JEE Journal of Ecological Engineering

Journal of Ecological Engineering 2022, 23(10), 89–97
https://doi.org/10.12911/22998993/152282
ISSN 2299–8993, License CC-BY 4.0

Received: 2022.07.08
Accepted: 2022.08.12
Published: 2022.09.01

Quasi Real-Time X-Ray Fluorescence Spectrometer in Source Apportionment of Particulate Matter in a Typical Suburban Area

Tomasz Mach[1], Justyna Rybak[1], Jan Bihałowicz[2*], Wioletta Rogula-Kozłowska[2]

[1] Faculty of Environmental Engineering, Wroclaw University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

[2] The Main School of Fire Service, ul. Słowackiego 52/54, 01-629 Warsaw, Poland

[*] Corresponding author's e-mail: jbihalowicz@sgsp.edu.pl

ABSTRACT

The article studies the data from a weekly campaign devoted to the study of the elemental composition of PM_{10} in a selected receptor, in a suburban area (Mazowieckie Voivodeship). The sampling point was located at the intersection of main roads and in the vicinity of a typical single-family housing, not far from the electrified Warsaw-Białystok railway line and a small heating plant. The research was carried out in the summer season, in order to minimize the impact of municipal emissions on the concentrations and elemental composition of PM_{10}. A Horiba PX-375 X-ray fluorescence spectrometer was used to measure the one-hour concentrations of elements related to PM_{10}. On the basis of the obtained results, the enrichment factors for PM_{10} in the analyzed elements (EF) were calculated and the principal components analysis (PCA) was performed. It was found that although the elemental composition of PM_{10} in all tested time intervals was noticeably influenced by the emissions from transport, the municipal emissions had a significant impact on the elemental composition, especially those related to coal combustion, and thus the concentration of PM_{10} during the study period. It seems that the possibility of observing the influence of all relevant sources on the composition and concentration of PM_{10} was possible owing to the use of hourly-averaged measurements of the elemental composition of PM_{10}. In the case of daily averaged measurements, in a receptor with such PM_{10} elemental profile, it would be impossible to determine the periods, in which specific – qualitatively completely different – emission sources dominate.

Keywords: atmospheric aerosol; traffic emissions; enrichment factor; 24-h concentrations; diurnal variability; PX-375; XRF analysis.

INTRODUCTION

The elemental composition of particulate matter (PM) is one of its most important environmental and health characteristics, and also allows defining the origin of PM at a specific receptor. Knowing that the elemental composition of the PM that comes from a given emission source is more or less defined; this can be used to determine the origin of the PM in a given area. For this purpose, mathematical models are used (Hopke 2016). The data on the concentrations of elements in PM are used to assess its origin for two main reasons. Most of the elements that are part of PM are found in chemically stable compounds. These compounds, together with the particulate matter, are transported from the emitters to the receptor in a similar chemical form and in amounts depending on the number of PM particles, emitted by the sources containing these elements (Pernigotti, Belis, and Spanó 2016; Zhu et al. 2018). The situation is different in the case of carbon, sulfur and nitrogen compounds, the presence of which in PM depends not only on the number of stable compounds emitted in PM, but also on the presence of gaseous organic and inorganic substances – secondary aerosol precursors in the atmosphere, as well as on meteorological factors determining the changes in volatile and semi-volatile compounds in the atmosphere (Hallquist et al. 2009). The second reason is that some elements can be effective markers of a specific

PM source. These are the elements characteristic of only one source or group of PM sources, which makes it possible to distinguish a given source from others, e.g., the presence of silicon or aluminum is characteristic of PM from soil or sand erosion, and also from biomass combustion (Liang et al. 2019). Sometimes, the mass ratios of the trace elements it contains are also used to assess the origin of PM (Pervez et al. 2018). In conclusion, the comprehensive assessment of the origin of PM, based on the concentrations of the elements identified in it, and using various approaches and modeling, is particularly effective in the areas where elemental profiles from various sources are highly diversified and repeatable over a long period of time (Pokorná, Hovorka, and Hopke 2016). In order to use these models correctly and to obtain the right conclusions, it is necessary to collect a large amount of data. This, in turn, depends on many factors: the meteorological and emission characteristics of the area or the model used. In the area where PM emissions from different sources overlap or where one source is clearly dominant, the correct determination of the origin of PM may be very difficult or even impossible (Rogula-Kozłowska et al. 2013, 2016). In such regions, the data on element concentrations from averaged measurements, at intervals shorter than 24 hours, may be more useful in assessing the origin of PM than the typically collected daily data. It is clear that the concentration, chemical composition and elemental profiles of PM can change dynamically throughout the day, which is related to, i.a. variable impact of road and municipal emissions. Conventional methods of testing the elemental composition of PM usually make it impossible to analyze the concentrations at shorter intervals than a day or even week. The possibility of correct application of conventional methods is determined by the amount of collected and analyzed material, which in this case is the mass of PM. Nevertheless, there are highly sensitive analytical techniques that allow reaching sampling resolution higher than daily, including energy dispersive X-ray spectroscopy (EDXRF). Due to the possibility of testing advanced and relatively recently existing on the market measuring equipment – the EDXRF spectrometer, working in short averaging periods (e.g. 30-min, 1-hour), in this study, it was planned to conduct a measurement campaign in a selected receptor, averaging over time 1-hr concentrations using EDXRF. The measurement point was located where emissions are defined by traffic, at a road junction where congestion is formed. A detailed hourly analysis of the content of elements in PM allowed for the examination of the impact of road traffic on the composition of PM. The variability was determined and the origin of the PM was assessed through the determination of the enrichment factors of the elements in PM, as well as the principal component analysis.

METHODS AND MATERIALS

Location and time of measurements

Measurements were carried out for 7 days, in August 2020, in the Mazowieckie Voivodeship, Wołomin poviat (Wołomin County), in the Wołomin commune, at the intersection of provincial road 634 and poviat roads. One of the largest shops – within 2 km – was located 40 m from the measuring point. The lack of a well-developed public transport network means that with a large number of customers, temporary traffic stops often occur, related to entering a car park, joining traffic and stopping at pedestrian crossings, through which store customers pass. Traffic jams form at the intersection where the measuring equipment was standing, reaching about 500–1000 m in length during rush hours. Despite the fact that the measurements were performed in the administrative area of the village, the buildings there showed a typical suburban character – loose single-family housing. There are water, sewage and gas installations in the village. In addition, at a distance of 500 m from the sampling point, there is the electrified Warsaw-Białystok railway line, and at a distance of 1250 m in a straight line, there is a heating plant smokestack, 120 m above ground level, discharging fumes from the complex with a rated power of 64.57 MW (ZEC Wołomin 2022). During the measurement period, the plant was involved in the supply of hot water to recipients in the Wołomin commune. In addition, many residents in the vicinity of the measuring point have individual natural gas-powered hot water systems. The minimum temperature during the measurements exceeded 14°C; therefore, the influence of individual heating on the air quality was negligible (IMGW-PIB 2021).

Due to the fact that the place selected for the study is exposed to high emissions from communication sources, and the study time was selected

so that the impact of individual heating was negligible, the day was divided into four equal intervals corresponding to the different types of traffic and lifestyle of residents. The starting hours of the intervals have been adopted, i.a. on the basis of (Mach, Bihałowicz, and Bihałowicz 2021). The first period (I) – night – covered the hours 22:01 to 4:00. During this time period, both the traffic and the need for domestic hot water are minimal. The second period (II) – morning – began at 4:01 am and ended at 10:00. Road traffic at the measurement site begins early in the morning, as the road by the sampling point is one of the main access roads for residents of the Wołomin County to work and study places in the Warsaw agglomeration. The third period (III) – afternoon hours – covered the hours 10:01–16:00, in which road traffic remains at a constant, quite intense level, but there are no road jams, and the emission related to the demand for hot water is low, because only a few residents stay at home during the day. The fourth period (IV) – evening – covered the hours 16:01–22:00.

Measurement method

During the measurements, the concentration of PM_{10} (μg/m^3) and the concentration of selected elements in PM_{10}, also expressed in mass units per unit volume, were tested. The measurements were performed in a continuous way using a Horiba PX-375 XRF analyzer (HORIBA ltd, Kyoto, Japan). During the measurements, the concentrations of Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Al, Si, S, K and Ca were analyzed. PX-375 allows collecting an atmospheric PM sample on the surface of a non-woven, elementally pure Teflon fiber (PTFE) tape. The mass of PM collected in the sample was determined by beta ray attenuation. After the mass of PM was determined, the tape was moved under EDXRF spectrometer equipped with a palladium lamp, so that the element concentrations were determined. The samples were taken for 60 minutes at a flow of 16.7 l/min. Then, after collection, they were induced and analyzed by EDXRF for 2000 s. The EDXRF system was additionally equipped with a camera that allows controlling the position of the sample in relation to the spectrometer. In order to control the quality of the collected spectra, the NIST SRM 2783 calibration material was used.

The sensitivity of the spectrometer – the lower detection limit – was dependent on the tested element, and with the parameters used in the experiment it was: for 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), and for Zn (1.25 ng/m^3). The data were collected for 7 full days, yielding 168 measurement points.

Analysis of the obtained results

In order to determine the influence of anthropogenic sources on the elemental composition of PM_{10}, the enrichment factors *EF* (Barbieri 2016) were used. *EF* (Formula 1) is defined as the ratio of the anthropogenic impact factor CF_n for the element n divided by the same factor for the reference element CF_{ref}. The *CF* factor is the ratio of the concentration of an element in PM_{10} C_n divided by the concentration in the environment (background) $C_{n,b}$, as shown in Eq (1).

$$EF_n = \frac{CF_n}{CF_{ref}} = \frac{\frac{C_n}{C_{n,b}}}{\frac{C_{ref}}{C_{ref,b}}} \quad (1)$$

The concentrations of elements in the upper Earth's crust (Hans Wedepohl 1995) were adopted as the values representing the concentration in the environment. Aluminum is often used as the reference element (Reimann and Caritat 2000; Rybak et al. 2020; Stojanowska et al. 2021). The obtained values of the *EF* coefficients were divided into five classes, according to (YONGMING et al. 2006), where the enrichment of PM with a specific element is:

- for EF ≤ 2 minimal enrichment,
- for 2 ≤ 5< EF moderate enrichment,
- for 5 < EF ≤ 20 significant enrichment,
- for 20 < EF 40 very high enrichment,
- for EF > 40 extremely high enrichment.

The *EF* analysis was performed separately for each time interval, providing the view into the temporal variability of the PM enrichment in individual elements. The next method used in the analysis was the principal components analysis of PCA. The successive principal components *PC* are the variables that account for less and less variability in the data set. PCA is a frequently used technique to reduce the dimensionality of the problems related to the elemental profile

(Bokwa 2008; Idriss et al. 2021; Kormoker et al. 2021; Li et al. 2020; Qu et al. 2018; Rybak et al. 2020). In this study, the content of 14 elements was analyzed and the dimensionality was reduced to 4, i.e., four main components were determined. Similarly, as in case of *EF*, it was done for each time interval separately. Data standardization was performed prior to *PC* designation.

Subsequently, the similarity of individual main components, i.e., *PC1* with *PC1* and *PC2* with *PC2* etc., between the time intervals was compared using the cosine similarity r_c (Jones and Furnas 1987), which for the *PC* is described by the Eq. (2), where PCn is the vector of the $n\text{-}th$ principal component, $t1$, $t2$ are two different time intervals. In Eq. (2), a modulus was introduced, in order to not distinguish the parallel and antiparallel principal components. The reason for choosing cosine similarity was that each *PC* is a vector; therefore the cosine of the angle between these vectors is a good measure of similarity, and in addition, this approach has already been used in previous works (Stojanowska et al. 2020).

$$r_C(PCn_{t1}, PCn_{t2}) = |PCn_{t1} \cdot PCn_{t2}| \qquad (2)$$

RESULTS AND DISCUSSION

Enrichment factors EFs

In order to determine the impact of selected emission sources on the elemental composition of PM_{10} and its concentration in the study area (road intersection in a suburban area), among others, enrichment factors EF were calculated. The results are shown in Table 1. PM_{10} does not indicate enrichment with respect to the composition of the upper Earth's crust, UCC, (Hans Wedepohl 1995) in potassium, silicon, titanium and vanadium. The EF values for these elements, which, regardless of the time of day, did not exceed 2 (Table 1), indicate that they are typical elements of the Earth's crust. It can therefore be assumed that they come from natural sources (Majewski and Rogula-Kozłowska 2016; Rogula-Kozłowska et al. 2016). It cannot be ruled out that these elements come from the resuspension of sand, soil and dust deposited on the crossroads and shoulders, instigated by intensive car traffic. On the basis of the determined values of the enrichment factors, PM_{10} was the most highly enriched in Zn and S; this is true for each averaging period and therefore it occurs irrespective of the time of day. This clearly shows that regardless of the averaging period of the results during the day, the emission related to coal combustion has a strong influence on the elemental composition of PM_{10}, and thus the concentration of PM_{10}.

This, in turn, suggests the influence of emissions from nearby buildings and heating plant on the composition and concentration of PM_{10} in the research area. Although the research was carried out in the warm period, when the impact of these sources should not be dominant (no emissions related to the heating of flats and houses, and municipal emissions determined mainly by processes related to water heating, cooking, etc.), they can be clearly observed. It is rather clear that when averaging the daily data on the elemental composition of PM_{10}, this impact could be masked by the traffic emission dominating in this area and in this period.

Regardless of the time of day, PM_{10} was significantly enriched in chromium and strongly enriched in copper. This, in turn, demonstrates the existing and clear influence of communication emissions on the composition of PM_{10}. In the morning and afternoon periods, this thesis is reinforced by the enrichment of PM_{10} with manganese and nickel. The traffic emission shown here is not

Table 1. Values of the enrichment coefficient for the tested elements, associated with PM_{10} mean values were calculated, for each hour during the day over the study period. Time periods: I – night, II – morning, III – noon, IV – evening

Period	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb	Si	S	K	Ca
I	○ 1	○ 2	◑ 8	○ 2	○ 1	○ 1	● 45	● 90	◕ 30	○ 1	● 381	○ 1	◔ 3
II	○ 0	○ 2	◑ 8	◔ 2	◔ 2	◔ 3	● 49	● 142	◕ 34	○ 1	● 475	○ 1	◔ 4
III	○ 0	○ 2	◑ 9	◔ 3	◔ 2	○ 1	◑ 11	● 123	◑ 19	○ 1	● 574	○ 1	◔ 4
IV	○ 0	○ 1	◑ 7	◔ 3	○ 2	○ 1	◕ 22	● 101	◕ 22	○ 1	● 402	○ 1	◔ 4

Note: The ○ symbol represents minimal enrichment, ◔ represents moderate enrichment, ◑–significant enrichment, ◕ – very high enrichment, ● – extremely high enrichment

only fuel combustion in engines, but most of all abrasion of vehicle components (wheels, brakes) and road surfaces. For example, while chromium is used in vehicle steel, also automotive cylinders are usually coated with a chrome layer (Moore, Polidori, and Sioutas 2011). The remaining elements are characterized by enrichment depending on the averaging time of the tests performed. It was found, i.a. that there is no manganese enrichment in PM_{10} at night, iron enrichment only in the morning and early afternoon hours, nickel – only in the morning, copper and lead – less enrichment during the day and evening. The presence of manganese and nickel is related to the combustion of gasoline (Moore et al. 2011). In turn, brake wear in road vehicles is an important source of copper concentration in the atmosphere (Hulskotte et al. 2007). Iron is the most abundant metal in nature. Low cost and high strength make it an essential element in many engineering structures, and is widely used in the construction of machines and vehicles. Although the consumption of unleaded gasoline has decreased, the presence of lead in the air is still high and is associated with heavy vehicle traffic (Moore et al. 2011). The relationship between the lead concentration in the air and the emissions from coal combustion is also known (Rogula-Kozłowska et al. 2012, 2013; Rogula-Kozłowska, Majewski, and Czechowski 2015).

In summary, the observed hourly variability may result from the congestion and traffic peaks that could be observed in the study area (morning peak, more intense traffic in the afternoon and more extended afternoon peak).

Share of PM_{10} emission sources

In order to identify the main sources of PM_{10} in the investigated suburban area, the main component analysis (PCA; Table 2) was used. Principal components for 14 elements were analyzed and four main components (PC1–PC4) were identified. The components were determined, as in the case of EF, separately for each time interval. The similarity of each component for the four time zones was compared using cosine similarity (Table 3).

In the case of the main component of PC1, the highest similarity was obtained for the time intervals III (noon) and IV (evening) (above 0.9; Table 3). The cosine similarity of PC1 for the remaining ranges was above 0.8, which suggests that PC1 represents a constant and intense source of emissions, independent of the period of the day. The general analysis of PCA shows that there were no strongly correlated elements in any time interval with PC1. Almost all elements determined are correlated with PC1 at the level of 0.1–0.4 (Table 2). These higher correlation values, regardless of the time of day, were recorded for Si, Al, Cr, V, Mn, Fe and Ca. It seems that PC1 may indicate a source of the road dust mixture enriched with elements typical for transport emissions (Majewski and Rogula-Kozłowska 2016; Penkała, Ogrodnik, and Rogula-Kozłowska 2018). PC1 contributes to the variance from 0.32 (morning (II)) to 0.5 (night (I)).

In the case of PC2, the greatest similarity was noted for the periods: night (I) and morning (II) – see Table 3; all the observed cosine similarities did not exceed the value of 0.63. For these periods, the share of PC2 in the variance is 0.16 (Table 2). Judging by the fact that V, Cr, S and K were the most strongly correlated with this component during the night and morning, it can be suspected that PC2 in these two periods represents the effect of heating, namely carbon combustion, on the elemental composition and PM_{10} concentration in the research area. In particular, this is evidenced by the correlations of PC2 with S and K (Li et al. 2010), which in the case of the conducted research may indicate that an important source of PM_{10} and the elements related to it, is a heating plant or residential buildings located in a short distance (water heating, cooking). Sulfur and potassium (especially potassium) may also be released during the combustion of biomass, waste and garbage in small-sized installations, i.e. home furnaces and local boiler houses (Samek et al. 2016). These sources cannot be excluded in the case of the conducted research, because there are single-family houses in the area that may be a source of this type of pollution. Moreover, the source of sulfur in PM_{10} may be secondary inorganic aerosols (sulphates), also released from the above-mentioned sources (Cesari et al. 2016).

There was no similarity between PC2 determined for noon (III) and evening (IV) (Table 3), which may indicate the presence of other, dominant emission sources in periods I and II, than those in periods III and IV. Specifically, it seems that these sources also differ in periods III and IV. In the afternoon (III) period, Ti, Fe and Ca were the most strongly correlated with PC2, and in the evening (IV) period, Ti, V and Cr were the most

strongly correlated with PC2 (Table 2). Both in the first and the second period of the day, it seems that PC2 can be characterized by a communication source. In the afternoon, it is more focused on the erosion of various elements of vehicles and surfaces, and in the evening, on the emissions related to fuel combustion in car engines (Pant and Harrison 2013; Rodriguez et al. 2004; Sternbeck, Sjödin, and Andréasson 2002). The share of this component in the variance in periods III and IV ranges from 0.13–0.15 (Table 2).

The main component of PC3 was characterized by the greatest cosine similarity in the morning (II) and noon (III) periods, which indicates PC3 as a common source of emissions for these periods. However, in each of these periods, different elements were correlated with PC3 (Table 2). In period II (morning), Ni, S and K were correlated with PC3, and in period III (noon) – V and Cr. It seems obvious that PC3 in the morning can be identified with municipal emission (similarly to PC2 during the night (I) and in the morning (II)), and in the afternoon (III) PC3 may indicate communication emission (analogous to PC2 in the evening (IV). No significant similarities were found with PC3 at other times of the day (Table 3). During the night (I), PC3 was most strongly correlated with Cu, Zn and Pb, and in the evening period with V, Cr and Ni (Table 2). Thus, in the evening period, analogically to the previous considerations, the traffic emissions related to fuel combustion in engines were identified, and during the night also traffic emissions, but related more to the typical erosion of brake pads (Pant and Harrison 2013; Rodriguez et al. 2004; Sternbeck et al. 2002).

The main component of PC4 with the lowest share of cumulative variance (Table 2) was characterized by the greatest cosine similarity in the periods: night (I) and noon (III), and morning (II) and noon (III) (Table 3). In the period I and III, PC4 was most strongly correlated with Ni and Zn. In period II (morning), the correlation of PC4 with Zn and Pb is observed. At night (period (IV)), the only notable correlations with PC4 are for Zn, Pb and Mn (Table 2). Taking into account completely different dependencies in the previous components, where the impact of communication and municipal emissions was identified, it is clear that a different source of emissions was qualitatively identified in PC4.

Probably with varying strength depending on the time of day, the elemental composition and PM_{10} concentration in this area are influenced by the nearby small, local non-ferrous metals processing point (70 m from the measurement point to the north), the paint shop located about 300 m to the south-west east as well as a tire repair and car repair shops (from 200 to 500 m to the west)

Table 2. Summary of the results of the principal component analysis (PCA) performed on the time intervals related to the elemental composition of PM_{10}. Time periods: I – night, II – morning, III – noon, IV – evening

Time interval	Component	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb	Al	Si	S	K	Ca	PC VAR
I	PC1	0.31	0.34	0.34	0.34	0.26	0.06	0.10	0.19	-0.06	0.36	0.31	-0.02	0.34	0.30	0.50
	PC2	0.32	0.21	0.22	0.07	-0.41	-0.24	0.16	-0.21	-0.06	0.04	-0.35	0.42	0.25	-0.38	0.16
	PC3	-0.02	-0.08	-0.09	-0.03	0.04	-0.21	0.56	0.47	0.63	-0.05	-0.05	0.06	0.04	-0.03	0.13
	PC4	-0.07	0.16	0.13	-0.17	-0.12	0.85	0.15	0.31	-0.07	-0.04	-0.14	0.12	-0.02	-0.18	0.07
II	PC1	0.00	0.16	0.18	0.33	0.44	-0.06	-0.04	0.09	0.18	0.44	0.45	0.04	0.14	0.43	0.32
	PC2	0.00	0.59	0.58	-0.09	-0.10	0.02	0.28	-0.05	-0.18	0.04	-0.14	0.25	0.28	-0.17	0.16
	PC3	0.00	-0.23	-0.20	0.24	-0.03	0.32	-0.33	-0.17	-0.10	0.20	-0.12	0.54	0.48	-0.17	0.13
	PC4	0.00	-0.05	-0.06	-0.15	-0.01	-0.02	0.14	0.68	0.61	0.02	-0.14	0.17	0.19	-0.18	0.12
III	PC1	0.08	0.22	0.23	0.35	0.36	0.15	0.18	0.20	0.10	0.39	0.37	0.27	0.26	0.32	0.39
	PC2	0.32	-0.31	-0.28	0.06	0.31	-0.31	-0.01	-0.07	-0.32	-0.01	0.29	-0.39	-0.20	0.38	0.15
	PC3	0.01	0.57	0.58	-0.13	0.06	-0.20	-0.24	-0.21	-0.15	-0.08	0.02	-0.24	-0.26	0.15	0.11
	PC4	0.41	0.08	0.01	-0.09	0.04	0.48	0.17	0.33	0.33	-0.19	-0.11	-0.11	-0.52	0.13	0.09
IV	PC1	0.18	0.25	0.26	0.30	0.35	0.07	0.28	0.27	0.23	0.34	0.35	0.14	0.26	0.32	0.48
	PC2	0.41	0.42	0.41	-0.16	-0.09	-0.23	0.12	-0.33	-0.39	-0.03	-0.04	-0.32	0.14	-0.02	0.13
	PC3	-0.28	0.39	0.37	-0.02	0.15	0.40	0.29	0.08	0.08	-0.32	-0.30	0.18	-0.29	-0.22	0.09
	PC4	0.01	0.09	0.13	0.27	0.12	-0.35	-0.25	0.34	0.27	-0.25	-0.05	-0.55	-0.37	0.12	0.09

Note: PC VAR – variance described by a component.

Table 3. Cosine similarity of principal components between time intervals

PC1					PC2				
	I	II	III	IV		I	II	III	IV
I	1.000	0.808	0.889	0.900	I	1.000	0.635	0.500	0.420
II		1.000	0.887	0.866	II		1.000	0.592	0.588
III			1.000	0.964	III			1.000	0.138
IV				1.000	IV				1.000
PC3					PC4				
	I	II	III	IV		I	II	III	IV
I	1.000	0.314	0.400	0.145	I	1.000	0.251	0.504	0.345
II		1.000	0.508	0.187	II		1.000	0.314	0.126
III			1.000	0.283	III			1.000	0.292
IV				1.000	IV				1.000

(Kaivosoja et al. 2013; Yang et al. 2019). The share of PC4 in the variance, depending on the time of day, is from 0.07 to 0.12.

CONCLUSIONS

In the research, the data from the period of a seven-day measurement campaign conducted in the suburban area was used. It was shown that in a typical suburban area, in the central part of Poland, the impact of emissions from transport on the elemental composition of PM_{10} can be observed in practically all tested time intervals, which is directly related to the nature of the examined place (location near a large intersection). Most car drivers who pass there are probably professionally or otherwise connected with Warsaw, e.g., they commute to work or for other purposes to the capital every day, which has a significant impact on the pollution of the studied area. Additionally, the emissions related to the proximity of ZEC Wołomin are a significant source (about 1.4 km in a straight line there is the ZEC Wołomin smokestack) and they have a significant impact on the elemental composition of PM_{10} during the study period. There was also a clear influence of small, local production and service facilities. It is highly likely that if a similar analysis of the origin of PM_{10} in the same measurement period were performed on the basis of daily averaged data, on the elemental composition of PM_{10}, the impact of non-communication emission sources in this research area would not be noticed. This shows that sampling with high temporal resolution constitutes a much better, cheaper and more efficient (short 7-day campaign) method of collecting data to assess the origin of PM in an urban or suburban area.

Acknowledgments

This research was carried out as a part of the "Implementation doctorate-edition II Faculty W-7 (03DW/0001/18)" project, financed by the National Centre for Research and Development.

The research results were connected with the project OPUS 12 "Transitions of some chemical elements (metals and metalloids) during migration on the way emitter–atmosphere–soil", financed by National Science Centre, Poland, 2016/23/B/ST10/02789.

The authors acknowledge the companies HORIBA and MLU-recordum Environmental Monitoring Solutions GmbH for supplying the measurement equipment (PX-375 Horiba, Japan).

REFERENCES

1. Barbieri, M. 2016. The Importance of Enrichment Factor (EF) and Geoaccumulation Index (Igeo) to Evaluate the Soil Contamination. Journal of Geology & Geophysics, 5.
2. Bokwa, A. 2008. Environmental Impacts of Long-Term Air Pollution Changes in Kraków, Poland. Polish Journal of Environmental Studies, 17.
3. Cesari, D., Amato, F., Pandolfi, M., Alastuey, A., Querol, X., Contini, D. 2016. An inter-comparison of PM10 source apportionment using PCA and PMF receptor models in three European sites. Environmental Science and Pollution Research, 23, 15133–15148.
4. Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N.M., George, C., Goldstein, A.H., Hamilton,

J.F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M.E., Jimenez, J.L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T.F., Monod, A., Prévôt, A.S.H., Seinfeld, J.H., Surratt, J.D., Szmigielski, R., Wildt, J. 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. Atmospheric Chemistry and Physics, 9, 5155–5236.

5. Hans Wedepohl, K. 1995. The composition of the continental crust. Geochimica et Cosmochimica Acta.
6. Hopke, P.K. 2016. Review of receptor modeling methods for source apportionment. Journal of the Air and Waste Management Association.
7. Hulskotte, J.H.J., van der Gon, H.A.C.D., Visschedijk, A.J.H., Schaap, M. 2007. Brake wear from vehicles as an important source of diffuse copper pollution. In: Water Science and Technology.
8. Idriss, I.E.A., Abdel-Azim, M., Karar, K.I., Osman, S., Idris, A.M. 2021. Isotopic and chemical facies for assessing the shallow water table aquifer quality in Goly Region, White Nile State, Sudan: focusing on nitrate source apportionment and human health risk. Toxin Reviews, 40, 764–776.
9. IMGW-PIB. 2021. Dane publiczne IMGW-PIB.
10. Jones, W.P., Furnas, G.W. 1987. Pictures of relevance: A geometric analysis of similarity measures. Journal of the American Society for Information Science, 38, 420–442.
11. Kaivosoja, T., Jalava, P.I., Lamberg, H., Virén, A., Tapanainen, M., Torvela, T., Tapper, U., Sippula, O., Tissari, J., Hillamo, R., Hirvonen, M.R., Jokiniemi, J. 2013. Comparison of emissions and toxicological properties of fine particles from wood and oil boilers in small (20–25 kW) and medium (5–10 MW) scale. Atmospheric Environment, 77, 193–201.
12. Kormoker, T., Proshad, R., Islam, M.S., Shamsuzzoha, M., Akter, A., Tusher, T.R. 2021. Concentrations, source apportionment and potential health risk of toxic metals in foodstuffs of Bangladesh. Toxin Reviews, 40, 1447–1460.
13. Li, J., Deng, Q., Lu, C., Huang, B. 2010. Chemical compositions and source apportionment of atmospheric PM10 in suburban area of Changsha, China. Journal of Central South University of Technology, 17, 509–515.
14. Li, Q., Zhang, H., Guo, S., Fu, K., Liao, L., Xu, Y., Cheng, S. 2020. Groundwater pollution source apportionment using principal component analysis in a multiple land-use area in southwestern China. Environmental Science and Pollution Research, 27, 9000–9011.
15. Liang, S.Y., Cui, J.L., Bi, X.Y., Luo, X.S., Li, X.D. 2019. Deciphering source contributions of trace metal contamination in urban soil, road dust, and foliar dust of Guangzhou, southern China. Science of the Total Environment.
16. Mach, T., Bihałowicz, J., Bihałowicz, J.S. 2021. Dobowa i godzinowa zmienność stężeń Pb, Ni, Zn, Mn i V w powietrzu atmosferycznym: badania pilotażowe w wybranym receptorze centralnej Polski. In: Energetyka i ochrona środowiska – współczesne rozwiązania i perspektywy na przyszłość. Wydawnictwo Naukowe TYGIEL, 145–163.
17. Majewski, G., Rogula-Kozłowska, W. 2016. The elemental composition and origin of fine ambient particles in the largest Polish conurbation: first results from the short-term winter campaign. Theoretical and Applied Climatology, 125, 79–92.
18. Moore, K., Polidori, A., Sioutas, C. 2011. Toxicological Assessment of Particulate Emissions from the Exhaust of Old and New Model Heavy- and Light-Duty Vehicles. This research was sponsored by the U.S. Department of Transportation.
19. Pant, P., Harrison, R.M. 2013. Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: A review. Atmospheric Environment.
20. Penkała, M., Ogrodnik, P., Rogula-Kozłowska, W. 2018. Particulate Matter from the Road Surface Abrasion as a Problem of Non-Exhaust Emission Control. Environments, 5, 9.
21. Pernigotti, D., Belis, C.A., Spanó, L. 2016. SPECIEUROPE: The European data base for PM source profiles. Atmospheric Pollution Research.
22. Pervez, S., Bano, S., Watson, J.G., Chow, J.C., Matawle, J.L., Shrivastava, A., Tiwari, S., Pervez, Y.F. 2018. Source Profiles for PM10–2.5 Resuspended Dust and Vehicle Exhaust Emissions in Central India. Aerosol and Air Quality Research, 18, 1660–1672.
23. Pokorná, P., Hovorka, J., Hopke, P.K. 2016. Elemental composition and source identification of very fine aerosol particles in a European air pollution hot-spot. Atmospheric Pollution Research.
24. Qu, M., Wang, Y., Huang, B., Zhao, Y. 2018. Source apportionment of soil heavy metals using robust absolute principal component scores-robust geographically weighted regression (RAPCS-RGWR) receptor model. Science of The Total Environment, 626, 203–210.
25. Reimann, C., Caritat, P. de. 2000. Intrinsic Flaws of Element Enrichment Factors (EFs) in Environmental Geochemistry. Environmental Science & Technology, 34, 5084–5091.
26. Rodriguez, S., Querol, X., Alastuey, A., Viana, M., Alarcon, M., Mantilla, E., Ruiz, C. 2004. Comparative PM10–PM2.5 source contribution study at rural, urban and industrial sites during PM episodes in Eastern Spain. Science of The Total Environment, 328, 95–113.

27. Rogula-Kozłowska, W., Błaszczak, B., Szopa, S., Klejnowski, K., Sówka, I., Zwoździak, A., Jabłońska, M., Mathews, B. 2013. PM2.5 in the central part of Upper Silesia, Poland: Concentrations, elemental composition, and mobility of components. Environmental Monitoring and Assessment.
28. Rogula-Kozłowska, W., Klejnowski, K., Rogula-Kopiec, P., Mathews, B., Szopa, S. 2012. A Study on the Seasonal Mass Closure of Ambient Fine and Coarse Dusts in Zabrze, Poland. Bulletin of Environmental Contamination and Toxicology, 88, 722–729.
29. Rogula-Kozłowska, W., Majewski, G., Błaszczak, B., Klejnowski, K., Rogula-Kopiec, P. 2016. Origin-oriented elemental profile of fine ambient particulate matter in central European suburban conditions. International Journal of Environmental Research and Public Health, 13.
30. Rogula-Kozłowska, W., Majewski, G., Czechowski, P.O. 2015. The size distribution and origin of elements bound to ambient particles: a case study of a Polish urban area. Environmental Monitoring and Assessment.
31. Rybak, J., Wróbel, M., Bihalowicz, J.S., Rogula-Kozlowska, W. 2020. Selected metals in Urban road dust: Upper and lower silesia case study. Atmosphere, 11, 290.
32. Samek, L., Gdowik, A., Ogarek, J., Furman, L. 2016. Elemental composition and rough source apportionment of fine particulate matter in air in Cracow, Poland. Environment Protection Engineering.
33. Sternbeck, J., Sjödin, Å., Andréasson, K. 2002. Metal emissions from road traffic and the influence of resuspension – Results from two tunnel studies. Atmospheric Environment.
34. Stojanowska, A., Mach, T., Olszowski, T., Bihałowicz, J.S., Górka, M., Rybak, J., Rajfur, M., Świsłowski, P. 2021. Air Pollution Research Based on Spider Web and Parallel Continuous Particulate Monitoring–A Comparison Study Coupled with Identification of Sources. Minerals, 11, 812.
35. Stojanowska, A., Rybak, J., Bożym, M., Olszowski, T., Bihałowicz, J.S. 2020. Spider Webs and Lichens as Bioindicators of Heavy Metals: A Comparison Study in the Vicinity of a Copper Smelter (Poland). Sustainability, 12, 8066.
36. Yang, H.-H., Gupta, S. K., Dhital, N. B., Lee, K.-T., Hsieh, Y.-S., Huang, S.-C. 2019. Establishment of Indicatory Metals for Filterable and Condensable PM2.5 Emitted from Important Stationary Emission Sources. Energy & Fuels, 33, 10878–10887.
37. Yongming, H., Peixuan, D., Junji, C., Posmentier, E. 2006. Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. Science of The Total Environment, 355, 176–186.
38. ZEC Wołomin. 2022. System ciepłowniczy – ZEC Wołomin.
39. Zhu, Y., Huang, L., Li, J., Ying, Q., Zhang, H., Liu, X., Liao, H., Li, N., Liu, Z., Mao, Y., Fang, H., & Hu, J. 2018. Sources of particulate matter in China: Insights from source apportionment studies published in 1987–2017. Environment International. Elsevier Ltd.