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Article

Impact of municipal, road traffic and natural sources on PM10: the hourly variability at a rural site in Poland

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Abstract: The paper presents data from a monthly campaign for the elemental composition of PM10 in a specific receptor Kotórz Mały (Opole Voivodeship) located in the vicinity of a moderately inhabited rural area, measured in one-hour samples with the use of the PX-375 analyzer by the Horiba company. The hourly variability of SO_2, NO, NO_2, CO, O_3 concentrations as well as the variability of meteorological parameters were also determined. On average, during the entire measurement period, the elements related to PM10 can be arranged in the following order: As<V<Ni<Pb<Cr<Mn<Cu<Ti<Zn<K<Fe<Ca<Al<Si<S. Trace elements, including toxic elements, such as As, V, Ni, Pb, Cr, Mn, were present in low concentrations, not exceeding 10 ng/m^3 (average daily value). These elements had fairly even concentrations, daily and hourly. The concentrations of the main elements in the PM10 in the receptor are subject to strong hourly changes related not only to changes in the structure of the sources identified in the statistical analysis, but mainly to wind speed and direction changes (soil and sand particles pick-up and inflow of pollutants from coal combustion). It has been shown that the transport emission in the receptor can have an intense effect on PM10 in the afternoon.

Keywords: atmospheric aerosol; municipal and traffic emissions; natural sources; enrichment factor; coal and gasoline combustion; 24-h concentrations; diurnal variability; PX-375; XRF analysis.

1. Introduction

Particulate matter (PM) elemental composition is one of its critical characteristics determined to characterize the environmental and health effects of PM as well as to define PM origin at a particular receptor. Taking advantage of the fact that the elemental composition of PM leaving the emission source is more or less defined, the information about it can be used to identify the origin of PM in almost any area. Various types of mathematical models are used for this purpose [1–5]. Data on element concentrations of PM are used to evaluate the origin of PM for two main reasons. Except for light elements, mainly carbon, nitrogen and sulphur, most of the elements that build PM, under atmospheric conditions, occur in chemically stable compounds. These compounds, along with PM particles, are transported from the emitters to the receptor in more or less the same chemical form and in an amount that strictly depends on the number of PM particles emitted by these emitters which contain these elements [6–9]. The situation is different with carbon, sulphur and nitrogen compounds, their amount in PM in a specific receptor depends not only on the number of stable compounds in PM emitted from sources affecting this receptor, but mainly on the presence of gaseous organic and inorganic precursors of secondary aerosols in the atmosphere and on meteorological factors determining the intensity and direction of changes of volatile and semi-volatile compounds in the atmosphere [10–13]. The second reason why the knowledge of elemental composition facilitates the understanding of the temporal and spatial variability of PM origin in different regions is that some elements are effective markers of specific PM sources. More specifically, we can say that there are elements characteristic for only one source/emitter or a group of similar PM sources that allow distinguishing a given source / group of sources from others. For example, silicon or aluminium is used as a marker for PM emitted from soil erosion or sand, next potassium is used as a marker for PM derived from biomass combustion [7,14–16]. Until recently, lead has been successfully used as a marker for PM emissions from gasoline combustion in car engines [17–19]. Sometimes the mass ratios of trace elements contained in PM are used to assess the origin of PM in a given area, as their characteristic values for PM emitted from different sources are known [1,20]. Nowadays, it is known that the assessment of the origin of PM based on data on the elemental composition of PM and various approaches and mathematical models is more effective in areas where the elemental profiles of PM emitted from different sources are highly varied and more or less repeatable over a longer period of time[1–3,21].

For the correct use of these models and for obtaining the right conclusions from the results, it is necessary to collect a large amount of data. The number of data depends on many factors; in addition to the meteorological and emission characteristics of the area, it also depends on the model used.

In areas where PM emissions from different sources overlap and/or one source is clearly dominant, the correct determination of the origin of PM may be very difficult or even impossible [22–25]. Probably, in such regions, data from averaging measurements over time intervals shorter than 24 hours could be more useful to assess the origin of PM based on the elemental composition of PM. Previous studies have shown, for example, that concentrations and chemical composition, including the elemental profile of PM, dynamically change throughout the day, hour by hour, and the main causes of this variability are road and municipal emissions. Unfortunately, it is often technically impossible to determine the elemental composition of PM in samples taken for an hour. Data on the elemental composition of PM in short periods of time comes almost exclusively from studies conducted with automatic measurements using the XRF technique. So far, such research has never been conducted in Poland. Meanwhile, in almost all regions of Poland, in terms of PM origin, difficulties have been noted in performing such an analysis (PM origin analysis) based on daily data on the elemental composition of PM. This paper presents and analyses data from a monthly measurement campaign for the elemental composition of PM10 measured in one-hour samples (averaged every hour). The data were used to assess the origin of PM10 in a rural area in southern Poland. The variability of the elemental composition of PM10, determining the variability of the participation of individual sources in the concentrations of PM10 in a specific receptor, was examined.

2. Materials and Methods

Sampling site

As the receptor, the measurement point in the northern part of the village was selected, which is situated near a moderately inhabited rural area (Kotórz Mały, Opolskie Voivodeship; Figure 1) surrounded by meadows, low shrubs and trees (50^{O}73’66.02” N; 18^{O}05’06.80” E, 162 m. a. s. l.). Kotórz Mały is a small village with a population of around 1000 inhabitants, which is located 15 km from Opole, in south-west direction, with 122 000 inhabitants. In this village one car service and two carpentries are situated which are equipped with dust collection systems of high efficiency. Apart from these, there are no local sources of air contamination in Kotórz Mały. As typical for Poland, natural emissions are the main sources of aerosol during warm seasons, while domestic heating systems are the main local source of air contamination during cold season [26]. Two national roads are situated in the range of few kilometers from the village: in north-west road No. 45 with a traffic density of approx. 8,000 vehicles/day and in south –east road No. 46 with 9500 vehicles/day (data from General Director for National Roads and Motorways https://www.gddkia.gov.pl/userfiles/articles/g/generalny-pomiar-ruchu-w-2015_15598//SYNTEZA/WYNIKI_GPR2015_DK.pdf),

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Figure 1. Location of the measuring point in Kotórz Mały.

Measurement method

PM10 mass and elemental concentrations of Al, As, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, S, Si, Ti, V, Zn were measured hourly with an online XRF (PX-375 Horiba, Japan). The online PX-375 monitor applies reel-to-reel filter tape sampling, with beta-ray attenuation analysis to determine the total PM10 mass. The nondestructive energy-dispersive X-ray fluorescence spectroscopy (EDXRF) analysis was applied to determine the selected element concentrations. The EDXRF unit contains a complementary metal–oxide–semiconductor (CMOS) camera for sample images. PM10 inlet and filter tape was used for air at a flow rate of 16.7 L/min, assuming a deposit of approximately 11.1 mm in diameter. After the collection of single sample at every 60 min, beta-ray attenuation EDXRF analyses were performed for 500 s (15kV or 50kV depending on the element), respectively, per hourly sample, coinciding with the collection of the subsequent sample.

NIST certified standard material, SRM 2783 (air particulate matter on filter media), was used to assess the elemental quantification of X-ray spectra and to get a quality control measure. In addition, the lowest detection limits (LLD as a double the standard deviation of blank analyzed) were Al (56.7 ng/m^3), As (3.7 ng/m^3), Ca (1.1 ng/m^3), Cr (2.05 ng/m^3), Cu (1.85 ng/m^3), Fe (7.00 ng/m^3), K (4.8 ng/m^3), Mn (1.45 ng/m^3), Ni (0.9 ng/m^3), Pb (1.05 ng/m^3), S (1.55 ng/m^3), Si (8.85 ng/m^3), Ti (0.25 ng/m^3), V (1.7 ng/m^3), Zn (1.25 ng/m^3).

The measurements lasted from 3 to 31 July 2018. In addition to the concentration of PM10 and the elemental composition of PM10, the hourly variability of the concentrations was also examined during the measurement campaign:

- SO_2 (automatic analyzer Monitoring für Leben und Umwelt API-MLU100; in accordance with PN-EN 14212 (Atmospheric air quality. Standard fluorescent UV method for determining the concentration of sulfur dioxide); the detection limit and measurement accuracy is 2.850 μg/m^3) ,

- NO/NO_2 (automatic analyzer Monitoring für Leben und Umwelt MLU200E; in accordance with PN-EN 14211 (Atmospheric air quality. Standard chemiluminescent method for measuring the concentration of monoxide and nitrogen dioxide; the limit of detection and measurement accuracy is 1.025 μg/m^3),

- O_3 (automatic analyzer Monitoring für Leben und Umwelt MLU400E; in accordance with PN-EN 14625 (Atmospheric air quality. Standard method for measuring ozone concentration using UV photometry); the limit of detection and measurement accuracy is 4.280 μg/m^3),

- CO (automatic analyzer Monitoring für Leben und Umwelt MLU400E; in accordance with PN-EN 14626 (Ambient air quality. Standard method for the determination of carbon monoxide using non-dispersive infrared spectroscopy); the limit of detection and measurement accuracy is 0.125 mg/m^3),

- meteorological parameters (air temperature, humidity, wind speed and direction, atmospheric pressure and precipitation) according to instructions of the network of state weather stations operated by the Institute of Meteorology and Water Management (IMWM).

Results analyses

First, the hourly data on each measured day were averaged. Descriptive statistics of all parameters tested in the measurement period averaged to the 24-hour value are presented in Table 1.

Table 1. Descriptive statistics of daily concentrations of the tested parameters

Parameter	Statistics				
	N	Average	Minimum	Maximum	Standard deviation
PM10, μg/m^3	29	20.8	7.1	48.4	7.5
Al, ng/m^3	29	357.2	76.4	675.0	154.9
As, ng/m^3	29	0.5	<LLD	4.5	1.0
Ca, ng/m^3	29	256.2	64.6	517.5	134.1
Cr, ng/m^3	29	6.1	5.2	7.3	0.5
Cu, ng/m^3	29	11.2	7.1	22.8	3.1
Fe, ng/m^3	29	195.2	63.9	355.4	77.1
K, ng/m^3	29	76.7	5.4	132.5	34.3
Mn, ng/m^3	29	6.9	3.0	12.7	2.5
Ni, ng/m^3	29	5.4	4.5	8.5	0.9

NO, µg/m^3	29	1.0	0.5	2.8	0.5
NO$_2$, µg/m^3	29	6.2	3.1	8.2	1.3
O$_3$, µg/m^3	29	25.1	19.3	33.1	3.8
Pb, ng/m^3	29	6.1	1.4	14.9	3.9
S, ng/m^3	29	1485.5	556.7	2352.4	487.4
Si, ng/m^3	29	770.3	98.5	1722.8	455.8
SO$_2$, µg/m^3	29	3.4	1.8	4.9	0.9
Ti, ng/m^3	29	12.8	0.3	54.8	11.7
V, ng/m^3	29	2.1	1.8	2.5	0.2
Zn, ng/m^3	29	14.5	4.4	37.6	7.7
CO, µg/m^3	29	0.4	0.2	0.5	0.1
Temperature max. °C	29	27.8	19.0	32.6	3.4
Temperature min. °C	29	14.8	10.5	18.6	2.2
Temperature average. °C	29	21.1	16.8	25.6	2.3
Humidity %	29	67.6	47.7	97.7	13.8
Wind speed m/s	29	7.1	4.2	11.7	1.9
Atmospheric pressure, hPa	29	1013.7	1008.2	1017.4	2.4
Precipitation, mm	29	1.7	0.0	12.0	3.6

In the case of the concentration of PM10 and PM10-bound elements, the hourly variability of the concentrations during the day was also tested (Figures 2, 3). For this purpose, the average concentrations determined for each hour were averaged over the entire measurement period (29 concentrations for 0.00 hour; 29 for 01.00 hour, etc.).

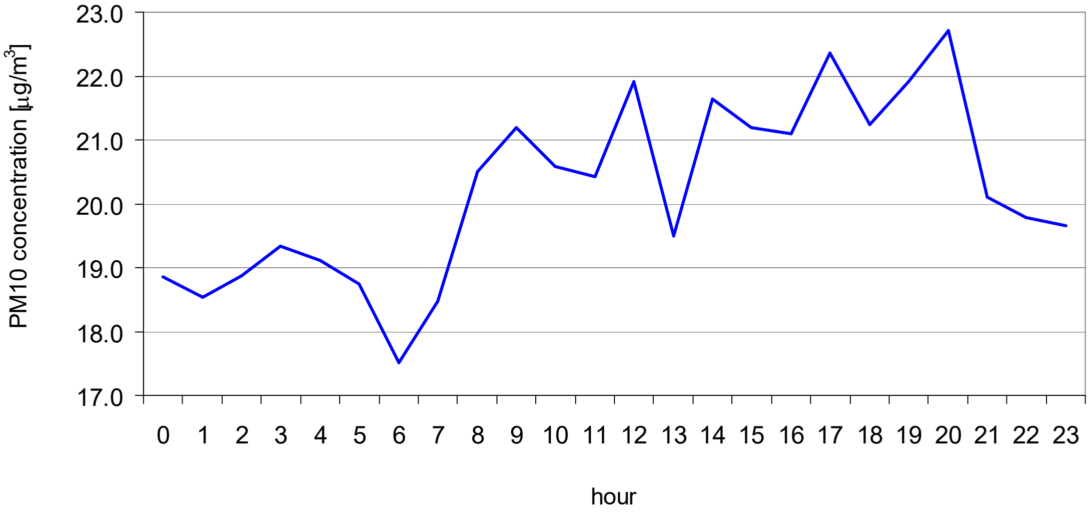

Figure 2. The average hourly PM10 concentrations averaged for the entire measurement period (03-31.07.2019) in the receptor.

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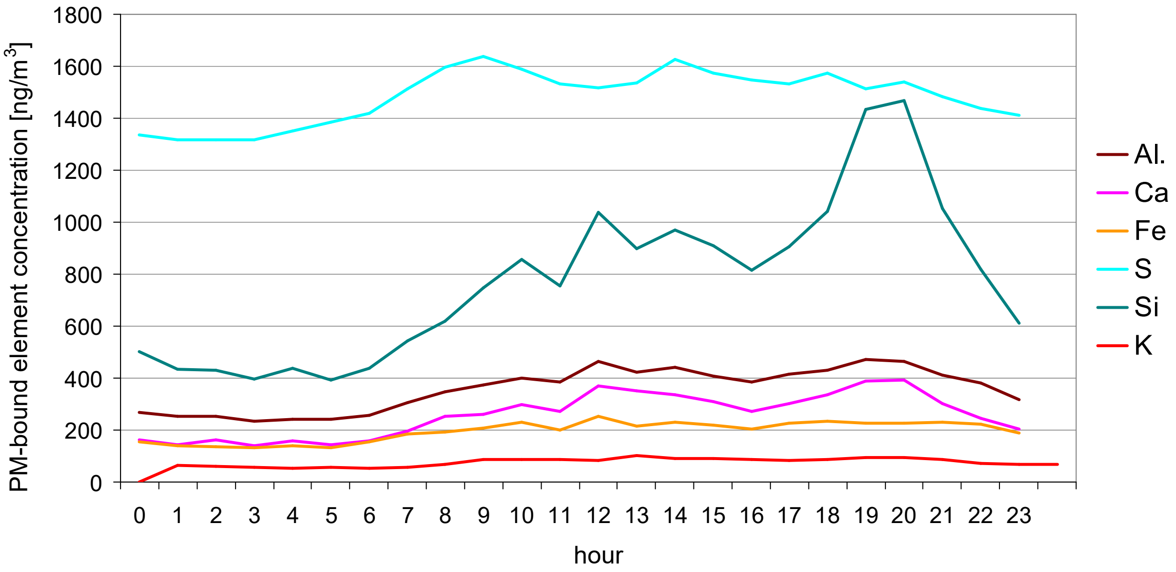
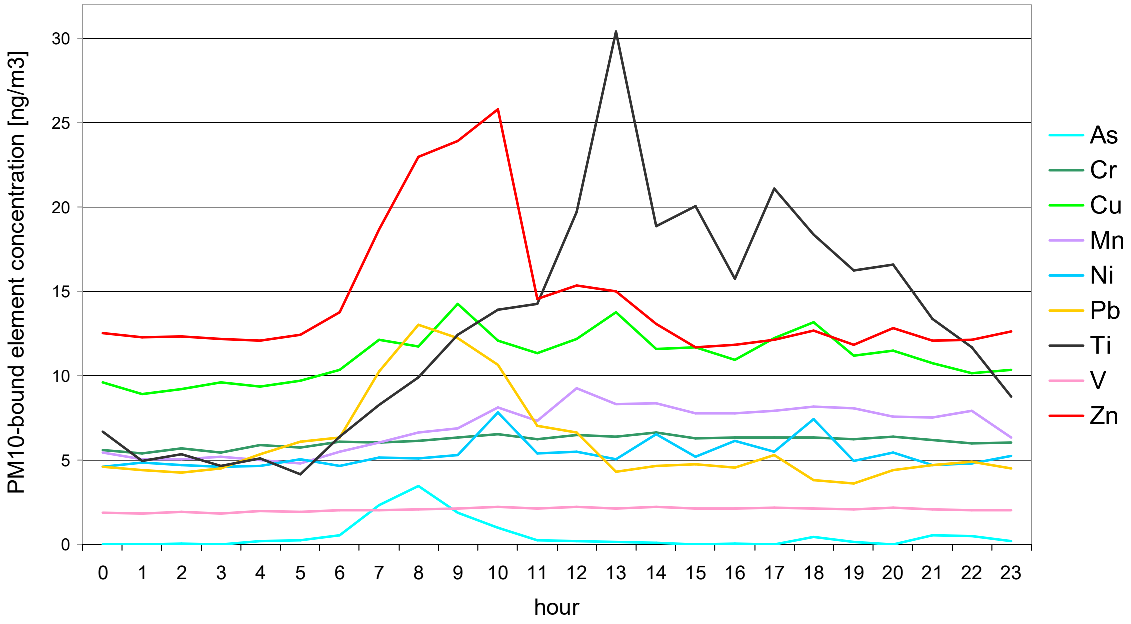


a)



b)

Figure 3. The average hourly concentrations Al, Ca, Fe, S, Si and K (a) and As, Cr, Cu, Mn, Ni, Pb, Ti, V and Zn (b) averaged for the entire measurement period (03-31.07.2019) in the receptor.

The so-called enrichment factor (EF) was then calculated for each element measured independently for the averaged concentration of the element in each hour of the day and for the averaged concentration of the element in the entire measurement period. The method of calculating EF for the elements and the assumptions for the calculations were done in the same way as in the previous works [22–24,27–29]. By using the enrichment factor it was possible to assess quantitatively the strength of the anthropogenic effect influencing the PM10-bound element concentrations.

In the next step, a principal component analysis (PCA) was applied to the 15x29 data matrix [23,24] representing the 1-hour PM10-bound element concentrations.

All calculations were performed using Statistica 8.0 software (StatSoft, Tulsa, OK, USA).

3. Results and 4. Discussion

3.1. Concentrations of PM10

The twenty-four-hour concentrations of PM10 in Kotórz Mały ranged from 7.1 to 48.4 μg/m^3 (Table 1). The mean PM10 concentration for the entire measurement period was equal to 20.8 μg/m^3. It was below the daily PM10 concentration limit established by the European Commission (50 μg/m^3; not to be exceeded on more than 35 days per year) [30]. PM10 concentrations fluctuated throughout the day, although the changes were relatively small (± 5 μg/m^3) (Figure 2). The lowest concentrations of PM10 were recorded between 00.00-06.00 a.m. and the highest between 02.00 p.m.-09.00 p.m. The fact that the measurements were conducted in the summer, the slight variability of PM10 concentrations during the day and the location of the receptor between two national roads, i.e., road No. 45 with a traffic density of approx. 8,000 vehicles/day (approx. 3 km in a straight line towards north-west) and road No. 46 with a traffic volume of 9500 vehicles/day (approx. 6 km in a straight line towards the south-east) (data from 2015 data from General Director for National Roads and Motorways https://www.gddkia.gov.pl/userfiles/articles/g/generalny-pomiar-ruchu-w-2015_15598//SYNTEZA/WYNIKI_GPR2015_DK.pdf), allow us to assume that the PM10 concentrations in the receptor were mainly determined by traffic emission, and their peaks in the afternoon hours were caused by the increased traffic intensity related to the movement from work and to work (2nd shift). This is also indicated by the wind rose of PM10 pollution (Figure 4) according to which the highest concentrations of PM10 were observed at the inflow of air masses from the NNW and NE directions, where the above routes run. PM10 concentrations above the average (> 20 μg/m^3) were also recorded with the inflow of air masses from the SE direction. This may also indicate the impact on the PM10 concentration in the receptor of emission sources present in the Opole agglomeration, located 15 km from the receptor in the south-east direction. Although the measurements were carried out in the summer, the so-called low-stack emission related to the combustion of solid fuels in individual home furnaces (e.g. to heat the bathwater, satisfy heating needs) can be taken into account as an additional source of PM10 in the evenings, especially since in the analyzed measurement period there were days when the air temperature was below 15°C.

The mean concentration of PM10 in the receptor did not differ much from the PM10 concentrations registered in the non-heating season in other locations in Poland, e.g. at two rural sites in Upper Silesia, Poland (2013; 16.14-27.89 μg/m^3) [31], in the industrial district of Sosnowiec city, Poland (2017, 20 μg/m³) [32], in a health resort in Krynica Zdrój, Poland (2016, 15.2 μg/m³) [33], in small cities around Kraków agglomeration (2017, 23.31 μg/m³) [34] and urban areas of Wrocław and Poznań, Poland (2016, approx. 18 μg/m³ in both cities) [35]. The mean PM_{10} concentration in Kotórz Mały was comparable to the concentration of PM_{10} recorded in summer in the agricultural areas of the Netherlands (2011, 21 μg/m³) and to the mean annual concentrations of PM_{10} in selected European cities (Vien, Brussel, London; 2014, 23-25 μg/m³ [36]; it was low compared to the values registered at various European locations, such as Istanbul, Turkey (2014, 58 μg/m³) [37], and Žilina, Slovakia (2017, 86 μg/m³) [38]. The relatively low concentration of PM_{10} in the receptor was probably influenced by the existence of a natural forest barrier (approx. 0.8 km in a straight line), lack of local industries or enterprises that substantially affect air quality (closest industrial activity approx. 13 km from the receptor) and the high average wind speed (7.1 m/s) which in the analyzed measurement period was more than twice as high as the average annual wind speed in Poland (2.6 m/s in summer; 3.8 m/s in winter). High wind speed could stimulate the air mixing processes, causing the migration of pollutants from the receptor to other areas, but it should also be taken into account that it could favor the inflow of pollutants from neighboring areas, e.g. the Opole agglomeration.

In this study, the concentrations of gaseous PM precursors, i.e., nitrogen oxides (NO_x), sulfur oxides (SO_2), as well as ozone (O_3) and carbon monoxide (CO) were also analyzed (Table 1). The average concentration of NO, NO_2, SO_2, O_3 and CO in the receptor take values: 1.0 μg/m³, 6.2 μg/m³, 3.4 μg/m³, 25.1 μg/m³ and 0.4 μg/m³ respectively and they were lower than concentrations recorded in other parts of the Poland, i.e. in the central agglomeration of Silesia (summer 2017, NO_x approx. 30 μg/m³) [39], in Warsaw agglomeration (summer 2014, NO_2=18.5 μg/m³, NO_x=22.5 μg/m³, SO_2=4 μg/m³, O_3=62.2 μg/m³) [40] and two cities in northern Poland (Tczew i Sopot) (warm season 2014; NO_2 = 10.3 μg/m³ (Tczew) and 10.0 μg/m³ (Sopot); SO_2=3.9 μg/m³ (Tczew) and 3.6 μg/m³ (Sopot), CO = 225 μg/m³ (Tczew) and 247 μg/m³ (Sopot) [41]. The increased intensity of photochemical reactions induced by solar irradiation in the sunny months, the use of gasoline-powered mechanical vehicles in summer, and the lack of the need to heat most of the buildings could have resulted in low concentrations of gaseous pollutants in the receptor [42]. The concentrations of the considered gaseous pollutants were also below the limit values set out in European law [30].

It is important to investigate the relationship between the concentrations of the studied gaseous substances and PM10, but this was not the subject of this study. Moreover, it would be necessary to collect data from a longer period. Herein, the studies on gaseous pollutants served, as well as the knowledge of the average meteorological parameters during the research period, to assess the aero-sanitary air conditions during the research period. They were typical for the summer period in Poland, and taking into account the state of air quality in other regions of the southern part of Poland in the summer, it can be assessed even as much better [40,43–45].

3.2. PM10-bound elements

The mean concentrations of the selected PM10-bound elements fluctuated within wide limits and took values from 0.5 ng/m³ (As) to 1485.5 ng/m³ (S). The masses of 15

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PM10-bound elements collectively accounted on average for 15% of the PM10 mass. S, Si and, Al were the most abundant among the determining elements. Their average mass percentages in the total PM10 mass were 7%, 4% and 2%, respectively. On average, during the entire monthly measurement period, the elements related to PM_{10} tested in the study can be arranged in the following order: As<V<Ni<Pb<Cr<Mn<Cu<Ti<Zn<K<Fe<Ca<Al<Si<S (Table 1). Most of these elements had fairly even concentrations, both daily and hourly (Table 1; Figure 3). Slight increases in the concentrations of most elements were observed between 12.00 p.m.-02.00 p.m. and between 06.00 p.m.-08.00 p.m. (Figure 3) except for Si, Zn, Ti, As and Pb, for which the concentration jumps were higher compared to the other elements. For Zn and Ti, almost twofold increase in concentration was recorded, respectively, in the hours 06.00-10.00 a.m., 11.00 a.m.-01.00 p.m., for Si between 06.00 p.m. a 08.00 p.m. and for As and Pb at 08.00 a.m. In general, trace elements, including the toxic ones, such as As, V, Ni, Pb, Cr, Mn were present in very low concentrations, not exceeding 10 ng/m^3 (mean daily value); the mean concentrations of As, Ni, and Pb in Kotórz Mały did not exceed the permissible values of annual concentrations established by the European Commission (6 ng/m^3, 20 ng/m^3, and 0.5 µg/m^3, respectively)[30]. The concentrations of the majority of tested PM10-bound elements were much lower than those previously recorded in other regions of Poland (Table 2). The concentrations of PM10-bound Si, K, Al, Ti, Fe Ca, Mn were determined by natural sources. This is indicated by EF values which, regardless of the time of day, do not exceed 10 during the entire measurement period (Table 3). Si, K, Al, Ti, Fe Ca are typical crustal elements, therefore it can be assumed that they were derived from the resuspension of crustal and soil matter [22,24,25,46]. When analyzing the changes in EFs during the day, it should be noted that EF for Al, Fe, Mn at 11.00 p.m.-08.00 a.m and Ti at 01.00 p.m were higher than the values of EF averaged for the entire measurement period. This may indicate the impact of an additional source of contamination in the considered hours. This will be explained in detail later in the manuscript using the PCA analysis. The concentrations of the remaining PM10-bound elements, i.e. S, Cu, Pb, Ni, Zn, As, Cr were strongly influenced by anthropogenic sources (EF_x> 10; Table 3). EF values for these elements changed during the day, with the highest values (higher than the average for the entire measurement period) recorded between 12.00 a.m-11.00 a.m. This may indicate a strong impact of several anthropogenic sources in this hour range, e.g. combustion of fuels by vehicles, abrasion of vehicle elements (wheels, brakes) and road surfaces, the inflow of polluted air masses from urbanized areas and low-stack emission [47–51]. An interesting case is V and As. The EFs for these elements indicate that at certain times of the day (V 07.00 p.m.-08.00 p.m.; As at 05.00 p.m.) their concentrations were strongly influenced by natural sources, and in others by anthropogenic sources. EFs greater than 10 for these elements in the rest of the day do not exclude that during these hours they also did not come from natural sources, e.g., soil re-suspension, but then the impact of anthropogenic sources (like road traffic or coal combustion) was more intensive [47,52,53].

Table 2. The mean concentration of PM10 and PM10-bound elements at various sites in Poland.

Sampling site (city, type)	***Measurement period***	***PM10 [μg/m³]***	***Concentration [ng/m³]***											
			As	**Ca**	**Cr**	**Cu**	**Fe**	**K**	**Mn**	**Ni**	**Pb**	**Ti**	**V**	**Zn**
Kotórz Mały, this study	*Summer2018*	*21*	*0.5*	*256.2*	*6.1*	*11.2*	*195.2*	*76.7*	*6.9*	*5.4*	*6.1*	*12.8*	*2.1*	*14.5*
Warsaw, urban area [54]	summer 2017	40		228.9	52.5	16.2	145.9		21.4	10.8	17.2			
Wadowice, urban area [55]	winter 2017	174	11.0	590.0	4.0	27.0	760.0	1400.0	27.0	4.2	120.0	56.0	15.0	360.0
Poznań, urban area [35]	summer 2017	17		2611.0				48.0						
Wrocław, urban area [35]	summer 2016	17		1080.0				300.0						
Poznań, urban area[56]	2010-2016	17	1.0							1.2				
Upper Silesia, rural area [57]	spring 2014	23	0.8		239.4	2.5	217.3		12.3	6.2	20.4			72.7
Kraków, urban area [58]	winter 2015	30-95		580.0	10.1	23.6		160.0	22.5	3.2	45.7	73.5	3.9	148.6

Table 3. The enrichment factors (EF) for the PM_{10}-bound elements, averaged for each hour of the day and the measurement period.

Period/Element	Al	As	Ca	Cr	Cu	Fe	K	Mn	Ni	Pb	S	Si	Ti	V	Zn
0	2.1	0.0	3.3	97.3	406.8	3.1	1.3	6.2	150.3	164.2	849.0	1.0	1.3	21.6	146.3
1	2.3	0.0	3.4	108.2	437.1	3.2	1.5	6.7	182.4	181.3	969.3	1.0	1.1	24.1	165.6
2	2.3	24.2	3.9	114.5	454.3	3.1	1.4	6.8	179.2	176.1	976.8	1.0	1.2	25.6	167.3
3	2.3	0.0	3.6	119.1	515.5	3.3	1.4	7.5	189.4	203.7	1057.8	1.0	1.1	26.4	179.2
4	2.2	64.2	3.7	116.8	454.3	3.2	1.4	6.6	174.2	217.7	985.9	1.0	1.1	26.0	161.2
5	2.4	92.0	3.7	127.1	526.0	3.4	1.4	7.1	210.9	278.5	1128.0	1.0	1.0	28.6	185.1
6	2.3	195.7	3.8	120.2	500.3	3.4	1.4	7.2	174.0	258.4	1029.0	1.0	1.4	26.8	183.5
7	2.2	655.8	3.7	97.0	474.9	3.3	1.4	6.4	155.0	337.2	889.0	1.0	1.5	21.4	201.2
8	2.2	855.5	4.2	86.3	403.1	3.1	1.5	6.2	134.6	376.5	821.5	1.0	1.6	19.1	216.8
9	2.0	382.2	3.6	73.7	406.2	2.7	1.2	5.3	115.4	292.6	699.0	1.0	1.6	16.4	187.0
10	1.8	179.0	3.6	65.9	299.1	2.7	1.1	5.4	148.9	221.3	590.0	1.0	1.6	14.7	175.6
11	2.0	46.3	3.7	71.7	318.6	2.6	1.2	5.6	116.5	166.7	646.1	1.0	1.8	16.0	112.8

12	1.8	26.9	3.7	54.4	248.6	2.4	1.1	5.1	86.3	114.0	465.7	1.0	1.8	12.2	86.5
13	1.8	24.6	4.0	61.7	326.5	2.4	1.1	5.4	92.0	85.9	545.7	1.0	3.3	13.6	97.8
14	1.8	17.8	3.6	59.2	253.5	2.3	1.0	5.0	109.6	85.3	534.2	1.0	1.9	13.2	78.5
15	1.8	0.0	3.5	60.0	272.3	2.4	1.0	4.9	93.5	93.7	550.3	1.0	2.1	13.3	74.8
16	1.9	11.7	3.4	67.5	284.3	2.5	1.1	5.5	123.3	100.2	603.2	1.0	1.9	14.9	84.8
17	1.8	3.3	3.4	60.7	286.4	2.4	1.0	5.0	99.4	104.7	539.3	1.0	2.3	13.7	78.3
18	1.6	67.6	3.3	52.7	268.7	2.2	0.9	4.5	116.2	65.3	480.5	1.0	1.7	11.8	71.0
19	1.3	16.5	2.8	37.7	165.8	1.5	0.7	3.2	56.6	45.2	335.9	1.0	1.1	8.3	48.1
20	1.2	0.0	2.7	37.8	166.6	1.5	0.6	3.0	60.5	53.9	334.2	1.0	1.1	8.4	51.0
21	1.5	79.7	3.0	50.9	216.7	2.2	0.7	4.1	72.6	79.9	448.1	1.0	1.2	11.4	66.9
22	1.8	91.1	3.1	63.3	263.2	2.7	0.9	5.6	95.5	107.3	558.3	1.0	1.4	14.1	86.3
23	2.0	50.6	3.5	85.8	359.7	3.1	1.2	6.0	140.6	131.5	738.2	1.0	1.4	19.3	120.7
3-31.07 (average)	1.8	98.5	3.4	68.7	308.6	2.5	1.1	5.2	114.4	141.4	614.1	1.0	1.6	15.6	109.9

Source apportionment of PM10

The principal component analysis (PCA) was applied to assess the correlations between different PM10-bound elements and identify the main sources of PM10 in Kotórz Mały. Fifteen variables (Al, As, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, S, Si, Ti, V, Zn) were included in this analysis. This analysis was divided into individual hours of the day due to the different hourly trends observed in these constituents (Figure 5). For a better interpretation of PCA results, the enrichment factors (EFs) for PM10-bound elements (Table 3), the distribution of element concentrations for particular wind directions (Figure 4), conclusions were drawn by the authors of previous studies [24,29,59], as well as conclusions from studies conducted by other researches were also taken into account.

As a result of the PCA, five principal components (PC1-PC5) were identified with eigenvalues higher than 1.0 (according to the Kaiser criterion). Together they explain on average 97.4% of the cumulative variance in the dataset (Figure 5). The most important is the first main component, which explains on average 42.7% of the variability, the second component explains 17.6% of the variability, the third 13.3%, the fourth 12.7%, and the fifth 11.1%.

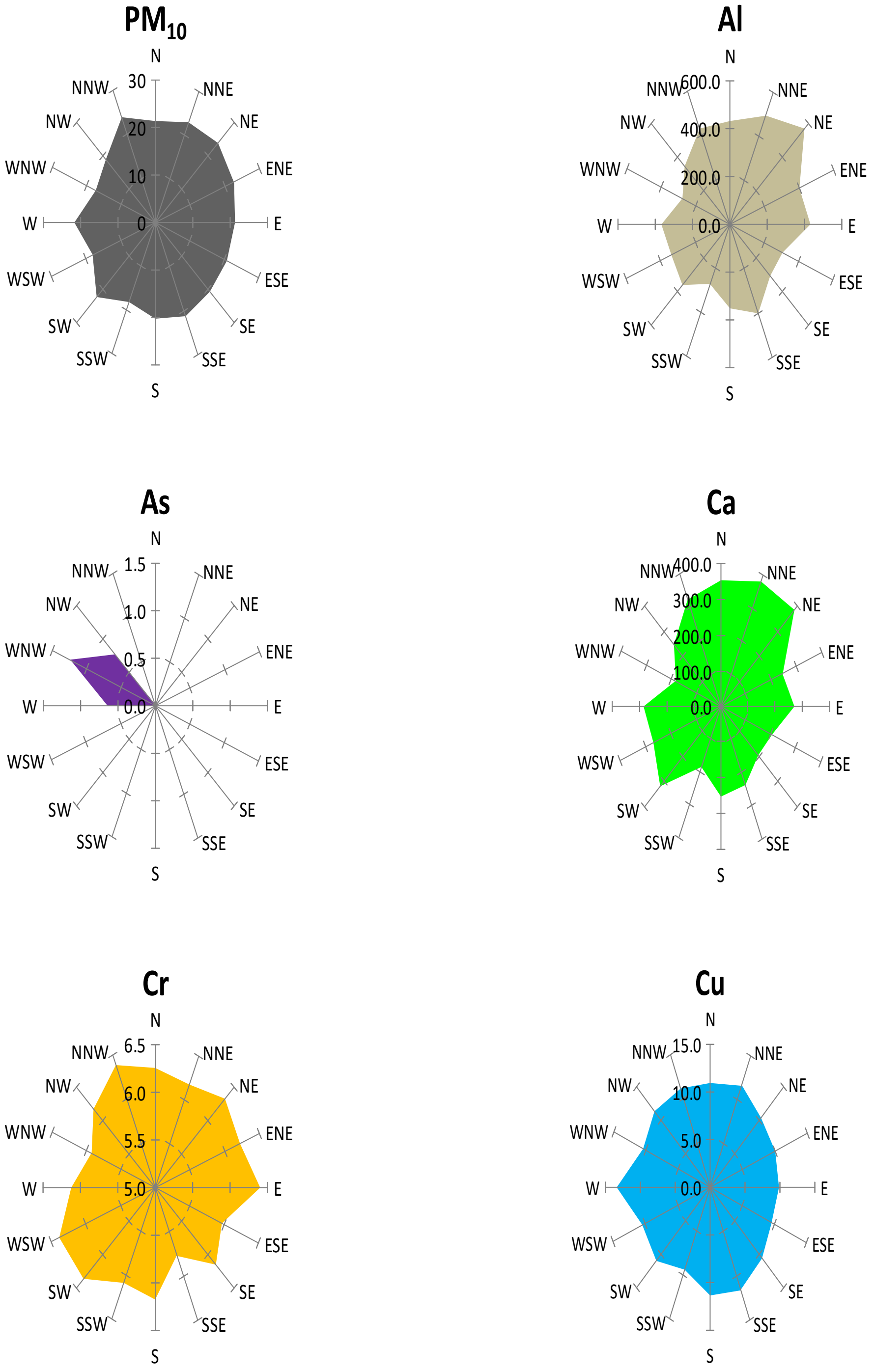
Fourteen elements, i.e. V, Cr, Mn, Ni, Cu, Zn, As, Pb, Al, Si, K, Ca, Fe, Ti were strongly correlated (factor loadings ≥0.7) with PC1. The vast majority of these elements (Al, Ca, K, Mn, Fe, Si, Ti) were of natural origin (EFs <10, Table 3) and their highest concentrations were observed when there was an inflow of air masses from NNE and NE directions (Figure 4). Crops, forest and lake are located in these directions. The above premises and the conclusions of other researchers[19,38,60–62] indicate that Al, Ca, K, Mn, Fe, Si, Ti came from the resuspension of soil and mechanical abrasion processes of crustal materials. Moreover, following to Gustafsson et al.[63] and Li et al. [64], it can be concluded that Al, Si and K could also have been derived from the abrasion of the pavement. The research presented by [22,65–68] shows that the remaining elements correlated with PC1 i.e. V, Cr, Ni, Cu, Zn, As, and Pb were likely traffic-related pollutants deposited in soils whose particles have been entrained by wind or field work. Therefore, it can be assumed that PM_{10} identified in PC1 came from mineral matter. As shown by the hourly correlations of these elements with PC1, this source affected PM10 concentrations in the receptor throughout the day, with the more intensive interaction occurring at 12.00 a.m., 03.00 p.m. and 05.00 p.m-06.00 p.m.

Such elements as V, Cr, Ni, Cu, Zn, As, Pb, Al, Si, S, K, Fe were strongly correlated with PC2. The concentrations of Cr and V during the day were at a relatively constant level (Figure 3), and their slight increases were observed with the air inflow from the NNW, SW, WSW and E directions (Figure 4). The highest mean concentrations of Pb were observed when there was an inflow of air masses from the SE, S, SW, SSE directions; Zn from the SW, S, ESE directions; As from the WNW direction; Cu from the W direction, and Ni from the ESE direction (Figure 4). In the NNW, SW, WSW directions there is the national road No. 45 and in the S, SSE, SE directions, the national road No. 46; towards SW, WSW is located the Opole agglomeration. Taking into account that the group of Pb, Cu, Zn, Cr and Ni is mostly representative for vehicle exhaust and road dust [46,69–71], Cu, Zn are characteristic markers of brake lining wear, and Zn additionally tire wear [19,72] and zinc compounds are also used as antioxidant and detergent improving the quality of automotive grease, it can be assumed that PM10 identified in PC2 originate from traffic emissions. This source had the most intense influence on the concentrations of PM_{10} in the receptor at 12.00 a.m., 03.00 p.m. and 05.00 p.m-06.00 p.m. These are the times of the day when traffic is usually heaviest due to the movement of city inhabitants to work, schools, kindergartens etc. During these hours, PC2 explains the most, approx. 30% of the variance in PM_{10} emission.

Six elements were strongly correlated with PC3, i.e. S, V, Cr, Zn, As, Pb (Figure 5). S is a characteristic PM component for areas where coal and fine coal are used for energy purposes [64,73]. It is also a characteristic metal released during biomass, waste and garbage burning in small-scale installations, i.e. domestic stoves/local boiler houses [25,74,75]. Moreover, the source of S may be secondary inorganic aerosols (sulphates), also released from the above-mentioned sources [76]. Zn and Pb associated with coarse dust, apart from traffic emissions, may come from biomass burning [25,61]. According to the research described in [65,77], another source of Cr and V is fossil fuel and fuel oil combustion. The highest concentrations of S were recorded between 10.00 a.m. and 06.00 p.m. at the inflow of air from the directions NE and NNE (Figure 4), where the neighboring village is located. Zn and Pb concentrations between 10.00 p.m. at 03.00 a.m., i.e. in the hours when these elements showed a strong correlation with PC3, which also corresponded to the inflow of air masses from the NE direction (Figure 4). The above observations allow us to conclude that PM10 identified in PC3 came from the low-stack emission from sources located in the NE direction from the receptor and this source explains the largest amount of variation in the early morning hours (04.00 a.m.-07.00 a.m.). The effect of municipal emissions, which can represented by PC3, in Kotórz Mały in this period was not large compared to the impact of natural sources (soil/mineral matter) and road traffic (exhaust and non-exhaust emission). This is obvious as the research was carried out in the summer period when there is no strong low-stack emission impact related to home heating [26]. Nevertheless, also in the summer period, due to the strong correlation of PC3 with the characteristic elements, it can be noted that in households at suburban areas this type of emission is still important. Taking into account the variability of the importance of PC3 during the day, it can be suggested that it is associated with the burning of various types of biomass waste and other organic materials and their derivatives, either when cleaning gardens, fields or during recreation activities (grilling, bonfires, etc.) [78–81].

PC4 explains the smaller amount of variance (12.7%) compared to PC1. His variances were in the range 8.0% (at 07.00 a.m.) to 14.9% (at 11.00 a.m.). PC4 was the most strongly correlated with V, Cr, Ni, Cu, Zn, As and S. Concentrations recorded in hours corresponding to the correlations of individual elements with PC4 indicate the inflow of air masses mainly from the SE, SSE, SW, WSW directions. In addition to roads with heavy traffic, 12 km in a straight line from the receptor towards SW there is an opencast mine of carbonate rocks called the Odra Quarry, while 13.5 km in a straight line towards the SE Mala Panew ironworks in Ozimek is located. These observations allow assuming that PC4 reflects the industrial source of PM_{10} in the receptor. Additionally, it is proved by strong correlations of PC4 with Ni, which is a component of metal products [82,83] and with As, Cu, V and Cr which are related to the production of ceramics, cement and metal smelting [83–85].

The last extracted principal component is PC5. Only two elements (Zn and S) were strongly correlated with PC5. The source identified in PC5 explains approx. 13% of the variance in PM_{10} emission only at 11.00 p.m. At that time, the mean Zn and S concentrations were 12.5 ng/m^3 and 1400 ng/m^3, respectively. Such values of these two elements were recorded when there was an air inflow from the NW direction. As described in [26] the northern part of Kotórz Mały is characterized by rural development, which predominantly uses obsolete individual heating systems (hard coal, 91%, wood, 6%, only 2% of non-emission heating systems). This allows us to assume that PM_{10} identified in PC5 is probably originated from fossil fuel and/or biomass combustion in local households [73]. Most probably, the hourly variability of the concentrations of the examined elements, for Zn and S, different than for other elements correlated with PC3, resulted in the isolation of an additional component of PC5. This component, however, undoubtedly, similarly to PC3, is related to municipal emission.


PM_{10}
N
NNE
NE
ENE
E
ESE
SE
SSE
S
SSW
SW
WSW
W
WNW
NW
NNW
30
20
10
0
Al
600.0
400.0
200.0
0.0
As
1.5
1.0
0.5
0.0
Ca
400.0
300.0
200.0
100.0
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Cr
6.5
6.0
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Cu
15.0
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0.0

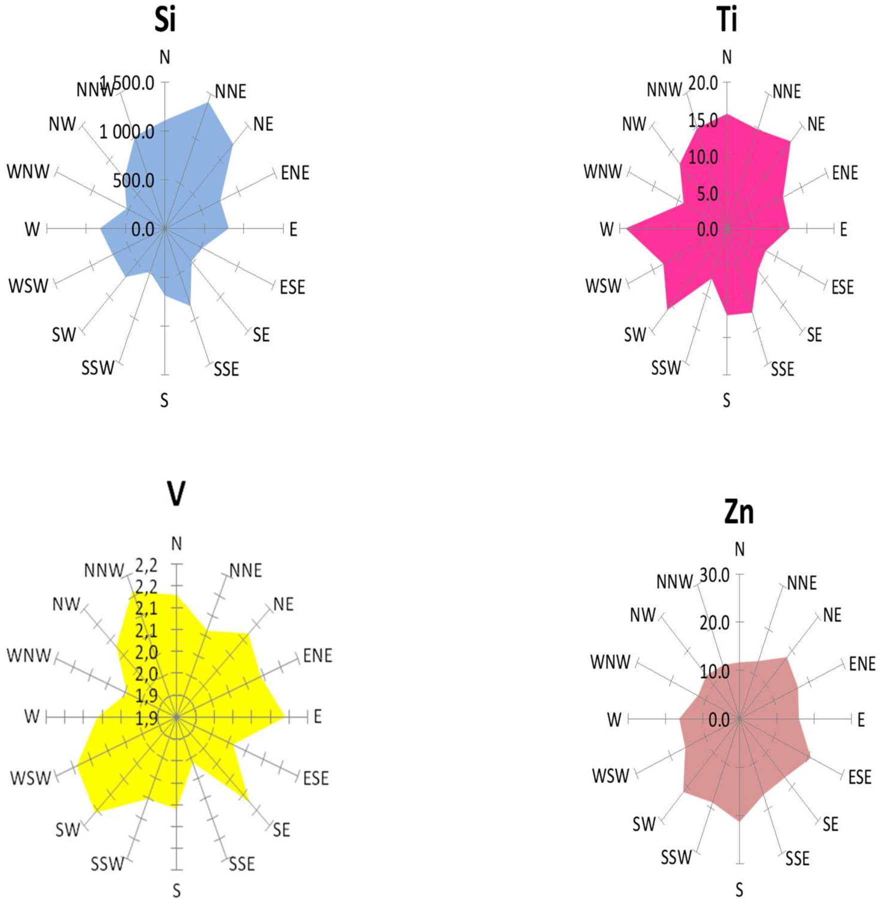
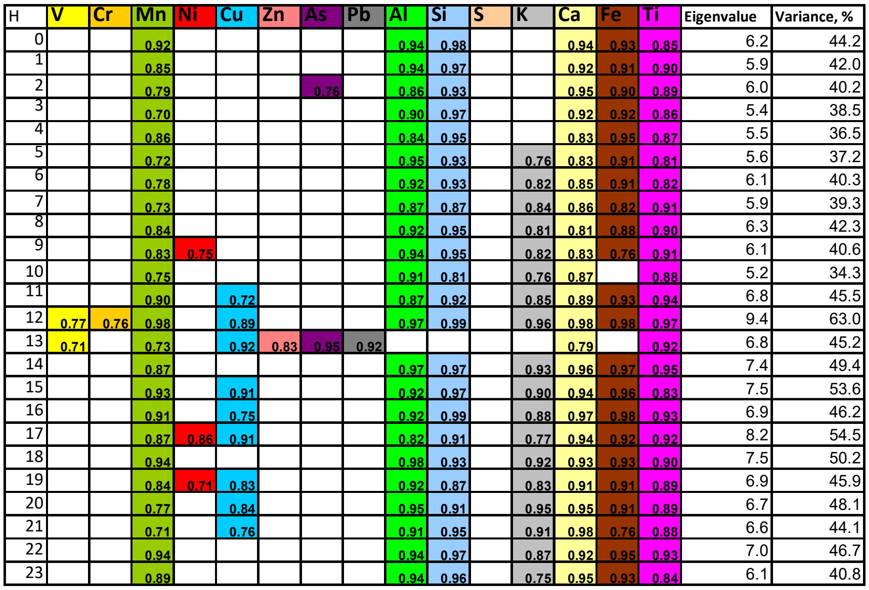


Fig. 4. Average concentrations of PM10 and PM10-bound elements related to wind direction in the measurement period.

PC1



H	V	Cr	Mn	Ni	Cu	Zn	As	Pb	Al	Si	S	K	Ca	Fe	Ti	Eigenvalue	Variance, %
0			0.92						0.94	0.98			0.94	0.93	0.85	6.2	44.2
1			0.85						0.94	0.97			0.92	0.91	0.90	5.9	42.0
2			0.79				0.76		0.86	0.93			0.95	0.90	0.89	6.0	40.2
3			0.70						0.90	0.97			0.92	0.92	0.86	5.4	38.5
4			0.86						0.84	0.95			0.83	0.95	0.87	5.5	36.5
5			0.72						0.95	0.93		0.76	0.83	0.91	0.81	5.6	37.2
6			0.78						0.92	0.93		0.82	0.85	0.91	0.82	6.1	40.3
7			0.73						0.87	0.87		0.84	0.86	0.82	0.91	5.9	39.3
8			0.84						0.92	0.95		0.81	0.81	0.88	0.90	6.3	42.3
9			0.83	0.75					0.94	0.95		0.82	0.83	0.76	0.91	6.1	40.6
10			0.75						0.91	0.81		0.76	0.87		0.88	5.2	34.3
11			0.90		0.72				0.87	0.92		0.85	0.89	0.93	0.94	6.8	45.5
12	0.77	0.76	0.98		0.89				0.97	0.99		0.96	0.98	0.98	0.97	9.4	63.0
13	0.71		0.73		0.92	0.83	0.95	0.92					0.79		0.92	6.8	45.2
14			0.87						0.97	0.97		0.93	0.96	0.97	0.95	7.4	49.4
15			0.93		0.91				0.92	0.97		0.90	0.94	0.96	0.83	7.5	53.6
16			0.91		0.75				0.92	0.99		0.88	0.97	0.98	0.93	6.9	46.2
17			0.87	0.86	0.91				0.82	0.91		0.77	0.94	0.92	0.92	8.2	54.5
18			0.94						0.98	0.93		0.92	0.93	0.93	0.90	7.5	50.2
19			0.84	0.71	0.83				0.92	0.87		0.83	0.91	0.91	0.89	6.9	45.9
20			0.77		0.84				0.95	0.91		0.95	0.95	0.91	0.89	6.7	48.1
21			0.71		0.76				0.91	0.95		0.91	0.98	0.76	0.88	6.6	44.1
22			0.94						0.94	0.97		0.87	0.92	0.95	0.93	7.0	46.7
23			0.89						0.94	0.96		0.75	0.95	0.93	0.84	6.1	40.8

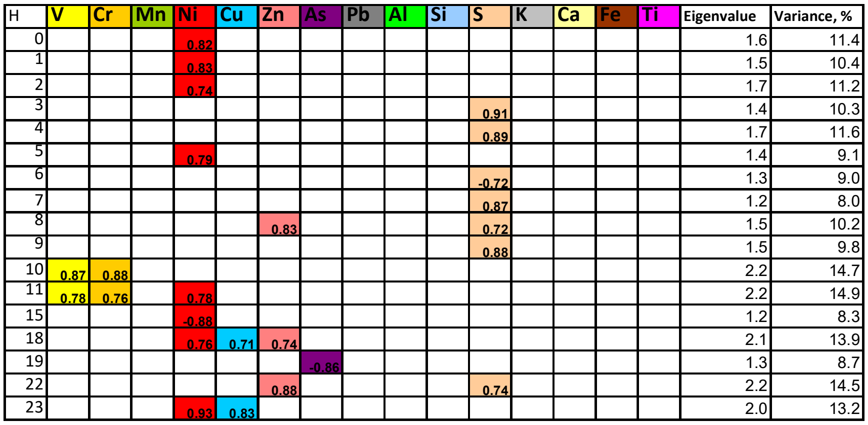
PC2

H	V	Cr	Mn	Ni	Cu	Zn	As	Pb	Al	Si	S	K	Ca	Fe	Ti	Eigenvalue	Variance, %
0	0.95	0.97														2.4	17.2
1	0.96	0.97														2.3	16.4
2	0.95	0.95														2.7	17.7
3	0.96	0.97														2.6	18.5
4					0.76		0.81	0.90								2.4	16.0
5	0.96	0.95														2.4	16.1
6							0.85	0.95								2.2	14.7
7					0.81		0.82	0.95								2.5	16.9
8							0.90	0.93								2.3	15.1
9						0.80	0.89	0.92								2.7	18.1
10				0.79	0.73	0.93	0.87	0.94						0.71		4.6	30.9
11							-0.93	-0.96								2.1	14.1
12							0.92	0.72								2.1	14.0
13									0.91	0.90		0.91		0.89		5.2	34.5
14	0.73	0.74					0.93	0.91								3.6	23.7
15	0.97	0.94														2.2	15.6
16	0.92	0.93														2.6	17.2
17						0.78										1.9	12.7
18							0.88	0.96								2.0	13.2
19						0.90		0.84			0.71					2.1	14.2
20						0.93	0.94				0.72					2.4	17.1
21						0.72	0.70	0.94								2.8	18.9
22	0.94	0.93														2.3	15.4
23	0.96	0.96														2.2	14.5

PC3

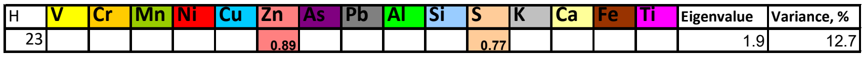
H	V	Cr	Mn	Ni	Cu	Zn	As	Pb	Al	Si	S	K	Ca	Fe	Ti	Eigenvalue	Variance, %
0						0.83		0.77								1.9	13.6
1						0.87										1.8	13.1
2						0.81										1.7	11.1
3						0.84		0.874								2.0	14.5
4	0.97	0.97														2.4	15.9
5								0.88								2.2	14.7
6	0.95	0.95														2.2	14.8
7	0.90	0.91														2.5	16.7
8	0.96	0.97														2.2	14.7
9	0.86	0.89														2.5	16.4
10											0.96					1.3	8.5
11											0.85					1.7	11.3
12						0.74					0.87					1.4	9.5
13											-0.91					1.3	8.9
14						0.79					0.90					2.0	13.2
15						0.74					0.82					1.5	10.9
16						0.80										2.0	13.2
17							0.76									2.1	13.7
18	0.71										-0.75					1.8	11.8
19	0.93	0.91														2.3	15.3
20	0.92	0.93														2.2	15.4
21	0.90	0.91														3.0	19.9
22							0.95	0.75								1.7	11.0
23							0.95	0.85								1.7	11.3

PC4



H	V	Cr	Mn	Ni	Cu	Zn	As	Pb	Al	Si	S	K	Ca	Fe	Ti	Eigenvalue	Variance, %
0				0.82												1.6	11.4
1				0.83												1.5	10.4
2				0.74												1.7	11.2
3											0.91					1.4	10.3
4											0.89					1.7	11.6
5				0.79												1.4	9.1
6											-0.72					1.3	9.0
7											0.87					1.2	8.0
8						0.83					0.72					1.5	10.2
9											0.88					1.5	9.8
10	0.87	0.88														2.2	14.7
11	0.78	0.76		0.78												2.2	14.9
15				-0.88												1.2	8.3
18				0.76	0.71	0.74										2.1	13.9
19							-0.86									1.3	8.7
22						0.88					0.74					2.2	14.5
23				0.93	0.83											2.0	13.2

PC5



H	V	Cr	Mn	Ni	Cu	Zn	As	Pb	Al	Si	S	K	Ca	Fe	Ti	Eigenvalue	Variance, %
23						0.89					0.77					1.9	12.7

Figure 5. A summary of the results of the principal components analysis (PCA) performed for hourly data with the elemental composition of PM10. For each hour, 29 data were used, and the tables summarized only those elements that were always correlated with the variables PC1-PC5 (correlation coefficient r> 0.7).

5. Conclusions

Regardless of the fact that in this study we used data from the summer period, it was shown that in the receptor characterizing a typical rural area in the southern part of Poland, the impact of carbon emissions on the elemental composition of PM10 can be noticed almost every hour of the day. During the measurement period, especially at night and in the early morning hours, an evident influence of municipal emission on the elemental composition of PM10 was observed. However, the natural emission (soil, sand) and exhaust and non-exhaust emission from road traffic had a stronger and dominant influence on the elemental composition of PM10 during the research period. It is highly probable that if the analysis of the origin of PM10 in this measurement period was carried out on the basis of daily data with the elemental composition of PM10, as is usually the case, the influence of other sources would not be noticed. Thus, it has been shown that using hourly concentrations of selected elements, it is possible to assess the origin of PM10 dust and the variability of the share of selected sources in shaping PM10 concentrations over the course of a day, even with the use of data from a relatively short measurement period.

As it results from the conducted PCA, the number of variances explained by particular main components varies in individual hours, which means the variability of the impact of various emission sources during the day. Besides, the conducted research and observations allow concluding that PCs are characterized by PM_{10} sources whose efficiency changed with not only the wind direction but also its speed, which determines the distances to which pollutants are transferred.

Author Contributions: Conceptualization, W.R.K and T.M.; methodology, G.M., P.R.K., K.B.; validation, T.M., P.R.K. and G.M.; formal analysis, G.M.; investigation, T.M.; resources, K.B.; writing—original draft preparation, W.R.K. and K.B.; writing—review and editing, J.R.; supervision, J.R. W. R.K. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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