Environment Protection Engineering

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ELEMENTAL COMPOSITION AND ORIGIN OF PM10 IN A FIRE STATION IN POLAND. REAL-TIME RESULTS FROM THE XRF ANALYSIS

This work presents the first results of the metal in particulate matter PM10 analysis and source apportionment in one of the fire station garages in Poland. The study's novelty includes the high temporal resolution of the elemental composition of PM-bound metals since the gamma-ray fluorescence spectrometer with the high temporal resolution was used in the study. The concentrations of PM10 were measured at the same time using the method of beta-ray attenuation. The concentrations of PM10 and PM-bound metals were analyzed with a temporal resolution of 4 h. To identify the source apportionment of metals, three commonly used models were applied: principal component analysis (PCA), EPA UNMIX, and EPA PMF (positive matrix factorization). The concentrations of the investigated metals have high temporal variations while the concentrations of PM10 were low in the garage. The enrichment of PM10 was very high or high, especially in sulfur, zinc, arsenic, nickel, cadmium, and lead. PCA analysis, as well as UNMIX and PMF, showed a high impact of factors related to sulfur on the variability. It showed the impact of combustion, including combustion of liquid fuels, in fire engines may have a crucial impact on air pollution in the fire station. The PMF analysis allowed us also to identify factors responsible for external anthropogenic emissions on concentrations inside the garage. Other identified sources of PM10 and PM10-bound elements are mineral dust, and road dust related to non-exhaust emission, originating inside the firehouse (resuspension and abrasion) as well as from outside.

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1. INTRODUCTION

It was found that some cancers and other health conditions such as cardiac events are very common among firefighters as they are exposed to combustion products, i.e., different chemicals in the vapor state and particulate phase, mainly through inhalation, although ingestion and dermal way are also possible [1]. Air pollutants are the main cause of health issues and numerous studies have proved a strong association between high concentrations of ambient particulate and mortality rates. The smoke deriving from fires can be a reason for the sudden death of both: firefighters and victims due to inhalation of toxic gases [2].

Fire smoke contains particulate matter (PM) of different particle sizes, various substances in a gaseous phase, PM-bound compounds such as toxic and carcinogenic polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and metals [3]. Toxic compounds are also found on firefighters' personal protective equipment (PPE) and clothing [1]. What is more, the storage location of PPE and clothing in the fire station can be a key issue as well as the effectiveness of post-fire decontamination or laundering which can highly contribute to the contamination of fire stations [1]. Some studies suggest that the contamination of clothing and equipment of firefighters on the scene of a fire can also contribute to the contamination of fire stations [4]. Moreover, diesel engine exhaust from fire appliances may play a significant role in a potential health risk for firefighters [5].

Therefore, models that can predict the variability of elemental composition and origin of PM concentrations in fire stations would be a very important and crucial tool for protecting human life. What is more, designing a warning system could greatly facilitate achieving this goal.

Receptor models, which attribute concentrations to sources based on statists and meteorological data, give a piece of clear information on the sources of aerosols [6]. Several receptor models, i.e., principal component analysis (PCA) [7], and UNMIX [8] are very useful in providing an easy and reliable tool for classifying sources [9], and positive matrix factorization (PMF) [10]. PCA, UNMIX, and PMF analyses depend on the covariance matrix. All three models are good at finding the dominant source categories of aerosols [11]. There are also other receptor models in use, although in models applied in this study, the data concerning the elemental composition of PM are sufficient for the reliable prediction of the variability of elemental composition and origin of PM. However, in other models, different parameters are also needed such as carbon contribution, etc.

For this purpose, a fast and comprehensive assessment of the origin of PM based on the concentration of elements obtained from the measurements averaged in intervals of less than 24 hours would be the most effective tool. It can be achieved with automatic measurements based on the X-Ray fluorescence (XRF) technique. The data obtained with this tool could supply a piece of reliable information that can enable future actions to be taken against possible health risks among firefighters.

The aim of our study was to assess the elemental composition and origin of PM10 in a selected fire station in Poland with the application of three different receptor models for source apportionment. Such studies have never been conducted before in Poland and can serve as inputs in the proposal of the warning system of ambient PM10 concentrations in fire stations.

2. METHODS

Measurements. During the measurements, the concentration of PM10 and the mass concentrations of some elements in PM10 have been studied in a selected fire station's garage in Poland. The fire station was located in Warsaw, in a typical residential district with single-family as well as multiple-family housing, where air quality is dependent mainly on emissions related to energy production and transport emissions. The measurements were carried out in the period from 24.06 to 08.07 (2020), i.e., full 336 hours.

Measurements were performed using the 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 measured. PX-375 collects PM on non-woven, elementally clean surface Teflon fiber tapes (PTFE). The mass of PM collected in the sample was determined with β radiation attenuation. Then the tape was moved so that using an X-ray fluorescence energy dispersion spectrometer (EDXRF) equipped with a palladium lamp to find the concentration of elements. Samples were taken for 60 min and a flow of 16.7 dm^3/min. After collection, they were excited and analyzed by EDXRF for 2000 s. System EDXRF was additionally equipped with a camera that allowed one to control the position of the sample relative to the spectrometer. To control the quality of the collected spectra, the National Institute of Technology (NIST) Standard Reference Material (SRM) 2783 was used. The sensitivity of the spectrometer – the lower detection limit – was dependent on the examined element, and parameters used in the experiment were (in ng/m^3) 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.

Source apportionment. The data collected by the Horiba PX-375 were analyzed employing statistical models. The correlations between the observed concentrations of elements were examined using Pearson's coefficient of correlation *r* available through package Seaborn package [12]. The significance of the correlations was also evaluated using this package. We evaluated significance at three levels α – 0.1, 0.05, and 0.01.

The enrichment of the elements in the PM10 was assessed using Enrichment Factor (*EF*) [13] with the conservative reference element – aluminum,

$$EF_i = \left(\frac{C_i}{C_{Al}} \right) \times \left(\frac{B_{Al}}{B_i} \right) \tag{1}$$

where C_i is the concentration of element i in the sample, C_{Al} is the concentration of aluminum in the sample, B_i and B_{Al} are concentrations of these elements in the upper crust according to Wedepohl [14].

The classes of the enrichment factor of PM10-bound elements

Value	Class
$EF \leq 2$	natural origin (soil, sand, etc.)
$2 < EF \leq 5$	deficiency to minimal enrichment
$5 < EF \leq 20$	moderate enrichment
$20 < EF \leq 40$	significant enrichment
$40 < EF \leq 100$	very high enrichment
$EF > 100$	extremely high enrichment

The classes of enrichment are presented in Table 1. The classical principal component analysis, PCA, was performed to identify the directions, along which the variance of data points is minimized to reduce the dimensionality of data points that were originally from $\mathbb{R}_+^{15}$ space. The number of principal components (PC) in PCA can be between 1 and 15, however, 15 is useless since it does not reduce the dimensionality. As the criterion for the choice of the number of PC, we used the explained variance in a dataset with an arbitrarily chosen level minimum of 99%. The PCA analysis was performed using the KNIME Analytics Platform [15].

Since PCA is limited, we used EPA UNMIX 6.0 model 6 [16]. EPA UNMIX decomposes the matrix $X_{m \times n}$ of m samples of n elements as a product of two matrices $G_{m \times p}$ representing fractions of each of p sources in m samples and matrix $F_{p \times n}$ which consists of n elements emission profiles of each of p sources. The fundamental difference from PCA is that these two matrices are non-negative since the contributions as well as emission profiles have to have physical meaning. The objective of the procedure is to minimize the difference E between X and FG

$$X = FG + E \tag{2}$$

The next model used is EPA PMF 5.0 [17]. It is a common practice, observed in many works [18] that UNMIX and PMF are used in parallel for source apportionment. EPA PMF also solves the equation; however, the main difference is the presence of measurement uncertainties for individual samples and elements. The model objective is to minimize the sum over all samples and elements Q

$$Q = \sum_i \sum_j \left(\frac{x_j^i - \sum_k g_k^i f_j^k}{u_j^i} \right) \tag{3}$$

where i refers to numbering samples, j numbering elements, and k numbering source profiles.

3. RESULTS AND DISCUSSION

3.1. CHARACTERISTICS OF THE DATA

Table 2 presents statistical characteristics for the measured parameters, i.e., the concentrations of PM10 and elements related to PM10.

Table 2

Statistical characteristics for the measured parameters
– the concentrations of PM10 ($\mu g/m^3$) and elements related to PM10 (ng/m^3)

Parameter	Minimum[a]	25th percentile	Median	75th percentile	Maximum	Mean	Standard deviation
PM10	4.83	7.64	10.64	12.66	19.35	10.66	3.53
Ti	0	0	0.07	1.77	20.21	1.92	4.26
V	0	0.03	0.15	0.29	1.6	0.2	0.26
Cr	0	0.05	0.41	0.84	4.52	0.59	0.74
Mn	0	1.01	1.68	2.18	7.55	2.1	1.8
Fe	0	54.04	77.31	96.5	263.71	84.96	47.62
Ni	0	0	0.11	0.34	0.83	0.19	0.23
Cu	0	0.87	1.77	4.26	7.15	2.44	1.89
Zn	0.11	5.26	6.83	13.3	461.21	47.29	107.41
As	0	0	0	0.07	9.47	0.71	1.86
Pb	0	1.14	2.09	3.63	37.25	4.93	8.17
Al	0	62.69	83.62	103.14	195.02	82.48	39.04
Si	10.72	77.89	90.82	111.07	232.58	96.89	39.21
S	29.21	602.84	933.78	1219.07	3077.42	992.62	541.19
K	0	8.42	15.84	20.38	51.62	16.25	11.17
Ca	9.83	36.76	43.4	59.02	303.45	60.4	55.66

[a]0 was assumed for every concentration at a level lower than the limit of quantification for a given element.

During the study period, PM10 concentrations inside the rescue and firefighting firehouse were relatively low. On average, one-hour PM10 concentrations did not exceed 11 $\mu g/m^3$ and ranged from about 5 $\mu g/m^3$ to 19 $\mu g/m^3$. In general, sulfur, calcium, silicon, aluminum, zinc, and iron dominated the dust.
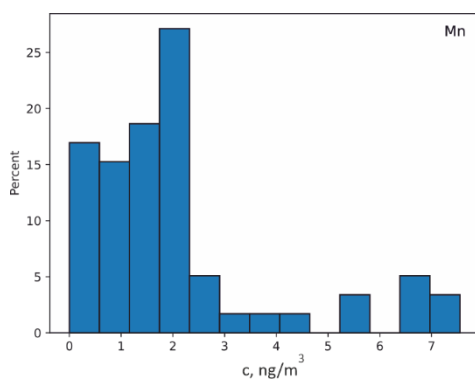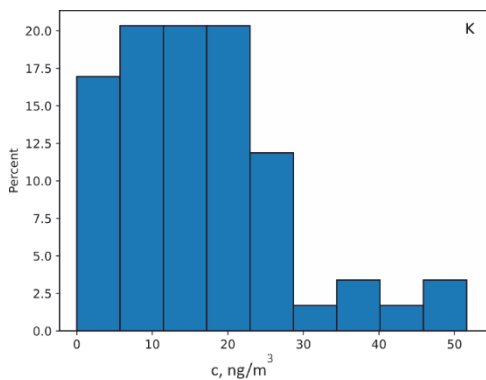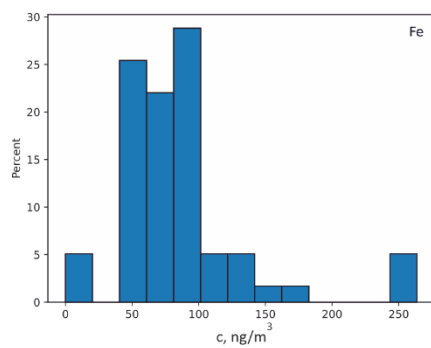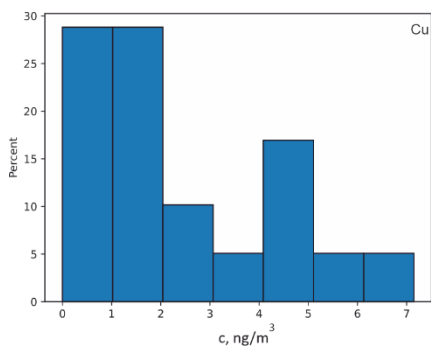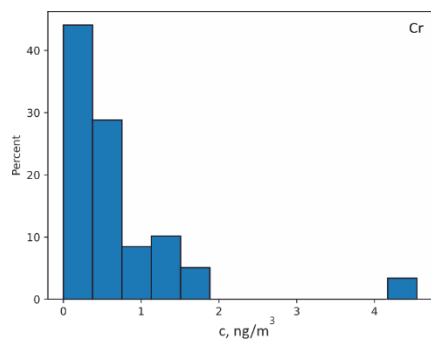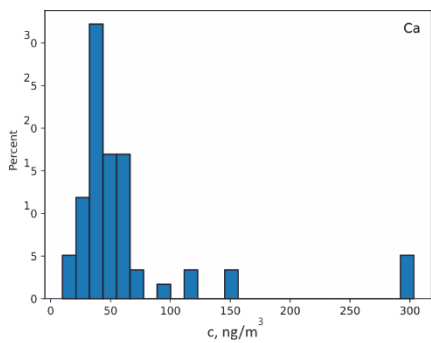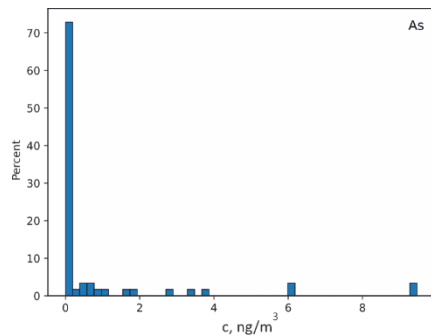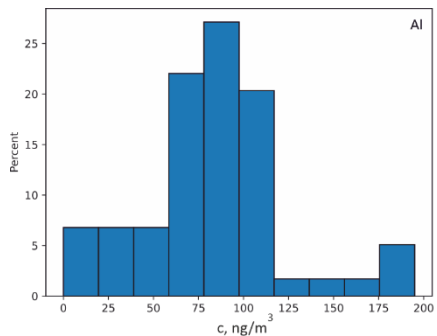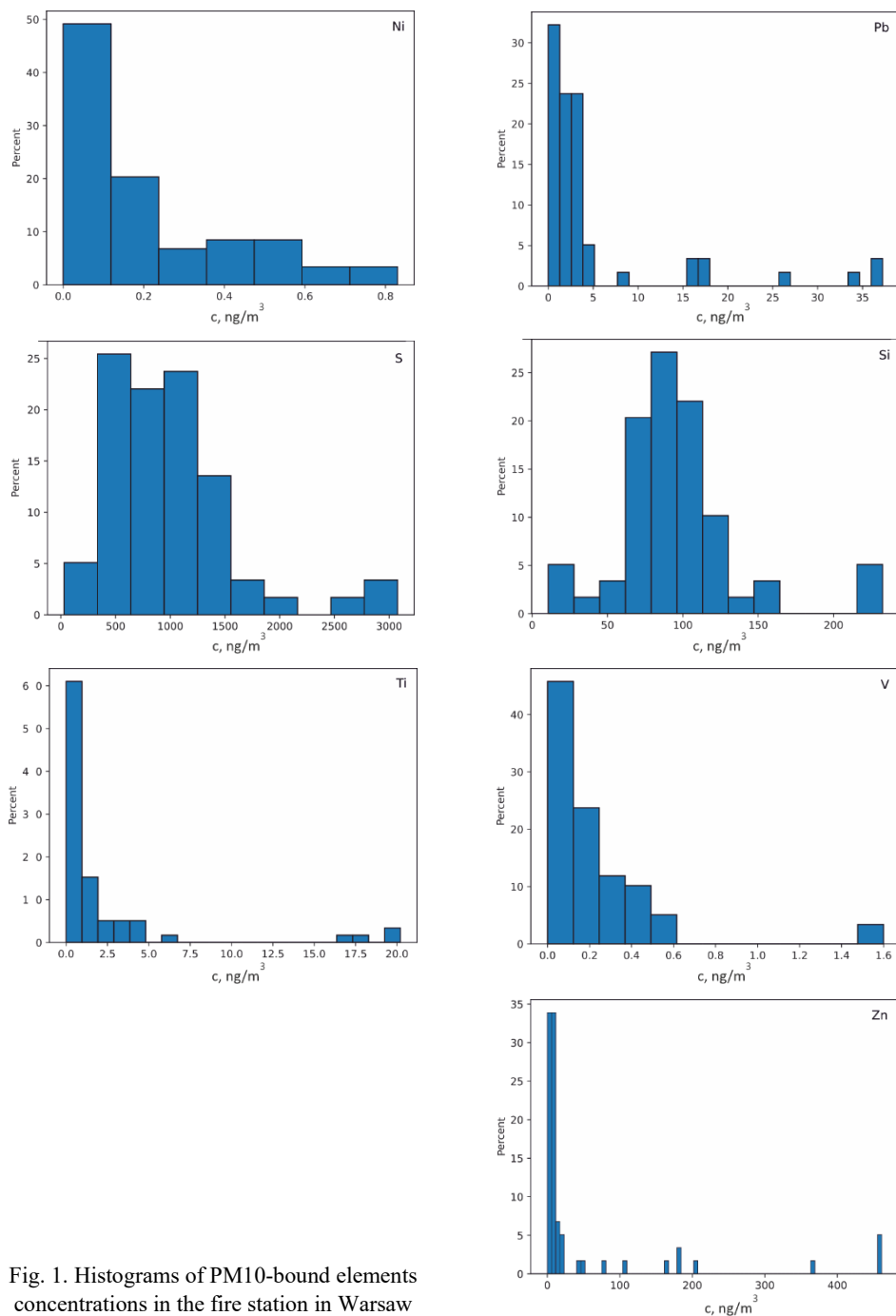
Fig. 1. Histograms of PM10-bound elements concentrations in the fire station in Warsaw

The elemental composition of PM10 indoors was different from that outdoors; this applies to both PM10 previously studied in different parts of Warsaw [19] and in other parts of Poland and the world [20]. Throughout the measurement period, a strong hourly variability of concentrations was observed for PM10 and for almost all elements associated with it, mainly for those with relatively high concentrations, such as sulfur, potassium, silicon, or zinc. The concentrations of these elements were higher in those periods when cleaning of fire trucks and personal protective equipment was carried out, and in the hours when cars and rescue teams left or returned to/from field operations. Figure 1 presents histograms of the elemental concentrations to show in which concentration ranges PM10-bound elements occur most often. This information is crucial in creating scenarios of users' exposure – firefighters – to the impact of toxic and potentially toxic elements in the studied fire station [21].

Statistically significant correlations were observed between the elements with the highest concentrations (Table 3). A very high correlation among datasets has been recorded. There are 84 statistically significant (70% of all possible) correlations at $p < 0.1$. Out of these 84, the biggest group are correlations significant at $p < 0.01$ – 50 correlations while 24 correlations are significant at $p = 0.05$. The strongest correlations relate to sulfur, aluminum, zinc, and iron. Sulfur concentrations are also correlated with concentrations of arsenic, lead, copper, and manganese. This shows a strong diversification of sulfur sources and other elements in the studied firehouse.

Table 3

Pearson's correlation matrix ($p < 0.05$) among hourly concentrations of the analyzed elements in the selected rescue and firefighting firehouse in the central part of Poland

	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Pb	Al	Si	S	K
V	0.07													
Cr	0.07	**0.99**												
Mn	0.02	**0.56**	**0.59**											
Fe	**0.44**	**0.32**	**0.38**	**0.42**										
Ni	–0.04	–0.03	0.00	**0.23**	**0.26**									
Cu	0.10	**0.25**	**0.30**	**0.54**	**0.62**	**0.29**								
Zn	–0.10	**0.28**	**0.30**	**0.81**	**0.23**	**0.27**	**0.56**							
As	–0.11	**0.23**	**0.25**	**0.70**	**0.23**	**0.28**	**0.49**	**0.91**						
Pb	–0.06	**0.26**	**0.28**	**0.82**	**0.28**	**0.30**	**0.58**	**0.97**	**0.92**					
Al	**0.25**	0.10	0.12	**0.41**	**0.59**	**0.31**	**0.48**	**0.44**	**0.48**	**0.54**				
Si	**0.31**	**0.58**	**0.61**	**0.31**	**0.67**	0.07	**0.28**	–0.06	0.02	0.00	**0.37**			
S	0.16	**0.28**	**0.29**	**0.50**	**0.43**	**0.24**	**0.41**	**0.49**	**0.56**	**0.60**	**0.84**	**0.41**		
K	**0.30**	0.02	0.02	**0.42**	**0.27**	**0.22**	**0.39**	**0.49**	**0.48**	**0.56**	**0.56**	0.12	**0.50**	
Cd	**0.87**	0.19	0.17	0.11	**0.29**	–0.07	0.03	–0.09	–0.11	–0.07	0.14	**0.38**	0.14	**0.30**

Means statistical significance at $p < 0.05$ in bold.

It should be underlined that the enrichment of PM10 in sulfur, arsenic, copper and zinc is extremely high (Fig. 2). Therefore, it is clear that these elements are of anthropogenic origin. Probably they come from the same source. To assess this the PCA results were analyzed (Fig. 3).
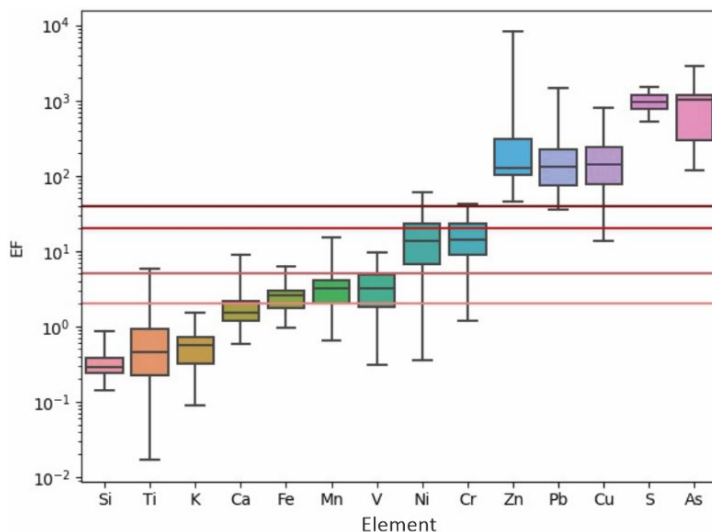

Fig. 2. Enrichment factor (*EF*) for PM10-bound elements in the indoor air of a selected firehouse in a central part of Poland (boxplots do not include points for which the concertation of the *i*th element was zero, the vertical scale is logarithmic, and the whiskers are from minimum to maximum values)
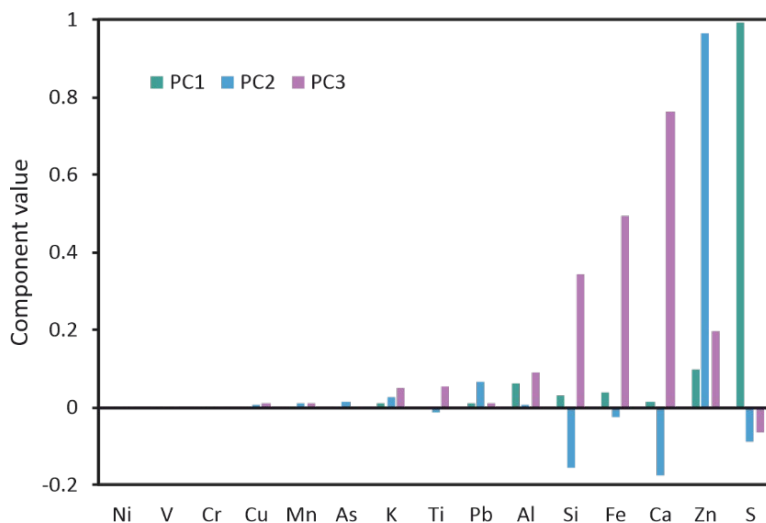

Fig. 3. Results of PCA analysis for PM10-bound elements in the indoor air of a selected firehouse in a central part of Poland

Sulfur is correlated the most with PC1, zinc with PC2. The third part of PC3 is strongly related to calcium, silicon, and iron. Considering the earlier issues regarding the enrichment of PM10 , this may indicate the existence of three basic sources of PM10 in the air of the studied firehouse. The first may be combustion processes, including oil [22] and other materials. Personal protective equipment, including special clothing, could be a source of secondary emission of certain compounds and dust, which is unusual for other rooms [3]. Our studies were carried out in the firehouse where, on the one hand, processes and emissions in the garage had an impact on air quality, and on the other hand, the measurement point was located close to the storage area for rescue and fire-fighting equipment, personal protective equipment and special clothes. In this area, firefighters change clothes before and after the rescue operation. During these activities, periodic increases in sulfur concentrations were observed, which may confirm that part of this element is carried in the firemen's equipment from the outside to the inside on special clothes and other equipment. The second main component may be related to the movement of vehicles inside the garage of the firehouse and the related other types of emissions (dust from the abrasion of brakes, tires, body parts, etc.) [23]. This can be proven by the fact that the zinc enrichment of PM10 was very high at the study site (Fig. 2) and therefore the zinc was not of natural origin. In the case of elements related to the third component – iron, silicon, and calcium – PM10 did not show a strong enrichment with these elements, and therefore this component can be considered a natural origin. These can be soil and sand particles, carried from the outside to the inside as well as particles subjected to resuspension inside the studied firehouse. It is obvious that all particles and elements are strongly mixed. Nevertheless, thanks to a simple analysis of the PM10 elemental composition from a very short series of measurements, conclusions can be drawn about the origin of the dust inside the studied firehouse. This is also confirmed by the fact that three main components attributed to 99% of the variance. It is also clear that the correlations among principal components are completely different in the case of the analyzed room than those observed in indoor air studies [24]. This is in line with expectations and thus confirms that in the case of a specific firehouse and with the use of measuring equipment that allows one to obtain measurements from short time intervals, a very short measurement period is sufficient to collect data suitable for conducting source apportionment. Such an approach seems adequate given that in such rooms the contribution of various sources in shaping the PM concentration changes in short periods (during the day depending on the activity inside). It is not the same as in atmospheric air when longer periods are needed – a month, a season, as it is shaped by changes in ambient temperature or changes in transport emissions due to the holiday season, etc.

3.2. UNMIX MODEL

The UNMIX model is similar to PCA, with the constraints on positive values of coefficients. The source profiles of four components are presented in Fig. 4. The constraint of positive coefficients significantly changed the source profiles. The variability

explained by principal components (PCs) is now divided in a few sources. Source #1 is the main source of titanium but also is responsible for almost half of the calcium, and some of the iron emission.
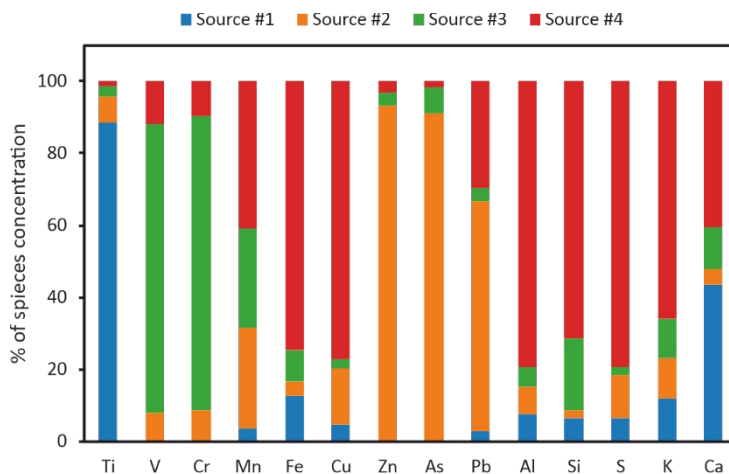

Fig. 4. Source profiles obtained in EPA UNMIX

According to the SPECIEUROPE, source profiles for Europe database [25] the important sources of titanium are combustion and dust. Source #2 is mainly responsible for zinc, arsenic, and lead emission which are also from the combustion of fuels. Source #3 is responsible mainly for chromium, vanadium, and manganese, which can be identified as elements from the abrasion of automotive elements and other non-combustion transport sources while source #4 is responsible for iron, copper, aluminum, and sulfur. Source #4 is responsible for the contribution of crustal elements as well as anthropogenic enriched elements. The analysis with the UNMIX allowed one to differentiate the sources.

3.3. PMF ANALYSIS

Similar conclusions can be drawn by studying PMF results (Fig. 5). PMF analysis allowed us to select four factors. Each of them corresponds to a different, not necessarily independent, source of PM10 and PM10-bound elements. In the first factor, sulfur, nickel, and aluminum have the highest share. Therefore, the previous conclusion about the predominant share of combustion processes and about carrying sulfur compounds on firemen's equipment and clothes in shaping the concentrations of these elements and dust inside the firehouse is correct. Considering the combustion of fuel oil and petroleum we deal with characteristic elements – sulfur and nickel [26]. The first factor in the case of the three mentioned elements reflects from about 60% (sulfur) to 45% (Ni) of their concentration (Fig. 6). However, the share of this factor is smaller in the case of

vanadium, chromium, iron or lead concentrations. This confirms that this factor can be identified with the combustion of fuels and other materials. It is similar to source #4 in UNMIX, however, the introduction of the uncertainties related to the X-ray analysis changes the contribution of this factor to the given elements – Mn from source #4 is not present in factor 1 while species concentration of iron, copper and aluminum are significantly lower in this factor.
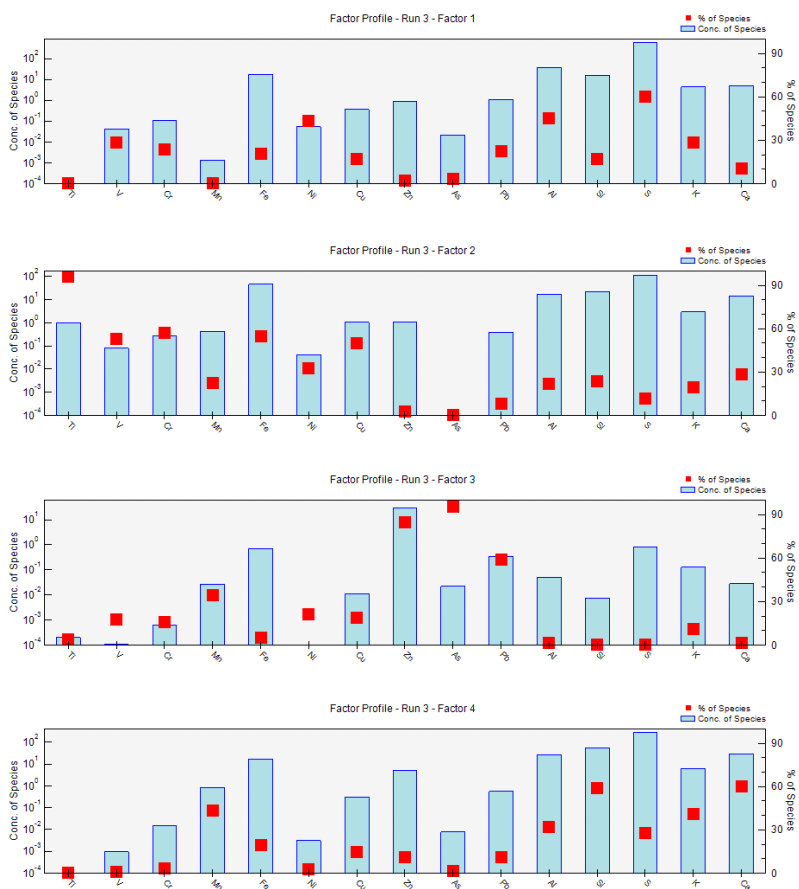

Fig. 5. Results of PMF analysis for PM10-bound elements in the indoor air of a selected firehouse in a central part of Poland (concentration of species in arbitrary units)

The second factor uses from over 90% (titanium), through 50–60% (vanadium, chromium, iron, copper) to 20–30% (nickel, aluminum, silicon, potassium, calcium) concentrations of the studied elements. Their common source may be a mixture of road dust related to traffic emissions not deriving from exhaust emissions. Factor 2 is like source #3 which includes more elements from non-exhaust emission than source #3.

Combustion may also involve a third factor that uses over 90% concentrations of arsenic and zinc as well as 60% lead concentrations. It is difficult to define what type of combustion is and what is the specific source, but based on the definite elements, we can suggest that it is most likely a factor characterizing the impact of external anthropogenic emission of PM10 and PM10-bound elements from the combustion of fossil fuels, especially coal from energy production. This is an important conclusion showing the impact of atmospheric air on the quality of indoor air not only in typical rooms such as schools, flats, or kindergartens [27] but also in specific rooms such as rescue and firefighting firehouses with many internal sources of pollutant emissions.
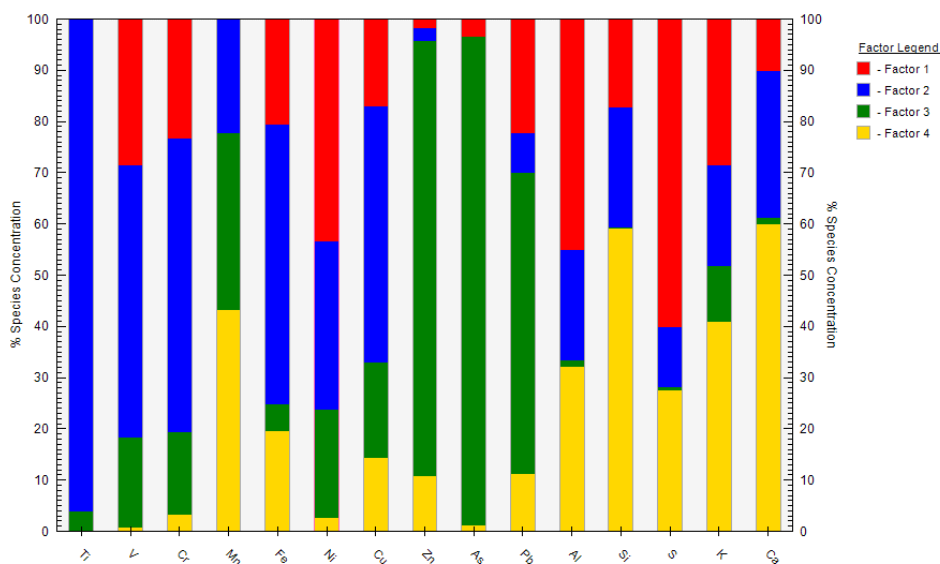

Fig. 6. The share of factors in PMF analysis in the concentrations of the studied elements

It should be underlined that the separation of this specific third factor allows one to show exactly how effective a tool in the analysis of PM origin can be UNMIX and PMF compared to simple PCA. Negative coefficients in the PCA, especially for PC2, for calcium and silicon biased the decomposition. The UNMIX source #2 and PMF factor 3, which are similar, were only identifiable with these techniques.

The fourth factor identified in PMF analysis is a factor that mainly uses the concentrations of typical crustal elements, which may partly be derived from natural sources, such as aluminum, silicon, calcium, and potassium. Factor four also uses sulfur and manganese concentrations partly which indicates the possibility of transferring their anthropogenic compounds or other elements on mineral aluminosilicate particles coming from natural sources. The comparison of sources found in UNMIX and in PMF shows no exact correspondence. It is like source #4 but in different proportions.

4. CONCLUSIONS

The paper presents the results of the first measurement of PM10-bound elements in a selected rescue and a typical firefighting firehouse it in Poland. The data from a two--week measurement campaign were analysed using PCA, PMF and UNMIX to demonstrate the origin of PM and PM-bound elements in the firehouse.

The concentrations of PM10 and most of the 14 studied elements in PM10 (Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb, Al., Si, S, K) are not high. Some differences and strong variability of hourly concentrations were noticed. Although the data came from a short measurement series, their high time resolution, and thus many individual data, allowed us the assessment of the PM10 origin and PM10-bound elements in the indoor air of the firehouse. Applying three different models to the collected data set gave similar results. First of all, it was found that the main source of PM10 and PM10-bound elements is anthropogenic emission. Most of the elements in PM10 were characterized by high and very high enrichment factors. Sulfur had the highest concentrations of all determined elements. Its concentrations also changed in the three models probably due to a strong enrichment of PM10 with sulfur which came from the fuel combustion in fire engine engines as well as from fuel oil emission. PMF model also allowed one to find specific relationships between sulfur and several trace elements indicating the influence of external emissions from fuel combustion on internal concentrations of PM10 and PM10--bound elements. Identified dependencies indicate the presence of mineral dust and dust from non-exhaust communication emissions in the firehouse. It is also possible that some of the elements and dust derive from the outside, and they were carried on vehicles or on firemen's equipment and clothes. However, to confirm this, further studies should be carried out at different points of firehouses and in different averaging periods.

Undoubtedly, in the case of high correlations among the dataset which are statistically significant, the PCA analysis cannot be applied in source apportionment. The correlations in the dataset cause almost whole variability to be explained by the first principal component. The other problem with the interpretation of PCs lies in possible negative values of coefficients in PCs. The step forward to better source apportionment is the application of UNMIX model that constrains the non-negativity of coefficients. It led to the essential change in the decomposition and resulted in sources that can be physically interpreted. The application of the PMF model for source apportionment allowed one to include the uncertainties related to the X-ray analysis precision. The results of the PMF analysis were slightly different from the results of UNMIX but they were comparable – the difference was not as big as in the case between PCA and UNMIX or PCA and PMF.

Independently of the model used, it is necessary to know PM elemental profiles from various sources. So far, they are well recognized for certain sources of atmospheric dust, such as the combustion of liquid and solid fuels (both in car engines and for mu-

nicipal and living purposes), industrial emissions, emissions from mechanical processes, including those related to car traffic, and many others. Elemental profiles of PM indoors are poorly recognized. Few studies have been done on indoor dust so far. However, data on the physical and chemical properties of dust generated from specific sources, including those found in rescue and firefighting firehouses are lacking. Regardless of the object that is analyzed in terms of the origin of indoor air pollution, the important starting point is to determine these sources and examine the properties of dust generated.

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