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Distribution of EC and OC temperature fractions in different research materials

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Abstract: The aim of the study was to assess the profile of EC (elemental carbon) and OC (organic carbon) temperature fractions in PM₁ and PM_{2.5} samples and in wet deposition samples (material collected on a filter). The research was conducted at the urban background station in Zabrze (southern Poland) in the period of Oct 2020–Oct 2021. PM samples were collected with high-volume samplers; the automatic precipitation collector NSA 181 by Eigenbrodt was used to collect the deposition samples. Concentrations of EC and OC were determined using thermal-optical method (carbon analyzer from Sunset Laboratory Inc., “eusaar_2” protocol). Regardless of the type of research material, organic carbon constituted the dominant part of the carbonaceous matter, and this dominance was more visible in the non-heating season. The profile of temperature fractions of OC and EC was clearly different for dust washed out by precipitation. Noteworthy is a much lower content of pyrolytic carbon (PC) in OC, which can be explained by the fact that PC is most often combined with the water soluble organic carbon. In addition, a high proportion of the OC3 fraction was observed, followed by OC4, which may indicate that these fractions are of a more regional origin. With regard to the EC fractions, the differences are less visible and concern, in particular, the higher share of EC4 and the lower of EC2. The obtained results may be a valuable source of information about the actual status of the carbonaceous matter and its transformation in the atmosphere.

Introduction

The deterioration of air quality and the increase in damage to ecosystems caused by the emission and subsequent deposition of particulate matter (PM) are currently among the main environmental problems (EEA 2022, Michalski & Pecyna-Utylska 2022). Among the various chemical species, carbonaceous matter is often the dominant part of the PM mass (Chow et al. 2015). The proportion of carbon compounds is generally higher in the finer fractions, accounting for an average of 20–60% of PM_{2.5} (particles with aerodynamic diameter < 2.5 μm) (Li et al. 2018). This share varies considerably in different regions of the world – generally higher values have been found in locations strongly influenced by anthropogenic emission sources, such as: road traffic, industrial plants, and fossil fuels combustion in households (Reizer and Juda-Rezler, 2016).

Due to the high variety of compounds, especially organic ones, that make up the content of total carbon (TC), chemical analyzes often focus on determining the concentration of its two main components – elemental carbon (EC) and organic carbon (OC). Most measurement techniques involve taking PM samples on the filter material (quartz or glass filters are recommended) and measuring the carbon content of the filter or the attenuation intensity of the light reflected or transmitted through the filter (Chow et al. 2015). Among these, thermal-

-optical analysis, based on the determination of reflectance (Thermal Optical Reflectance, TOR) or transmittance (Thermal Optical Transmittance, TOT), is the most commonly used. Currently, this method is considered as the standard (Karanasiou et al. 2015), and the use of specific temperature protocols – differing in temperature thresholds, their number and duration – enables the separation and determination of the concentration of OC and EC temperature fractions.

Carbonaceous matter, despite its documented impact on the climate, environment and population health, is still not fully understood and many things need to be discovered or clarified. This work focused on the analysis of carbonaceous matter, including the profile of OC and EC temperature fractions in the research material with different characteristics – these were both PM₁ and PM_{2.5} samples as well as wet deposition samples (suspension collected on the filters). According to the literature data, these temperature fractions have often been used in studies on the determination of sources of particulate matter emissions (e.g. Cao et al. 2006, Kim et al. 2011, dos Santos et al. 2016, Aswini et al. 2019, Tohidi et al. 2022), but the authors do not always agree on the true origin of the OC and EC fractions in PM. Moreover, the comparison of the results of different studies is often difficult due to the use of different temperature protocols in thermal-optical analysis (Błaszczak and Mathews 2020). For the above reasons, the authors of the article decided to additionally look at the characteristics of the

carbonaceous material in the dust washed out by precipitation, which is a much more processed material. To the best of our knowledge, such studies have not been conducted so far, so the obtained results can be considered innovative. On the one hand, they will provide important information on the sources of carbonaceous compounds in the atmospheric dust, including the role of local and/or more distant emitters. On the other hand, they make an important scientific contribution to the knowledge about the transformation of carbonaceous matter in the atmosphere and the carbon cycle in the environment.

Methodology

Characteristics of the measurement campaign and the study area

Measurements were carried out at the urban background station belonging to the Institute of Environmental Engineering of the Polish Academy of Sciences in Zabrze (IEE PAS). The research area lies in the western part of the Silesian Voivodeship (Southern Poland), within the Upper Silesian Industrial District (USID) (Figure 1), considered to be one of the most densely populated and polluted regions of Poland (Ziola et al. 2021). The nearest surroundings of the station are: a) to the north: a national road No 88 with heavy traffic (~400 m); b) to the east: residential buildings, commercial and service facilities and a provincial road with heavy traffic (~200 m); c) to the south: blocks of flats and houses (~200–300 m); d) to the west: housing estates and allotments (~200 m). 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.

The research material consisted of samples of PM_{10} and $PM_{2.5}$ particulate matter and wet deposition samples (suspension collected on the filter). In the case of PM_{10} samples were taken on a daily basis, with the use of high-volume samplers (Digitel DHA-80); dust was collected on quartz fiber filters of 150 mm in diameter (Whatman QMA®). $PM_{2.5}$ concentrations were determined according to the EN 12341:2014 standard, using

Sartorius CP 225D-OCE microbalance (resolution: 10 μ g). Conditioning, weighing and storage of both non-exposed and exposed filters were conducted in the weighing room – at fixed conditions of temperature (19–21°C) and relative humidity (45–50%).

Continuous systematic measurements of fine particulate matter – for the purposes of the implementation of statutory tasks – have been started in May 2020 ($PM_{2.5}$) and December 2017 (PM_{10}). In addition, at the beginning of Feb 2020, continuous measurements of wet deposition were launched. For this purpose, the NSA 181 automatic precipitation collector by Eigenbrodt was used, and its operation was carried out in a 1-week system. After 1 week, the wet deposition sample was transferred to the laboratory, where the volume of rainwater was determined at first. Then the sample was placed in the refrigerator, and a further procedure depended on the amount of rainwater collected – in the case of a small amount of rainfall, the weekly sample was combined with the subsequent weekly sample(s). Finally, the wet deposition sample was filtered on a quartz fiber filter of 47 mm in diameter (Whatman QMA®). After a conditioning period of minimum 48 hours, the filters with the suspension were weighed using Mettler Toledo AT20 microbalance (resolution: 2 μ g). The weight of the suspension was determined on the basis of the difference between the weight of the loaded and unloaded filters.

For the purposes of the study, data from the annual period Oct 2020–Oct 2021 were presented – in order to capture the entire heating (H) and non-heating (NH) seasons. These periods were distinguished on the basis of the average daily air temperature, and 10°C was adopted as the delimiting value (see also Figure 2, section 3.1). Basic information on the research material is summarized in Table 1. The table also shows the mean values of the selected meteorological parameters, calculated on the basis of measurements made with the Vantage Pro weather station installed at the urban background station in Zabrze. Other auxiliary data – used in the interpretation of the test results – were taken from the general public database



Fig. 1. Location of the urban background station in Zabrze and a view of the immediate surroundings and measuring equipment

of the Chief Inspectorate for Environmental Protection (CIEP) (<https://powietrze.gios.gov.pl/pjp/current>). They included the concentration of gaseous (SO₂, NO, NO₂, NO_x, O₃, CO) and particulate (PM_{2.5}, PM₁₀) pollutants measured in parallel at the CIEP station, located approximately 70 m from the IEE PAS building. All data collected during the annual measurement period were stored in the internal IEE PAS database. The MSEXcel 2013 (Redmond, Washington, DC, USA) and Statistica 13.0 (Stat Soft, Cracow, Poland) software packages were used for statistical analysis.

Determination of the content of carbonaceous matter

The content of EC and OC was determined using a thermal-optical carbon analyzer with FID detection – Model 4L Main Oven Assembly (Sunset Laboratory Inc). Dust samples – in the form of 1.0 cm² sections of the filters – were analyzed in two stages. First, the organic fraction was released as a result of gradual heating of the sample in the helium stream. In the next step, the filter section was heated in an oxidizing helium-oxygen mixture to release elemental carbon. A detailed analytical procedure is presented in Błaszczak and Mathews (2020).

In this study, the analysis was carried out using the „eusaar_2” protocol, which was developed as a proposed standard method for European monitoring stations under the EUSAAR (European Supersites for Atmospheric Aerosol Research) project. In total, the concentration and relative content of nine temperature-resolved carbon fractions are provided, including: a) 4 fractions of organic carbon (OC1, OC2, OC3 and OC4), which express the amount of OC released from the sample during its heating in the helium stream – respectively at temperature steps: 200°C, 300°C, 450°C and 650°C; b) pyrolytic carbon (PC fraction), which expresses the amount of organic compounds converted to elemental carbon in the first step of the analysis; c) 4 fractions of elemental carbon (EC1, EC2, EC3, EC4), released from the filter in a helium-oxygen atmosphere, at 4 temperature steps (500°C, 550°C, 700°C, 850°C). Total OC is defined as:

$$OC = OC1 + OC2 + OC3 + OC4 + PC,$$

total EC is defined as:

$$EC = EC1 + EC2 + EC3 + EC4 - PC,$$

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

Results and discussion

Air pollution with particulate matter against the meteorological situation

The temporal variation of fine PM concentrations and wet deposition of dust (D_w) during the entire measurement period is shown in Figure 2. As meteorological parameters essentially influence the levels of atmospheric pollutants, the mean value of temperature and the sum of precipitation are also presented. All presented parameters were related to the deposition sampling periods, to achieve a better temporal resolution. Descriptive statistics for daily averaged PM₁ and PM_{2.5} concentrations and weekly averaged D_w levels are summarized in Table 2. Finally, the correlation between the PM levels measured in this study and the concentrations of selected gaseous and particulate pollutants as well as the values of meteorological parameters was examined (Spearman’s rank correlation, α = 0.05) (Table 3).

The obtained results showed that the concentrations of PM₁ and PM_{2.5} in the studied area fluctuated within wide limits and showed a clear seasonal variability. The average concentration of PM_{2.5} in the entire measurement period amounted to 24 μg·m⁻³ and was by ~ 20% higher than the limit value for the annual mean concentration (20 μg·m⁻³) (Directive 2008/50/EC). Significantly worse living conditions of the inhabitants of the analyzed area, related to exposure to fine PM, occurred in the heating season, when the concentration of PM_{2.5} and PM₁ was on average 35 and 13 μg·m⁻³, respectively. In the non-heating season, these values were much lower and amounted to 11 μg·m⁻³ (PM_{2.5}) and 6 μg·m⁻³ (PM₁).

The reason for the observed seasonal differences may be the result of several factors, the most important being the local emission sources and the meteorological situation (Zioła et al. 2021). In this work, it was confirmed that the main parameter determining the levels of atmospheric pollutants is air temperature, which correlated negatively with PM₁ and PM_{2.5} concentrations (Table 3). A drop in air temperature in

Table 1. General information about measurement campaign and research material

Research material	Sampling cycle	No. of samples	T [°C] ^{b)}	RH [%] ^{b)}	WS [m·s ⁻¹] ^{b)}	WD ^{d)}	Pr [mm] ^{e)}
Heating season (5/10/20–02/05/21)							
PM ₁	24 h	204	4.13	84.83	1.83 (9.62%) ^{c)}	SSW (16.69%) SW (13.93%) NW (11.17%)	343.33
PM _{2.5}		203					
Wet deposition	(1–4) week ^{a)}	12					
Non-heating season (03/05/20–03/10/21)							
PM ₁	24 h	154	17.02	75.81	1.46 (18.15%) ^{c)}	NNW (18.05%) SSW (11.15%) NW (10.09%)	451.11
PM _{2.5}		153					
Wet deposition	(1–4) week ^{a)}	12					

Designations: T – air temperature; RH – relative humidity; WS – wind speed; WD – wind direction; Pr – precipitation

^{a)} depending on the amount of rainwater; ^{b)} mean value over the measurement period; ^{c)} contribution of wind calms in the entire measurement period;

^{d)} the frequencies of winds prevailing in the measurement period are given; ^{e)} the sum of atmospheric precipitation in the measurement period, estimated on the basis of wet deposition measurements

the autumn-winter period causes an increase in the intensity of combustion of fossil fuels and biomass – considered the dominant PM anthropogenic sources at this time of the year – and, consequently, an increase in the concentration of ambient PM. The concentration of other pollutants also increases, as evidenced by the high positive correlations between fine PM and other measured gaseous and particulate substances, apart from ozone.

Seasonal variability of the wet deposition of dust shows an opposite tendency compared to the PM concentrations, which is already indicated by the analysis of Figure 2. During the heating season, the total loading of dust brought by precipitation in the study area was 8.89 kg·ha⁻¹; in the

non-heating season; this value was almost twice as high and amounted to 15.31 kg·ha⁻¹. It is generally recognized that an increase in precipitation intensity contributes to a more efficient removal of atmospheric aerosol particles, and thus to a decrease in PM concentrations. The sum of atmospheric precipitation in the study area was higher in the non-heating season (451.11 mm) compared to the heating one (343.33 mm) (Table 1). The most wet periods were the turn of August and September 2021 (70.80 mm, 1 week), following by early August (69.47 mm, 1 week) and the first half of October (2 weeks, 89.38 mm). Low concentrations of PM₁ and PM_{2.5} were recorded in the indicated periods, although the wet deposition of dust was also relatively low. The driest period lasted from

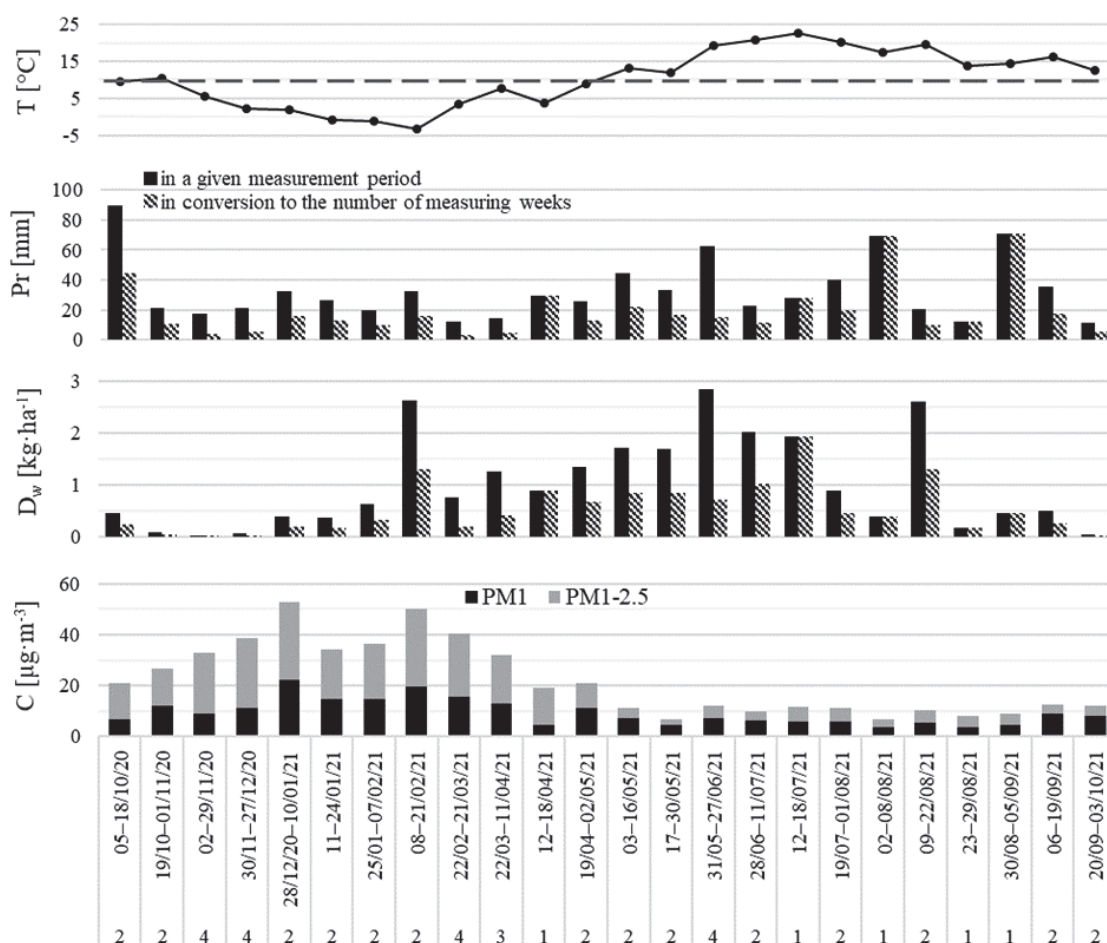


Fig. 2. Average air temperature [°C], sum of atmospheric precipitation [mm], wet deposition of dust [kg·ha⁻¹] and average concentration (C) of PM₁ and PM_{2.5} [µg·m⁻³] at the urban background station in Zabrze

Table 2. Concentration of PM₁ and PM_{2.5} particulate matter against the value of PM₁/PM_{2.5} ratio and wet deposition of dust in the study area

Parameter	Unit	H (5/10/20–02/05/21)		NH (03/05/20–03/10/21)	
		Ave±SD	Range	Ave±SD	Range
PM ₁	µg·m ⁻³	12.87±8.52	2.04–63.02	6.29±2.63	2.03–15.45
PM _{2.5}	µg·m ⁻³	34.85±21.08	5.80–133.68	10.50±3.62	3.52–20.26
PM ₁ /PM _{2.5}	–	0.38±0.08	0.24–0.54	0.58±0.08	0.45–0.72
D _w	kg·ha ⁻¹	0.74±0.74 (8.89) ^{a)}	0.004–2.63	1.28±0.98 (15.31) ^{a)}	0.05–2.86

^{a)} the sum of wet deposition of TSP in the measurement period
Designations: H – heating season; NH – non-heating season

late February to mid-April, when only 26.99 mm of rain fell in 7 weeks. The PM concentrations were then moderate or high, while the wet deposition of dust was moderate or relatively low. The highest values of D_w – calculated on the number of measurement weeks – were found in the period 12-18/07/21 (1.94 kg·ha⁻¹), then in February (08-21/02) and August (09-22/08), with moderate amounts of precipitation.

Summarizing the above considerations, it can be concluded that there is no strong and clear relationship between the sum of precipitation and PM concentration or wet deposition of dust, which could explain the lack of a significant statistical correlation between these variables (Table 3). Thus, the obtained results showed that there are other factors, apart from precipitation, determining the intensity of wet deposition of dust, and the atmospheric transformation processes should be considered one of the most important. The high degree of processing of the dust removed by precipitation can be confirmed by a very high positive correlation between D_w and ozone, noted in both averaging periods (Table 3). The variable activity of local emission sources is also significant, as evidenced by the presence of a high positive correlation between the PM concentration and the wind speed recorded for the data set from the entire measurement period (Table 3).

Concentration of carbonaceous matter in PM₁, PM_{2.5} and wet deposition samples

Descriptive statistics for the average concentrations and shares of carbonaceous matter in the analyzed research material are summarized in Table 4. It was found that carbonaceous compounds constituted a significant part of the particulate matter and dust washed out by precipitation. Taking into account the entire measurement period, the average concentration of total carbon was 5.74 μg·m⁻³ (PM₁), 12.09 μg·m⁻³ (PM_{2.5}) and 1.17 mg·l⁻¹ (D_w), which corresponded to the contribution at the level of 56.78%, 47.47% and 42.02%, respectively (Table 4). The concentrations of the analyzed compounds in PM₁ and PM_{2.5} showed a characteristic seasonal variability, being the combined effect of the activity of anthropogenic sources changing throughout the year and the variability of

meteorological conditions (Reizer and Juda-Rezler, 2016). The levels of carbonaceous aerosol were mainly influenced by the immission situation in the autumn-winter period (low air temperatures, the impact of emissions from fossil fuel combustion), when the maximum TC concentrations reached 39.23 and 66.54 μg·m⁻³, in PM₁ and PM_{2.5}, respectively. In the case of PM₁ fraction, the average concentration of OC in the heating season (5.97 μg·m⁻³) was more than twice as high as in the non-heating season (2.63 μg·m⁻³), while the average concentration of EC was 1.72 and 0.53 μg·m⁻³, respectively (more than a 3-fold difference). Seasonal differences were even more visible for the PM_{2.5}, with average OC concentrations of 14.39 μg·m⁻³ (H) and 3.96 μg·m⁻³ (NH), and average EC concentrations of 3.07 μg·m⁻³ (H) and 0.73 μg·m⁻³ (NH).

With regard to wet deposition samples, the seasonal variability of the levels of carbonaceous compounds was much less pronounced – the average TC concentration in the heating season (1.26 mg·l⁻¹) was only slightly higher compared to the non-heating one (1.07 mg·l⁻¹); the same trend was also observed for organic and elemental carbon. While the activity of local emission sources is much higher in the cold season, the intensity of precipitation is then significantly lower (Table 1). In the non-heating season, the intensity of precipitation increases and, consequently, the load of dust removed from the atmosphere, which results in a relatively high concentration of carbonaceous matter.

The obtained results showed that the variability of the concentrations of the analyzed compounds may have a strong influence on the dust concentrations, which has a direct impact on the shares of these components in PM₁, PM_{2.5} and D_w samples (Figure 3). Regardless of the research material, the dominance of organic carbon over elemental carbon was clearly visible, as evidenced by the high values of the OC/EC ratio (Table 4). The share of OC in TC increased in the non-heating season, due to the occurrence of conditions favoring the formation of secondary organic aerosols (SOA) (i.e. high air temperature, high intensity of solar radiation). The share of EC showed a different seasonal variability – higher values in the heating season should be associated with the presence

Table 3. Correlation of PM₁, PM_{2.5} and wet deposition of dust with concentrations of other atmospheric pollutants and the values of meteorological parameters

Averaging period	Research material	D_w^*	PM ₁	PM _{2.5}	PM ₁₀	CO	SO ₂	NO ₂	NO _x	O ₃	BC	T	V
ALL	PM ₁		x	+++	+++	++	++	++	++	–	+++	--	+
	PM _{2.5}		+++	x	+++	++	++	++	++	–	+++	--	+
	D_w^*	x							(–)	++			
H	PM ₁		x	++	++	++	++	++	+		++	–	
	PM _{2.5}		++	x	+++	+++	++	++	+++		+++	--	
	D_w^*	x								++			
NH	PM ₁		x	++	+++						++		
	PM _{2.5}		++	x	+++						+		
	D_w^*	x								+++			

* Wet deposition samples (suspension collected on the filter)

Designations: ALL – entire measurement period; H – heating season; NH – non-heating season

„+++”: $r \geq 0.90$; „++”: $0.70 \leq r < 0.90$; „+”: $0.50 \leq r < 0.70$; „(+)”: $0.30 \leq r < 0.50$

„--”: $-0.90 < r \leq -0.70$; „-”: $-0.70 < r \leq -0.50$; „(-)”: $-0.50 < r \leq -0.30$

the relations with correlation coefficient $r \geq 0.70$ and $r \leq -0.70$ are highlighted in gray

of an additional source of EC in winter, apart from road traffic, i.e., fuel combustion for heating purposes (Błaszczak and Mathews, 2020). The relatively high proportion of EC in TC for the PM₁ fraction can be explained by the fact that EC tends to accumulate in the finest PM particles (Freney et al. 2011). Particles of this size can persist in the air for relatively long time and are more difficult to remove from the atmosphere, which may, in part, explain the relatively low proportion of EC in wet deposition samples.

Profile of OC and EC temperature fractions – characteristics and main differences

For a more in-depth characterization of carbonaceous matter in various research materials, the content of nine carbon temperature fractions was analyzed, paying particular attention to the observed differences and their possible causes. The contribution of different OC and EC fractions to total organic and elemental carbon, respectively, averaged over the heating and non-heating season, is shown in Figure 4. As can be seen, the PM₁ and PM_{2.5} samples – although they differed in the

share of individual fractions in OC and EC – also showed many common features. Taking into account the entire measurement period, OC2, OC4 and PC clearly dominated over the remaining OC fractions. Pyrolytic carbon had the largest share in OC in the heating season, with average PC/OC ratios of ~33% (PM₁) and ~41% (PM_{2.5}), respectively. In the non-heating season, the share of PC in OC was much lower, while the importance of OC2, OC4 – and to a lesser extent OC3 – increased, with average shares of these fractions in PM₁ amounting to ~32% (OC2), ~25% (OC4) and ~19% (OC3), and in PM_{2.5} – ~36%, ~21% and ~18%, respectively. The share of the most volatile OC fraction (OC1) was relatively low and averaged (all periods) ~15% (PM₁) and ~13% (PM_{2.5}).

Regardless of the averaging period (heating and non-heating season), EC2 and EC3 fractions had the largest share in total EC, with comparable shares for PM₁ and PM_{2.5}, amounting to on average ~38% (EC2) and ~40% (EC3). These fractions showed different seasonal fluctuations, with higher shares of EC2 in the heating season and EC3 in the non-heating one. The EC1/EC ratio averaged ~13% (PM₁) and

Table 4. Average concentrations of EC, OC and TC along with the average values of OC/EC ratio and the contributions of TC in total PM mass

Research material	Parameter	Unit	H (5/10/20–02/05/21)		NH (03/05/20–03/10/21)	
			Ave±SD	Range	Ave±SD	Range
PM ₁	OC	µg·m ⁻³	5.97±4.16	1.33–33.06	2.63±1.05	0.98–5.95
	EC	µg·m ⁻³	1.72±1.03	0.02–6.17	0.53±0.34	0.00–1.87
	TC	µg·m ⁻³	7.69±5.12	1.47–39.23	3.17±1.34	1.09–7.56
	OC/EC	–	3.54±0.87	1.32–10.00	6.01±3.00	2.63–24.42
	TC/PM	%	61.26±12.14	16.26–92.37	50.85±7.41	27.13–83.86
PM _{2.5}	OC	µg·m ⁻³	14.59±10.54	2.22–58.12	3.96±1.39	1.20–8.07
	EC	µg·m ⁻³	3.07±1.62	0.36–8.43	0.73±0.42	0.08–2.32
	TC	µg·m ⁻³	17.66±12.00	2.71–66.54	4.69±1.69	1.57–10.39
	OC/EC	–	4.65±2.26	2.34–30.83	6.81±4.30	1.95–32.14
	TC/PM	%	49.31±10.15	10.19–72.49	45.03±7.02	26.27–67.05
D _w *	OC	µg·m ⁻³	1.13±1.08	0.09–3.64	0.97±0.69	0.24–2.08
	EC	µg·m ⁻³	0.14±0.08	0.01–0.24	0.10±0.08	0.03–0.25
	TC	µg·m ⁻³	1.26±1.13	0.10–3.85	1.07±0.76	0.27–2.33
	OC/EC	–	7.58±4.61	2.35–17.14	9.97±3.17	5.51–16.45
	TC/PM	%	48.35±15.90	27.35–80.61	35.69±16.48	14.73–78.28

* Wet deposition samples (suspension collected on the filter)
Designations: H – heating season; NH – non-heating season

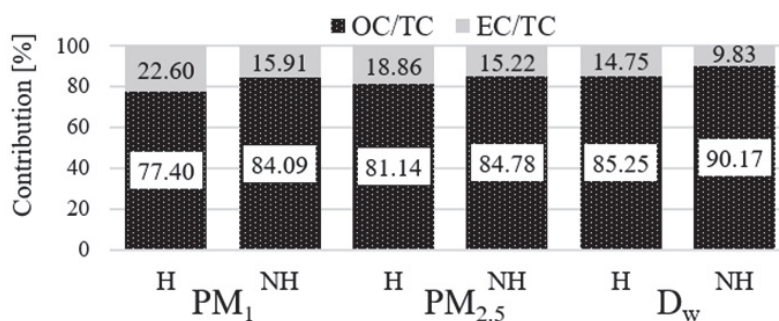


Fig. 3. Average values of EC and OC contributions in TC, separately for PM₁, PM_{2.5} and wet deposition samples
Designations: H – heating season; NH – non-heating season

~16% ($PM_{2.5}$) and reached higher values in the heating season, similarly to the EC2/EC ratio. The share of the least volatile EC4 fraction was relatively low (on average: ~8% (PM_1), ~6% ($PM_{2.5}$)), however, it showed significant temporal fluctuations – in the heating season it was on average less than 3% (PM_1) and 2% ($PM_{2.5}$), while in the non-heating season it increased to ~16% and 11%, respectively.

The obtained results are consistent with the results presented in Błaszczak & Mathews (2020), in which a lot of attention was devoted to identifying possible origins of the OC and EC temperature fractions in PM from selected urban and rural background sites in southern Poland. However, the profile of carbon fractions was clearly different in the case of dust washed out by precipitation, especially in relation to organic carbon. Particularly noteworthy is the much lower content of PC in OC, with an average share of ~12%. This is most likely due to the fact that PC is most connected with water soluble organic carbon (WSOC) – compounds emitted from fossil fuel and biomass combustion sources, which are important precursors of secondary organic aerosol (Zhu et al. 2014, dos Santos et al. 2016, Aswini et al. 2019). The dominant OC fractions were OC3, followed by OC4, with average shares ~50% and ~30%, respectively. The lack of clear seasonal variability of OC3 and OC4 shares and its much higher levels compared to those for PM_1 and $PM_{2.5}$ indicate that these OC fractions could have a more regional or long-range transport origin (Vodička et al. 2015). In many works, the occurrence of OC3, OC4 and OC2 was attributed to aged aerosols related to photochemical reactions and chemical aging processes occurring in the atmosphere (Li et al. 2018, Aswini et al. 2019). On the other hand, high shares of OC2 and OC1 were often observed in fresh vehicle exhaust (Vodička et al. 2015, Zhu et al. 2014) or emissions from biomass burning (Kim et al. 2011, Aswini et al. 2019). The OC1/OC and OC2/OC ratios in dust washed out by precipitation were much lower compared to PM_1 and $PM_{2.5}$, and did not exceed ~7% (OC2) and ~0.5%

(OC1) on average. This is probably due to the high volatility of these OC fractions, which well explains their low shares in samples taken in a weekly or even longer cycle (Dillner et al. 2009, Tohidi et al. 2022).

Relatively few works concerned the issue of the share of individual EC fractions in total EC or TC, however the research material was only particulate matter samples. No doubt EC is emitted into the atmosphere exclusively as primary aerosol from incomplete combustion processes of biomass or fossil fuels (Chow et al. 2015). Elemental carbon is also a chemically inert compound and insoluble in water (Zioła et al. 2021), which explains the high similarity of the EC profile in the deposition samples with that of PM_1 and $PM_{2.5}$. EC3 remained the dominant EC fraction, with an average share of ~39%. The differences concerned the lower share of the EC2, and the higher share of EC4, with average levels of ~23% and ~24%. The values of the EC1/EC ratio were comparable for PM_1 , $PM_{2.5}$ and D_w , and averaged ~14%.

Literature data are also inconsistent about the emission sources of the EC fractions (Błaszczak & Mathews 2020). The occurrence of individual EC fractions was attributed, for example, to diesel vehicle exhaust (EC2–EC4) (Cao et al. 2006, Sahu et al. 2011), gasoline emissions (EC1–EC3) (Cao et al. 2006, Zhu et al. 2010, Bautista VII et al. 2014), coal combustion and biomass burning (EC2, EC3) (Lim et al. 2012, Aswini et al. 2019) or industrial sources (EC4) (Cao et al. 2004, Yan et al. 2019). Indicating the exact sources would require additional chemical analyzes and in-depth analyzes of the emission situation in the study area. However, seasonal variability of the shares of EC fractions may provide some additional insight. Higher levels of EC1 and EC2 in EC recorded for PM_1 and $PM_{2.5}$ in the heating season could suggest a greater importance of coal and biomass combustion in households (so-called low-level emission sources). In turn, higher shares of EC3 and EC4 in the non-heating season could indicate road traffic and industry as the dominant emissions sources of these

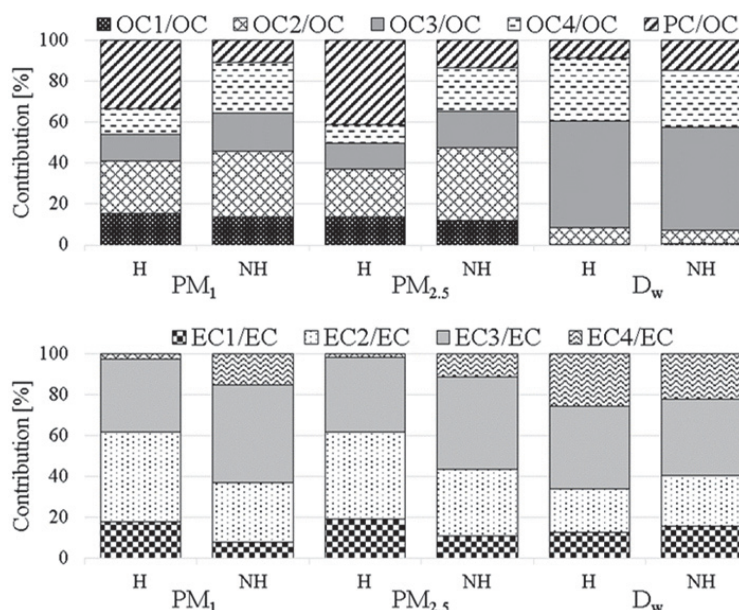


Fig. 4. Contributions of individual fractions of organic carbon (OC1-OC4, PC) and elemental carbon (EC1-EC4), in the total concentration of OC and EC, respectively, separately for PM_1 , $PM_{2.5}$ and wet deposition samples
Designations: H – heating season; NH – non-heating season

carbon fractions (Yan et al. 2019). The importance of road dust from re-suspension as a source of EC₄ could be supported by the high EC₄/EC ratios in the case of dust washed out by precipitation, which also includes particles of larger sizes.

Finally, a Spearman's rank correlation ($\alpha = 0.05$) was carried out between the concentrations of individual carbon fractions and their relationship with the concentrations of other atmospheric pollutants was examined. It was found that both for particulate matter and dust from wet deposition, there were strong relationships ($r > 0.70$) between all OC and EC fractions; the only exceptions were fractions whose content was very low – EC₄ (PM₁, PM_{2.5}) and OC₁ (D_w). The OC and EC fractions contained in PM₁ and PM_{2.5} correlated strongly with most gaseous pollutants, thus indicating that these constituents had one or more co-genetic sources. High positive correlations were recorded especially in the heating season, with the exception of ozone. In the non-heating season, strong relationships were maintained only for carbon monoxide, nitrogen oxides and black carbon.

The results of the correlation analysis for dust from wet deposition should be treated with great caution, due to the small number of samples (12 per season) and a weekly sampling cycle. The obtained results give a more general picture of dependencies that may occur and should be confirmed by further studies of a longer duration time. In contrast to PM₁ and PM_{2.5}, the OC and EC fractions correlated strongly with only a few gaseous pollutants. In the non-heating season, there was a strong positive correlation between sulphur dioxide and the total EC as well as most carbon fractions, which could emphasize the importance of industrial sources located in close proximity to the measurement station. Interestingly, in the spring-summer period, a strong negative correlation ($r < -0.60$) was also noted between OC₂, OC₃, EC₁, total OC and nitrogen oxides. Taking into account the weekly sampling cycle of the wet deposition samples, the explanation may be the photochemical reactions of nitrogen oxides leading to the formation of ozone, which occur particularly intensively at high air temperatures and strong insolation. This hypothesis can be confirmed by the high positive correlation between most carbon fractions and ozone, which persists regardless of the averaging period.

Conclusions

In this article, for the first time, a comparison of the content of carbonaceous matter and the profile of organic and elemental carbon was carried out in samples of fine particulate matter (PM₁, PM_{2.5}) and dust from wet deposition. The research material was collected during the one-year measurement period at the urban background station in Zabrze (southern Poland). The concentration of fine PM in the study area was relatively high and showed characteristic seasonal variability, with higher levels in the heating season compared to the non-heating one. Conversely, a higher loading of dust brought by precipitation was observed in the non-heating season, however, the temporal variation of the dust levels and related carbon compounds was determined by factors other than just the intensity of precipitation, including atmospheric transformation processes and activity of local emission sources.

It was proved that regardless of the averaging period, the common feature of PM₁, PM_{2.5} and wet deposition samples was

a clear dominance of OC over EC. The OC and EC profile was similar for PM₁ and PM_{2.5} – the highest share in total OC was found in OC₂, OC₄ and PC, while EC₂ and EC₃ were the dominant EC fractions. The OC profile in dust from wet deposition was dominated by OC₃, followed by OC₄; the share of PC was much lower. More similarities were noted for the EC profile, due to its chemical inertness and insolubility in water, and the differences concerned the lower share of EC₂, and the higher share of EC₄.

The different OC and EC profile for the deposition samples could result from various factors, including larger particle sizes, the presence of particles of biological origin, a high degree of processing of the research material and the method of averaging the measurement results (weekly sampling cycle). The results presented in the work should be treated as a preliminary recognition of an extremely important research issue, which are the sources of origin and transformation of carbonaceous aerosol in the atmospheric air. The actual explanation of the possible causes of the observed differences in the characteristics of the carbonaceous material contained in particulate matter and dust washed out by atmospheric precipitation requires continuation of research in the future and the extension of their scope. In particular, it is recommended to pay great attention to the analysis of meteorological conditions *in situ* and the emission situation of the study area, which together will allow to verify the possible impact of long-distance transport and local emitters on the structure of carbonaceous matter.

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Dystrybucja frakcji temperaturowych EC i OC w różnych materiałach badawczych

Streszczenie: Celem badań była ocena profilu frakcji temperaturowych EC (węgiel elementarny) i OC (węgiel organiczny) w próbkach PM₁ i PM_{2.5} oraz w próbkach depozycji mokrej (materiał zgromadzony na sączku). Badania przeprowadzono na stacji tła miejskiego w Zabrze w okresie X 2020–X 2021. Próbkę PM pobierano za pomocą poborników wysoko-objętościowych. Do poboru próbek depozycji zastosowano automatyczny kolektor opadów NSA 181 firmy Eigenbrodt. Stężenia EC i OC oznaczono metodą termiczno-optyczną (analyzer węgla firmy Sunset Laboratory Inc., protokół „eusaar_2”). Niezależnie od rodzaju materiału badawczego węgiel organiczny stanowił dominującą część materii węglowej, a dominacja ta była bardziej widoczna w sezonie niegrzewczym. Profil frakcji temperaturowych OC i EC różnił się wyraźnie dla pyłu z depozycji mokrej. Na uwagę zasługuje znacznie niższa zawartość węgla pirolitycznego (PC) w OC, co można tłumaczyć tym, że PC jest najczęściej łączony z rozpuszczalnym w wodzie węglem organicznym. Ponadto zaobserwowano wysoki udział frakcji OC₃, a następnie OC₄, co może wskazywać na bardziej regionalne pochodzenie tych frakcji. W przypadku frakcji EC różnice są mniej widoczne i dotyczą w szczególności wyższego udziału EC₄ i mniejszego EC₂. Uzyskane wyniki mogą być cennym źródłem informacji o materii węglowej i przemianom jakim podlega w atmosferze.