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ORIGINAL PAPER

# Source apportionment of the PM10 fraction of particulate matter collected in Kraków, Poland

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**Abstract.** Samples of PM10 fraction of air particulates were collected during the winter of 2010 at two different sites in the City of Kraków, Poland. One site was located nearby a steel mill (Nowa Huta district) and the second one was situated at a distance of 10 km from the first site (Krowodrza district). The measured mass concentrations of PM10 fraction were in the range of 33 to 358 μg/m$^3$. They exceeded the permissible daily limit value of 50 μg/m$^3$. The Voivodship Inspectorate for Environmental Protection in Kraków was in charge of collecting samples as well as determining mass concentrations. Assessment of elemental concentrations and statistical analyses were performed at the University of Science and Technology in Kraków. Mean concentrations of Ti, Cu, Br and Pb were almost the same at both sites, while those of K, Ca and Zn were two times higher at Nowa Huta than at Krowodrza. Cr, Mn and Fe mass concentrations were also higher at Nowa Huta site; the values were a factor of three higher for Cr and Mn and factor of four for Fe. Factor analysis (FA) and multilinear regression analysis (MLRA) were used to determine source contributions to ambient PM10. The measurements were based on PM10 composition data which included elemental concentrations. Local combustion, industry and other, not identified sources, such as secondary aerosols, were the factors that highly contributed to the pollution of PM10 during winter time. For the site at Nowa Huta 53.1% of pollution was attributable to combustion and traffic, 28.5% was due to industry and wood combustion, and 18.3% were not identified. For the Krowodrza site, industry and wood combustion contributed 46.1%, combustion and traffic 50.4% and other, not identified sources 3.5% of the total PM10. Examination of meteorological data suggested that the concentration of potassium was inversely proportional to ambient air temperature at both sites. A wood combustion was identified as possible source of potassium in PM10.

**Key words:** air pollution • energy dispersive X-ray fluorescence (EDXRF) • elemental concentration • particulate matter • statistical analyses • PCA – principal component factor analysis • MLRA – multilinear regression analysis

## Introduction

Air pollution is one of many factors which may cause serious health problems [5, 8, 11, 13]. It can negatively influence respiratory and cardiovascular morbidity and mortality in humans. Air pollution is caused by gaseous ($SO_2$, $NO_x$) and particulate matter (soot, toxic metals) pollutants. The effects on human health are related to chemical and physical properties of particulate matter [4]. Particle size fractions of 1, 2.5 and 10 μm have different influence on the respiratory system [9]. The chemical content of particulate matter is very important; it has a significant effect on particulate matter (PM) toxicity [9]. Ambient PM originates from various sources, for example: industry, traffic and soil. For the most part, urban air is polluted by sources originating in industrial activities and from automotive traffic. Urban environments also tend to have the highest level of air pollution, which affects the people

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who live in those areas. The influence of air pollution on people's health is significant and, therefore, it is necessary to conduct research in this field on routine basis. By applying various statistical methods to the data of elemental content of PM it is possible to identify the sources of PM. Elements present in PM serve as the tracers of sources of pollution in such research [1, 9, 14, 18].

In the present study urban air pollution at two different sites in the City of Kraków, Poland was investigated. One site was situated near the large industrial object (steel mill) while the second one was located about 10 km from the first one, close to the city center. Mass concentrations and elemental concentrations of PM10 were determined for each site. On the basis of the results source identification and apportionment of PM10 were performed by statistical analyses, which included the use of PCA – principal component analysis, and MLRA – multilinear regression analysis. The results obtained for the two sites were compared.

## Experimental

### Sampling

Sampling sites were located within the agglomeration of the City of Kraków. The first one was situated in the Nowa Huta district (50°04'06"N and 20°03'07"E), in close proximity to a large industrial area. The second one was located in the Krowodrza district (50°05'15"N and 19°55'34"E ) which is a residential area, close to the City center. Samples of PM10 were collected on each day from the 15th of January until the 11th of February, 2010. Duration of collecting one sample was 24 h. Leckel LVS samplers fitted with QMA filters were used to collect samples at the flow rate of 2.3 $m^3$/h. A total of 50 samples of PM10 were collected. The Voivodship Inspectorate for Environmental Protection in Kraków was responsible for collection of PM10 samples.

### Chemical analysis

Elemental concentrations on each loaded filter were determined using energy dispersive X-ray fluorescence (EDXRF) technique in the laboratory of Faculty of Physics and Applied Computer Science at the AGH University of Science and Technology (Kraków, Poland) [16]. Mass concentrations of the following elements were measured: K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Br, Pb and As. The laboratory is equipped with a multifunctional energy dispersive X-ray fluorescence system. It consists of a micro-beam X-ray fluorescence spectrometer with capillary X-ray optics, a broad X-ray beam from Mo secondary target for X-ray fluorescence (XRF) analysis of bulk samples and total reflection X-ray setup. A 2 kW power, Mo-anode X-ray tube is a source of X-rays. The X-rays excited in samples are detected by a Si(Li) detector with the resolution of 170 eV at the energy 5.9 keV. Data acquisition was performed with a Canberra spectrometry system. The measurements were carried out in the following conditions: high voltage – 55 kV, tube current – 40 mA, measuring time – 10 000 s per sample. Measurements were carried out in the air atmosphere. In order to calculate the concentrations of different elements on the filters, the spectrometer was calibrated using thin-film standards (Micromatter, USA). Calibration was verified by analysis of NIST Standard Reference Material 2783 (air particulate on filter media) [7]. The XRF spectra were quantitatively analyzed with the QXAS package [19].

### Air mass back trajectories

Backward trajectories, ending in Kraków, on 27th January 2010 and at the height of 1000 m, were calculated with the Hysplit Model [6].

### Statistical analysis

To further identify PM10 emission sources, factor analysis (STATISTICA software) was applied to the element concentration data obtained at both sites. Multilinear regression analysis was performed to evaluate the contribution of each source group to the PM10 concentration. Factor analysis (FA) was performed according to the method described in [17]. This was performed by utilizing the orthogonal transformation method with Varimax rotation and retention of principal components whose eigenvalues were greater than unit. Factor loadings indicate the correlation of each pollutant species with each component and are related to the source emission composition. Absolute zero values were calculated and applied to give absolute FA scores, which were used to perform further research on the regression of mass to apportion PM10 to source categories and locations under study.

## Results and discussion

The mass concentrations obtained at Nowa Huta and Krowodrza districts are presented in Fig. 1. These values varied from 39 to 358 and from 32 to 355 $\mu g/m^3$, respectively. The mean mass concentration for the testing period at Nowa Huta site was equal to 124 $\mu g/m^3$ whereas the mean at Krowodrza site came to be 92 $\mu g/m^3$, the former being only slightly higher than the latter. The highest values were observed at both sites on the 27th of January 2010. On that day the wind speed was low (0.9 m/s) and air mass came from the North (Fig. 2). That day main contribution resulted from combustion and traffic (87.4% for Nowa Huta and 85.7% for Krowodrza) followed by industry and wood combustion (4.1% for Nowa Huta and 13.3% for Krowodrza) and from unidentified source shown 8.5% for Nowa Huta and 1% for Krowodrza (Figs. 4c and 4d). Very high values of mass concentrations were also measured at Nowa Huta on the other two days, 24th of January and 5th of February. However, on those two days the values at the Krowodrza site were much lower. This result suggest that on those two days the source of PM10 was closer to the Nowa Huta sampling site. On those two days the contribution of industial and wood combustion sources increased to about 30% for Nowa

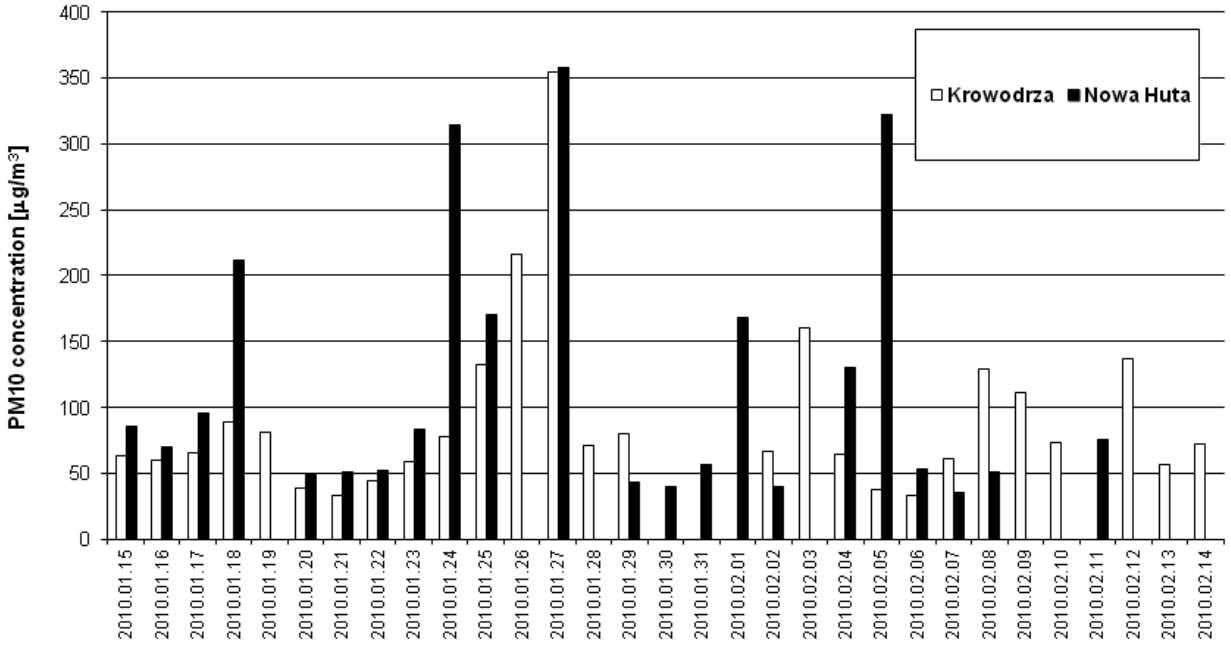


**Fig. 1.** PM10 concentrations at Krowodrza and Nowa Huta testing sites.

Huta and about 60% for Krowodrza. Simultaneously, sources identified as combustion and traffic lowered to 60% at Nowa Huta and 20% at Krowodrza (it is not shown in the paper).

Mean elemental concentrations of PM10 for both sites are presented in Table 1. It can be seen that the mean concentrations of Ti, Cu, Br and Pb were almost the same for both sites. On the other hand, the mean concentrations of K, Ca and Zn were two times higher for Nowa Huta than for Krowodrza while the values of Mn and Cr were three times and those of Fe four times higher for Nowa Huta than for Krowodrza. Table 1 contains also limit values for all analyzed elements [2] together with maximum elemental concentrations and date of collecting samples. On 27th January 2010, the concentrations of almost all analyzed elements were the same for both sites. The exception was Pb, which had a much higher concentration at Krowodrza on that day. At Krowodrza on 27th January for all analyzed elements the concentration was the highest. At Nowa Huta on 15th January, the concentration of Cr was very high. That day air mass was coming from the South-East direction. Also at Nowa Huta on 27th January, the concentrations of Cu, Zn, Br were the highest. At this site concentrations of K, Ca, Ti and Pb had the highest values on 5th February 2010 (Table 1). Mean concentrations of all elements at both sites reported in this study were much greater than those reported by Almeida *et al*. [1] for urban locations in Portugal and by Pey *et al*. [12] for Spanish urban sites. The only exceptions were Ca and Cu, the former having a higher concentration both in Spain and Portugal and the latter only in Spain. Studies conducted by Roosli *et al*. [15] in Switzerland showed the results similar to those obtained at Krowodrza site, except for Cu and Zn. In our study Zn concentration was higher than that in Switzerland and Cu concentration was lower in Kraków than in Switzerland. The copper and lead levels reported by Manoli *et al*. [10] for Thessaloniki, Greece, were higher than presented here for both sites located in Kraków. Our results of the elemental concentrations at both locations did not exceed the limit values (Table 1). Figures 3a and 3b show for both sites variation of potassium concentrations and ambient air temperature as a function of date of test. As is evident from these graphs, potassium is inversely correlated with temperature of ambient air. Since potassium is the tracer element of wood combustion processes, it is natural to expect elevated levels of potassium in air on colder days.

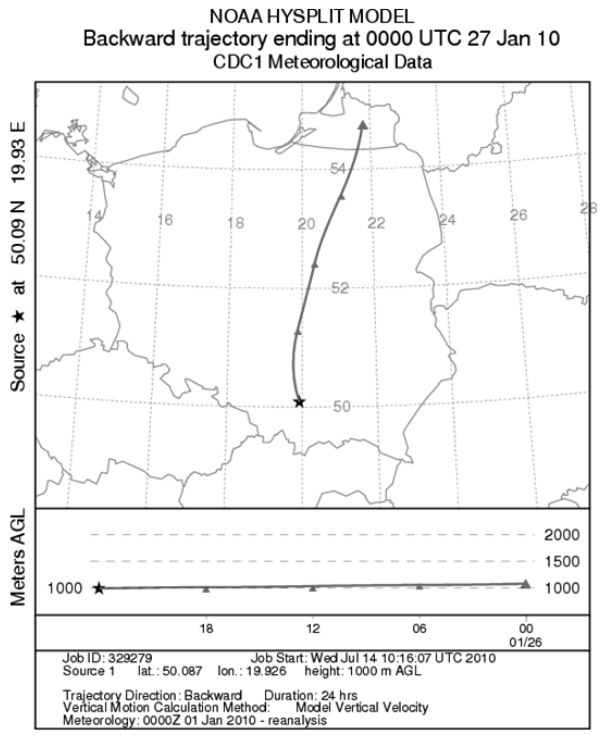


**Fig. 2.** Backward trajectories at 1000 m height.

The results of principal component analysis were shown in Table 2. Two PCA factors were obtained for

**Table 1.** Concentrations of PM10 (μg/m³) and elemental concentrations of PM10 at Nowa Huta and Krowodrza testing sites, (ng/m³)

| Element | Nowa Huta mean | Krowodrza mean | Nowa Huta max | Date | Krowodrza max | Date | Ratio mean Nowa Huta / mean Krowodrza | Limit value |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| PM10 | 124 ± 81 | 92 ± 45 | 358 | 27 Jan 2010 | 355 | 27 Jan 2010 | 1.35 | 50 |
| K | 737 ± 536 | 339 ± 199 | 1 659 ± 237 | 5 Feb 2010 | 1 040 ± 190 | 27 Jan 2010 | 2.17 | not included |
| Ca | 858 ± 533 | 342 ± 118 | 1 432 ± 285 | 5 Feb 2010 | 1 140 ± 14 | 26 Jan 2010 | 2.51 | not included |
| Ti | 66 ± 39 | 63 ± 18 | 213 ± 23 | 5 Feb 2010 | 105 ± 15 | 27 Jan 2010 | 1.05 | 3 800 |
| Cr | 47 ± 45 | 17 ± 8 | 332 ± 20 | 15 Jan 2010 | 49 ± 10 | 27 Jan 2010 | 2.76 | 2 500 |
| Mn | 118 ± 68 | 39 ± 15 | 377 ± 44 | 18 Jan 2010 | 80 ± 10 | 27 Jan 2010 | 3.03 | 1 000 |
| Fe | 2 960 ± 1 846 | 743 ± 350 | 8 447 ± 683 | 18 Jan 2010 | 1 785 ± 152 | 27 Jan 2010 | 3.98 | 10 000 |
| Cu | 31 ± 23 | 23 ± 13 | 90 ± 8 | 27 Jan 2010 | 75 ± 7 | 27 Jan 2010 | 1.35 | 600 |
| Zn | 422 ± 261 | 223 ± 122 | 1 128 ± 94 | 27 Jan 2010 | 1 054 ± 87 | 27 Jan 2010 | 1.89 | 3 800 |
| Br | 51 ± 33 | 37 ± 19 | 172 ± 14 | 27 Jan 2010 | 179 ± 14 | 27 Jan 2010 | 1.38 | 2 500 |
| Pb | 108 ± 54 | 68 ± 46 | 302 ± 18 | 5 Feb 2010 | 342 ± 22 | 27 Jan 2010 | 1.59 | 500 |

*Note: values ± in column 4 and 6 are standard deviations of EDXRF measurements and ± in column 2 and 3 represents the variability of elemental concentrations in all collected samples.

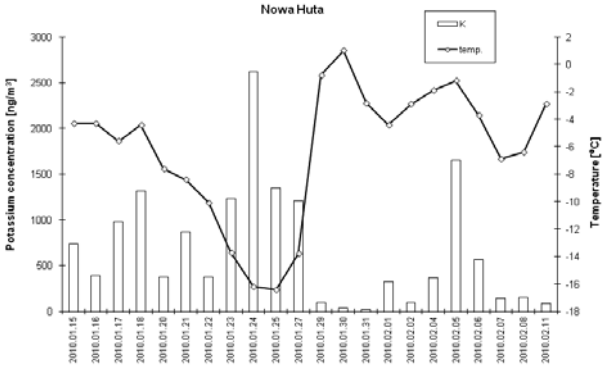


**Fig. 3a.** Daily air temperature and concentration of potassium in PM at Nowa Huta site.

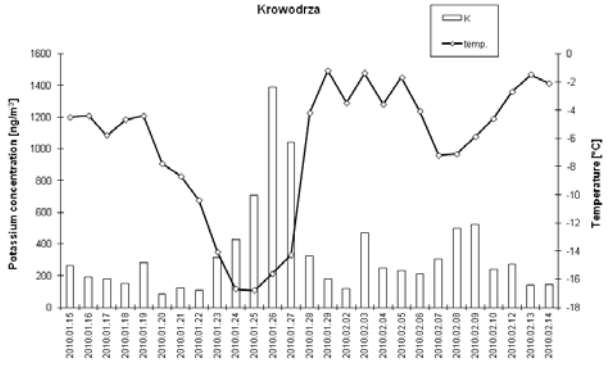


**Fig. 3b.** Daily air temperature and concentration of potassium in PM at Krowodrza site.

both sites. For the Krowodrza site, the tracer elements (those with high correlation coefficients) were: Pb, Br, Zn, Cu and As. The main sources of pollution identified on the basis of the presence of these elements, can be combustion (coal, fuel) and automotive traffic (factor 1 in Table 2) [18]. The presence of copper in particulate matter can be attributed to wearing of brake pads [10], while zinc may be a wear product of tire rubber [10]. For the second PCA factor the tracers were: Ca, K and Fe. The presence of these elements points to industrial and wood combustion as pollution sources. Hansen *et al*. [3] showed that wood combustion fly ash contains potassium and calcium. The sources identified for the Nowa Huta site are similar to those at the Krowodrza site. The first factor was connected with industry and wood combustion (factor 1 in Table 2). The tracer elements were Fe, Mn, Ca and K. The second one, associated with combustion and traffic, was characterized by

**Table 2.** Factor loadings of element data from the Nowa Huta and Krowodrza sites

| Element | Nowa Huta | | Krowodrza | |
|---|---|---|---|---|
| | Industry/wood combustion Factor 1 | Combustion/traffic Factor 2 | Combustion/traffic Factor 1 | Industry/wood combustion Factor 2 |
| 1 | 2 | 3 | 4 | 5 |
| K | **0.77** | 0.53 | 0.54 | **0.77** |
| Ca | **0.91** | 0.20 | 0.03 | **0.90** |
| Mn | **0.92** | 0.12 | 0.51 | 0.58 |
| Fe | **0.95** | 0.18 | 0.61 | **0.69** |
| Cu | 0.02 | **0.91** | **0.82** | 0.36 |
| Zn | 0.24 | **0.84** | **0.92** | 0.34 |
| Br | 0.36 | **0.88** | **0.92** | 0.31 |
| Pb | 0.61 | 0.30 | **0.93** | 0.16 |
| As | 0.49 | **0.70** | **0.82** | 0.20 |
| Variance (%) | 0.44 | 0.36 | 0.54 | 0.29 |

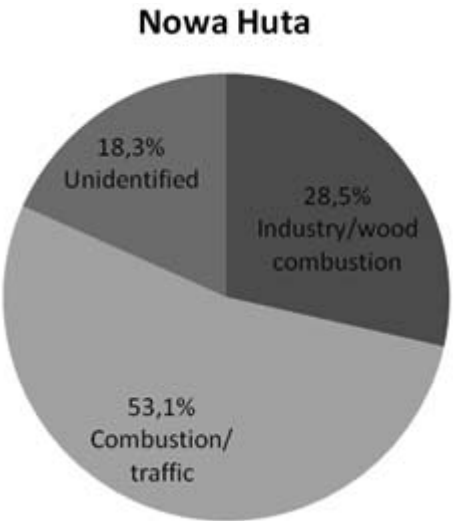


**Fig. 4a.** Contribution of sources to total PM measured at Nowa Huta site.

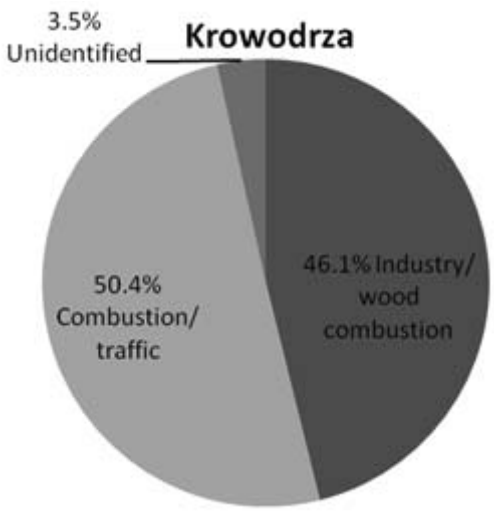


**Fig. 4b.** Contribution of sources to total PM measured at Krowodrza site.

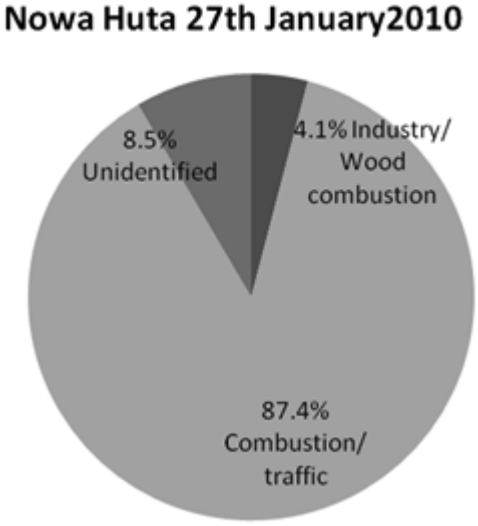


**Fig. 4c.** Contribution of sources to total PM measured at Nowa Huta site on 27th January 2010.

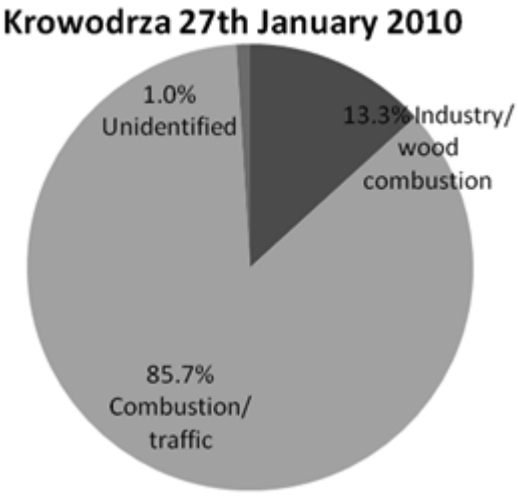


**Fig. 4d.** Contribution of sources to total PM measured at Krowodrza site on 27th of January 2010.

Cu, Br, Zn and As. In our study mass concentrations of Cu, Br, Pb and PM10 were strongly correlated with $NO_x$ and $SO_2$ concentrations (not reported in this paper) which suggested that automotive traffic and combustion processes were the origin of these elements.

Multilinear regression analysis was performed for each sample and each site and the results showing the mean values for each site are presented in Figs. 4a and 4b. At the Nowa Huta sampling site, the industry and wood combustion factor contributed 28.5%, the coal and/or fuel combustion and automotive traffic 53.1% and unidentified sources 18.3% to the total PM10 pollution. It is possible that the unidentified sources are due to the formation of secondary aerosols. At the Krowodrza sampling site, the industry and wood combustion factor contributed 46.1%, the coal and/or fuel combustion and traffic 50.4% and unidentified sources 3.5% to the total pollution. On 27th January, mass concentrations were the highest at both sites and almost all elemental concentrations as well as the contributions of sources were approximately the same. For the Nowa Huta site, industry and wood combustion contributed 4.1%, combustion and traffic 87.5% and unidentified sources 8.5%. For the Krowodrza site, combustion and traffic constituted 86% of the total PM10 pollution, industry and wood combustion 13.3% and unidentified sources 0.7%. On that day the coal and/or fuel combustion and automotive traffic were the most significant sources of air pollution. The air temperature in Kraków on that day was very low and the local heating including coal fired furnaces and heating from electropower, plant were used.

## Conclusions

Samples of PM10 were collected over the period of 4 weeks in winter of 2010 at two sites in the City of Kraków. One was located at Nowa Huta district and the other 10 km closer to the centre, at the Krowodrza district. PM10 concentrations were higher at Nowa Huta than they were at Krowodrza. Elemental concentration of Fe was four times higher at Nowa Huta than at Krowodrza and for Mn and Cr it was three times higher at

Nowa Huta than at Krowodrza. These elements have higher concentrations at Nowa Huta because sampling site is located nearby a steel mill. For other elements the differences were less significant. Statistical analyses suggest that combustion and automotive traffic had the highest contribution to air pollution, followed by industry and wood combustion and secondary aerosols. In Kraków a lot of people still use a low quality coal for heating in furnaces at homes.

The method of X-ray fluorescence may be used to perform analysis of elemental concentrations in PM. Statistical analyses based on concentrations of elements in PM allow to identify sources of air pollution. Previous paper [16] contains characterization of fine and coarse fractions of particulate matter together with meteorological parameters. So, it concerns characteristic of fractions with a diameter below 2.5 μm, between 2.5 and 10 μm and above 10 μm. For this work, however, according to the EU regulations, the present author collected samples of PM10 (particulate matter with the diameter below 10 μm) at two different sites of Kraków. The author successfully applied statistical analyses for source identification and apportionment.

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