

Seasonal variation of the elemental composition of particulate matter collected in a small town near Warszawa, Poland

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Abstract. Four seasonal sampling campaigns successively in April, July, September 2008 and February 2009 took place at Świder, a town located to the south-east of Warszawa, Poland. Three particle size fractions of particulate matter were collected by a NILU (The Norwegian Institute for Air Protection, Norway) sampler. The following elements were determined by the energy dispersive X-ray fluorescence (EDXRF) method: K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Br and Pb. The highest mean mass concentrations in fine and medium fractions were observed in April 2008 and February 2009. For a coarse fraction, the highest values of mass concentrations were observed in April and September 2008. Ca, Mn and Fe existed mainly in the coarse fraction. These elements probably came from the southern direction. Zn was divided between three fractions equally. In February 2009 the highest Zn concentrations were observed in the medium fraction. Pb existed mainly in the fine and medium fractions. The highest values of Pb concentrations were observed in February 2009. Bromium existed in the fine fraction. Correlations were observed between Ca, Mn and Fe concentrations. Correlation factors were about 0.8 for the coarse fraction. For other analyzed elements, the correlation coefficients were small. Basing on the backward trajectories and elemental concentrations of particulate matter (PM), it was confirmed that in winter the main influence on air quality is caused by pollution coming from coal combustion in local houses, heat and power plants working in urban areas. In summer the main influence on air quality is caused by pollution from sources in rural cultivable areas. The improvement of air quality is possible by decreasing the emission, using coal with a small level of harmful compounds and whole elimination of plant preventive agents and using fertilizers with a small content of unwanted elements.

Key words: air pollution • particulate matter • mass concentrations • elemental concentrations • EDXRF

Introduction

Air pollution has been widely investigated in many regions of the world. It is very important to know its level since particulate matter pollution has an influence on human health. Especially particulate matter with particle diameters below 2.5 μm influences human health. Some illnesses, for example respiratory diseases and cancer can appear after a long exposure to ambient particulate matter pollution [6, 11, 14, 20]. Particulate matter pollution depends on emission sources in the investigated regions (like: traffic, domestic heating, industry) and re-suspended dust and crustal material and long-range transport of pollutants. It is also connected with meteorological parameters. It is very important to know the level of particulate matter pollution in other countries in order to compare and evaluate its influence. There are some characterization of PM in Greece [7, 8, 16, 17], Hungary [3], UK [1, 9, 10, 15, 19], the Czech Republic [4, 5, 24], Sweden [18], Italy [2, 21], Switzerland [13, 22]. The above-mentioned studies were performed in urban and rural areas. Atmospheric PM is a complex mixture of elemental and organic carbon, ammonium, nitrates, sulphates, mineral dust, trace elements and water [13]. Information about the concentration of PM,

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Table 1. Mass concentrations of PM collected at Świder

	April 2008	July 2008	September 2008	February 2009
			Fine	
Mean mass concentration ($\mu\text{g}/\text{m}^3$)	6.4	3.6	4.3	4.8
			Medium	
Mean mass concentration ($\mu\text{g}/\text{m}^3$)	5.9	5.2	4.5	7.9
			Coarse	
Mean mass concentration ($\mu\text{g}/\text{m}^3$)	9.8	5.3	6.1	4.8

its size, chemical composition and chemical speciation of particles in PM can help to explain the problem of its toxicity. This paper describes size fractionated PM collected in a small town located near Warszawa, Poland. The place is a health resort, 44% of the town area is covered by forest. Simultaneously, there are houses heated by poor quality coal and wood. Three particle size fractions were collected: fine (particle diameter below $2.5 \mu\text{m}$), medium (particle diameter between 2.5 and $10 \mu\text{m}$) and coarse (particle diameter above $10 \mu\text{m}$). Sampling campaigns took place in four seasons of the year: April, July and September 2008 and February 2009. Seasonal mass concentrations were evaluated. Elemental concentrations were determined by EDXRF method. Correlations were calculated between internal elemental concentrations, elemental concentrations and meteorological parameters.

Experimental

Sampling

Four sampling campaigns took place in April, July, September 2008 and February 2009. The place where the samples were collected was a small town located 25 km to the south-east of Warszawa in Poland. Sampling site is located in the middle of Poland. Sampler (product NILU) was mounted at the level of the first floor. Samples of particulate matter were collected in three particle size fractions. Fine fraction consisted of particles diameter below $2.5 \mu\text{m}$, medium fraction consisted of particles between 2.5 and $10 \mu\text{m}$ and coarse above $10 \mu\text{m}$. Nuclepore filters were used as the supports. The time of collecting samples was 24 h. Total airflow was about 70 m^3 per sample [23]. Filters were weighed on a balance before and after collection of PM on the balance. Mass concentration of PM were evaluated.

Analytical method

Elemental concentrations were determined by the EDXRF method in the laboratory of Faculty of Physics and Applied Computer Science, AGH University of Science and Technology in Kraków (Poland). Measurements were carried out on a multifunctional EDXRF spectrometer. The spectrometer consists of a micro-beam X-ray fluorescence (XRF) 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. For the air particulate

matter analysis, the secondary target EDXRF method was used. Mo tube was used as the source of X-rays with a power of 2 kW. The X-rays were detected by a Si (Li) detector. The energy resolution of the detector was 170 eV for the energy 5.9 of keV. The measurements were carried out under the following conditions of X-ray tube: voltage – 55 kV, current – 40 mA, measuring time – 10 000 s. Measurements were done in air atmosphere. In order to calculate the concentrations of different elements in the filters, the spectrometer was calibrated using standards with a matrix similar to that of the samples to be analyzed. Thin film samples produced by Micromatter were used for calibration of the spectrometer. The calibration was tested by measurements using SRM 2783 (NIST product). The XRF spectra were quantitatively analyzed by the use of the quantitative X-ray analysis system (QXAS) package [25].

Results and discussion

Table 1 presents the mass concentrations of three particle size fractions of PM. The highest values of mass concentrations in the fine fraction were observed in April 2008 and February 2009. In the medium fraction the highest values were reached in February 2009, slightly lower in April 2008. In the coarse fraction, the largest values were observed in April 2008, the smallest in February 2009. These results show that the largest values of mass concentrations for the fine fraction were observed during cold season. This is connected with the heating in houses and in local heat and power plants. The wind speed was low, approximately 1–2 m/s during this campaign. High mass concentrations in the coarse fraction observed in April can be connected with meteorological parameters. During this campaign, the southeaster wind was blowing with a speed of 2–4 m/s. High wind speed causes transport of the PM coarse fraction. The values of mass concentrations at Świder are smaller than in urban areas in Greece [16, 17], UK [9, 10, 15], Italy [2] and Hungary [3]. The values for Świder are smaller than for the urban and larger than for rural areas in Switzerland [13], but for rural areas in the Czech Republic they are comparable [5]. Backward trajectories (Fig. 2) during April and February campaigns show that the air came from the north and south of Poland [12]. Figure 1 contains concentrations of K, Ca, Cr, Fe, Mn, Cu, Zn, Br and Pb in collected particulate matter. Table 2 contains meteorological parameters measured at the sampling place. Table 3 includes the detection limits for all analyzed elements. Concentrations of K, Mn, Cr, Cu are close to detection limits. The highest values of K concentrations were ob-

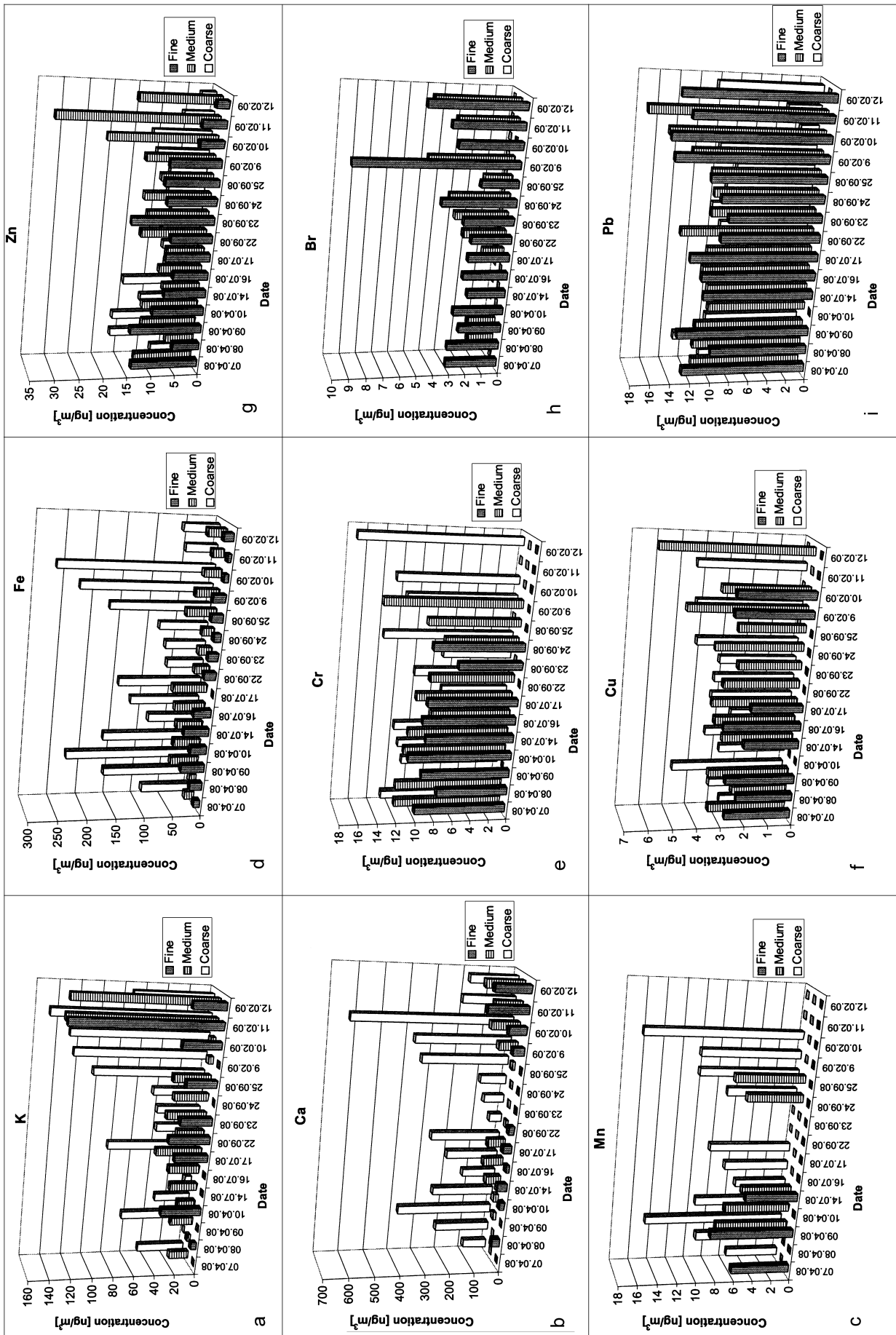


Fig. 1. Elemental concentration of PM collected at Swider.

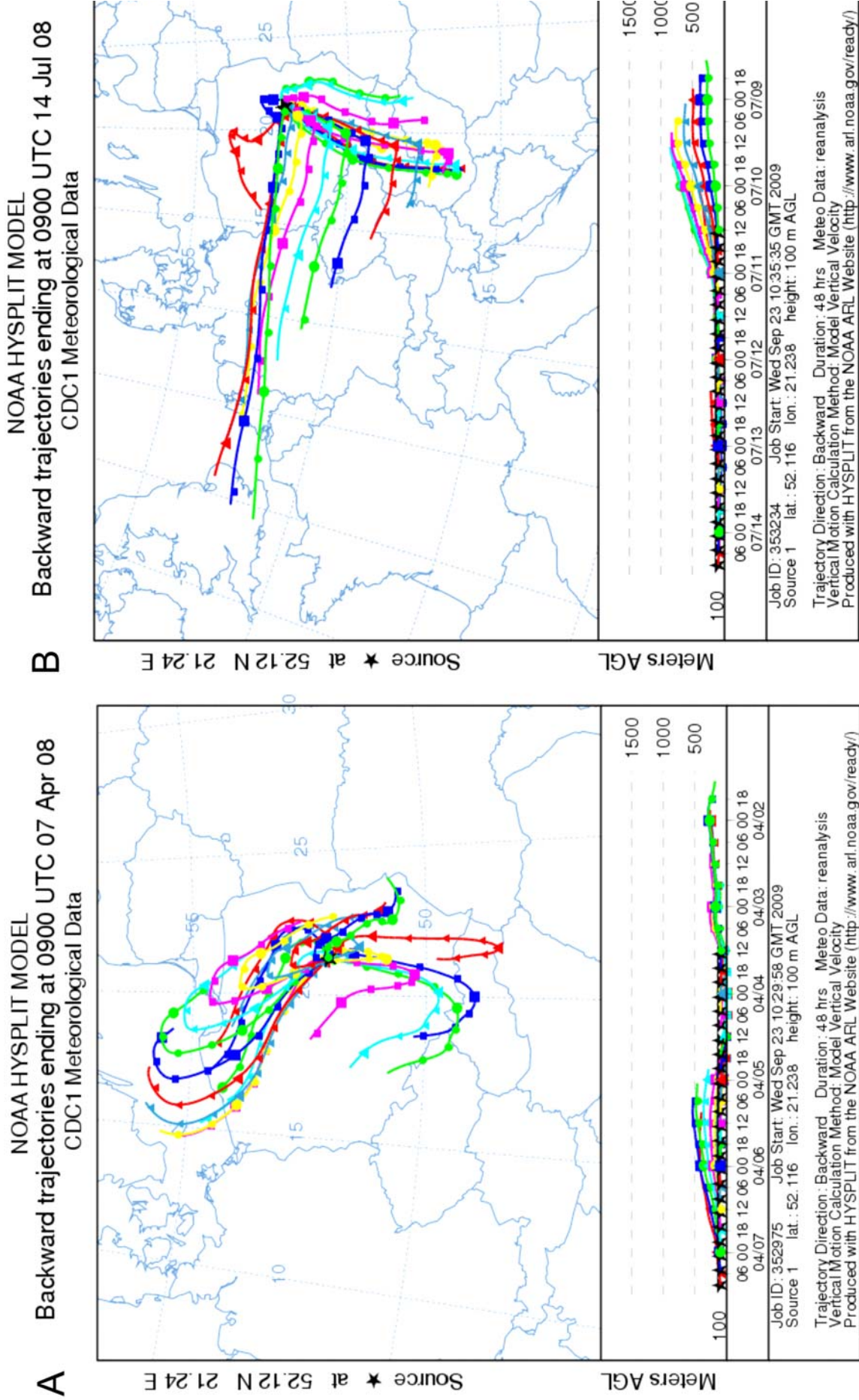


Fig. 2. Backward trajectories for Świder. (A) – April 2008, (B) – July 2008.

Table 2. Meteorological parameters observed at Świder

Date	Temperature (°C)	Wind speed (m/s)	Wind direction
7 April 2008	6	2	S
8 April 2008	4	4	S/W
9 April 2008	6	2	S
10 April 2008	12	3	S/W, N/W
14 July 2008	18	3	W/N
15 July 2008	18	3	N, W/N
16 July 2008	18	1	W/N
17 July 2008	18	2	W/N
22 September 2008	8	1	W/S, W/N
23 September 2008	10	1	E, N
24 September 2008	10	1	N/E, N
25 September 2008	10	1	N/E
9 February 2009	0.6	2	N/W
10 February 2009	-0.5	2	S/E
11 February 2009	2.3	2	S
12 February 2009	0.8	1	W

Table 3. Detection limits of air particulate matter in ng/m³

Element	Fine fraction	Medium fraction	Coarse fraction
K	6.9	6.6	10.4
Ca	4.5	5.9	15.1
Cr	7.0	7.5	9.1
Mn	6.0	6.5	7.3
Fe	1.8	2.5	3.8
Cu	2.3	2.7	3.0
Zn	1.6	1.8	2.1
Br	1.1	1.3	1.5
Pb	2.8	3.2	3.7

Table 4. Correlation coefficients between analyzed elements

Elements	Correlation coefficients		
	Fine fraction	Medium fraction	Coarse fraction
Ca-Cr	-0.560	-0.381	-0.033
Ca-Mn	-0.279	-0.402	0.807
Ca-Fe	-0.328	0.184	0.900
Ca-Cu	-0.203	0.309	-0.347
Ca-Zn	-0.744	0.512	0.341
Ca-Br	0.367	0.224	0.168
Ca-Pb	0.379	-0.198	-0.505
Cr-Mn	0.427	0.077	0.082
Cr-Fe	0.323	0.182	0.042
Cr-Cu	0.253	-0.021	-0.084
Cr-Zn	0.439	-0.592	0.071
Cr-Br	-0.441	-0.239	-0.058
Cr-Pb	-0.480	0.061	0.274
Mn-Fe	0.532	0.422	0.933
Mn-Cu	0.427	-0.248	-0.099
Mn-Zn	0.466	-0.261	0.626
Mn-Br	-0.258	-0.219	0.384
Mn-Pb	0.162	-0.099	-0.181
Fe-Cu	0.221	0.091	-0.139
Fe-Zn	0.240	-0.367	0.569
Fe-Br	-0.163	-0.289	0.351
Fe-Pb	-0.259	-0.160	-0.197
Cu-Zn	0.021	-0.249	0.323
Cu-Br	0.130	0.372	0.288
Cu-Pb	0.431	-0.564	0.210
Zn-Br	-0.192	0.352	0.720
Zn-Pb	-0.265	0.380	0.213
Br-Pb	0.364	-0.239	0.441

served in February 2009. This element appeared in all fractions. This may be due to the heating in houses as well as local heat and power plants. Concentrations of Ca, Fe and Mn have the same trend – they exist mainly in the coarse fraction. The high values of Ca, Mn, and Fe concentrations were observed on 9th of April, 25th of September 2008 and on 9th, 10th of February 2009. The highest values were observed on 10th of February 2009 for Ca – 630 ng/m³, for Mn – 16 ng/m³ and for Fe – 270 ng/m³. On this day the southeaster wind was blowing with a speed of 2 m/s. Ca, Mn and Fe were identified as soil dust elements. They can also be resuspended by cars or transported when the wind speed is strong. Harrison *et al.* [10] determined elemental concentrations of PM in wintertime. The following values were obtained: for Ca – 76 ng/m³, for Fe – 204 ng/m³ and Mn – 6.4 ng/m³. In our experiment we had for Ca – 300 ng/m³, for Fe – 43 ng/m³ and Mn was below detection limit. The highest values of Cu concentrations were observed in the medium fraction in February 2009. On 9th and 12th of February the wind was blowing from North/West and West with a speed of 1–2 m/s. During the rest of sampling campaigns Cu appeared equally in all fractions.

The highest value of Cu concentration was 6 ng/m³. Zinc was divided in all fractions equally. The highest Zn concentrations in the medium fraction were observed on 10 and 11th February 2009. They amounted to 20 and 30 ng/m³, respectively. During those days, the wind blew from South/East and South with a speed of 2 m/s. No correlation between Cu, Zn concentrations and meteorological parameters could be observed. Pb and Br were present in the fine and medium fractions. High concentrations of Pb and Br were in February 2009 (on 9th February the concentration of Br was 9 ng/m³ in the fine fraction and on 11th February Pb concentration was 17 ng/m³ in medium fraction). Trace element concentrations at Świder were comparable with those reported by Harrison for the UK [10]. Manoli [17] for Greece has found higher elemental concentration of PM. Branis [5] in the Czech Republic obtained comparable results for a rural place. The results for Pb in Italy [2] were also reported. Larger Pb concentrations in winter and comparable to our in summer were observed. Our results for Cu and Pb are smaller for urban and larger than for rural places in Switzerland [13]. The calculation of correlation coefficients between elemental concentrations was performed. Table 4 shows the values of correlation coefficients for the analyzed elements. A high correlation coefficient (about 0.8) appeared for Ca, Mn and Fe in the coarse fraction. This means that these elements can originate from the same source. For other analyzed elements, the correlation coefficients were small.

Conclusions

Seasonal changes of chemical composition of different particle size fractions of particulate matter were observed. The highest values of mass concentrations in the fine fraction were observed during cold seasons (April 2008, February 2009). These resulted from higher emission of PM from house heating and local heat and power plants. The coarse fraction had the

lowest mass concentration in February 2009. Elements like: Ca, Mn, Fe existed mainly in the coarse fraction. When the South/East wind speed was higher (2 m/s), the concentrations of Ca, Mn and Fe were higher. Soil dust elements were found. These elements can be transported from a long distance or re-suspended by cars. The correlation coefficients between concentrations of Ca, Mn and Fe were high. They amounted to 0.8. This means that these elements have the same source. Concentrations of Cu, Zn, Br and Pb were high in February 2009. No correlation between concentrations of these elements were observed.

On the basis of backward trajectories and elemental concentrations of PM, it was confirmed that in winter the main influence on air quality is caused by pollution originating from coal combustion in local houses as well as heat and power plants working in urban areas. In summer the main influence on air quality is caused by pollution from sources in rural cultivable areas. The improvement of air quality is possible by decreasing the emission, using coal with a lowered level of harmful compounds and the total elimination of plant preventive agents and fertilizers with low level of unwanted elements.

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