7.92 and 2.51 $\mu\text{g m}^{-3}$, respectively. Even if the SIA/PM_{2.5} ratio in such days (average: ~22%) was lower than in normal days during the heating season (average: ~26%), the structure of SIA was very similar—the key component of SIA were nitrates with average share in PM_{2.5} of ~11%. Interestingly, the values of SIA/ion ratio increased during high pollution days (average: ~71%), compared to those for normal days in the heating period (~64%). This could indicate that as the pollution level increased, the intensity of formation of SIA also increased, mainly thanks to enhanced heterogeneous conversion of NO_x . It should be noted that in conditions of high relative humidity (Table 2), heterogeneous reactions on pre-existing particles are more intense rather than homogeneous conversions (Song *et al.*, 2019; Wang *et al.*, 2019).

With regard to the other ions listed in Table 3, the chemical profile of PM_{2.5} during high pollution days was enriched in Cl^- and to a lesser extent in K^+ . This suggested that the increased intensity of biomass burning and the use of coal for energy purposes could have contributed to enhanced PM_{2.5} concentrations (Liu *et al.*, 2015). The analysis of PM_{2.5} ionic balance also proves the specificity of PM_{2.5} chemical composition during high pollution events. At high PM_{2.5} concentrations, atmosphere was ammonia-rich, as indicated by relatively low value of the $\text{SO}_4^{2-}/\text{NH}_4^+$ ratio (average: 0.85). Despite this, the amount of NH_4^+ ions was insufficient for complete neutralization of sulfuric acid (H_2SO_4) and nitric acid (HNO_3) in atmospheric dust. It was supported by relatively low values of the $\Sigma_{\text{cat}}/\Sigma_{\text{an}}$ ratios (average: 0.86), indicating the acidic nature of the aerosols—in contrast to other averaging periods—due to high levels of secondary inorganic ions formed in heterogeneous reactions that are particularly intense during high pollution days. The deficit of cations (excess of anions) could probably be attributed to hydrogen ions (H^+), since the sum of the crustal and trace elements is usually only a small percentage of PM_{2.5} mass (Błaszczak *et al.*, 2016a).

Table 3. Concentrations (in $\mu\text{g m}^{-3}$) of $\text{PM}_{2.5}$ and $\text{PM}_{2.5}$ -related components during days with $\text{PM}_{2.5} > 50 \mu\text{g m}^{-3}$ in relation to data from other averaging periods.

Specification	$\text{PM}_{2.5} > 50 \mu\text{g m}^{-3}$ ($n = 38$)		2018 ($n = 153$)		Heating ($n = 72$)		Non-heating ($n = 81$)		Concentration ratios	
	Ave $\pm$ SD	Range	Ave $\pm$ SD		Ave $\pm$ SD		Ave $\pm$ SD		E/(ALL-E)	E/(H-E)
$\text{PM}_{2.5}$	70.81 $\pm$ 22.82	50.20–129.85	26.90 $\pm$ 22.31		39.37 $\pm$ 25.89		14.74 $\pm$ 5.53		3.62	2.68
OC	32.12 $\pm$ 12.87 (~45%)	11.79–61.42	9.97 $\pm$ 10.78 (~33%)		16.56 $\pm$ 12.71 (~41%)		4.12 $\pm$ 1.96 (~27%)		4.84	2.96
EC	4.79 $\pm$ 2.03 (~7%)	2.06–11.22	1.73 $\pm$ 1.72 (~6%)		2.86 $\pm$ 1.89 (~8%)		0.72 $\pm$ 0.51 (~4%)		3.79	2.22
TC	36.91 $\pm$ 14.04 (~52%)	13.85–70.36	11.70 $\pm$ 12.32 (~39%)		19.41 $\pm$ 14.29 (~49%)		4.84 $\pm$ 2.40 (~31%)		4.67	2.84
OC/EC	7.20 $\pm$ 2.97	3.67–13.52	6.36 $\pm$ 2.66		5.75 $\pm$ 2.09		6.89 $\pm$ 2.99		1.16	1.39
SOC	14.59 $\pm$ 11.00 (~20%)	0.04–44.80	3.70 $\pm$ 6.04 (~12%)		6.13 $\pm$ 8.12 (~13%)		1.54 $\pm$ 0.89 (~11%)		7.07	4.90
POC	17.53 $\pm$ 7.44 (~25%)	7.53–41.05	6.27 $\pm$ 6.26 (~22%)		10.42 $\pm$ 6.90 (~28%)		2.58 $\pm$ 1.73 (~16%)		3.83	2.23
SO_4^{2-}	5.86 $\pm$ 2.53 (~8%)	2.11–11.48	2.89 $\pm$ 1.80 (~13%)		3.59 $\pm$ 2.28 (~10%)		2.26 $\pm$ 0.85 (~15%)		2.40	2.13
NO_3^-	7.92 $\pm$ 5.34 (~11%)	2.05–20.38	2.56 $\pm$ 3.11 (~9%)		4.20 $\pm$ 3.82 (~11%)		1.11 $\pm$ 0.93 (~7%)		4.50	2.78
nss- SO_4^{2-}	5.54 $\pm$ 2.52 (~8%)	1.91–11.06	2.67 $\pm$ 1.77 (~12%)		3.31 $\pm$ 2.24 (~9%)		2.10 $\pm$ 0.89 (~14%)		2.47	2.24
NH_4^+	2.51 $\pm$ 0.62 (~4%)	1.38–3.76	1.09 $\pm$ 0.74 (~4%)		1.52 $\pm$ 0.85 (~4%)		0.71 $\pm$ 0.31 (~5%)		2.86	2.17
SIA	15.97 $\pm$ 7.98 (~22%)	5.33–33.73	6.33 $\pm$ 5.24 (~25%)		9.03 $\pm$ 6.49 (~25%)		3.93 $\pm$ 1.54 (~26%)		3.27	2.46
ss- SO_4^{2-}	0.32 $\pm$ 0.12 (< 1%)	0.12–0.52	0.22 $\pm$ 0.14 (~1%)		0.28 $\pm$ 0.15 (~1%)		0.16 $\pm$ 0.11 (~1%)		1.59	1.20
Cl ⁻	2.91 $\pm$ 1.26 (~4%)	0.93–4.91	0.95 $\pm$ 1.01 (~4%)		1.56 $\pm$ 1.18 (~4%)		0.40 $\pm$ 0.18 (~3%)		4.48	2.71
Na ⁺	1.30 $\pm$ 0.49 (~2%)	0.51–2.10	0.88 $\pm$ 0.58 (~4%)		1.14 $\pm$ 0.60 (~4%)		0.65 $\pm$ 0.45 (~5%)		1.59	1.20
K ⁺	0.46 $\pm$ 0.18 (~1%)	0.20–0.94	0.21 $\pm$ 0.16 (~1%)		0.30 $\pm$ 0.18 (~1%)		0.12 $\pm$ 0.06 (~1%)		2.73	1.88
Ca ²⁺	0.91 $\pm$ 0.55 (~1%)	0.28–1.83	0.70 $\pm$ 0.42 (~4%)		0.75 $\pm$ 0.47 (~3%)		0.66 $\pm$ 0.37 (~5%)		1.36	1.29
Mg ²⁺	0.06 $\pm$ 0.04 (< 1%)	0.01–0.16	0.04 $\pm$ 0.04 (< 1%)		0.05 $\pm$ 0.04 (< 1%)		0.03 $\pm$ 0.04 (< 1%)		1.74	1.32
Ions	21.94 $\pm$ 8.67 (~31%)	10.68–40.71	9.32 $\pm$ 6.60 (~39%)		13.11 $\pm$ 7.86 (~38%)		5.95 $\pm$ 1.86 (~41%)		2.96	2.21
$\Sigma_{\text{cat}}/\Sigma_{\text{an}}$	0.86 $\pm$ 0.26	0.43–1.48	1.30 $\pm$ 0.40		1.15 $\pm$ 0.39		1.43 $\pm$ 0.36		0.63	0.69
$\text{SO}_4^{2-}/\text{NH}_4^+$	0.85 $\pm$ 0.23	0.40–1.26	1.13 $\pm$ 0.45		0.94 $\pm$ 0.34		1.31 $\pm$ 0.46		0.73	0.88
Others	11.96 $\pm$ 5.04 (~17%)	4.23–23.17	5.22 $\pm$ 4.36 (~21%)		5.79 $\pm$ 5.29 (~13%)		4.72 $\pm$ 3.27 (~28%)		2.84	3.38

Designations: n : number of samples; Ave $\pm$ SD: average $\pm$ standard deviation; Range: minimum–maximum; in round brackets the average share of a substance in $\text{PM}_{2.5}$ is given; E/(ALL-E): ratio of average concentration of a given substance during days with $\text{PM}_{2.5} > 50 \mu\text{g m}^{-3}$ to concentration of this substance during the normal days ($\text{PM}_{2.5} > 50 \mu\text{g m}^{-3}$) in the annual measurement period; E/(H-E): ratio of average concentration of a given substance during days with $\text{PM}_{2.5} > 50 \mu\text{g m}^{-3}$ to concentration of this substance during the normal days ($\text{PM}_{2.5} > 50 \mu\text{g m}^{-3}$) in the heating season.
Bold and underlined type indicates statistically significant differences between daily averaged concentrations of a given substance recorded during the compared periods (the non-parametric U Mann–Whitney test; $\alpha = 0.05$).

To get a further insight into the variability of $PM_{2.5}$ chemical composition, we also classified $PM_{2.5}$ pollution into different categories. Mean percentages of the main chemical components of $PM_{2.5}$ —carbonaceous matter (EC, POC, SOC), secondary inorganic ions ($nss\text{-}SO_4^{2-}$, NO_3^- , NH_4^+) and Cl^- ions—under different pollution levels are presented in Fig. 4. Other ions were omitted in the considerations, because their share in the total $PM_{2.5}$ mass during high pollution days was small and did not exceed 2% (Table 3).

It was generally found that the share of carbonaceous matter increased with the increase of $PM_{2.5}$ concentration. During the clean periods ($PM_{2.5} < 10 \mu g m^{-3}$), the share of TC was low (average: $\sim 34\%$), especially in the case of EC (average: $\sim 5\%$) and POC (average: $\sim 17\%$). The highest POC and EC shares were recorded at $PM_{2.5}$ concentrations in the range of $35\text{--}50 \mu g m^{-3}$, with average values of $\sim 32\%$ and $\sim 9\%$, respectively. The increase in the SOC share in $PM_{2.5}$ together with the increase in the pollution level was more pronounced compared to primary carbon compounds. As a result, at the highest $PM_{2.5}$ concentrations ($PM_{2.5} \geq 70 \mu g m^{-3}$), the SOC share (average: $\sim 25\%$) was higher than the POC share (average: $\sim 22\%$).

In general, the share of SIA decreased with the increase of $PM_{2.5}$ concentrations; however, differences were observed when considering the shares of individual inorganic ions. The highest share of $nss\text{-}SO_4^{2-}$ in $PM_{2.5}$ (average: $\sim 14\%$) was recorded at the lowest concentrations of $PM_{2.5}$ ($< 10 \mu g m^{-3}$), which could affect the high SIA content in $PM_{2.5}$ for the given concentration range. Also in this case the highest shares of Cl^- ions were recorded (average: $\sim 6\%$). The share of NH_4^+ ions was less variable, with the highest levels (average: $\sim 5\%$) observed at $PM_{2.5}$ concentrations in the range of $10\text{--}15 \mu g m^{-3}$. Nitrates were distinguished by increasing share with an increase in the pollution level, reflecting an elevated production of heterogeneous reactions. The highest share of NO_3^- (average: $\sim 14\%$) was found at $PM_{2.5}$ concentrations of $\geq 70 \mu g m^{-3}$, similar to the share of SOC.

The obtained results suggest that high concentration of $PM_{2.5}$ in Racibórz were mainly caused by secondary aerosol, especially secondary organic carbon and, to a lesser extent, nitrates. A high share of TC, especially OC, was also found at various measurement stations located in Poland, representing both urban backgrounds, e.g., Katowice (Rogula-Kozłowska *et al.*, 2014) and Warsaw (Juda-Rezler *et al.*, 2011), and rural backgrounds, e.g., Diabla Góra (Juda-Rezler *et al.*, 2011) and Czerniawa (Reizer and Juda-Rezler, 2016). On the other hand, the importance of SIA as a factor responsible for increased concentrations of $PM_{2.5}$ has been emphasized in many scientific publications (e.g., Weijers *et al.*, 2010; Rodelas *et al.*, 2019; Wang *et al.*, 2019). This has confirmed the fact that Poland is a specific country in terms of emission conditions, which also has an undeniable effect on the chemical composition of the atmospheric aerosol.

Correlations among $PM_{2.5}$ Chemical Components and their Relation with Meteorological Parameters

In this work, the interrelationships between the concentrations of $PM_{2.5}$ chemical components were examined using Spearman's rank correlation ($\alpha = 0.05$). A non-parametric correlation matrix was constructed separately for the data set from high pollution days and normal days in the heating season (Table 4) to capture the specifics of both periods.

$PM_{2.5}$ concentrations showed a strong positive correlation with carbonaceous aerosol, while during high pollution days the correlation was maintained only in the case of OC ($r = 0.79$). In such periods no statistically significant relationship was found between OC and EC, which proves the presence of mixed emission sources of these substances (Mancilla *et al.*, 2015). For example, the significant positive correlation between Ca^{2+} and Mg^{2+} and primary carbon compounds (EC, POC) during high pollution days may indicate a common source of origin—emissions from car engines and road abrasion (Rodríguez *et al.*, 2004). On the other hand, neither

Fig. 4. Contributions (%) of carbonaceous compounds (EC, SOC and POC) and inorganic ions ($nss\text{-}SO_4^{2-}$, NO_3^- , NH_4^+ and Cl^-) in $PM_{2.5}$ for different concentration ranges.

Table 4. Non-parametric (Spearman) correlation matrix ($\alpha = 0.05$) between concentrations of PM_{2.5} and its main components, separately for high pollution days and normal days in the heating season.

Variable	High pollution days (PM _{2.5} > 50 µg m ⁻³)										
	PM _{2.5}	EC	OC	SOC	POC	nss-SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	SIA	Cl ⁻	Mg ²⁺
PM _{2.5}											
EC	0.90										
OC	0.96	0.92									
SOC	0.55	0.27	0.58								
POC	0.90	1.00	0.92	0.27							
nss-SO ₄ ²⁻	0.79	0.63	0.70	0.51	0.63						
NO ₃ ⁻	0.66	0.54	0.62	0.48	0.54	0.47					
NH ₄ ⁺	0.88	0.71	0.82	0.60	0.71	0.85	0.78				
SIA	0.85	0.70	0.78	0.56	0.70	0.85	0.84	0.97			
Cl ⁻	0.74	0.65	0.71	0.40	0.65	0.55	0.49	0.71	0.62		
Na ⁺	0.31	0.33	0.31	0.08	0.33	0.17	0.29	0.26	0.26	0.57	
K ⁺	0.73	0.66	0.71	0.41	0.66	0.67	0.31	0.58	0.56	0.51	0.23
Ca ²⁺	0.25	0.39	0.20	-0.29	0.39	0.21	0.17	0.16	0.21	0.19	-0.29
Mg ²⁺	0.21	0.22	0.16	-0.03	0.22	0.33	0.02	0.17	0.18	0.23	0.58

Bold type indicates that the correlation is statistically significant ($\alpha = 0.05$).

EC and POC nor Ca²⁺ and Mg²⁺ showed statistically significant associations with PM_{2.5} in such periods, and therefore the role of these sources in shaping high PM_{2.5} concentrations could be negligible. Conversely, the relatively high positive correlation between SOC and PM_{2.5} ($r = 0.61$) indicated the importance of SOA formation processes (Mancilla *et al.*, 2015).

In addition to SOC, SIA also had a significant effect on high PM_{2.5} concentrations, specifically, NO₃⁻ ($r = 0.60$) and, to a lesser extent, NH₄⁺ ($r = 0.46$). In both averaging periods, strong positive correlation was noted between the nss-SO₄²⁻ and NO₃⁻, suggesting a significant content of aged particles in the ambient air, which is typical for non-urban areas such as Racibórz (Heo *et al.*, 2013; Rogula-Kozłowska *et al.*, 2014). This is confirmed by the high correlation of NH₄⁺ with nss-SO₄²⁻ and NO₃⁻ ($r = 0.74$ – 0.85). Moreover, during days with PM_{2.5} > 50 µg m⁻³ there were no statistically significant relationships between SIA and other analyzed ions as well as between SIA and SOC, which could indicate that the SIA concentrations are less impacted by local emissions in such periods (Freney *et al.*, 2011; Heo *et al.*, 2013). On the other hand, the effect of local sources—such as coal combustion in households (Rodelas *et al.*, 2019)—on SOC levels is confirmed by the strong correlation between SOC and Cl⁻ ($r = 0.61$).

A non-parametric (Spearman) correlation analysis ($\alpha = 0.05$) between weather parameters and PM_{2.5} chemical composition data was also performed in order to identify the factors affecting the variability of concentrations of the analyzed substances (Table 5). During periods of elevated PM_{2.5} concentration, no statistically significant relationships were found between the analyzed PM components, and precipitation, solar radiation intensity, atmospheric pressure and wind speed. This may be due to much lower values of these parameters during high pollution days or to their small variability (see also Section 3.2). The impact of wind speed was revealed in the formal days of the heating season, with negative values of correlation coefficients. This is probably due to the cleaning function of wind—high wind speeds favor the dispersion of atmospheric pollutants, while low wind speeds allow pollutant levels to rise (Galindo *et al.*, 2011).

During the high pollution days, the correlation with air temperature was maintained only for PM_{2.5} ($r = -0.48$), EC and POC ($r = -0.60$), Cl⁻ ($r = -0.57$) and Na⁺ ($r = -0.48$). The lack of statistically significant relations with temperature for most of the analyzed components may indicate that other factors, such as long-range transport events, regional recirculation episodes or complex photochemical reactions, to a greater extent could affect high concentrations of these substances (Galindo *et al.*, 2011; Heo *et al.*, 2013). Interestingly, for most of the analyzed substances, there were no statistically significant relationships with relative humidity. In view of the above considerations (see Section 3.3), this is particularly surprising in relation to secondary PM_{2.5} components. It should be remembered that the resolution of the chemical analysis data could have an effect on the results obtained—every second daily sample was analyzed. Therefore, to examine the relationships between relative humidity, and SIA and SOC levels thoroughly, further studies are needed.

Table 5. Non-parametric (Spearman) correlation matrix ($\alpha = 0.05$) between concentrations of $PM_{2.5}$ and its main components and selected meteorological parameters, separately for high pollution days and normal days in the heating season.

Variable	High pollution days ($PM_{2.5} > 50 \mu g m^{-3}$)							Normal days ($PM_{2.5} \leq 50 \mu g m^{-3}$)						
	T	Pr	Ins	Vis	WS	RH	Ps	T	Pr	Ins	Vis	WS	RH	Ps
$PM_{2.5}$	-0.48	0.08	0.10	-0.44	-0.08	0.01	-0.12	-0.21	-0.28	-0.08	-0.81	-0.62	0.14	0.31
EC	-0.60	-0.17	0.25	0.32	0.37	-0.59	-0.28	-0.15	-0.34	0.06	-0.64	-0.61	0.00	0.24
OC	-0.34	0.08	0.00	-0.29	-0.19	0.08	-0.15	-0.24	-0.30	-0.06	-0.74	-0.61	0.14	0.24
SOC	-0.01	0.22	-0.19	-0.45	-0.38	0.43	-0.07	-0.21	-0.16	-0.22	-0.55	-0.33	0.34	0.10
POC	-0.60	-0.17	0.25	0.32	0.37	-0.59	-0.28	-0.15	-0.34	0.06	-0.64	-0.61	0.00	0.24
$nss-SO_4^{2-}$	-0.22	-0.16	0.05	-0.54	-0.19	0.01	-0.03	-0.14	-0.22	-0.20	-0.83	-0.52	0.18	0.35
NO_3^-	-0.09	0.01	-0.06	-0.59	-0.24	0.17	-0.26	-0.46	-0.17	-0.22	-0.61	-0.32	0.21	0.03
NH_4^+	-0.18	0.04	-0.22	-0.74	-0.11	0.31	-0.22	-0.37	-0.12	-0.35	-0.87	-0.49	0.30	0.14
SIA	-0.16	-0.04	-0.07	-0.66	-0.28	0.17	-0.14	-0.35	-0.22	-0.27	-0.84	-0.50	0.23	0.18
Cl^-	-0.57	-0.13	0.02	-0.19	-0.01	-0.17	-0.07	-0.35	-0.03	-0.33	-0.63	-0.42	0.28	0.20
Na^+	-0.48	-0.21	0.20	-0.01	0.26	-0.30	-0.09	-0.43	-0.01	-0.04	-0.19	-0.15	-0.05	0.18
K^+	0.21	0.08	0.04	-0.26	-0.38	0.17	0.41	0.01	-0.24	0.12	-0.56	-0.40	0.00	0.38
Ca^{2+}	-0.17	-0.07	0.16	0.37	0.27	-0.49	-0.25	-0.02	-0.11	0.22	-0.07	-0.27	-0.26	0.15
Mg^{2+}	-0.16	0.02	0.00	0.35	0.14	-0.32	-0.06	-0.05	-0.10	0.20	-0.04	-0.07	-0.48	0.28

Designations: T: temperature; Pr: precipitation; Ins: insolation; Vis: visibility; WS: wind speed; RH: relative humidity; Ps: atmospheric pressure. Bold type indicates that the correlation is statistically significant ($\alpha = 0.05$).

Nevertheless, a significant positive correlation with visibility was noted only for SOC ($r = -0.45$) and secondary inorganic ions ($r = -0.59$ to -0.74). The results obtained in the study are consistent with literature data (e.g., Lin *et al.*, 2014; Wang *et al.*, 2019) and confirm that the secondary aerosol was the major contributor to atmospheric visibility deterioration during high pollution events.

The Role of Atmospheric Circulation during Periods of High $PM_{2.5}$ Concentration

Due to the clear weakness of the relationship of measured chemical components with meteorological parameters during the periods of elevated $PM_{2.5}$ concentrations, the variability of the share of $PM_{2.5}$ main components (SIA, EC + POC, SOC) was checked against the atmospheric circulation types in the heating season (Fig. 5). The classification of circulation types according to Lityński (1969) was used in the study. It belongs to the group of automatic (objective) classifications and has been routinely used in the IMWM-NRI measurement network. This classification contains 27 types of circulation, including 8 cyclonic, 8 anticyclonic and 8 zero-types for a given inflow of air (N, NE, E, SE, S, SW, W, NW) as well as 3 types without an identified inflow of air mass—zero cyclone (0c; center of low pressure), zero saddle (0o) and zero anticyclonic (0a; center of high pressure).

The highest $PM_{2.5}$ concentrations were associated with the inflow of air masses from the SE, and were primarily caused by the increased content of carbonaceous compounds. TC concentrations peaked on 04 and 06 Mar (Episode 4); however, these days differed in the direction of air mass inflow and the concentrations of primary and secondary compounds. On 04 Mar, with the E_c circulation type, very high concentrations of EC ($11.22 \mu g m^{-3}$) and POC ($41.05 \mu g m^{-3}$) were noted, indicating a significant impact of local emission sources—National Freeway No. 45. This statement was confirmed by the maximum EC and POC shares in $PM_{2.5}$ recorded on 28 Feb ($\sim 41\%$ and $\sim 11\%$, respectively), with the E_a circulation type. Equally high share of EC + POC was found on 26 Feb with the inflow of air masses from the NE direction, which indicated an additional impact of the city center of Racibórz (~ 2.5 km northeast of the station).

Generally, POC clearly dominated over SOC, although the situation is different if we look at individual days of the heating season (Fig. 5). For example, on 06 Mar, with an inflow of air masses from the SE, the SOC concentration ($44.80 \mu g m^{-3}$) was more than 2.5 times higher than POC, with contribution in $PM_{2.5}$ of $\sim 35\%$. Equally high SOC shares in $PM_{2.5}$ were found on 27 Jan, 10 Nov and 28 Nov, with similar advection directions. Therefore, high concentrations and shares of SOC during high pollution days were probably caused by regional transport of pollutants from the Rybnicko-Jastrzębska agglomeration—an important industrial center of southern Poland—or the inflow of polluted air masses from the Czech Republic. The impact of local emission sources was also not without significance, as was evidenced by the high/moderate TC shares recorded for types with no distinct inflow direction (e.g., 19 Jan, 23 Jan, 28 Mar).

In general, the SIA concentrations were ~ 2 times lower compared to TC concentrations (Table 3); however, this

Fig. 5. Concentrations of the total carbon (TC) and secondary inorganic aerosol during heating period of 2018 with an indication of the atmospheric circulation types and high pollution days: (a) Jan–Mar and (b) Oct–Dec.

situation changed significantly on particular days (Fig. 5). The highest concentration of SIA ($33.73 \mu\text{g m}^{-3}$) was found on 06 Mar (circulation type: SE_c), although the share of SIA remained at moderate level ($\sim 26\%$). A very high share of

SIA ($\sim 44\%$) was recorded on 08 Feb (Episode 2), with S₀ circulation type—this indicated an inflow of polluted air masses from the Czech Republic (Ostrava). The highest share of SIA in PM_{2.5} from Racibórz ($\sim 45\%$) was registered

on 04 Feb (circulation type: NE₀), at low PM_{2.5} concentration and moderate TC share. A high share of SIA in PM_{2.5} (~42%) was also noted on 19 Oct, with the N_a circulation type, relatively high PM_{2.5} concentration and a minimum share of TC (~28%). The results obtained may indicate a large role of regional transport of pollutants from the area of Kędzierzyn-Koźle (~30 km north of the station), where large sources of the chemical industry are located. The inflow of gaseous precursors from the Upper Silesian Industrial District could have also a potentially large impact on the high share of SIA in PM_{2.5}.

CONCLUSIONS

To better comprehend the factors leading to periods of high pollution, we analyzed daily measurements of PM_{2.5} conducted during 2018 at a suburban background station in Racibórz, which is located in Silesia Province, one of the most polluted regions of Poland. The concentrations of PM_{2.5} and its chemical components varied during the study period, exhibiting characteristic seasonal trends associated with variations in the emission intensity of PM and its precursors from anthropogenic sources as well as changes in the prevailing meteorological conditions. The inhabitants of the analyzed area experienced much worse living conditions during the heating season, when the PM_{2.5} concentration exceeded the European standard (25 w) on ~66% of the sampled days.

We identified 7 PM_{2.5} episodes, which critically affected the air quality in Racibórz. In general, the TC fraction grew (to an average of ~52%) during the polluted periods (PM_{2.5} > 50 w) owing to the increased OC (average: ~45%). When the PM_{2.5} concentrations reached their maximum values (≥ 70 w), the percentage of SOC (contrary to that of POC) rose dramatically. In addition, the ionic portion was dominated by secondary inorganic ions, including NO₃⁻, a key component of SIA, on polluted days. Overall, the fraction of SIA decreased as the level of pollution increased; however, we observed differences in this variability between the individual species.

Although specific weather conditions during the cold season were shown to favor the occurrence of PM_{2.5} episodes, obviously weak correlations between certain meteorological parameters and the PM_{2.5} component concentrations reveal the potential influence of regional and long-range transport events as well as the importance of secondary aerosol formation. We found that inflowing air masses from the following areas may have significantly contributed to air pollution in Racibórz: a) the Rybnicko-Jastrzębska agglomeration (SOC), b) the Czech Republic (Ostrava and Opava; SIA and SOC); and c) Kędzierzyn-Koźle and the Upper Silesian Industrial District (SIA). Local emission sources (e.g., road transport and fossil fuel combustion) also played a role, as evidenced by the high proportions of EC and POC in the PM_{2.5} mass.

These results suggest that elevated concentrations of PM_{2.5} in Racibórz and at similar sites in Poland are mainly due to secondary organic carbon and, to a lesser extent, NO₃⁻, which confirms the specificity of this nation's emission conditions, namely, the heavy use of fossil fuels in energy

consumption, and electricity and heat production. This study provides valuable scientific data for developing strategies and programs to protect air quality, which should particularly focus on abating emissions of PM's gaseous precursors. Regional and long-range transport should also be considered as potential factors, especially in non-urban areas.

ACKNOWLEDGMENTS

This work was supported by the Institute of Environmental Engineering of the Polish Academy of Sciences basic (statutory) Research Project No. 1a-119/2018 (*Temporal and spatial variability of the chemical composition of atmospheric aerosols as a tool for assessing the effects of implementing air protection programs in Poland*, 2018–2020). The authors also gratefully acknowledge the Institute of Meteorology and Water Management–National Research Institute for the provision of the meteorological data.

REFERENCES

- Błaszczak, B., Rogula-Kozłowska, W., Mathews, B., Juda-Rezler, K., Klejnowski, K. and Rogula-Kopiec, P. (2016). Chemical compositions of PM_{2.5} at two non-urban sites from the polluted region in Europe. *Aerosol Air Qual. Res.* 16: 2333–2348. <https://doi.org/10.4209/aaqr.2015.09.0538>
- Błaszczak, B., Widziewicz-Rzońca, K., Ziola, N., Klejnowski, K. and Juda-Rezler, K. (2019). Chemical characteristics of fine particulate matter in Poland in relation with data from selected rural and urban background stations in Europe. *Appl. Sci.* 9: 98. <https://doi.org/10.3390/app9010098>
- Castro, L.M., Pio, C.A., Harrison, R.M. and Smith, D.J.T. (1999). Carbonaceous aerosol in urban and rural European atmospheres: Estimation of secondary organic carbon concentrations. *Atmos. Environ.* 33: 2771–2781. [https://doi.org/10.1016/S1352-2310\(98\)00331-8](https://doi.org/10.1016/S1352-2310(98)00331-8)
- Dai, Q., Bi, X., Liu, B., Li, L., Ding, J., Song, W., Bi, S., Schulze, B.C., Song, C., Wu, J., Zhang, Y., Feng, Y. and Hopke, P.K. (2018). Chemical nature of PM_{2.5} and PM₁₀ in Xi'an, China: Insights into primary emissions and secondary particle formation. *Environ. Pollut.* 240: 155–166. <https://doi.org/10.1016/j.envpol.2018.04.111>
- Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on Ambient Air Quality and Cleaner Air for Europe; 2005/0183/COD; Council of the European Union: City, Country, 2008.
- Fiore, A.M., Naik, V. and Leibensperger, E.M. (2015). Air quality and climate connections. *J. Air Waste Manage. Assoc.* 65: 645–685. <https://doi.org/10.1080/10962247.2015.1040526>
- Freney, E.J., Sellegri, K., Canonaco, F., Boulon, J., Hervo, M., Weigel, R., Pichon, J.M., Colomb, A., Prévôt, A.S.H. and Laj, P. (2011). Seasonal variations in aerosol particle composition at the Puy-de-Dôme research station in France. *Atmos. Chem. Phys.* 11: 13047–13059. <https://doi.org/10.5194/acp-11-13047-2011>
- Galindo, N., Varea, M., Gil-Moltó, J., Yubero, E. and Nicolás, J. (2011). The influence of meteorology on

- particulate matter concentrations at an urban mediterranean location. *Water Air Soil Pollut.* 215: 365–372. <https://doi.org/10.1007/s11270-010-0484-z>
- Hassan, S.K. and Khoder, M.I. (2017). Chemical characteristics of atmospheric PM_{2.5} loads during air pollution episodes in Giza, Egypt. *Atmos. Environ.* 150: 346–355. <https://doi.org/10.1016/j.atmosenv.2016.11.026>
- Heo, J., McGinnis, J.E., de Foy, B. and Schauer, J.J. (2013). Identification of potential source areas for elevated PM_{2.5}, nitrate and sulfate concentrations. *Atmos. Environ.* 71: 187197. <https://doi.org/10.1016/j.atmosenv.2013.02.008>
- Jones, A.M. and Harrison, R.M. (2005). Interpretation of particulate elemental and organic carbon concentrations at rural, urban and kerbside sites. *Atmos. Environ.* 39: 7114–7126. <https://doi.org/10.1016/j.atmosenv.2005.08.017>
- Juda-Rezler, K., Reizer, M. and Oudinet, J.P. (2011). Determination and analysis of PM₁₀ source apportionment during episodes of air pollution in Central Eastern European urban areas: The case of wintertime 2006. *Atmos. Environ.* 45: 6557–6566. <https://doi.org/10.1016/j.atmosenv.2011.08.020>
- Kassomenos, P.A., Vardoulakis, S., Chaloulakou, A., Pscholidou, A.K., Grivas, G., Borge, R. and Lumbreras, J. (2014). Study of PM₁₀ and PM_{2.5} levels in three European cities: Analysis of intra and inter urban variations. *Atmos. Environ.* 87: 153–163. <https://doi.org/10.1016/j.atmosenv.2014.01.004>
- Khan, Md.B., Masiol, M., Formenton, G., Di Gilio, A., de Gennaro, G., Agostinelli, C. and Pavoni, B. (2016). Carbonaceous PM_{2.5} and secondary organic aerosol across the Veneto region (NE Italy). *Sci. Total Environ.* 542: 172–181. <https://doi.org/10.1016/j.scitotenv.2015.10.103>
- Kim, K.H., Kabir, E. and Kabir, S. (2015). A review on the human health impact of airborne particulate matter. *Environ. Int.* 74: 136–143. <https://doi.org/10.1016/j.envint.2014.10.005>
- Lin, Y., Huang, K., Zhuang, G., Fu, J.S., Wang, Q., Liu, T., Deng, C. and Fu, Q. (2014). A multi-year evolution of aerosol chemistry impacting visibility and haze formation over an Eastern Asia megacity, Shanghai. *Atmos. Environ.* 92: 76–86. <https://doi.org/10.1016/j.atmosenv.2014.04.007>
- Lityński, J. (1969). Numerical classification of circulation types and types of weather for Poland [in Polish]. *PIHM Studies* 97: 3–14.
- Liu, G., Li, J., Wu, D. and Xu, H. (2015). Chemical composition and source apportionment of the ambient PM_{2.5} in Hangzhou, China. *Particuology* 18: 135–143. <https://doi.org/10.1016/j.partic.2014.03.011>
- Ma, Q., Wu, Y., Zhang, D., Wang, X., Xia, Y., Liu, X., Tian, P., Han, Z., Xia, X., Wang, Y. and Zhang, R. (2017). Roles of regional transport and heterogeneous reactions in the PM_{2.5} increase during winter haze episodes in Beijing. *Sci. Total Environ.* 599–600: 246–253. <https://doi.org/10.1016/j.scitotenv.2017.04.193>
- Maciejewska, K., Juda-Rezler, K., Reizer, M. and Klejnowski, K. (2015). Modelling of black carbon statistical distribution and return periods of extreme concentrations. *Environ. Modell. Software* 74: 212–226. <https://doi.org/10.1016/j.envsoft.2015.04.016>
- Mancilla, Y., Herckes, P., Fraser, M.P. and Mendoza, A. (2015). Secondary organic aerosol contributions to PM_{2.5} in Monterrey, Mexico: Temporal and seasonal variation. *Atmos. Res.* 153: 348–359. <https://doi.org/10.1016/j.atmosres.2014.09.009>
- Pavuluri, C.M., Kawamura, K., Aggarwal, S.G. and Swaminathan, T. (2011). Characteristics, seasonality and sources of carbonaceous and ionic components in the tropical aerosols from Indian region. *Atmos. Chem. Phys.* 11: 8215–8230. <https://doi.org/10.5194/acp-11-8215-2011>
- PN-EN 12341:2014-07: Ambient air – Standard gravimetric measurement method to determine the concentration of mass fractions PM₁₀ or PM_{2.5} particulate matter.
- Rai, P.K. (2016). Impacts of particulate matter pollution on plants: Implications for environmental biomonitoring. *Ecotoxicol. Environ. Saf.* 129: 120–136. <https://doi.org/10.1016/j.ecoenv.2016.03.012>
- Rao, N.V., Rajasekhar, M. and Rao, G.C. (2014). Detrimental effect of air pollution, corrosion on building materials and historical structures. *Am. J. Eng. Res.* 03: 359–364.
- Reizer, M. and Juda-Rezler, K. (2016). Explaining the high PM₁₀ concentrations observed in Polish urban areas. *Air Qual. Atmos. Health* 9: 517–531. <https://doi.org/10.1007/s11869-015-0358-z>
- Rodelas, R.R., Perdrix, E., Herbin, B. and Riffault, V. (2019). Characterization and variability of inorganic aerosols and their gaseous precursors at a suburban site in northern France over one year (2015–2016). *Atmos. Environ.* 200: 142–157. <https://doi.org/10.1016/j.atmosenv.2018.11.041>
- Rodríguez, S., Querol, X., Alastuey, A., Viana, M.M., Alcorcón, M., Mantila, E. and Ruiz, C.R. (2004). Comparative PM₁₀–PM_{2.5} source contribution study at rural urban and industrial sites during PM episodes in Eastern Spain. *Sci. Total Environ.* 328: 95–113. [https://doi.org/10.1016/S0048-9697\(03\)00411-X](https://doi.org/10.1016/S0048-9697(03)00411-X)
- Rogula-Kozłowska, W., Klejnowski, K., Rogula-Kopiec, P., Ośródk, L., Krajny, E., Błaszczak, B. and Mathews, B. (2014). Spatial and seasonal variability of the mass concentrations and chemical composition of PM_{2.5} in Poland. *Air Qual. Atmos. Health* 7: 41–58. <https://doi.org/10.1007/s11869-013-0222-y>
- Romer, E. (1949). *Climate regions of Poland*. Works of the Wrocław Scientific Society B20, Wrocław. (in Polish)
- Sillanpää, M., Hillamo, R., Saarikoski, S., Frey, A., Pennanen, A., Makkonen, U., Spolnik, Z., Van Grieken, R., Braniš, M., Brunekreef, B., Chalbot, M.C., Kuhlbusch, T., Sunyer, J., Kerminen, V.M., Kulmala, M. and Salonen, R.O. (2006). Chemical composition and mass closure of particulate matter at six urban sites in Europe. *Atmos. Environ.* 40: 212–223. <https://doi.org/10.1016/j.atmosenv.2006.01.063>
- Song, X., Li, J., Shao, L., Zheng, Q. and Zhang, D. (2019). Inorganic ion chemistry of local particulate matter in a populated city of North China at light, medium, and severe pollution levels. *Sci. Total Environ.* 690: 566–574. <https://doi.org/10.1016/j.scitotenv.2018.09.033>
- U.S. EPA (2016). *Integrated Review Plan for the National*

- Ambient Air Quality Standards for Particulate Matter. Publication No. EPA-452/R-16-005.* U.S. Environmental Protection Agency Office of Air Quality Planning and Standards Health and Environmental Impacts Division Research Triangle Park, NC, USA, December 2016.
- Wang, S., Yin, S., Zhang, R., Yang, L., Zhao, Q., Zhang, L., Yan, Q., Jiang, N. and Tang, X. (2019). Insight into the formation of secondary inorganic aerosol based on high-time-resolution data during haze episodes and snowfall periods in Zhengzhou, China. *Sci. Total Environ.* 660: 47–56. <https://doi.org/10.1016/j.scitotenv.2018.12.465>
- Weijers, E.P., Sahan, E., ten Brink, H.M., Schaap, M., Matthijssen, J., Otjes, R.P. and van Arkel, F. (2010). *Contribution of secondary inorganic aerosols to PM₁₀ and PM_{2.5} in the Netherlands; measurement and modelling results.* Netherlands Environmental Assessment Agency, Bilthoven, The Netherlands. <https://www.pbl.nl/en/publications/Contribution-of-secondary-inorganic-aerosols-to-PM10-and-PM2-5-in-the-Netherlands>
- World Health Organization (WHO) (2013). *Health Effects of Particulate Matter. Policy implications for countries in eastern Europe, Caucasus and central Asia*; WHO Regional Office for Europe, Copenhagen, Denmark. <https://www.euro.who.int/en/health-topics/environment-and-health/air-quality/publications/2013/health-effects-of-particulate-matter.-policy-implications-for-countries-in-eastern-europe,-caucasus-and-central-asia-2013>
- Received for review, January 10, 2020*
Revised, June 5, 2020
Accepted, August 5, 2020