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## CHEMICAL CHARACTERIZATION AND SOURCE IDENTIFICATION OF PARTICULATE MATTER PM<sub>10</sub> IN A RURAL AND URBAN SITE IN POLAND

The measurements of PM<sub>10</sub> at two sites in Poland – a typical village and a big city considered urban background – indicated only a small difference in PM<sub>10</sub> concentrations. In summer time, the concentrations of PM<sub>10</sub> did not exceed the daily limit value of 50 µg/m<sup>3</sup> while in wintertime, the daily limit value was exceeded for almost all sampling days for both sites. Source contributions to ambient PM<sub>10</sub> were determined with factor analysis (FA) and multilinear regression analysis (MLRA) based on PM<sub>10</sub> composition data including concentrations of K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Br, Pb and As. In the winter, local combustion sources contributed with 61% and 79% to total mass in the urban and rural sites, respectively, reflecting serious local or even regional problem associated with PM<sub>10</sub> pollution. The episodic presence of As, the commonly known toxic element, requires a detailed study for better understanding of its temporal distribution both in the rural and urban atmosphere.

### 1. INTRODUCTION

The interest in atmospheric aerosol is high because of its impact on human health and its possible role in climate change. It has also a distinctive effect on visibility and contributes to soiling of monuments [1]. Many epidemiological studies have shown the association between health effects and particulate matter (PM) in ambient air [2, 3]. Health effects of PM are likely to depend on several factors, however, ambient concentrations, size and composition of the particles belong to the most important ones. Determination of composition of atmospheric aerosols, and particularly concentrations of trace elements is important because of toxic effects of aerosols composition

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on human health. Thus, for a targeted reduction of PM concentrations in the air, it is very crucial to know the sources and their contribution to the PM levels. Some mathematical methods are available to evaluate possible sources of PM using the concentration data set of various elements in aerosol samples [4].

Recently most studies on PM have been associated with urban sites, however people in an agriculturally used region are also exposed to PM from both naturally occurring processes and human activities [2, 5–8]. Therefore, more research is needed to better understand this problem and to evaluate the health risk of PM both for the inhabitants of rural settlements and cities.

In this work, the elemental composition of PM of the diameter below 10  $\mu\text{m}$  (PM<sub>10</sub>) samples originating from a typical village and a big city in Poland have been compared for two different seasons. One sampling site has been categorized as urban background (in Cracow, Poland) and the second as rural background (in Brzezina, Poland). Major sources of PM<sub>10</sub> are identified using factor analysis (FA). Mass contributions of identified PM<sub>10</sub> sources have been evaluated by multilinear regression analysis (MLRA).

## 2. MATERIALS AND METHODS

*Sampling.* Locations of sampling sites were selected such that the sites would be representative of urban and rural background air pollution. An urban site (Cracow, 50°04'06" N, 20°03'07" E) was located in the district Nowa Huta, in a build-up area with a park in the vicinity. An industrial area was located about 600 m East of the data recording site. A rural site (Brzezina; 51°12'12" N, 16°49'38" E) was situated in a garden at the outskirts of the village Brzezina. In the urban site 24-hour PM<sub>10</sub> samples were collected for two weeks in June 2009 and in January 2010 by a high-volume Digitel AG Sampler with the flow rate of 30 m<sup>3</sup>/h. As a support Whatman QMA (quartz microfiber) filters were used. In a rural site aerosol PM<sub>10</sub> was collected for two weeks in August 2009, and in February 2010 on a daily basis with a sampler TRC TECORA Co., Italy (Charlie model). The sampling rate was set at 2.3 m<sup>3</sup>/h. Sampling substrates were Teflon-membrane 47 mm in diameter filters (Whatman PTFE, 2  $\mu\text{m}$  pore size).

*Chemical analysis.* Filters were weighted to evaluate the PM<sub>10</sub> mass on a microbalance in a controlled clean room. Filter weight before and after sampling was obtained as the average of three measurements. Concentrations of following elements were determined: K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Br, Pb and As. Samples of PM<sub>10</sub> were taken for XRF as a bulk. X-Ray fluorescence analyses were performed in the laboratory of the Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Cracow, Poland. A multifunctional energy dispersive X-

ray fluorescence spectrometer was used. It consisted of micro-beam X-ray fluorescence spectrometer with capillary X-ray optics, a broad X-ray beam from Mo secondary target for XRF analysis of bulk samples and total reflection X-ray technique. Mo tube was a source of X-rays. The tube had the power of 2kW. Excited X-rays were detected by the Si(Li) detector with the resolution of 170 eV at the energy 5.9 keV. Data collections were done by the Canberra system. The measurements were carried out in the air atmosphere under the following conditions: voltage – 55 kV, current – 40 mA, measuring time – 10 000 s. For calibration of the spectrometer thin-film standards (Micromatter, USA) were used. The XRF spectra were quantitatively analyzed by the use of the QXAS package. The details of sampling and the accuracy of analytical methods is given in [9]. In our source apportionment studies, only elements that were above the detection limit in over 50% of the samples were included.

*Statistical analysis.* To further identify PM10 emission sources, factor analysis (STATISTICA software) was applied to the element concentration data obtained at both sites, urban and rural. Multilinear regression analysis was performed for evaluation the contribution of each source group to the PM concentration. The method was developed by [10], in which FA was conducted, absolute zero values calculated and applied to give absolute FA scores, followed by a regression of the mass to apportion PM10 to source categories and locations under study.

### 3. RESULTS AND DISCUSSION

PM10 mean mass concentrations, standard deviations and extreme values for the rural and urban sites are shown in Fig. 1. For the air quality management, the levels of pollutants are commonly compared with national or international standards or limit values. For PM10 concentrations, the daily EU mean limit value is  $50 \mu\text{g}/\text{m}^3$  and the number of allowed exceedances is 35 days per year. In summertime, both for the rural and urban sites, there were observed comparable levels of PM10 mass concentrations and they did not exceed  $50 \mu\text{g}/\text{m}^3$ . They varied from 15 to  $45 \mu\text{g}/\text{m}^3$  (Fig. 1). At the rural site, the PM10 concentrations were somewhat lower with the mean of  $23 \mu\text{g}/\text{m}^3$  as compared to the mean of  $26 \mu\text{g}/\text{m}^3$  at the urban site. Wintertime mean concentrations reached 4 and 5 times the summertime ones for the rural site and urban, respectively. The limit value of  $50 \mu\text{g}/\text{m}^3$  was exceeded almost all days for both sites. Strong fluctuations of the concentrations can be demonstrated by the standard deviation divided by the mean. The wintertime variability in Cracow was 78%, e.g. much higher as compared to 37% in Brzezina. The highest PM10 mass concentration ( $356 \mu\text{g}/\text{m}^3$ ) was monitored in Cracow on 27 January. Air masses came from the North, the wind speed was very low, temperature remained also very low on this day (minimum  $-16^\circ\text{C}$ ). Weather conditions were favourable for the accumulation of pollutants in the

shallow mixing layer in winter. Thus, this PM<sub>10</sub> peak concentration was most likely due to a combination of increased emission from heating sources coupled with meteorological conditions that limited pollutant dispersion. PM<sub>10</sub> concentrations in the urban site in this study were much higher than those measured in the Czech Republic [5, 6], Switzerland [2] and in some other European countries [1] but comparable to Greece [11] during cold season. In the rural location, our results were similar to the PM<sub>10</sub> levels monitored in the Czech Republic [5, 6]. In general, these comparisons above showed that during the winter very high PM<sub>10</sub> concentrations were monitored both in the urban and rural site under study.

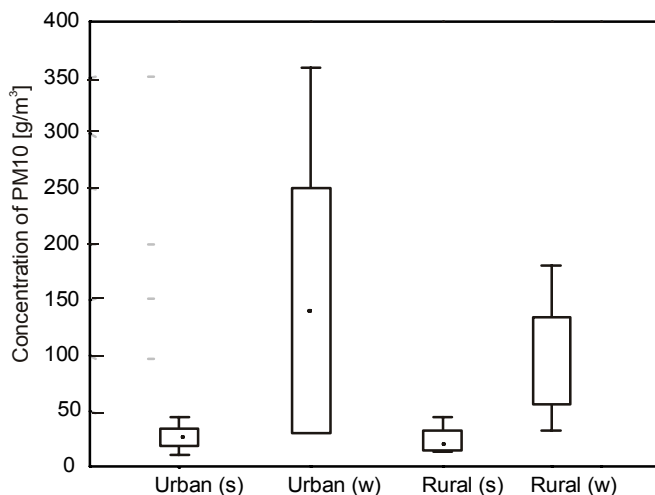


Fig. 1. PM concentrations at two locations: rural and urban for summer (s) and winter (w) periods presented by box-whisker plots. Graph shows minimum and maximum (whiskers), standard deviation (boxes) and means (middle points)

Table 1 presents the PM<sub>10</sub> mean, minimum and maximum concentrations for each of the species measured in Cracow and Brzezina. Obvious seasonal differences were observed in the ambient levels of trace elements, with the highest wintertime concentrations of all elements except Cu in the urban site. In summertime higher K concentrations were observed in the rural site, whereas Ca, Cr, Fe, Zn and Br in the urban site. The concentrations of Ti, Mn, Cu, Pb and As in the urban site in general appeared to be comparable to those in the rural site for the summer period.

Some selected elements are discussed at policy level in the European Union. Currently, there are only annual target values for Ni, As, Cd (they enter into force 1.1.2012) and a limit value for Pb. These elements should not exceed the annual standard of 20 ng/m<sup>3</sup>, 6 ng/m<sup>3</sup>, 5 ng/m<sup>3</sup> and 0.5 µg/m<sup>3</sup>, respectively. For Pb, the standard was higher than the observed concentrations. Cd and Ni were not detected in the samples. Nevertheless, the reported levels for As (Table 1) in some samples exceeded 6 ng/m<sup>3</sup>.

Table 1

Elemental concentrations of PM10 in urban and rural area [ng/m<sup>3</sup>]

Element	Summer					
	Urban			Rural		
	Mean	Minimum	Maximum	Mean	Minimum	Maximum
K	95	22	432	324	90	500
Ca	667	30	1740	474	105	1200
Ti	43	26	70	50	40	104
Cr	54	36	76	12.4	15	43
Mn	41	22	106	37	17	70
Fe	1124	150	3850	630	194	1384
Cu	13	5.8	26	11	5.3	21
Zn	74	20	317	44	9	128
Br	13	6.2	27	7.5	4.6	11.4
Pb	11	1	52	12.5	1.5	38
As	2.2	<LLD	6	3.5	<LLD	14
Element	Winter					
	Urban			Rural		
	Mean	Minimum	Maximum	Mean	Minimum	Maximum
K	1042	372	2620	648	380	1760
Ca	1216	300	1900	376	100	622
Ti	52	37	180	<LLD	<LLD	60
Cr	66	2	332	30	<LLD	103
Mn	164	85	377	40	27	163
Fe	4350	2554	8450	500	125	1400
Cu	24.6	10	90	32	15	68
Zn	442	155	1130	188	70	517
Br	61	18	173	28	8	70
Pb	121	50	200	85	19	232
As	21	10	39	4.3	<LLD	27

Wintertime urban concentrations of all elements in this study were much higher than those reported by Almeida et al. [4] for urban locations in Portugal and by Pey et al. [12] for Spanish urban sites (except for Cu), both for the winter periods. Branis and Domasowa [5] obtained lower values for rural locations during winter campaign in the Czech Republic. Studies conducted by Roosli et al. [2] in Switzerland showed similar results to our in urban environment. Karanosiou et al. [13] monitored higher summertime elemental concentrations in Athens, Greece as compared to those in Cracow. Manoli et al. [11] reported higher levels for Cu, Pb and lower for As, Cr, Mn, Zn and Fe at Thessaloniki, Greece than in Cracow (both for winter and summer).

Commonly researchers used two simple techniques to assess the contribution of various emission sources or categories to the observed pollutant concentrations, first from the correlation coefficients of each of these pollutants with each other, and then

applying principal component analysis PCA [14]. Such a correlation matrix for the summer period is shown in Tables 2 and 3 (similar results were obtained for the winter period, not shown). If some of these elements are associated with just one emission source or multiple similar sources, then they should strongly correlate. For the urban site, Ca, K, Fe, Mn and Zn have the strongest correlation (Table 2) and were clearly associated with just one type of the emission source; however, for other elements, the situation gets more uncertain and the errors in determining their corresponding relationships were much larger.

Table 2

Pearson's correlation coefficients between some elements in PM10 for the urban site (Cracow) summer 2009 (marked values with the significance level  $p < 0.005$ )

Element	K	Ca	Ti	Mn	Fe	Cu	Zn	Br
Ca	<b>0.71</b>							
Ti	-0.29	-0.25						
Mn	<b>0.82</b>	<b>0.84</b>	-0.16					
Fe	<b>0.91</b>	<b>0.85</b>	-0.36	0.92				
Cu	-0.15	0.34	0.15	0.07	-0.04			
Zn	0.73	0.67	-0.29	0.77	0.83	-0.03		
Br	0.13	0.52	0.01	0.39	0.34	0.46	0.50	
As	0.13	0.41	0.04	0.43	0.29	0.40	0.49	0.66

Table 3

Pearson's correlation coefficients between some elements in PM10 for the rural site (Brzezina), summer 2009 (marked values with the significance level  $p < 0.005$ )

Element	K	Ca	Ti	Mn	Fe	Cu	Zn	Br	Pb
Ca	<b>0.93</b>								
Ti	<b>0.75</b>	<b>0.79</b>							
Mn	<b>0.94</b>	<b>0.95</b>	0.65						
Fe	<b>0.90</b>	<b>0.97</b>	<b>0.84</b>	<b>0.92</b>					
Cu	0.38	0.54	0.51	0.43	0.59				
Zn	<b>0.75</b>	<b>0.87</b>	0.63	<b>0.81</b>	<b>0.87</b>	0.58			
Br	<b>0.76</b>	<b>0.83</b>	0.64	<b>0.80</b>	<b>0.82</b>	0.59	<b>0.81</b>		
Pb	<b>0.72</b>	<b>0.85</b>	<b>0.72</b>	<b>0.78</b>	<b>0.78</b>	0.54	<b>0.89</b>	<b>0.78</b>	
As	0.07	-0.01	0.31	-0.06	0.11	0.29	-0.08	0.13	0.01

Results for the rural environment (Table 3) show that most elements present in the aerosol are highly correlated with each other (except As and Cu), suggesting well-mixed components more likely controlled by similar processes of transport than attributed to one emission source. However in both cases, it was difficult to extract the types of emission sources, many of them contain the same elements. Soil particles are composed of oxides of Al, Si, Ca, Ti, Fe, K with many trace elements. These elements are also typical indicators of fly ash from coal combustion [15]. Resuspension of

roadway dust is also dominated by crustal elements Si, Fe, Ca, Na, Mg, Al and K [16]. Metals related to brake and tyre wear, and tailpipe emission are Cu, Zn, Pb, Sb, Br and Cd [16–18]. The municipal incineration sources are described by Cl, S, Fe, Br, and Zn [15, 19]. The ferrous metal source was mainly loaded with Fe, Mn and Zn [20].

Table 4

Factor loadings of element data from the urban site (Cracow)

Summer 2009				
Element	Steel works	Combustion /traffic	Crustal /soil	Commonality
K	<b>0.94</b>	0.13	0.08	0.91
Ca	<b>0.82</b>	0.39	0.04	0.83
Ti	0.27	0.04	<b>0.83</b>	0.76
Cr	0.19	0.32	<b>0.79</b>	0.76
Mn	<b>0.94</b>	0.19	0.12	0.93
Fe	<b>0.98</b>	0.08	0.10	0.97
Cu	0.12	0.76	0.23	0.64
Zn	<b>0.83</b>	0.28	0.18	0.80
Br	0.29	<b>0.83</b>	0.05	0.77
As	0.25	<b>0.81</b>	0.01	0.72
Variance, %	0.43	0.23	0.14	0.80
Winter 2009				
K	Combustion	Steel works	Commonality	
Ca	<b>0.86</b>	0.36	0.94	
Ti	0.34	<b>0.78</b>	0.99	
Cr				
Mn	0.17	<b>0.73</b>	0.93	
Fe	0.27	<b>0.83</b>	0.98	
Cu	0.42	<b>0.83</b>	0.99	
Zn	<b>0.93</b>	0.01	0.99	
Br	<b>0.93</b>	0.02	0.99	
As	0.26	0.52	0.62	
	<b>0.95</b>	0.06	0.90	
Variance, %	0.43	0.32	0.75	

In order to obtain more reliable estimates of different contributors to PM10 mass measured, FA was applied to identify major elements associated with sources. Then, a multilinear regression analysis was performed to assess the relative contribution of major air pollution sources at the receptor site. Trace elements were used as the markers for the above assessment. Table 4 shows the factor loadings from factor analysis for three components accounting for 81% of the total variance and two components accounting for 75% for the summertime and wintertime data from Cracow, respectively. In the summer, the first factor that explains 43.4% of the variance has high load-

ings of K, Ca, Mn, Fe, Zn. It is anticipated that the contribution is from the main type of the pollution source in this region, most likely industrial activities associated with the steel works (Nowa Huta steel mill). Interestingly, a high loading is found both for Fe, Mn, Zn and K, Ca. Its current association also suggests the contribution of fuel combustion (e.g. in a blast furnace) to atmospheric concentrations of these metals.

The second source profile is represented by high contribution of Cu, Br and As. Cu is emitted from metal brake wear [17], Br and As have been also detected in a vehicle emission source [15, 21]. Therefore, this source can be identified as vehicle emission.

The third factor is dominated by Ti and Cr. Atmospheric Ti is commonly considered a crustal element. Chromium belongs to the group of elements emitted from natural and anthropogenic sources in comparable amounts. The largest single sources are windblown dust and metallurgical processes [22]. Its current association with Ti may suggest that crustal soil is the dominant source for these metals in this urban site. No other typical crustal elements such as Al and Si were recorded. During the winter campaign, FA identified two main factors at the urban location (Table 4). Factor 1 is dominated by K, Cu, Zn, As and factor 2 by Ca, Cr, Mn, Fe. Factor 1 includes high factor loadings for As, Cu, Zn, K that are identified as markers for typical combustion sources (coal, wood) and/or vehicle emission. Factor 2 explains 32% of the variance and is recognized as industrial processes associated with the steel works. A crustal soil component remained unidentified as it could be insignificant during the winter with the snow layer on the ground. However, Cr has been identified as a soil element in the summer, but during the winter it was associated with other sources. Cr was related to emissions from metallurgical processes [22].

Relative impact of all source categories on PM<sub>10</sub> concentrations was almost equal in the summer and wintertime, whereas the ferrous metal source in summertime and combustion sources/traffic in wintertime were clearly the most important determinants of ambient PM<sub>10</sub>.

FA of Brzezina data for the summer and winter periods are shown in Table 5. Percentage of total variance in the analyzed data that is explained by two extracted factors is 77% and 76%, respectively. The commonalties for individual elements range from 0.97 (for Ca) to over 0.80 for the remaining six elements considered (K, Mn, Fe, Zn, Pb and As) for the summer period, and a little lower for the winter from 0.94 (Zn) to above 0.80 for K, Mn, Fe and Br. The general pattern of variable loadings in FA are similar for both seasons (Table 4). The first factor that explains 64% of total variance in the summer, and 61% in the winter, includes high factor loadings for almost all elements that some of them can be identified as indicators of different emission sources. In the summer, it was clearly a soil factor (K, Ca, Fe, Mn, Ti) with a range of other metals associated with road traffic (Zn, Br and Pb). It can be identified as well-mixed dust from agricultural operations and road traffic (regional background dust). But, the concentration values of K, Zn, Cu, Pb, Br in the winter differed several times from those in the summer, indicating greater influences by human activities.



Much higher concentrations of elements characteristic of different kinds of combustion processes demonstrate that local combustion sources, including biomass/refuse burning and coal combustion are of great importance in the winter. Crustal elements (Ca, Fe, Mn) along with Zn, Pb and Cu are typical markers for coal combustion, K for wood burning or generally biomass burning, and Zn, Br, Pb, K for incineration [23]. Wood burning along with domestic refuse and coal have been lately widely present in individual heating houses. This phenomenon undoubtedly contributes to high concentrations of PM10 and high abundance of many elements in air in the winter. It was a very cold winter, so heating in houses had high impact on PM10 mass concentrations.

Table 5

Factor loadings of element data from the rural site (Brzezina)

Summer 2009			
Element	Regional dust	Cu smelting	Commonality
K	<b>0.92</b>	0.10	0.85
Ca	<b>0.98</b>	0.08	0.97
Ti	<b>0.76</b>	0.40	0.73
Cr	0.47	0.05	0.23
Mn	<b>0.95</b>	0.02	0.91
Fe	<b>0.96</b>	0.21	0.96
Cu	0.48	0.54	0.53
Zn	<b>0.92</b>	0.03	0.84
Br	<b>0.86</b>	0.20	0.77
Pb	<b>0.87</b>	0.12	0.80
As	0.09	<b>0.95</b>	0.91
% Variance	0.64	0.13	0.77
Winter 2010			
Element	Combustion /incineration	Cu smelting	Commonality
K	<b>0.79</b>	0.42	0.80
Ca	0.63	0.54	0.68
Ti			
Cr	<b>0.71</b>	0.05	0.51
Mn	<b>0.87</b>	0.22	0.81
Fe	<b>0.90</b>	0.21	0.86
Cu	<b>0.82</b>	0.07	0.68
Zn	<b>0.95</b>	0.16	0.94
Br	<b>0.93</b>	0.11	0.88
Pb	<b>0.73</b>	0.45	0.74
As	0.07	<b>0.85</b>	0.74
% Variance	0.61	0.15	0.76

The second factor (15% of var.) was solely related to As. This is consistent with the lack of correlation found between As and the rest of the elements in this study (Table 3). This may suggest that the isolated emission source is a dominant source for As at this location, either due to episodic presence of As. There were only few days when As was detected with high concentrations and thus its behaviour can thus be interpreted with some confidence. However, it can be brought to the area from a distant sources since a copper smelter is located about 50 km in northwestern direction. In addition, areas that are near nonferrous metal smelters have reported extremely high arsenic air concentrations (EPA-454/R-98-013). This problem needs further investigation.

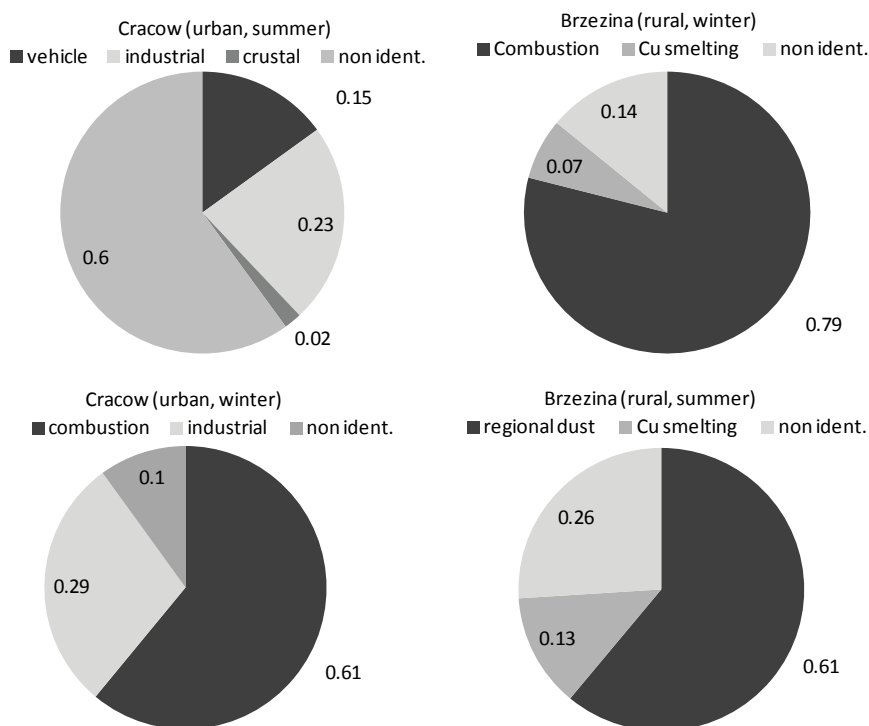


Fig. 2. Average contribution of various sources to PM10 mass concentrations monitored in the rural (Brzezina) and urban (Cracow) sites

The average mass contributions of each source to ambient PM10 in Cracow and Brzezina were calculated based on daily contributions (Fig. 2). Daily contributions were estimated using FA/MLRA methodology [10]. In Cracow, the average mass contribution of industrial emission sources was 23% in the summer and 29% in the winter, vehicle emission – 15% (in summertime) and combustion sources – 61% (in wintertime). Crustal soil contributed with 2% of total PM10 mass during the summer

campaign. In the summer, non-identified sources contributed with about 60% (10% in the winter). It was probably due to high concentrations of sulfates, nitrates and a certain amount of organic carbon which are characteristic secondary pollutants and are formed, especially in the summer, when solar radiation and temperature are high [22]. Contribution of vehicle emission was relatively low (15%) as for the urban atmosphere. However, vehicles emit not only particulate matter, but also large amount of gaseous pollutants which are transformed to secondary aerosols, including nitrates and organic carbon (probably contribute to unidentified aerosol mass).

In Brzezina, the contribution from regional background dust reached 61% PM10 mass concentrations in the summer campaign. Local combustion sources contributed with 79% in the winter, reflecting serious local or even regional problem associated with PM10 pollution. Probably impact of anthropogenic activities such as the smelting of metal ores was estimated as about 13% in the summer, and 7% in the winter. Unidentified PM10 sources dominated in the summer, 26% as compared to 14% in the winter.

#### 4. CONCLUSIONS

The PM10 elemental composition data collected at two sites; rural and urban ones were studied using FA/MLRA analysis to identify the possible sources and their contribution to ambient PM10 mass concentrations. The results of this study can be summarized as:

- During the winter, very high PM10 concentrations, exceeding the daily EU mean limit value, were monitored both in the urban and rural site.

- The industrial (steel works) source in summertime and combustion sources/traffic in wintertime were clearly the most important determinants of ambient PM10 in the urban site. In summer, non-identified sources contributed with about 60% (10% in winter). It was probably due to high concentrations of secondary pollutants.

- In the rural site, it was found that ambient PM10 sources showed significant seasonal variations in spite of similar characteristics. In the summer, regional background dust was identified as well-mixed dust from agricultural operations and road traffic. In the winter, wood burning along with domestic refuse and coal contributed to high concentrations of PM10. Regional impact of anthropogenic activities such as smelting of metal ores was also estimated, however, this problem needs further investigation.

- The episodic presence of As, a commonly known toxic element which causes adverse effects on human health, requires a detailed study for better understanding of its spatial and temporal distribution both in the rural and urban atmosphere.

It should be stressed that the present data only deal with the short measurements periods, and should not be generalized as such, nevertheless, the results present a realistic example of air pollution in a village and in a big city in Poland. In conclusion, we should be concerned about the particulate matter pollution not only in urban areas but

also in rural ones. The inhabitants can be exposed to comparable levels of inhalable PM10 particulate matter. Additionally, observed associations of health effects with PM10 exposure may be more closely related to specific chemical components than to PM10 mass concentrations. Thus, there is a great need to better characterize the metal emissions from different local and regional sources.

#### ACKNOWLEDGEMENTS

This work was partially financed by the International Atomic Energy Agency, project No. RER/2/005 and Polish Ministry of Science and Higher Education. The authors would like to thank the Environmental Protection Agency in Cracow for help in collection of samples.

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