

Article

# Characteristics of Carbonaceous Matter in Aerosol from Selected Urban and Rural Areas of Southern Poland

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**Abstract:** The purpose of this study is to obtain a detailed picture of the spatial and seasonal variability of carbonaceous matter in southern Poland. Particulate matter (PM) samples from eight selected urban and rural background sites were analyzed for organic carbon (OC) and elemental carbon (EC) (thermal-optical method, “eusaar\_2” protocol), and the content of secondary (SOC) and primary organic carbon (POC) was estimated. The OC and EC dynamics were further studied using each of the thermally-derived carbon fractions (OC1–4, PC, and EC1–4). Clear spatiotemporal variability of carbonaceous compounds concentrations was observed, with higher levels recorded during the heating season. The considered measurement sites differed particularly in the shares of SOC and POC, with higher values of POC contents especially in rural areas. In terms of the content of carbon fractions, the analyzed sites showed roughly the same characteristics, with PC, OC4, and OC2 as dominant fractions of OC and with clear dominance of EC3 and EC2 over other EC fractions. The results obtained as part of this work may be a valuable source of information about the actual status of the carbonaceous matter, which remains one of the least known components of atmospheric PM.

**Keywords:** carbonaceous matter; thermal-optical analysis; secondary and primary organic carbon; organic and elemental carbon fractions; rural and urban background; southern Poland

## 1. Introduction

Air pollution is currently one of the most serious environmental problems of all developed and developing countries, which affects both urban and rural areas [1–3]. 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. The composition of PM in the atmosphere consists of various chemical species, such as carbonaceous matter, inorganic ions, mineral dust, and sea salt aerosol, as well as trace elements and water [4,5]. Among the abovementioned substances, carbonaceous matter forms a large and often dominant part of PM, accounting for approximately 20–50% of the PM<sub>2.5</sub> mass concentration and somewhat less (20–35%) of PM<sub>10</sub> [6,7]. This proportion may increase even more during episodes of elevated PM concentrations [8–11].

As aerosols contain a complex mixture of organic compounds, their analyses are simplified by measuring the two main parts of the total carbon (TC), i.e., the organic and elemental carbon (OC and EC, respectively). Such a simplification is especially useful when their diurnal trends and long data series are studied [12,13]. The terms EC and BC have often been used loosely and interchangeably in the literature, and the difference between them relates to the analytical method applied to assess their content [14,15]. The term EC is based on thermal methods that allow the separation of EC and OC

from PM samples. BC means soot particles and refers to optical properties of aerosol particles which are determined by means optical methods.

Both EC and OC present in aerosols can originate from almost every thermal process involving carbonaceous matter. Elemental carbon is emitted only as a primary pollutant from incomplete combustion of carbon-based fuels, principally wood used for residential heating and fossil fuels used in transportation, power generation, and industrial processes [16]. In the atmosphere, EC occurs in an inert state; therefore, it can be a direct indicator of the degree of air pollution in urban areas [17]. The OC is mainly composed of primary organic carbon (POC), directly emitted into the air, and secondary organic carbon (SOC), produced in photochemical reactions of its gaseous precursors, including volatile organic compounds (VOCs) [15,18]. The components of OC are very complex and rich in toxic substances [18]. Many of them are known human mutagens and/or carcinogens, e.g., some polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) [13,19].

European Parliament and Council Directive 2008/50/EC requires the monitoring of organic and elemental carbon in PM<sub>2.5</sub> at selected rural background sites from mid-2010 [20]. The monitoring program of the convention on long-range transports of air pollutants (EMEP) also includes the measurement of OC and EC in PM<sub>10</sub> [15]. To determine, quantitatively, the concentrations of OC and EC, a variety of analytical techniques are used [4,14]. Among these, thermal-optical analysis, based on the determination of reflectance (Thermal Optical Reflectance (TOR)) or transmittance (Thermal Optical Transmittance (TOT)), is currently considered as a reference method [15,21,22]. It allows the performance of measurements according to several standard temperature protocols that differ in temperature thresholds, their quantity, and duration. The most commonly used thermal protocols include NIOSH, IMPROVE\_A, and EUSAAR\_2, which are comparable for TC concentrations, but the results vary significantly concerning OC and especially EC concentrations [15,23–25]. It should be mentioned that the EUSAAR\_2 protocol is one candidate for a future standard in Europe and is already in use in the infrastructure initiative called Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS). It enables better separation and determination of thermal OC and EC fractions than that provided by the NIOSH protocol that was often used in Europe previously. The use of lower temperature steps in the He-mode and longer residence times was aimed at the reduction of pyrolysis and at a more complete evolution of OC [21].

In spite of its dominant percentage in PM mass, the carbonaceous matter is not yet well understood [13,26,27]. It is known, however, that this component plays an important role in global processes related to radiative forcing and atmosphere optics, as well as its impact on population health [7,16,28,29]. Although EC represents generally a minor component of total carbon, it is the major absorber of visible light, and a driver of global warming [18,28]. On the other hand, organic carbon can influence visibility degradation and radiative transfer through the atmosphere by both scattering and absorption, depending on functional group composition and mixing with soot particles [30]. In addition, water-soluble organic carbon (WSOC), including dicarboxylic acids, may have a large contribution in cloud-related processes [26,31].

Apart from the climatic and human health reasons, better understanding of chemical characterization of carbonaceous matter is also important for identifying sources of atmospheric aerosols and developing effective prevention and mitigation strategies to protect air quality [7,13]. Many studies have focused on carbonaceous aerosol in recent years and they agreed that TC is the main contributors to PM mass, especially in the atmospheres of highly industrialized areas [32–35]. One of such European hot spots in relation to air quality is the area of southern Poland [36,37]. This region is characterized by a high degree of urbanization and numerous large urban centers—often densely populated and with many industrial plants (e.g., coking plants, mines, and iron foundries)—which contribute to high pollution of all components of the environment [37–39]. The unique position of hard coal as an energy source is the reason for the emission of large amounts of gaseous and particulate pollutants to the atmosphere. A significant threat to air quality is also public and individual transport,

as well as sources of so-called low emissions, especially the burning of fossil fuels and biomass in domestic furnaces and local boiler rooms. All this explains why PM concentrations in southern Poland still remain high compared to many European measurement stations, despite major economic changes in the region over the last three decades [36,40].

With regard to the above considerations, the main goal of this work was to describe the carbonaceous matter characteristics in the atmosphere of the selected measurement sites in southern Poland. The following specific issues were discussed within the study: (1) examination of the OC and EC concentrations, as well as their contributions in PM mass; (2) estimation of the content of secondary and primary organic carbon in PM samples from the considered areas; (3) investigation of the carbon distribution between the OC and EC temperature fractions; (4) assessment of seasonal and spatial variability of analyzed carbon compounds. Based on the obtained data, an additional attempt was made to indicate the possible source origins of carbonaceous matter in PM.

## 2. Methodology

### 2.1. Study Area

The current database of OC and EC measurements includes data collected over the years 2013–2020 at eight measurement sites located in different parts of the southern Poland. Detailed information on measurement campaigns is presented in Table 1, and the geographical location of measurement sites in Figure 1. Of the research locations, four sites represented rural/suburban background conditions, while another four met the requirements for urban background stations [40]. It should also be noted that within both types of sites there were more or less distinct differences in terms of topographical, emission, and land use conditions. Krynica-Zdrój (“Krynica”) is a well-known health resort in Poland situated within the “Beskid Sadecki” mountain range. The measurement site lies on a slope of a mountain valley, adjacent to the city’s residential buildings and the health resort area. Rokitno Szlacheckie (“Rokitno”) is a small village situated near Zawiercie (Silesian Voivodeship), in the area of zinc and lead ores occurrence. The measurement site is located on the territory of a former farm, in an open area. Although it represents typical conditions for rural locations, it may be exposed to influx of urban industrial pollution from other zones of the Silesian Voivodeship. Similar conditions are represented by the measurement site in Złoty Potok, considered to be the regional background point for the Silesian Voivodeship. Its immediate surroundings are meadows, arable fields and forests, and at a distance of ~150 m there is a forester’s lodge and several coal-fired summer houses. The nearest larger areas of low-rise buildings are located within a radius of ~1–1.5 km from the site. The suburban background site in Racibórz (“Racibórz-S”) differs from the others’ rural background sites by a relatively short distance to the city center (~2.5 km). This site is 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). Its direct surroundings are arable fields. The national road no. 45 and the nearest dispersed residential buildings are located ~100–250 m east of the site. Due to its specific location within the Moravian Gate, it is possible to directly investigate the impact of the long-range transport of pollutants from the Czech Republic. There is also an urban background site in Racibórz (“Racibórz-C”), located in the city center, on the territory of an elementary school. Its immediate surroundings are compact urban buildings, roads, and a railway station. Among the remaining urban background locations, Trzebinia and Skawina represent similar characteristics. Trzebinia is an industrial city and is situated at a relatively short distance from large economic centers: Katowice (~36 km) and Cracow (~37 km). The measurement site is located in the eastern part of the city, in close proximity to single-family and multi-family housings. In addition, there are numerous industrial plants within a radius of ~2–5 km from the station, including a refinery, a power plant, and cement and refractory production plants. Skawina is one of the urban centers of the Cracow agglomeration and is located ~13 km from the center of Cracow. The measurement site lies outside the city center, on the territory of the municipal stadium. As in the case of Trzebinia, in its close vicinity (within

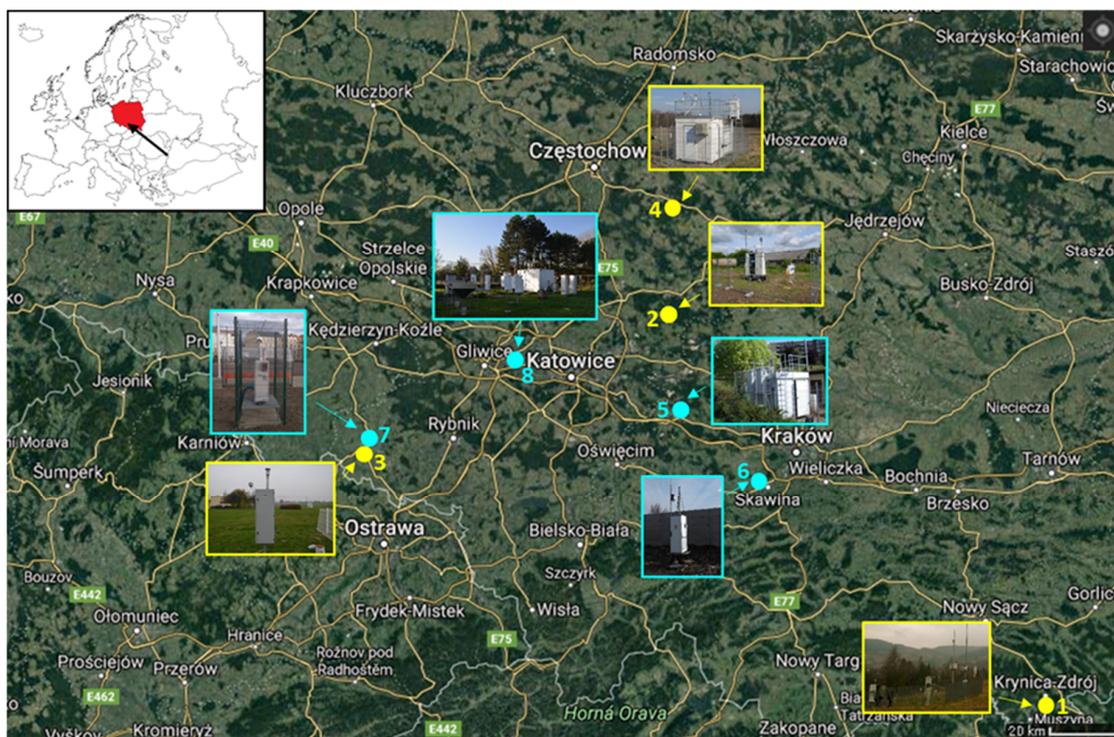
a radius of up to 2 km) there are numerous industrial plants, mainly from the steel industry sector, a power plant, and high-traffic roads. The urban background site in Zabrze lies in the heart of the Upper Silesia Agglomeration, which is densely populated and one of the most industrialized parts of Poland. The measurement site is located on the area belonging to the Institute of Environmental Engineering Polish Academy of Sciences (IEE PAS). The research area is surrounded by a national road with heavy traffic (~500 m north of the site), blocks of flats and houses (~300 m east of the site), and housing estates and allotments (~200 m west of the site). At a distance of ~1 km to the south and south-east of the site there is the center of Zabrze, with residential and commercial buildings.

**Table 1.** General information about measurement campaigns selected for research.

No	Station Name	Coordinates (Latitude, Longitude, Altitude ( <i>h</i> ))	Type of Station	Measurement Period ( <i>n</i> —Number of Samples)	Sampling Equipment	Measured PM Fraction
1	Krynica	49°24'28'' N 20°57'39'' E <i>h</i> = 582 m a.s.l.	rural background	02 January–29 December 2018 ( <i>n</i> = 359)	low-volume sampler PNS-15 (Atmoservice)	PM <sub>10</sub>
2	Rokitno	50°26'9'' N 19°25'29'' E <i>h</i> = 344 m a.s.l.	rural background	01 January–31 December 2019 ( <i>n</i> = 358)	high-volume sampler DHA-80 (Digitel)	PM <sub>10</sub>
3	Racibórz-S	50°3'39'' N 18°11'27'' E <i>h</i> = 203 m a.s.l.	near-city background	01 January–29 December 2019 ( <i>n</i> = 171)	low-volume sampler PNS-15 (Atmoservice)	PM <sub>2.5</sub>
4	Złoty Potok	50°42'39'' N 19°27'32'' E <i>h</i> = 291 m a.s.l.	rural background	01 January–31 March 2013 and 20 April–31 July 2019 ( <i>n</i> = 171)	low-volume sampler PNS-15 (Atmoservice)	PM <sub>2.5</sub>
5	Trzebinia	50°9'4'' N 19°28'39'' E <i>h</i> = 340 m a.s.l.	urban background	01 February–31 March 2013 and 01 May–31 July 2019 ( <i>n</i> = 135)	low-volume sampler μPNS LVS15 (Umwelttechnik MCZ)	PM <sub>2.5</sub>
6	Skawina	49°58'36'' N 19°48'49'' E <i>h</i> = 210 m a.s.l.	urban background	23 February 2019–11 January 2020 ( <i>n</i> = 179)	low-volume sampler μPNS LVS16 (Umwelttechnik MCZ)	PM <sub>10</sub>
7	Racibórz-C	50°5'24'' N 18°12'58'' E <i>h</i> = 190 m a.s.l.	urban background	01 January–31 December 2019 ( <i>n</i> = 179)	low-volume sampler PNS-15 (Atmoservice)	PM <sub>2.5</sub>
8	Zabrze	50°18'53'' N 18°46'17'' E <i>h</i> = 254 m a.s.l.	urban background	01 December 2017–31 March 2018 and 07 May–30 September 2019 ( <i>n</i> = 207 (PM <sub>1</sub> ); <i>n</i> = 257 (PM <sub>2.5</sub> ); <i>n</i> = 227 (PM <sub>10</sub> ))	high-volume sampler DHA-80 (Digitel) *	PM <sub>1</sub> , PM <sub>2.5</sub> , PM <sub>10</sub>

\* In the non-heating season, it is used interchangeably with low-volume samplers: FAI (PM<sub>1</sub>), PNS 15 (PM<sub>2.5</sub>, PM<sub>10</sub>), and Comde-Derenda GmbH (PM<sub>2.5</sub>).

PM samples were taken on a daily basis, which applies to all measurement sites selected for research. In the case of two sites in Racibórz, chemical composition analyzes were carried out for every second sample, hence the lower number of daily samples compared to other stations. The measurement results were averaged over the entire measurement period and in the heating (January–March and October–December) and non-heating (April–August) seasons. The adopted division, commonly used in the literature, was primarily dictated by differences in air temperatures and the resulting difference in energy demand and its consumption, which in turn contributes to the observed seasonal variability of the concentrations of PM and related components [9,37,42]. The measurement period usually covered a calendar year; in some cases it was shorter (Skawina, Trzebinia, Złoty Potok, and Zabrze). In relation to the Trzebinia and Złoty Potok, the measurements were part of a research and development project which aimed to analyze the concentration and percentage of the PM<sub>2.5</sub> main chemical components (carbonaceous matter and water-soluble ions) [3,37]. This paper presents only data on carbon compounds, including the concentrations and shares of OC and EC temperature fractions.



**Figure 1.** Location of the study area and measurement stations (1–8 in figure) selected for research. Source: Google Maps; photos: own collection and [41].

Daily PM samples were collected with the use of low- or high-volume samplers (see Table 1), equipped with sampling heads enabling the collection of PM<sub>1</sub> (Zabrze), PM<sub>2.5</sub> (Racibórz-S, Racibórz-C, Złoty Potok, and Zabrze) or PM<sub>10</sub> (Krynica, Rokitno, Skawina, and Zabrze) fractions. PM was collected on quartz fiber filters (Whatman QMA<sup>®</sup>) with a diameter of 47 mm (low-volume samplers) or 150 mm (high-volume samplers). A discussion of the methodology for determining PM concentrations and concentrations of carbonaceous compounds is provided in Section 2.2.

## 2.2. Analytical Procedures

The PM mass concentrations were obtained via the gravimetric method [43,44], with the use of Mettler Toledo (resolution 2 µg) and Sartorius (resolution, 100 µg) balances, respectively, for PM samples from low- and high-volume samplers. Conditioning, weighing, and storage of both non-exposed and exposed filters were conducted in the weighing room. The conditions in this room are regulated by an air conditioning device as well as humidity regulators (humidifier and dryer). This allows working to always be performed in similar conditions of temperature (20 ± 1 °C) and relative humidity (50 ± 5% RH). After weighing, the filters were prepared for chemical composition analysis. One section of 1.0 cm<sup>2</sup> was cut from each PM daily sample, which was submitted for analysis of organic and elemental carbon content. The remaining filter surface was stored in a refrigerator in marked Petri dishes and analyzed for other chemical components which were not the subject of this study. Only daily samples for which the measurement time was not less than 75% of the day were subjected to chemical analysis.

Measurements of OC and EC were performed using thermal-optical transmittance analysis (TOT), by means of carbon analyzer from Sunset Laboratory Inc. with flame ionization detection (FID). In TOT analysis, the carbonaceous material contained in PM samples collected on quartz-fiber filters evolves thermally under different temperature steps according to a prescribed temperature protocol. First, by the gradual heating of the sample (1.0 cm<sup>2</sup> sections of the quartz filters) in the helium stream, the organic carbon is released from the filter. In the next step, the filter section is heated in an oxidizing

helium-oxygen mixture to release elemental carbon. The compounds separated from the sample during the subsequent steps are quantitatively converted to CO<sub>2</sub> in an oxidizer oven with MnO<sub>2</sub> catalyst. The CO<sub>2</sub> produced during the analysis, in the presence of hydrogen and nickel catalyst, is reduced to methane, the amount of which is measured by a flame ionization detector. During the first stage of the analysis, there are some organic compounds that are converted to elemental carbon. This pyrolytic conversion is continuously monitored by measuring the transmission of a laser beam through the filter and automatically corrected. In addition to regular split point determination for the pyrolytic carbon (PC), there are many other steps to ensure an accurate determination of the EC and OC concentrations, such as: (a) regular analysis of blank filters; (b) periodic analysis of a calibration (control) sample of glucose solution of known concentration; (c) the use of auto-calibration of the apparatus (the inclusion of a fixed volume loop used to inject an external standard (Air Liquide) at the end of each analysis); (d) periodic analysis of certified reference material manufactured by NIST (RM 8785 NIST and RM 8786 NIST) with known carbon content (recovery of 90–102% and 98–124% was obtained, respectively, for organic and elemental carbon); (e) participation in inter-laboratory tests.

In this study, the analysis was performed using the “eusaar\_2” protocol (Table 2), which has been developed as a proposed standard method for European monitoring stations under the European Supersites for Atmospheric Aerosol Research (EUSAAR) project [21,22]. In total, nine temperature-resolved carbon fractions are provided: four organic carbons (OC1–4), four elemental carbons (EC1–4), and the pyrolytic carbon (PC). Total OC is operationally defined as:

$$\text{OC} = \text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{PC}, \quad (1)$$

total EC is defined as:

$$\text{EC} = \text{EC1} + \text{EC2} + \text{EC3} + \text{EC4} - \text{PC}, \quad (2)$$

and the total carbon concentration (TC) is the sum of OC and EC.

**Table 2.** Parameters of the analysis according with the EUSAAR 2 protocol. (OC1–4: four organic carbons, EC1–4: four elemental carbons).

Phase/Gas Stream	Temperature (°C)	Time (s)	Carbon Fraction
He	200	120	OC1
He	300	150	OC2
He	450	180	OC3
He	650	180	OC4
He/O <sub>2</sub>	500	120	EC1
He/O <sub>2</sub>	550	120	EC2
He/O <sub>2</sub>	700	70	EC3
He/O <sub>2</sub>	850	80	EC4

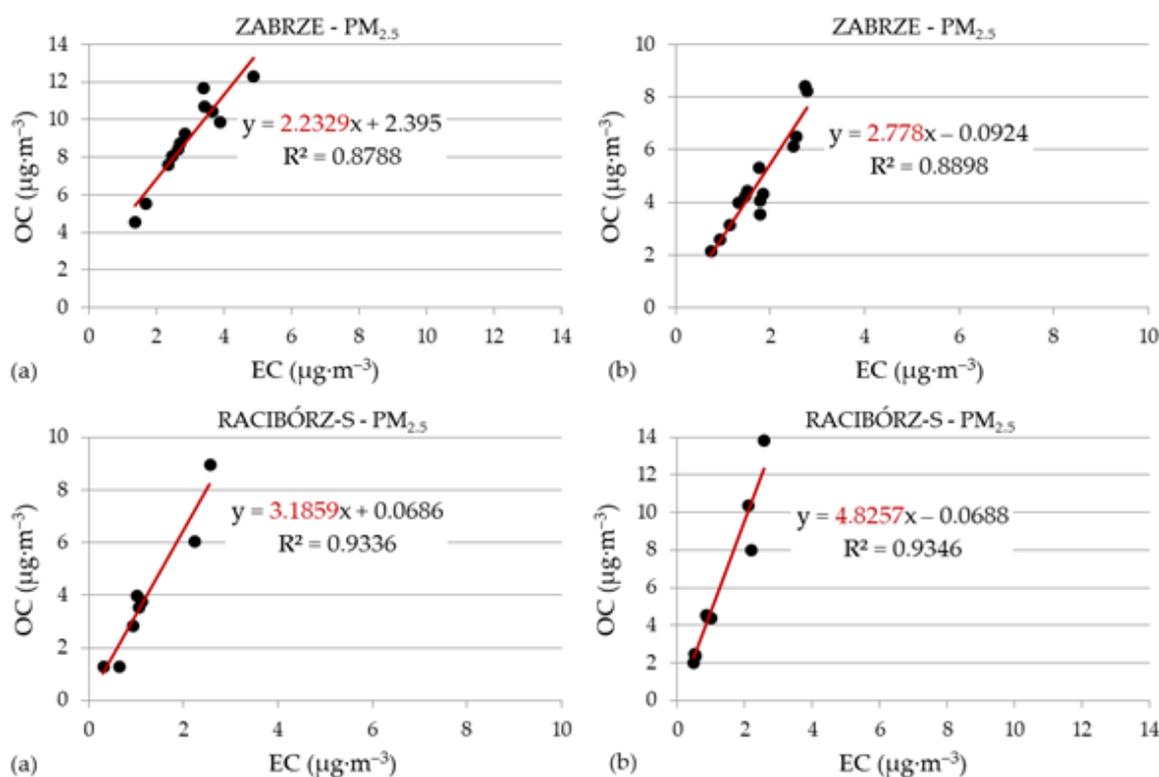
Based on measured OC and EC concentrations, a preliminary assessment of SOC and POC content in PM samples from each measurement site was made. It should be noted here that the quantitative estimation of the share of primary and secondary organic carbon associated with the aerosol is very difficult because there is no direct method of chemical analysis of SOC and POC concentrations [27,45,46]. Several indirect methods have been developed, among which the most common and the simplest method remains the use of EC as an indicator for POC (the so-called EC-tracer method) [47]. However, it requires meeting a number of conditions, including stability of relative contributions of primary carbonaceous sources to aerosol load in time and space. In addition, PM samples contaminated with wood burning emissions should be rejected in the calculation, because this type of emission source can have a significant impact on the OC/EC ratios. No such correction was performed within this work,

and to estimate the SOC and POC concentrations, the methodology used in the earlier work of the authors [37,48,49] was adopted—Equations (3) and (4):

$$\text{POC} = \text{EC} \cdot (\text{OC}/\text{EC})_{\text{pri}}, \quad (3)$$

$$\text{SOC} = \text{OC} - \text{POC}, \quad (4)$$

where  $(\text{OC}/\text{EC})_{\text{pri}}$  is the ratio of primary organic carbon to elemental carbon. To estimate the value of  $(\text{OC}/\text{EC})_{\text{pri}}$  ratio, a minimum slope method was applied, consisting of analyzing the correlation between OC and EC concentrations (Figure 2). Linear regression was performed for 10% of the samples with the lowest OC/EC ratio because, according to literature data [50,51], the value of the determination coefficient for this range of data will represent the impact of POC emission sources. In the present study, due to large discrepancies between the heating and non-heating seasons, the  $(\text{OC}/\text{EC})_{\text{pri}}$  ratios were determined separately for these periods. The only exceptions are the measurement sites in Trzebinia and Złoty Potok, where due to the relatively lower number of samples, the data set from the entire measuring period was used.



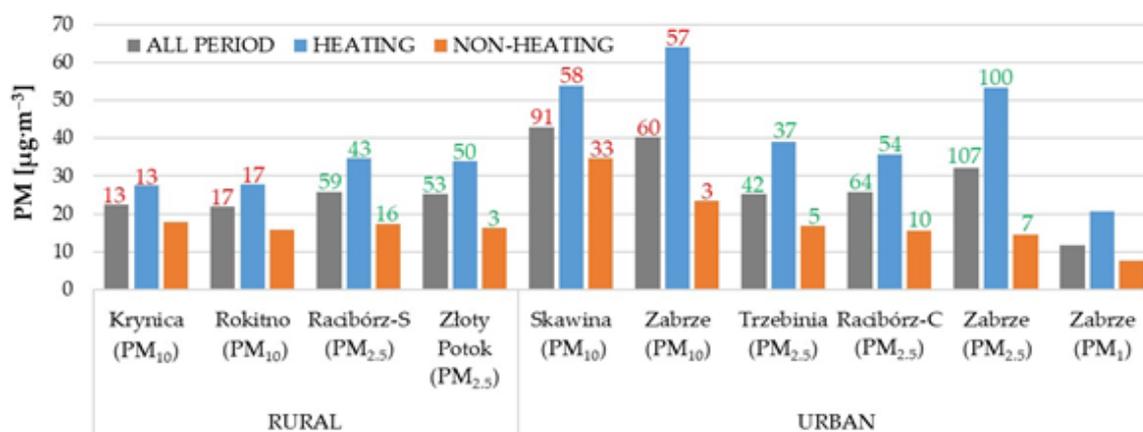
**Figure 2.** Linear relationship between OC and EC, taking into account 10% of the samples with the lowest values of the OC/EC ratio (measurement sites in Zabrze (PM<sub>2.5</sub>) and Racibórz-S (PM<sub>2.5</sub>)). (a) heating season; (b) non-heating season.

### 3. Results and Discussion

#### 3.1. Spatiotemporal Variations of the PM Mass Concentrations

Comparison of average PM concentrations recorded at measurement sites selected for research is presented in Figure 3, together with the frequency of exceeding the normative values for average daily concentrations. Among the rural background sites, the lowest PM concentrations were recorded in Rokitno (PM<sub>10</sub>) and Krynica (PM<sub>10</sub>) and they were on average (all period) 21.94 and 22.52  $\mu\text{g}\cdot\text{m}^{-3}$ , respectively. The number of exceedances of the limit value for the average daily PM<sub>10</sub> concentration ( $50 \mu\text{g}\cdot\text{m}^{-3}$ ) [20] at these sites was lower than 35, and therefore the air quality standards were not

violated. Interestingly, the PM concentrations observed in Racibórz-S and Złoty Potok were higher, although the measurements concerned the fine PM fraction. This indicates that the problem of air pollution with fine particulate matter was much more serious in these sites. Consequently, the average concentration of  $PM_{2.5}$  at these sites, taking into account the entire measurement period ( $25.73$  and  $25.16 \mu\text{g}\cdot\text{m}^{-3}$ , respectively), slightly exceeded the limit value for the average annual concentration of  $PM_{2.5}$  ( $25 \mu\text{g}\cdot\text{m}^{-3}$ ) [20]. Both in Racibórz and Złoty Potok, there was also a relatively high (>50 days) frequency of exceeding the value recommended by the WHO for the average daily concentration of  $PM_{2.5}$  ( $25 \mu\text{g}\cdot\text{m}^{-3}$ ) [52].



**Figure 3.** Average concentrations of PM from considered rural and urban background stations. The numbers above each bar symbolize the number of exceedances of the limit value for the average daily  $PM_{10}$  concentration [20] (red) and the recommended value for the average daily  $PM_{2.5}$  concentration [52] (green). Designations: ALL—all periods; H—heating season; NH—non-heating season.

Particulate matter concentrations recorded at the considered urban background sites were generally higher compared to the values recorded at rural background sites, which is consistent with the literature data [3]. Apart from the obvious reason of a much higher aggregation of emission sources, the compact development of urban areas largely hinders horizontal air ventilation [53,54], which has an undeniable impact on air quality. However, it should be noted that the average concentration of  $PM_{2.5}$  (all periods) in Trzebinia and Racibórz-C was comparable to the rural background sites in Racibórz and Złoty Potok. This demonstrates the high level of regional background for the area of southern Poland, which was mentioned in Ref [9,36,37].

The highest concentrations of  $PM_{2.5}$  were observed in Zabrze and they averaged  $32.21 \mu\text{g}\cdot\text{m}^{-3}$ . This site also recorded a very high frequency of exceeding the WHO recommended value for the average daily  $PM_{2.5}$  concentration of up to 107 days.  $PM_{2.5}$  was a significant part of the  $PM_{10}$ , with the average  $PM_{2.5}/PM_{10}$  ratio of 0.80 (all periods); however, higher values were recorded in the heating season (0.83, on average), compared to the non-heating one (0.62, on average). The  $PM_1$  fraction constituted a small part of the  $PM_{2.5}$  (36%, all periods, on average). This is not unusual because the finest PM particles have a dominant share in the PM number concentration, while their share in the total aerosol mass is often very small [55,56]. The ratios of  $PM_1/PM_{2.5}$  slightly increased during the non-heating season, which may be related to the intensive processes of secondary aerosol formation during this period [57,58]. The average concentration of  $PM_{10}$  in Zabrze (all periods) was  $40.38 \mu\text{g}\cdot\text{m}^{-3}$ , slightly less than in Skawina ( $42.96 \mu\text{g}\cdot\text{m}^{-3}$ ). It can be seen that the limit value for the average daily  $PM_{10}$  concentration has not been met at both stations, as well as the permissible frequency of exceeding the daily standard for  $PM_{10}$  [20]. Both the Zabrze and Skawina sites are located in a highly industrialized and densely populated area, and therefore, although they are official urban background sites, they may be under the influence of specific conditions resulting from traffic emissions and plume of urban-industrial pollution coming from other areas of the city.

Regardless of the site characteristics (urban/rural) and the measured PM fraction, there is a clear trend regarding the seasonal variability of particulate matter concentrations. For all stations, higher PM levels were recorded during the heating season compared to the non-heating one. These differences can be attributed to the emission situation in the cold season, including increased activity of local emission sources and a set of adverse meteorological conditions (e.g., lower wind speeds and mixing heights and frequent temperature inversions), which impede the dispersion and removal of pollutants [27,36]. Periodically occurring episodes of elevated concentrations of PM are characteristic for the climatic conditions of Poland and in cases of so-called large smog episodes; their range also includes areas with low building intensity [9]. The seasonal difference is generally more noticeable in the case of smaller fractions: PM<sub>2.5</sub> and PM<sub>1</sub> and urban background locations. For example, the ratio of average seasonal PM<sub>2.5</sub> concentrations (heating/non-heating) in Zabrze was ~3.7, while in Racibórz-S, this was ~2.0. For comparison, the same ratio for PM<sub>10</sub> in Krynica and Skawina was about ~1.6. Attention is drawn to the high PM<sub>10</sub> concentrations recorded at the latter site in the non-heating season (average: 34.60 µg·m<sup>-3</sup>), which indicated that mobile and industrial sources, as well as resuspension of road dust, could play an important role in air pollution by PM [8,27,35].

### 3.2. Concentrations and Contributions of OC and EC

The average concentration of the analyzed carbon compounds, throughout the entire measuring period and divided into the heating and non-heating seasons, is presented in Tables 3 and 4, respectively, for the rural and urban background sites. The obtained results are illustrated graphically in Figures 4 and 5, showing the course of the EC and OC concentration time series (with distinction of SOC and POC). The average shares of EC, SOC, and POC in the PM mass at individual measurement sites are shown in Figures 6 and 7.

In the case of rural background sites, the average TC concentration (all periods) ranged from 7.45 µg·m<sup>-3</sup> (Krynica, PM<sub>10</sub>) to 10.20 µg·m<sup>-3</sup> (Racibórz-S, PM<sub>2.5</sub>). At urban background sites, the average TC concentration reached values in the range of 5.64 µg·m<sup>-3</sup> (Zabrze, PM<sub>1</sub>) to 18.19 µg·m<sup>-3</sup> (Zabrze, PM<sub>10</sub>). Therefore, data collected in the frame of this work showed a large variation in carbonaceous aerosol concentrations in southern Poland, although some general regularities can also be seen. First of all, it should be noted that the TC concentrations recorded in the considered areas remained high compared to the values observed at many European stations, e.g., (a) in Czech Republic: Prague (urban background) (TC = 7.76 µg·m<sup>-3</sup> (heating season) and 3.93 µg·m<sup>-3</sup> (non-heating season)) and Košetice (rural background) (TC = 5.13 µg·m<sup>-3</sup> (heating season) and 3.50 µg·m<sup>-3</sup> (non-heating season)) [23]; (b) in France: Paris (TC = 5.13 and 3.40 µg·m<sup>-3</sup>, urban and suburban background, respectively) [59]; (c) in Hungary: K-Pusztá (rural background) (TC = 5.09 µg·m<sup>-3</sup>) [60] and Budapest (urban background) (TC = 7.46 µg·m<sup>-3</sup>) [61]; (d) in Italy: Venice (urban background) (TC = 5.80 µg·m<sup>-3</sup>) [62] and Monte Martano (rural background) (TC = 2.48 µg·m<sup>-3</sup>) [63].

Similar to the PM mass concentrations, higher concentrations of carbonaceous compounds were generally recorded at urban background locations. For example, the average TC concentration (all periods) at the Racibórz-C site (12.23 µg·m<sup>-3</sup>) was higher than the TC concentration recorded at the Racibórz-S site (10.20 µg·m<sup>-3</sup>), located at a distance of ~3 km. Spatial differences in TC concentrations were also observed for the PM<sub>10</sub> fraction, as evidenced by the results obtained at the measurement sites in Skawina (TC = 14.52 µg·m<sup>-3</sup>) and Zabrze (TC = 18.19 µg·m<sup>-3</sup>) as well as in Krynica (TC = 7.90 µg·m<sup>-3</sup>) and Rokitno (TC = 9.17 µg·m<sup>-3</sup>). It should be noted that the TC concentrations recorded at rural background sites in Złoty Potok and Racibórz-S were comparable to the values obtained in Trzebinia. This indicates that air pollution by PM and PM-related carbon compounds can be a significant problem not only in cities but also in rural areas, which are often considered less polluted in terms of air quality [37,64,65].

**Table 3.** Average concentrations of carbonaceous compounds ( $\mu\text{g}\cdot\text{m}^{-3}$ ), along with the average values of the OC/EC ratio at considered rural background sites.

Period	Measurement Site	OC	EC	TC	OC/EC	SOC	POC
All period	Krynica (PM <sub>10</sub> )	6.51 ± 4.69	0.94 ± 0.74	7.45 ± 5.34	7.90 ± 3.68	2.54 ± 2.54	3.97 ± 2.99
	Rokitno (PM <sub>10</sub> )	7.89 ± 5.96	1.28 ± 0.82	9.17 ± 6.71	6.30 ± 1.92	2.70 ± 3.37	5.19 ± 3.28
	Racibórz-S (PM <sub>2.5</sub> )	8.96 ± 9.84	1.25 ± 1.15	10.20 ± 10.88	7.50 ± 3.12	4.40 ± 6.96	4.56 ± 3.74
	Złoty Potok (PM <sub>2.5</sub> )	8.59 ± 6.97	1.48 ± 1.19	10.07 ± 8.12	5.88 ± 1.15	3.30 ± 3.06	5.29 ± 4.28
Heating season	Krynica (PM <sub>10</sub> )	8.85 ± 5.70	1.39 ± 0.83	10.23 ± 6.41	6.38 ± 1.60	3.16 ± 3.31	5.69 ± 3.39
	Rokitno (PM <sub>10</sub> )	10.95 ± 6.90	1.77 ± 0.83	12.71 ± 7.63	5.98 ± 1.80	3.86 ± 4.32	7.09 ± 3.37
	Racibórz-S (PM <sub>2.5</sub> )	13.16 ± 12.59	1.81 ± 1.34	14.98 ± 13.77	6.67 ± 2.43	7.41 ± 9.10	5.76 ± 4.29
	Złoty Potok (PM <sub>2.5</sub> )	12.69 ± 7.88	2.17 ± 1.35	14.86 ± 9.18	5.85 ± 1.06	4.90 ± 3.60	7.78 ± 4.85
Non-heating season	Krynica (PM <sub>10</sub> )	4.24 ± 1.18	0.51 ± 0.20	4.75 ± 1.27	9.37 ± 4.46	1.94 ± 1.17	2.30 ± 0.88
	Rokitno (PM <sub>10</sub> )	4.73 ± 1.88	0.78 ± 0.40	5.51 ± 2.22	6.63 ± 1.99	1.50 ± 1.01	3.24 ± 1.61
	Racibórz-S (PM <sub>2.5</sub> )	5.08 ± 3.11	0.72 ± 0.58	5.80 ± 3.66	8.26 ± 3.49	1.62 ± 1.04	3.46 ± 2.74
	Złoty Potok (PM <sub>2.5</sub> )	4.49 ± 1.23	0.79 ± 0.26	5.27 ± 1.42	5.92 ± 1.23	1.69 ± 0.82	2.80 ± 0.89

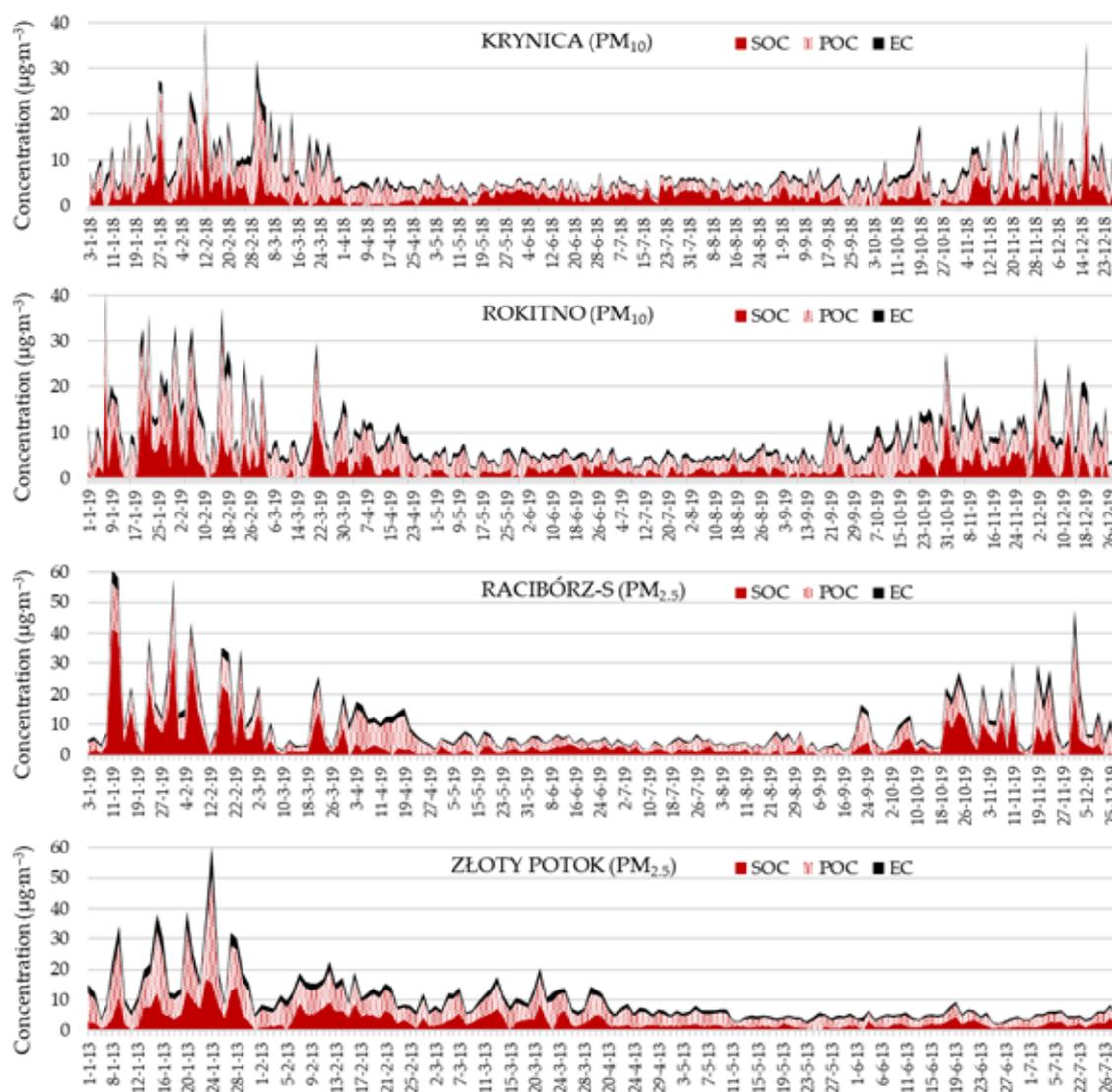
**Table 4.** Average concentrations of carbonaceous compounds ( $\mu\text{g}\cdot\text{m}^{-3}$ ), along with the average values of the OC/EC ratio at considered urban background sites.

Period	Measurement Site	OC	EC	TC	OC/EC	SOC	POC
All period	Skawina (PM <sub>10</sub> )	12.09 ± 10.50	2.43 ± 1.51	14.52 ± 11.80	4.87 ± 1.66	5.60 ± 7.32	6.49 ± 4.08
	Zabrze (PM <sub>10</sub> )	15.57 ± 17.76	2.62 ± 1.96	18.19 ± 19.46	5.50 ± 2.35	8.88 ± 14.00	6.69 ± 4.71
	Trzebinia (PM <sub>2.5</sub> )	8.60 ± 6.73	2.21 ± 2.90	10.81 ± 8.60	4.37 ± 1.35	7.12 ± 5.96	1.48 ± 1.93
	Racibórz-C (PM <sub>2.5</sub> )	10.62 ± 10.36	1.61 ± 1.20	12.23 ± 11.36	6.51 ± 3.06	5.94 ± 7.72	4.67 ± 3.57
	Zabrze (PM <sub>2.5</sub> )	13.19 ± 13.78	2.38 ± 1.89	15.57 ± 15.47	5.29 ± 2.06	7.59 ± 10.41	5.60 ± 4.07
	Zabrze (PM <sub>1</sub> )	4.60 ± 4.23	1.05 ± 0.93	5.64 ± 5.09	4.91 ± 1.74	1.73 ± 2.13	2.87 ± 2.51
Heating season	Skawina (PM <sub>10</sub> )	18.14 ± 13.24	3.28 ± 1.52	21.43 ± 14.58	5.10 ± 1.94	9.26 ± 9.86	8.88 ± 4.15
	Zabrze (PM <sub>10</sub> )	28.85 ± 21.03	4.31 ± 1.81	33.16 ± 22.47	6.27 ± 2.62	18.28 ± 17.75	10.57 ± 4.44
	Trzebinia (PM <sub>2.5</sub> )	15.39 ± 6.53	3.97 ± 4.15	19.35 ± 8.61	4.82 ± 1.35	12.74 ± 6.39	2.65 ± 2.77
	Racibórz-C (PM <sub>2.5</sub> )	15.84 ± 12.32	2.27 ± 1.30	18.11 ± 13.30	6.84 ± 3.75	9.15 ± 9.78	6.69 ± 3.86
	Zabrze (PM <sub>2.5</sub> )	23.63 ± 14.61	3.98 ± 1.64	27.61 ± 15.92	5.74 ± 2.28	14.75 ± 11.98	8.89 ± 3.66
	Zabrze (PM <sub>1</sub> )	8.62 ± 5.86	1.96 ± 1.14	10.59 ± 6.90	4.37 ± 1.08	3.29 ± 3.33	5.34 ± 3.09
Non-heating season	Skawina (PM <sub>10</sub> )	7.46 ± 3.34	1.77 ± 1.13	9.23 ± 4.37	4.69 ± 1.39	2.79 ± 1.49	4.66 ± 2.93
	Zabrze (PM <sub>10</sub> )	6.01 ± 2.64	1.41 ± 0.84	7.41 ± 3.40	4.94 ± 1.96	2.10 ± 1.20	3.90 ± 2.33
	Trzebinia (PM <sub>2.5</sub> )	4.48 ± 1.40	1.15 ± 0.38	5.63 ± 1.64	4.09 ± 1.28	3.71 ± 1.27	0.77 ± 0.25
	Racibórz-C (PM <sub>2.5</sub> )	5.33 ± 2.76	0.94 ± 0.55	6.27 ± 3.24	6.19 ± 2.14	2.70 ± 1.64	2.63 ± 1.52
	Zabrze (PM <sub>2.5</sub> )	4.47 ± 1.82	1.04 ± 0.60	5.50 ± 2.33	4.90 ± 1.79	1.62 ± 1.01	2.85 ± 1.63
	Zabrze (PM <sub>1</sub> )	2.88 ± 1.03	0.65 ± 0.40	3.53 ± 1.39	5.14 ± 1.91	1.06 ± 0.56	1.82 ± 1.11

Organic and elemental carbon were relevant species both in fine and coarse particulate matter. Due to the parallel measurements of PM<sub>1</sub>, PM<sub>2.5</sub>, and PM<sub>10</sub> concentrations in Zabrze, the distribution of carbonaceous material in various fractions of particulate matter could be examined. It was found that both OC and EC were mostly in the fine mode fraction, as evidenced by the OC<sub>PM2.5</sub>/OC<sub>PM10</sub> and ECP<sub>M2.5</sub>/EC<sub>PM10</sub> ratios, slightly higher in the heating season (0.82 and 0.92, respectively) compared to the non-heating one (0.74 for both ratios). OC and EC in PM<sub>1</sub> constituted only a small part of PM<sub>2.5</sub> mass, although the OC<sub>PM1</sub>/OC<sub>PM2.5</sub> and EC<sub>PM1</sub>/EC<sub>PM2.5</sub> ratios increased significantly during the non-heating season (on average, 0.64 and 0.63, respectively), which may suggest the impact of traffic emission sources and the importance of secondary aerosol formation processes [8,57,66].

Regardless of the type of the site and the measured PM fraction, the highest concentrations of carbonaceous compounds were always recorded during the heating season, when the maximum TC concentrations reached ~40  $\mu\text{g}\cdot\text{m}^{-3}$  (PM<sub>10</sub>, Rokitno and Krynica), ~61  $\mu\text{g}\cdot\text{m}^{-3}$  (PM<sub>2.5</sub>, Racibórz-S, Złoty Potok) (Figure 4), and in the case of urban background stations, ~43  $\mu\text{g}\cdot\text{m}^{-3}$  (Zabrze-PM<sub>1</sub>, Trzebinia-PM<sub>2.5</sub>), ~64  $\mu\text{g}\cdot\text{m}^{-3}$  (Racibórz-C, PM<sub>2.5</sub>), ~80  $\mu\text{g}\cdot\text{m}^{-3}$  (Skawina, PM<sub>10</sub>), ~90  $\mu\text{g}\cdot\text{m}^{-3}$  (Zabrze-PM<sub>2.5</sub>), and even ~116  $\mu\text{g}\cdot\text{m}^{-3}$  (Zabrze-PM<sub>10</sub>) (Figure 5). The results obtained are consistent with the literature data on the relatively regular occurrence of very unfavorable air quality conditions at the beginning and end of the year [2,35,36]. Seasonal variability concerned both organic and elemental carbon; however, more pronounced seasonal fluctuations were observed in urban areas, similar to PM mass concentrations; therefore, the OC and EC concentrations in PM<sub>2.5</sub> from Zabrze was, respectively, ~5.3 and ~3.8 times higher in the heating season, compared to the non-heating one. In the case of the PM<sub>10</sub> fraction, this difference was smaller, but still relatively high (on average, ~4.8 (OC) and ~3.1 (EC) times higher concentrations during the heating season). For comparison, the ratio of average seasonal

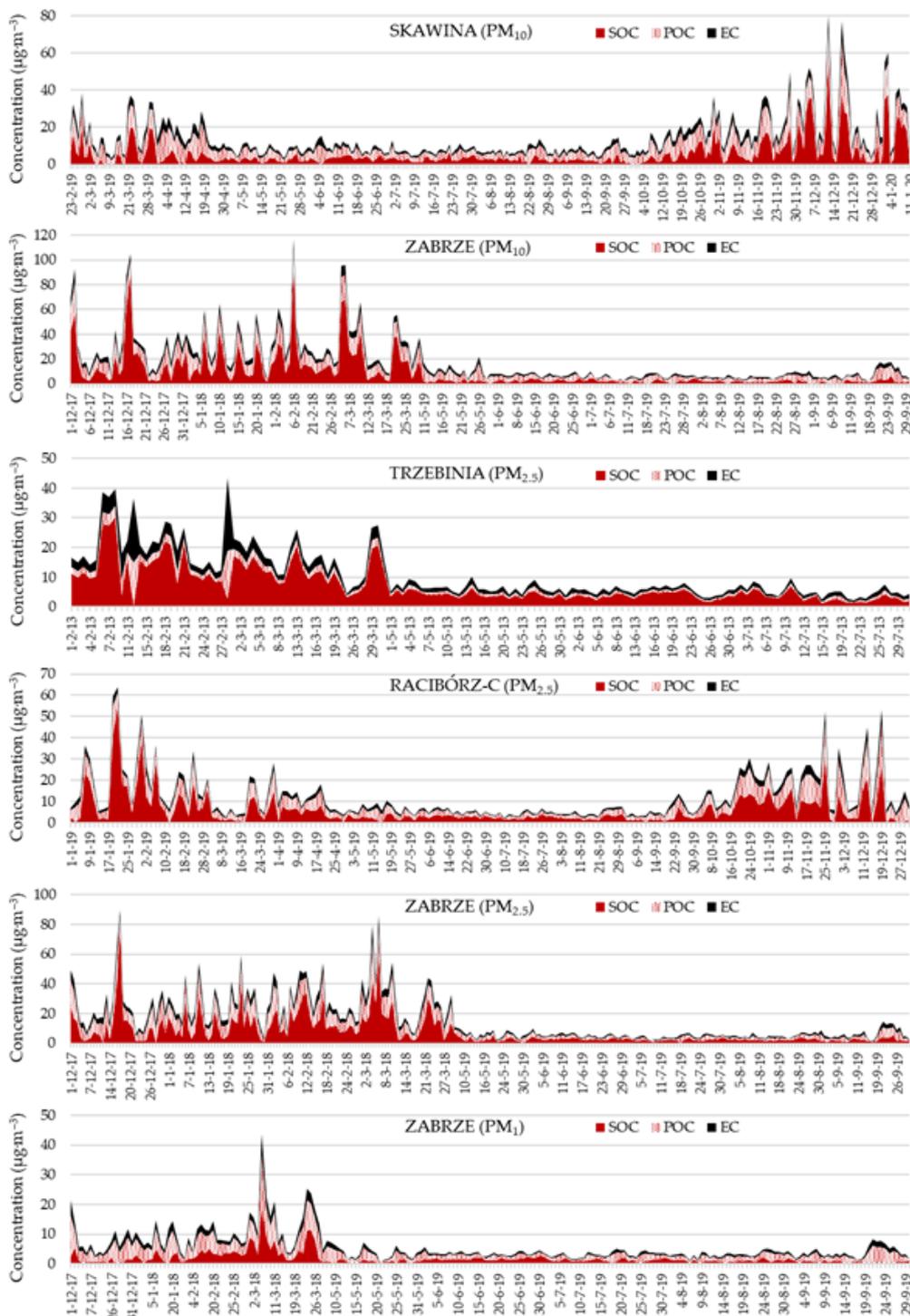
OC and EC (heating/non-heating) concentrations at the Racibórz-S site was 2.59 and 2.51, respectively, and at the Krynica site, 2.08 and 2.72, respectively.



**Figure 4.** Time series of daily averaged concentrations of SOC, POC and EC ( $\mu\text{g}\cdot\text{m}^{-3}$ ) at considered rural background sites.

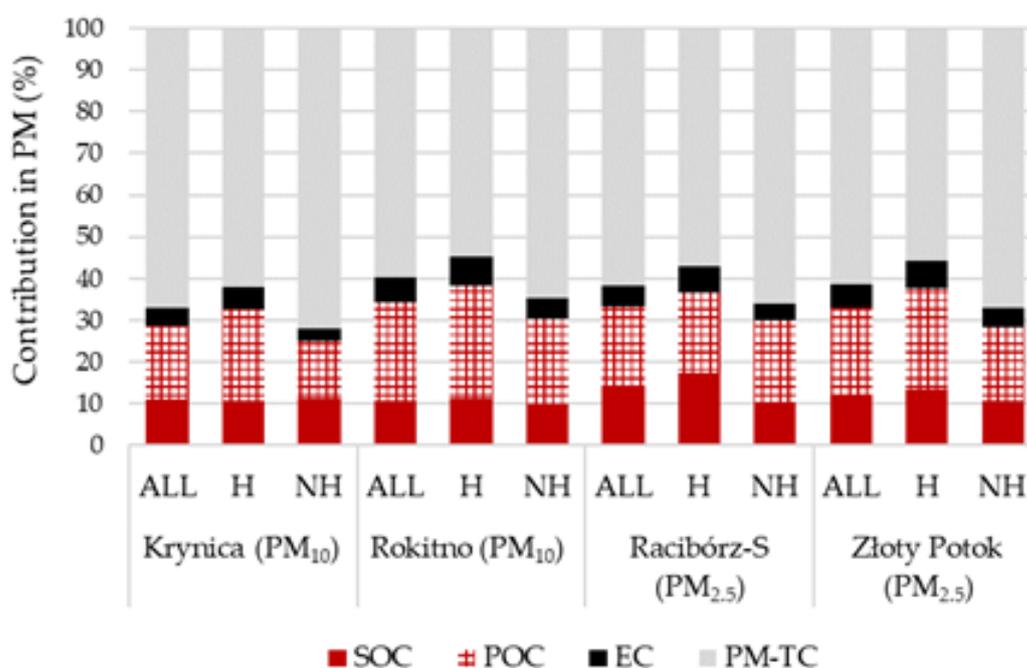
Both in the heating and non-heating seasons, organic carbon clearly dominated over elemental carbon, which applied to all measurement sites and all PM fractions. The high dominance of organic carbon and potential formation of secondary organic aerosol (SOA) are also demonstrated by high values of the OC/EC ratio (Tables 3 and 4). Considering the entire measurement period, the average OC/EC ratios ranged from 4.37 (Trzebinia,  $\text{PM}_{2.5}$ ) to 7.90 (Krynica,  $\text{PM}_{10}$ ) and were generally higher in rural areas. This indicates that in such locations, coal and biomass combustion has a major impact on air pollution with carbonaceous aerosol, while in urban areas, the more intense interaction of traffic sources (vehicle exhaust) may explain the lower values of the OC/EC ratio [46,67,68]. Both types of sites also differed in seasonal variability of the OC/EC ratios. For all rural locations, higher OC/EC ratios were recorded in the non-heating season, and the best example is the measurement site in Krynica, with average OC/EC ratios of 6.38 (heating season) and 9.37 (non-heating season). On the contrary, at most urban background sites, higher OC/EC ratios were observed in the heating season, and the largest seasonal differences were recorded at the urban background site in Zabrze for the  $\text{PM}_{10}$ , with average

OC/EC ratios of 6.27 (heating season) and 4.94 (non-heating season). The significant impact of local emission sources together with adverse meteorological conditions mean that the intensity of SOA formation processes in urban areas is generally higher during the heating season [32,36,69]. The only exception is the PM<sub>1</sub> in Zabrze, when slightly higher OC/EC ratios occurred in the non-heating season (average: 5.14) compared to heating one (4.37).

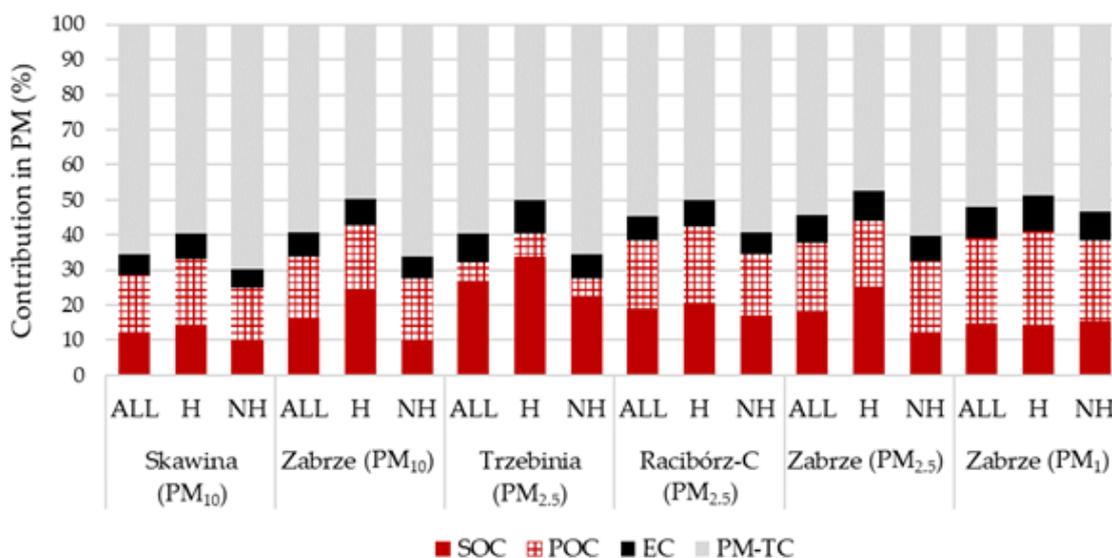


**Figure 5.** Time series of daily averaged concentrations of SOC, POC and EC ( $\mu\text{g}\cdot\text{m}^{-3}$ ) at considered urban background sites.

The obtained results showed that the fluctuations in daily EC and OC concentrations (Figures 4 and 5) can strongly influence the variability of PM concentrations, which has a direct impact on the share of these components in the total mass of PM (Figures 6 and 7). The average TC share in PM (all periods) ranged from ~33% (Krynica, PM<sub>10</sub>) to ~40% (Rokitno, PM<sub>10</sub>) (rural background) (Figure 6) and from ~35% (Skawina, PM<sub>10</sub>) up to ~48% (Zabrze, PM<sub>1</sub>) (urban background) (Figure 7). The contribution of TC in PM was primarily determined by fluctuations in the OC share, which generally accounted for over 30% of the PM mass, except for the measurement sites in Krynica and Skawina. The highest shares of OC in PM occurred in the heating season and ranged from ~33% (Krynica, PM<sub>10</sub>) to ~39% (Rokitno, PM<sub>10</sub>) (rural background) and from ~33% (Skawina, PM<sub>10</sub>) to ~44% (Zabrze, PM<sub>2.5</sub>) (urban background). In the non-heating season, the share of OC decreased on average up to ~25% (Krynica, PM<sub>10</sub> and Skawina, PM<sub>10</sub>); relatively high values of the OC/PM ratio compared to the other sites in this period were recorded in Zabrze (PM<sub>1</sub>, ~38%) and at two sites in Racibórz (~30% and ~35%, rural and urban background, respectively). High OC shares in PM during the autumn and winter months may result from high emissions of organic carbon compounds from the combustion of fossil fuels and biomass, the intensity of which increases during this period due to low air temperatures [26,36,70]. On the other hand, the relatively high share of OC in PM recorded during the non-heating season indicates that biological matter and secondary organic aerosol could also be important sources of organic matter [34,57,71].



**Figure 6.** Average contributions of carbonaceous compounds (EC, SO, POC) in PM mass (%) at considered rural background sites.



**Figure 7.** Average contributions of carbonaceous compounds (EC, SO, POC) in PM mass (%) at considered urban background sites.

Variations in the OC/PM ratio at all measurement sites were accompanied by changes in the EC/PM ratio. The EC share in PM was lower at rural background sites, where it reached average values (all periods) in the range of ~4% (Krynica, PM<sub>10</sub>) to ~6% (Rokitno, PM<sub>10</sub>; Złoty Potok, PM<sub>2.5</sub>) (Figure 6). At urban background sites, the EC share in PM ranged from ~6% (Skawina, PM<sub>10</sub>) to ~9% (Zabrze, PM<sub>1</sub>) (Figure 7). Seasonal variability of the EC/PM ratio was less pronounced than in the OC/PM ratio, although slightly higher values were recorded in the heating season at all sites, with the maximum for Zabrze (PM<sub>1</sub>) and Trzebinia (PM<sub>2.5</sub>) (on average, ~10%). Due to the relatively uniform share of traffic emissions during the year, which are the main source of EC, the observed seasonal variation of the EC/PM ratio should be associated with the presence of an additional source of elemental carbon in winter—combustion of fuels for heating purposes [37,62].

### 3.3. Assessment of Secondary and Primary Carbon Content

Research carried out as part of this work showed that the analyzed measurement sites differed particularly in the content of secondary and primary organic carbon. The average SOC concentrations throughout the entire measurement period ranged from 2.54  $\mu\text{g}\cdot\text{m}^{-3}$  (Krynica, PM<sub>10</sub>) to 4.40  $\mu\text{g}\cdot\text{m}^{-3}$  (Racibórz-S, PM<sub>2.5</sub>) (rural background) (Table 3) and from 1.73  $\mu\text{g}\cdot\text{m}^{-3}$  (Zabrze, PM<sub>1</sub>) to 8.88  $\mu\text{g}\cdot\text{m}^{-3}$  (Zabrze, PM<sub>10</sub>) (urban background) (Table 4). Average POC concentrations (all periods) ranged from 3.97  $\mu\text{g}\cdot\text{m}^{-3}$  (Krynica, PM<sub>10</sub>) to 5.29  $\mu\text{g}\cdot\text{m}^{-3}$  (Złoty Potok, PM<sub>2.5</sub>) (rural background) and from 1.48  $\mu\text{g}\cdot\text{m}^{-3}$  (Trzebinia, PM<sub>2.5</sub>) up to 6.69  $\mu\text{g}\cdot\text{m}^{-3}$  (Zabrze, PM<sub>10</sub>) (urban background). SOC and POC concentrations showed characteristic spatial and seasonal fluctuations that were consistent with fluctuations in PM, EC, and total OC concentrations. In order to investigate the differences between the measurement sites more thoroughly, the authors focused on analyzing the share of SOC and POC in the PM mass, including the assessment of its seasonal variability.

The obtained results showed that POC usually dominated over SOC, especially in rural background areas. The low share of SOC in this case could be due to the impact of regional and long-range transport processes that could be responsible for the high value of the  $(\text{OC}/\text{EC})_{\text{pri}}$  ratio used to assess the share of SOC and POC in PM [63]. The largest differences between the content of POC and SOC were observed in Rokitno (PM<sub>10</sub>), where the POC share was higher than SOC by ~13% (on average). The disproportion between POC and SOC content generally increased during the heating season, except for the Racibórz-S site, where the POC/PM<sub>2.5</sub> ratio remained relatively constant throughout the entire measurement period (on average: ~19%). As indicated by numerous literature data [57,64,71],

an occasional increase in the concentrations of PM and related carbon compounds in rural areas—often far away from large emission sources—is most often attributed to the influx of particles from more polluted areas. An equally important reason for the high TC content in PM is the combustion of fossil fuels in local sources, especially intense in the winter season [7,12,64,72]. It should be noted that in addition to hard coal, large amounts of biomass and lower-quality fuels are often burned in local heating stoves, and in extreme cases, plastics or other waste materials [37,64]. These processes often generate large amounts of primary organic matter, which lead to an increase in the POC share in atmospheric particles [73–75]. On the other hand, abundant vegetation in rural areas releases significant amounts of primary biological matter (e.g., fungal spores, plant debris, and plant waxes) and is a source of hydrocarbon emissions, especially during the warm period [76,77]. This could explain the high content of POC in the air of Zloty Potok and Racibórz during the non-heating season.

Higher shares of POC than SOC in PM were also identified in urban areas and a good example is the measurement site in Skawina, with average values of POC/PM<sub>10</sub> and SOC/PM<sub>10</sub> ratios (all period) at the level of ~17% and ~12%, respectively. The lower secondary formation is consistent with the high impact of primary sources at this site (Section 2.1). Among the considered urban areas, in Skawina, the lowest share of SOC in PM was observed (on average, ~12%); this share was higher in the heating season, however the difference between the content of POC and SOC in PM<sub>10</sub> remained stable in both seasons (~5%). Conversely, the disproportion between POC and SOC was more pronounced in the case of PM<sub>1</sub> in Zabrze, with average values of the POC/PM<sub>1</sub> and SOC/PM<sub>1</sub> ratios (all period) of ~24% and ~15%, respectively. It could confirm the important role of traffic emissions as a source of POC and PM<sub>1</sub>. Here, the dominance of POC over SOC also increased during the heating season, when the conditions of dispersion of pollutants are particularly unfavorable [27,36].

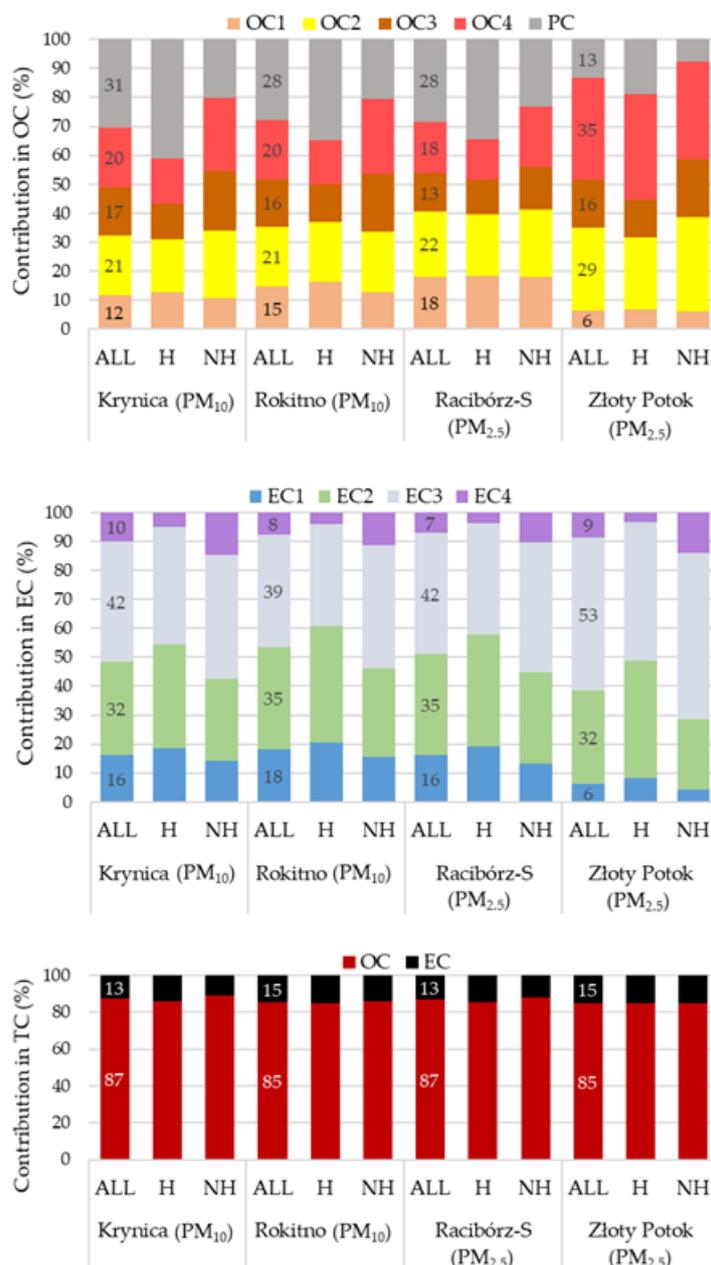
Interestingly, in relation to the PM<sub>2.5</sub> and PM<sub>10</sub> fractions measured in Zabrze, the situation was more complex. Considering the entire measurement period, the POC share was only slightly higher compared to SOC, with average values of ~20% and ~18% (PM<sub>2.5</sub>) and ~18% and ~16% (PM<sub>10</sub>), respectively. The dominance of POC over SOC was due to the high POC shares recorded in the non-heating season, which were higher (on average) by ~8% (PM<sub>2.5</sub>) and ~7% (PM<sub>10</sub>) than the SOC share. It could suggest an important role of local communication sources in air pollution by carbonaceous matter [15,24,27]. On the contrary, in the heating season the importance of secondary aerosol formation increased, as evidenced by the high SOC shares in PM<sub>2.5</sub> and PM<sub>10</sub> of ~25% and ~24%, respectively; for comparison, the POC shares in this period were ~19% (both fractions).

Comparable shares of SOC and POC in PM<sub>2.5</sub> were observed at the urban background site in Racibórz, with higher values recorded in the heating season (average ~20%) compared to non-heating one (~17%). In turn, the measurement station in Trzebinia stood out from the other urban sites with a very clear dominance of SOC over POC and the highest values of the SOC/PM<sub>2.5</sub> ratio, which were on average ~34% (heating season) and ~23% (non-heating season). This fact should be explained by the location conditions of measurement site, especially the close proximity of municipal emission sources that will have a dominant impact on air quality (see Section 2.1). Seasonal variation, although less pronounced, was also found for the POC share, with average values of ~6% and ~5%, respectively, in the heating and non-heating season.

It should be noted that conditions favorable to the formation of SOC (i.e., high air temperature, high wind speeds, and high intensity of solar radiation) persist in the non-heating season and determine the greater share of SOC in OC and PM [27,37,57]; examples include the measurement sites in Krynica (PM<sub>10</sub>) and Zabrze (PM<sub>1</sub>). The reasons for the increased share of SOC in the heating season should be primarily attributed to the significantly increased emission of SOC precursors in this period from numerous anthropogenic sources, especially municipal emissions. In addition, stable atmospheric conditions in winter (low air temperatures and stagnation of air masses) lead to a shift in the balance of VOC transformations towards the solid phase (associated with PM), which may explain the high SOC content in PM, recorded in various areas at this time of the year [27,76].

### 3.4. The Profile of the Carbon Fractions

In order to further analyze the carbonaceous matter characteristics at the measurement sites selected for research, the contents of the nine carbon temperature fractions were statistically analyzed. The spatial and seasonal variability of these components was assessed and, based on the obtained information and literature studies, an attempt was made to identify the possible origin sources of the analyzed temperature fractions. It should be noted here that the above carbon fractions are widely recognized as so-called fingerprints of emission sources and they were often used in research on PM source apportionment [15,18,23,24,78,79].



**Figure 8.** Profiles of nine temperature fractions against the share of OC and EC in total TC at the considered rural background sites.

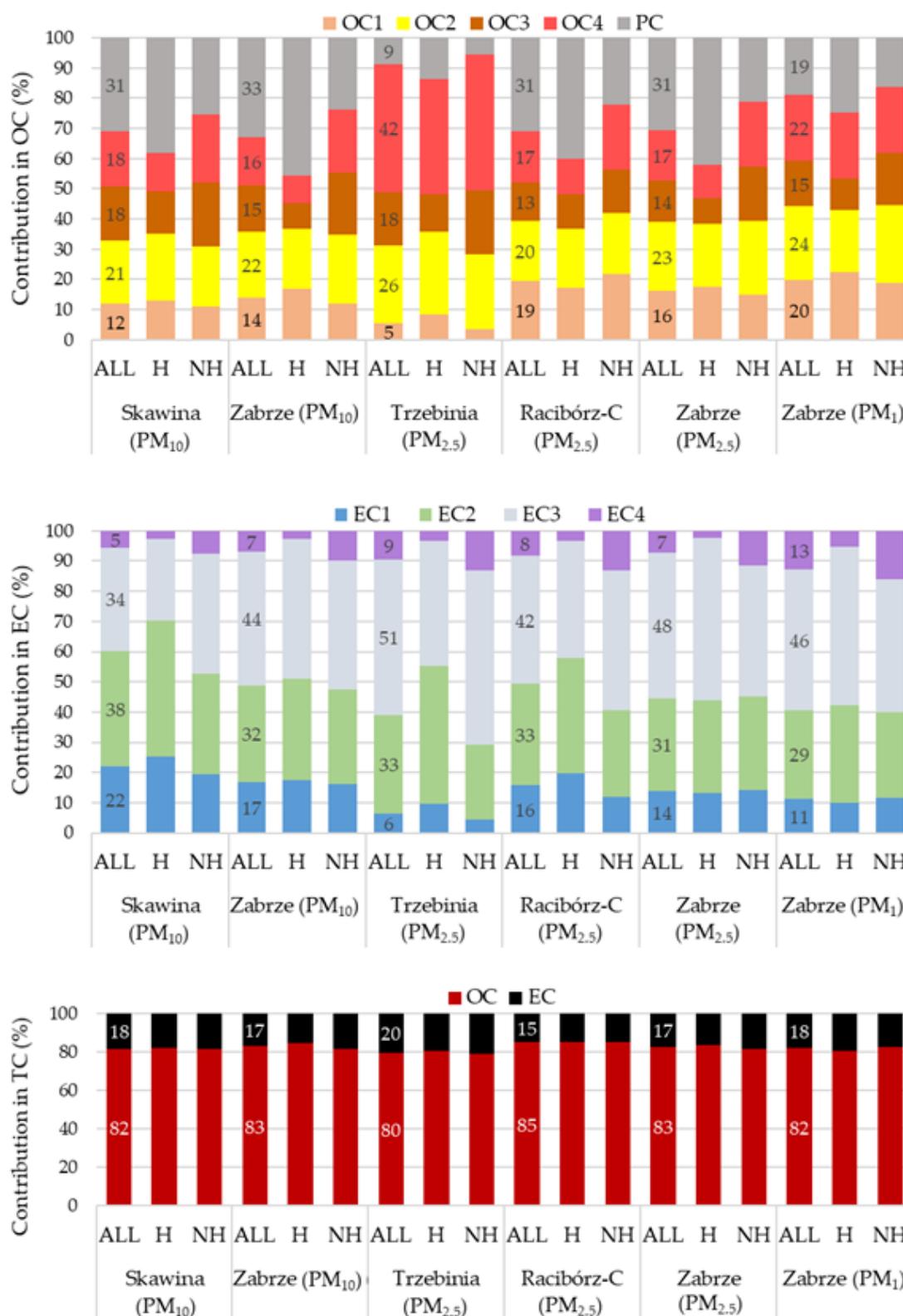


Figure 9. Profiles of nine temperature fractions against the share of OC and EC in total TC at the considered urban background sites.

The results presented in Figures 8 and 9 (rural and urban background, respectively) relate to the average shares of OC1–OC4 and PC in total OC (top), and average shares of EC1–EC4 in total EC

(center), against the average shares of OC and EC in total TC (down). Average values ( $\pm$  standard deviation) of the concentrations of all nine temperature fractions over the three averaging periods are shown in Table S1 and Table S2 in the Supplementary Materials.

In terms of the content of carbonaceous compounds, the considered sites showed roughly the same characteristics (Figures 8 and 9), so the composition of atmospheric pollution sources could be similar. Some differences were determined by location conditions, measured PM fraction, and season of the year. At all sites, OC constituted the dominant part of the TC (Section 3.2). Slightly higher OC shares were recorded in rural background locations, where average shares did not fall below 85%, reaching a maximum of 89% (Krynica, PM<sub>10</sub>, non-heating season). They were also relatively more uniform throughout the year compared to the urban background sites, where the average OC/TC shares ranged from 79% (Trzebinia, PM<sub>2.5</sub>, non-heating season) to 85% (Racibórz-C, PM<sub>2.5</sub>, at all averaging periods; Zabrze, PM<sub>10</sub>, heating season). For comparison, the EC share in TC was generally higher in urban areas, with average values ranging from 15% to 21%. In rural areas, the EC/TC ratio did not exceed 15% and was generally higher during the heating season, unlike most urban sites.

The research revealed that regardless of the location, the PC, followed by OC4 and OC2, was the dominant organic carbon fraction. In relation to rural background sites, the average share of PC in OC (all periods) ranged from ~13% (Złoty Potok, PM<sub>2.5</sub>) to ~31% (Krynica, PM<sub>10</sub>). At urban background sites, the diversity of PC shares was even more evident. The measurement site in Trzebinia with the lowest PC/OC ratio (on average, ~9%, all periods) stood out in particular. A relatively low share of PC in OC was recorded in Zabrze (PM<sub>1</sub>), which was on average (all periods) ~19%. Regardless of spatial differences, clearly higher PC shares in OC were observed in the heating season, which applied to all urban and rural background sites. Seasonal differences sometimes reached up to ~21–22% (Zabrze, PM<sub>2.5</sub>, and PM<sub>10</sub>, respectively) and seemed to be more visible in the case of the PM<sub>10</sub> fraction. An example could be the rural background site in Krynica, with average PC/OC ratios of ~41% (heating season) and ~20% (non-heating season). It should be noted that the PC fraction was often shown to be a main part of analyzed OC at various measurement stations in Europe, as described by, e.g., [73] and [80]. Source apportionment analyses connect PC mainly with water soluble organic carbon (WSOC), the main sources of which are residential heating, including biomass burning, and secondary organic aerosol [23,24]. This explains the high PC shares in OC recorded in both periods of the year, especially during the heating season, when the SOC shares in PM were also high (see Section 3.3).

The values of the OC4/OC ratio were relatively uniform, especially in rural areas, and for most sites they were on average (all periods) ~18–20% (rural background) and ~16–22% (urban background). The exceptions were two sites with very high average OC4 shares in OC: Złoty Potok (~35%, all periods) and Trzebinia (~42%, all periods). Seasonal variability of the OC4/OC ratio was generally consistent for all the considered sites, with higher values recorded in the non-heating season, except for the sites in Złoty Potok (PM<sub>2.5</sub>) and Zabrze (PM<sub>1</sub>). Similar seasonal fluctuations were also observed for the OC3 fraction, with smaller contributions and average shares (all periods) of ~13–17% (rural background) and ~13–18% (urban background). The relatively small spatial fluctuations between the sites may suggest that the OC3 and OC4 fractions could have a more regional or long-range transport origin [23], which is generally confirmed by the higher shares of these fractions in the non-heating season. Moreover, the high fractions of OC3 and OC4 were also associated with the impact of emissions from wood and coal combustion [81,82], which could explain the results observed in Złoty Potok. In turn, in some works [82,83], it was suggested that OC3 and OC4 are the main components of road dust and gasoline vehicle exhausts, which may be supported by a lack of clear seasonal variability of OC3/OC and OC4/OC ratios at the urban background site in Zabrze (all PM fractions).

The share of the OC2 fraction was generally comparable or slightly higher compared to the OC4, except for the measurement site in Trzebinia (PM<sub>2.5</sub>) and Złoty Potok (PM<sub>2.5</sub>). In relation to rural areas, the OC2/OC ratios amounted on average (all periods) to ~21–29% and were generally higher in the non-heating season, except for the site in Rokitno (PM<sub>10</sub>), with comparable values in both seasons. Similar shares of OC2 in OC were recorded at urban background sites, with average

values (all periods) of ~20–26%, although these sites differed in seasonal variation of the OC2/OC ratio. Sites located in close proximity to industrial emission sources—Trzebinia (PM<sub>2.5</sub>) and Skawina (PM<sub>10</sub>)—were characterized by slightly higher OC2/OC ratios during the heating season. In Racibórz-C site, there was no clear seasonal variability of the OC2/OC ratio, while in Zabrze (all PM fractions), a higher share of OC2/OC was recorded in the non-heating season, similar to that recorded at the rural background sites. In contrast to OC2 and OC3, the shares of OC1 in OC differed between the analyzed areas, from low levels, as in Trzebinia (average ~5%, all periods), to high shares in the case of the PM<sub>1</sub> in Zabrze (average ~20%, all periods). Spatial variability was also observed at rural background sites with average values of the OC1/OC ratio at the level of (all periods) ~6–18%. Higher OC1/OC ratios at all analyzed sites were found during the heating season, except for Racibórz-C, where the OC1 share in OC was ~5% higher in the non-heating season. The presence of the most volatile OC fractions was often attributed to the coal and/or biomass combustion factor [18,84] and was also associated with emissions from incinerators and/or oil combustion [85]. These sources support observed seasonal variability of the OC1/OC ratio. Moreover, the high shares of the OC2 and OC1 fractions was often observed in fresh vehicle exhaust and at poor dilution conditions [24,79], which in turn would explain the relatively high shares of OC1 in OC in Zabrze (PM<sub>1</sub>). It was generally found that high OC1/OC ratios, accompanied by high PC/OC ratios, suggest a significant interaction of local emission sources [23]. However, the behavior of the OC2 fraction (less visible spatial variations) in both urban and rural areas may indicate that it is of a more regional origin or can be subjected to long-range transport.

To further investigate the origin (primary/secondary) of the organic carbon fractions in the considered rural and urban areas, non-parametric Spearman correlation analysis ( $\alpha = 0.05$ ) was conducted between the concentrations of OC1–4, PC and the concentrations of EC and SOC. The results are presented in Table 5, separately for the data sets from the heating and non-heating season, due to the different emission specificity of these periods. As can be seen, in the heating season, most of the considered fractions present a very high positive correlation with SOC and EC; this applies to both urban and rural areas. It should be noted that during this period, when all emission sources are active, it is difficult to clearly distinguish the source of origin of the studied temperature fractions. More information can be obtained from the correlation analysis in the non-heating season, when, due to a very clear decline in the activity of fossil fuel combustion in local sources, it is possible to capture the impact of other sources such as communication as well as regional and long-range transport processes. For example, at the measurement site in Krynica (PM<sub>10</sub>), a general lack of strong relationships with EC and the presence of high correlation with SOC (especially OC2 and OC3 fractions) probably indicate that there was a significantly larger fraction of transported secondary aerosols or aged aerosols. The same may apply to the urban background site in Trzebinia; however, the OC4 fraction strongly correlated with EC, indicating its primary origin. The fact that the PC fraction does not correlate with EC suggests a secondary nature from potentially biogenic and/or anthropogenic sources [79]. On the other hand, in Rokitno, Skawina, and Zabrze (PM<sub>2.5</sub> and PM<sub>10</sub>) all distinguished temperature fractions correlated more strongly with EC, with the maximum  $r$  values for the fractions OC2 (0.70–0.79) and OC4 (Skawina) (0.72). This could indicate the prevailing presence of primary sources in the vicinity of the sites. At two measurement sites in Racibórz, positive relations with EC and SOC were maintained for all considered temperature fractions. Interestingly, in the case of rural background (Racibórz-S), temperature fractions correlated more strongly with EC, with the highest  $r$  values for OC1 (0.71), OC4 (0.81), and PC (0.87). This shows that these fractions are linked to well-processed primary aerosols from vehicular sources. On the contrary, at the urban background site (Racibórz-C), the OC1, OC2 and OC3 fractions strongly correlated with SOC ( $r = 0.74$ – $0.81$ ), suggesting that they are secondarily formed from anthropogenic gaseous precursors [23]. A very high positive correlation was noted between PC and EC ( $r = 0.81$ ), which indicates that the main source of the origin of PC at this site is vehicular emissions. The same was observed at the urban background site in Zabrze for the finest fraction of particulate matter (PM<sub>1</sub>) ( $r = 0.79$ ).

**Table 5.** Results of nonparametric (Spearman) correlation analysis ( $\alpha = 0.05$ ) between concentrations of OC1–4 and PC fractions and concentrations of SOC and EC.

Specification		Krynica					Rokitno				
		OC1	OC2	OC3	OC4	PC	OC1	OC2	OC3	OC4	PC
Heating	SOC	0.72	0.73	0.65	0.58	0.79	0.82	0.83	0.71	0.40	0.85
	EC	0.89	0.89	0.84	0.79	0.87	0.84	0.88	0.78	0.55	0.80
Non-heating	SOC	0.60	0.83	0.73		0.53		0.40			
	EC						0.68	0.70	0.51	0.66	0.64
Specification		Racibórz-S					Złoty Potok				
Heating	SOC	0.94	0.90	0.90	0.83	0.92	0.85	0.84	0.84	0.82	0.85
	EC	0.91	0.95	0.92	0.75	0.92	0.88	0.93	0.90	0.66	0.82
Non-heating	SOC	0.66	0.64	0.59	0.40	0.45	0.47	0.72	0.64	0.50	
	EC	0.71	0.69	0.67	0.81	0.87		0.63	0.50	0.84	0.45
Specification		Skawina					Zabrze (PM <sub>10</sub> )				
Heating	SOC	0.91	0.95	0.91	0.56	0.96	0.95	0.93	0.94	0.64	0.95
	EC	0.85	0.89	0.88	0.63	0.87	0.85	0.90	0.97	0.47	0.84
Non-heating	SOC		0.49	0.52		0.53	0.42	0.44	0.48		
	EC	0.59	0.79	0.59	0.72	0.57	0.69	0.77	0.62	0.51	0.64
Specification		Trzebinia					Racibórz-C				
Heating	SOC	0.83	0.74	0.83	0.81	0.86	0.93	0.88	0.86	0.73	0.89
	EC	0.51	0.90	0.75	0.76		0.75	0.87	0.81	0.49	0.78
Non-heating	SOC		0.85	0.81		0.60	0.74	0.79	0.81	0.63	0.65
	EC				0.74		0.64	0.70	0.59	0.61	0.81
Specification		Zabrze (PM <sub>2.5</sub> )					Zabrze (PM <sub>1</sub> )				
Heating	SOC	0.92	0.94	0.96	0.62	0.97	0.76	0.74	0.80	0.80	0.74
	EC	0.83	0.89	0.87	0.47	0.82	0.88	0.93	0.87	0.78	0.80
Non-heating	SOC	0.48	0.47	0.50	0.42					0.43	
	EC	0.53	0.70	0.59	0.45	0.69	0.49	0.66	0.66	0.49	0.79

Note: only correlation coefficients higher than 0.40 are indicated in the table; correlation coefficients higher than 0.70 are highlighted in gray.

Relatively few papers have raised the issue of the share of individual EC fractions in total EC or TC, probably due to methodological reasons. The total EC concentration, as given in Section 2.2, is the sum of the EC1–EC4 concentrations decreased by the concentration of PC. However, based on simple mathematical calculations, the authors estimated the profile of EC for all considered measurement sites, and the results are presented in Figures 8 and 9. As can be seen, both in urban and rural areas, EC3 clearly dominated in the total EC, followed by EC2. The shares of EC1 and EC4 were generally lower and, at both types of sites, often showed more pronounced spatial variations.

Individual EC fractions also differed in seasonal variability. Considering first the shares of EC1 and EC2, these were usually higher in the heating season, compared to the non-heating one. The only exceptions were PM<sub>1</sub> and PM<sub>2.5</sub> in Zabrze, with slightly higher shares of EC1 in EC recorded during the spring–summer months and comparable values of the EC2/OC ratio (PM<sub>2.5</sub>) in both seasons. Seasonal differences were less visible for the urban areas and EC1 fraction (max ~6%), while in the case of EC2 they reached up to ~17% (Złoty Potok, PM<sub>2.5</sub>). The average values of the EC1/EC ratio (all periods) ranged from ~5% (Złoty Potok, PM<sub>2.5</sub>) to ~18% (Rokitno, PM<sub>10</sub>) (rural background) and from ~5% (Trzebinia, PM<sub>2.5</sub>) up to ~22% (Skawina, PM<sub>10</sub>) (urban background). Interestingly the shares of EC2 in EC were more uniform and in rural areas these amounted to (all periods) ~32–35%. For most of the urban sites, quite lower values of the EC2/EC ratio were recorded, which ranged, on average (all periods), from ~29% (Zabrze, PM<sub>1</sub>) to ~33% (PM<sub>2.5</sub> in Trzebinia and Racibórz-C), except for the site in Skawina, with the highest share of EC2 in EC (~38%, on average).

In contrast to EC1 and EC2, at all rural background sites, the higher shares of the dominant EC fraction—EC3—were observed in the non-heating season. The average EC3/EC ratio in these types of areas was generally ~39–42% (all periods); however, it was very high at the measurement site in

Złoty Potok (on average, ~53%, all periods). In the cases of the considered urban areas, the average shares of EC3 in EC ranged from ~34% (Skawina, PM<sub>10</sub>) to ~51% (Trzebinia, PM<sub>2.5</sub>). The seasonal variability of the EC3/EC ratio was more diverse compared to the rural background sites. In Zabrze (all measured PM fractions), higher values of the EC3/EC ratio were recorded in the heating season, with seasonal differences being more visible for the smaller fractions (PM<sub>1</sub>, PM<sub>2.5</sub>). At the remaining urban background sites, clearly higher EC3 shares in the EC were recorded in the non-heating season. The EC4 shares in EC were generally lower compared to other EC fractions and were on average from ~7% (Racibórz-S, PM<sub>2.5</sub>) to ~10% (Krynica, PM<sub>10</sub>) (rural background) and from ~5% (Skawina, PM<sub>2.5</sub>) to ~13% (Zabrze, PM<sub>1</sub>) (urban background). Higher values of the EC4/EC ratio were observed in the non-heating season at all measurement sites, similarly as that observed in the case of the EC3/EC ratio.

It should be noted that the interpretation of the sources of the EC fractions is not a simple task, and literature studies have often given conflicting results. An additional and significant difficulty in interpreting the research results may be the use of different temperature protocols in thermal-optical analysis. For example, the clear dominance of the EC2 and EC3 fractions could indicate that the important pollution sources in analyzed areas were diesel vehicle exhaust, while gasoline exhaust emissions contributed less to carbonaceous aerosol in the air [18]. In other papers, it was pointed out that diesel emissions were identified based on the high contribution of high-temperature components of EC (EC3, EC4) [86,87]. In turn, in [32] it was also noted that gasoline emissions could also be responsible for high shares of the EC1–EC3 fractions. Despite these discrepancies, research studies generally agree that higher values of every EC temperature fraction are identified at the direct vehicular impacted sites [24,32,76]. This does not quite correspond to the results obtained in this study, as the EC temperature fraction profile was similar in rural and urban background sites. Higher shares of individual temperature fractions recorded in the non-heating season may support the influence of traffic emission sources. In this period, the impact of industrial emissions, which are responsible for relatively high EC4 contributions compared to other sources [83], could also be more apparent. On the other hand, high contents of EC2 and EC3 were also identified in emissions from coal combustion [83], which could be more explained by the high EC2/EC and EC3/EC ratios observed in the analyzed rural areas.

To examine the similarity between EC and OC emission sources, correlations between the concentrations of EC fractions and OC were compared (Spearman rank correlation,  $\alpha = 0.05$ ) (Table 6). Moreover, the relationship of the measured EC fractions with nitric oxide (NO), which is a better indicator of communication emissions than NO<sub>x</sub> (nitrogen oxides) and NO<sub>2</sub> (nitrogen dioxide) [88], was also examined. It was found that both during the heating and non-heating season, at all measurement sites, most of the EC fractions showed very strong positive relationships with organic carbon, thus indicating that these constituents had one or more co-genetic sources. The only exception was the EC4 fraction, in which concentrations were relatively lower (see Table S1). Particularly strong relations of the analyzed EC fractions were recorded in Racibórz (both rural and urban background sites) and Rokitno. Interestingly, strong relationships also maintained during the non-heating season, which pointed to the fact that in this period, emissions of EC are caused mainly by a local source (traffic). On the contrary, during this period the weaker relationships between EC fractions and OC were recorded in Trzebinia, which indicates a significant impact of secondary organic aerosol formation processes at this site. Among all EC fractions, usually the strongest relations with OC in the non-heating season were recorded for the dominant EC3 fraction, and further EC2, and the examples can be urban background sites in Skawina and Zabrze (all PM fractions).

As expected, in the case of the considered rural background sites, relatively strong relations with NO were recorded only in Rokitno (fractions EC1 and EC2, heating season) and in Złoty Potok. However, during the non-heating season, which is a more meaningful period for assessing the impact of traffic emissions, strong relations were maintained only in the latter site, and concerned the EC2 and EC3 fractions. For most urban background sites, all EC fractions generally showed a strong positive correlation with NO during the heating period, and the exceptions concerned only the EC4

fraction. In the spring and summer months, the situation was much more diverse. With respect to the measurement sites in Trzebinia and Skawina, vehicle exhaust emissions could be a source of EC3 and EC2 fractions, respectively. At the urban background site in Racibórz, moderately positive correlations were observed for all EC fractions. In the case of the measurement site in Zabrze, relatively strong positive relationships with OC were identified for EC1, EC2, and EC3 fractions, and the highest values of the correlation coefficient were found for the PM<sub>2.5</sub>.

**Table 6.** Results of nonparametric (Spearman) correlation analysis ( $\alpha = 0.05$ ) between concentrations of EC1-4 and PC fractions and concentrations of OC and NO.

Specification		Krynica				Rokitno			
		EC1	EC2	EC3	EC4	EC1	EC2	EC3	EC4
Heating	OC	0.94	0.98	0.95	0.51	0.93	0.94	0.93	0.72
	NO					0.46	0.47		
Non-heating	OC	0.68	0.74	0.78	0.42	0.85	0.85	0.86	0.45
	NO								
Specification		Racibórz-S				Złoty Potok			
		EC1	EC2	EC3	EC4	EC1	EC2	EC3	EC4
Heating	OC	0.97	0.97	0.96	0.80	0.93	0.94	0.94	
	NO					0.58	0.58	0.52	0.62
Non-heating	OC	0.92	0.92	0.91	0.71	0.64	0.65	0.67	0.55
	NO					0.52	0.61		
Specification		Skawina				Zabrze (PM <sub>10</sub> )			
		EC1	EC2	EC3	EC4	EC1	EC2	EC3	EC4
Heating	OC	0.95	0.97	0.78		0.86	0.93	0.88	0.45
	NO	0.72	0.69	0.58		0.79	0.79	0.75	0.52
Non-heating	OC	0.66	0.80	0.88	0.67	0.46	0.66	0.87	0.49
	NO		0.43			0.45	0.57	0.57	
Specification		Trzebinia				Racibórz-C			
		EC1	EC2	EC3	EC4	EC1	EC2	EC3	EC4
Heating	OC	0.86	0.88	0.83	0.47	0.95	0.92	0.89	0.51
	NO	0.72	0.73	0.75	0.54	0.85	0.80	0.83	0.40
Non-heating	OC		0.56	0.69		0.88	0.89	0.88	
	NO			0.42		0.43	0.46	0.47	0.41
Specification		Zabrze (PM <sub>2.5</sub> )				Zabrze (PM <sub>1</sub> )			
		EC1	EC2	EC3	EC4	EC1	EC2	EC3	EC4
Heating	OC	0.95	0.96	0.91		0.88	0.93	0.94	0.54
	NO	0.78	0.77	0.69	0.40	0.63	0.65	0.68	0.55
Non-heating	OC	0.53	0.70	0.83		0.57	0.69	0.82	
	NO	0.51	0.60	0.65		0.48	0.54	0.59	

Note: only correlation coefficients higher than 0.40 are indicated in the table; correlation coefficients higher than 0.70 are highlighted in gray.

#### 4. Conclusions

As part of this work, an extensive characterization of carbonaceous matter was carried out in PM samples collected during the different measurement campaigns (2013–2020) conducted at selected urban and rural background sites in southern Poland. In this study, the chemical analysis was performed using the thermo-optical method and “eusaar\_2” protocol, which has been developed as a proposed standard method for European monitoring stations under the EUSAAR project. It should be noted that the work is the first such thorough attempt to characterize carbonaceous compounds, including individual carbon temperature fractions, in a highly industrialized and urbanized area, which is an example of a European hot spot in relation to air quality.

Data collected in the frame of this work showed a large variation in carbonaceous aerosol concentrations in southern Poland. Nevertheless, TC concentrations remained relatively high compared to the values observed at many European stations, which may be due to the unique position of the use of hard coal as an energy source. Spatial and seasonal variability of the OC and EC levels were generally consistent with spatiotemporal fluctuations of the PM mass concentrations, with higher

levels recorded during the heating season and at urban background sites, where seasonal fluctuations of OC and EC concentrations were also more pronounced. The relatively high concentrations observed in rural background sites, often considered less polluted in terms of air quality, indicate the presence of a high regional background for the area of southern Poland.

Organic and elemental carbon were relevant species both in fine and coarse particulate matter. Regardless of the season, OC clearly dominated over EC, which applied to all measurement sites and all PM fractions. The high dominance of organic carbon and potential formation of secondary organic aerosol is demonstrated by high values of the OC/EC ratio, which, taking into account average values throughout the entire measurement period, did not fall below four. Higher values observed in rural areas indicated that in such locations, coal and biomass combustion plays a major impact on air pollution with carbonaceous aerosol. On the contrary, more intense interaction of traffic sources (vehicle exhaust) may explain the lower values of the OC/EC ratio recorded at the urban background sites.

The fluctuations in daily EC and OC concentrations strongly influenced the variability of PM concentrations, which had a direct impact on the share of these components in the total mass of PM. The average TC share in PM generally exceeded ~40%, except for the urban background site in Skawina and most rural background locations. The contribution of TC in PM was primarily determined by fluctuations in the OC shares, which were higher during the heating season, probably due to the increased intensity of the emission of organic carbon compounds from the combustion of fossil fuels and biomass. Slightly higher OC/TC ratios were recorded in rural background locations (on average, ~85–89%) compared to the urban background sites (on average, ~79–85%). For comparison, the EC share in TC was generally higher in urban areas (on average, ~15–21%) than in rural areas (on average <15%).

Despite the characteristic spatial and seasonal variations of the SOC and POC concentrations, analyzed measurement sites clearly differed in the share of these components in the PM mass. The obtained results showed that POC usually dominated over SOC, especially in rural background sites, which could be caused by the inflow of polluted air masses from urban areas and the impact of local combustion sources, including combustion of low-quality fuels. Moreover, the high POC content in the non-heating season pointed to the role of primary biological emissions from abundant vegetation in rural areas. Higher shares of POC than SOC in PM, which were more pronounced in the non-heating season, were also identified at urban background sites, especially those under dominant influence of primary emission sources such as communication (e.g., Zabrze, PM<sub>1</sub>) and industry (e.g., Skawina, PM<sub>10</sub>). On the contrary, in the heating season, the importance of calculated secondary aerosol increased, which should be associated mostly with the effects of fuel combustion for heating purposes (e.g., Trzebinia)—including the influence of wood burning emissions—and stable atmospheric conditions in winter (low air temperatures and stagnation of air masses), which lead to a shift in the balance of VOC transformations towards the solid phase. It could explain high calculated SOC content in PM, recorded in various areas at this time of the year.

In terms of the content of nine carbon fractions, the considered sites showed roughly the same characteristics, and slight differences were determined mainly by location conditions, measured PM fraction, and season of the year. Regardless of the location type, the PC, followed by OC<sub>4</sub> and OC<sub>2</sub>, was the dominant OC fraction. Clearly higher values of the PC/OC ratio were observed in the heating season, at all considered measurement sites, suggesting that residential heating, including biomass burning, and secondary organic aerosol could be an important source of PC. The relatively small spatial fluctuations of the OC<sub>4</sub>/OC and OC<sub>3</sub>/OC ratios may suggest a more regional or long-range transport origin of the OC<sub>3</sub> and OC<sub>4</sub> fractions, which is generally confirmed by the higher shares of these fractions in the non-heating season. The lack of clear seasonal variability for the OC<sub>3</sub> and OC<sub>4</sub> shares observed in Zabrze (all PM fractions) could indicate the impact of communication sources, including road dust and gasoline vehicle exhausts. The high content of OC<sub>2</sub> and OC<sub>1</sub> fractions in some areas and the observed seasonal variability was mainly associated with the impact of local emission sources, such as industry (e.g., Trzebinia, Skawina), coal and biomass combustion (e.g., Racibórz-C), or fresh vehicle exhaust and poor dilution conditions (e.g., Zabrze).

The profile of EC temperature fractions was also similar at all considered sites, with EC3 followed by EC2 as the dominant EC fractions. The shares of EC1 and EC4 were generally lower and, at both types of sites, often showed more pronounced spatial variations. Individual EC fractions also differed in seasonal variability. Higher shares of EC1 and EC2 fractions were generally observed during the heating season, contrary to the EC3 and EC4 fractions, with higher values in the non-heating season. Nevertheless, it was found that accurate determination of the emission sources of individual EC fractions is not a simple task, and a serious difficulty in interpreting the research results may be created by the use of different temperature protocols in thermal-optical analysis. The analysis of the correlation between the concentrations of EC fractions and OC showed that, at all measurement sites, most of the EC fractions showed very strong positive relationships with organic carbon, thus pointing to one or more co-genetic sources. Interestingly, strong relationships were also maintained during the non-heating season, which could indicate that, in this period, emissions of EC were caused mainly by a local source (traffic) (e.g., Zabrze). On the contrary, the weaker relationships between EC fractions and OC recorded in the non-heating season (e.g., Trzebinia) suggested a significant impact of secondary organic aerosol formation processes. The analysis of the correlation between EC fractions and NO<sub>x</sub>, which is a good indicator of traffic emissions, showed that the strongest relationships were mainly noted in urban areas, in the case of the EC2 and EC3 fractions.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4433/11/7/687/s1>, Table S1: Average concentrations of nine carbon fractions ( $\mu\text{g}\cdot\text{m}^{-3}$ ) at considered rural background sites, Table S2: Average concentrations of nine carbon fractions ( $\mu\text{g}\cdot\text{m}^{-3}$ ) at considered rural background sites.

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