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PM2.5 ELEMENTAL COMPOSITION
AND SOURCE APPORTIONMENT IN A RESIDENTIAL AREA
OF WROCŁAW, POLAND

Ambient PM2.5 aerosol samples were collected from Wroclaw residential area between January and April 2009, and their elemental compositions were studied. The mean mass concentration of PM2.5 was 36 ± 21 µg/m^3. Based on the variability in elemental composition of atmospheric aerosols, using principal component analysis (PCA) and multiple linear regression (MLRA), four main sources of fine particulate matter were identified: road dust (54%), combustion of liquid fuels (4%), soil /mineral material (15%); industrial emission (10%). Also in the analysis of these data, two road dust components were identified with one being associated with local wood burning and the other with road salt.

1. INTRODUCTION

Transportation and fossil fuel combustion have been recognized to be significant and increasing sources of atmospheric particulate matter worldwide. This problem has gained additional significance as ambient particles may cause adverse health effects [1–9]. It has been suggested that fine fractions (with the diameter below 2.5 µm, PM2.5) might induce various respiratory diseases, particularly bronchitis and reduction in lung function parameters. These effects were observed when the mean annual concentration of particulate matter was above 20 µg/m ^{3} for PM2.5 or 30 µg/m ^{3} for PM10 (with the diameter below 10 µm).

Wroclaw (51°07′ N, 17°02′ E, 116 m a.s.l.), with the total population of 634 000 inhabitants and the total area of 292.8 km^2, is the fourth largest city in Poland. As a city, it constitutes a homogeneous urban area with rural surroundings. The air quality

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in Wroclaw is determined by a large number of emission sources, among which road traffic seems to be the most important. Traffic density in the city is very high with a dramatic frequency of severe traffic jams. Wrocław's major industries were traditionally the electronics, thermal electric power plants, and chemical factories.

The above considerations have motivated a pilot study on the PM2.5 concentration levels and elemental composition of ambient aerosol in the residential area of the city. The study of elemental composition is also essential to elucidate the sources of particulate matter. Any strategy aimed at reducing pollutant levels in air demands the knowledge of chemical composition and the recognition of emission sources which significantly contribute to ambient pollutant concentrations.

2. EXPERIMENTAL

In order to assess the potential emission sources of PM2.5 in Wroclaw, a monitoring study was established to measure urban background concentrations in the city. In a residential area with mixed settings and allotments, PM2.5 was collected during 24 h periods from January to April, 2009.

The study employed modified IMPROVE (Interagency Monitoring of Protected Visual Environment) aerosol monitors, similar ones have been operating within the Programme IMPROVE in the United States for several years. Each of the modified IMPROVE samplers is equipped with PM2.5 Anderson inlet at approximately 3 m collecting PM2.5 on 47 mm Teflon filters (Whatman, 2 mm PTFE 46.2 mm, air flow 22.8 dm^3/min).

The filter samples were analyzed at the Crocker Nuclear Laboratory, University of California at Davis (UCD). Elemental composition analysis was performed using the technique of X-ray fluorescence XRF, proton induced X-ray energy (PIXE) and proton elastic scattering analysis (PESA). PESA is applicable for hydrogen determination in the sample. Total concentrations of 21 elements were analysed such as H, S, Cl, K, Ca, Ti, Fe, Mn, Cr, V, Ni, Cu, Zn, As, Pb, Br, Rb, Sr, Na, Al and Si.

Source categories for PM2.5 constituents were identified by means of the principal component analysis (PCA) using the orthogonal transformation method with varimax rotation. Multilinear regression analysis (MLRA) was applied to assess the contribution of each source group to the aerosol burden [10, 11].

3. RESULTS

Table 1 summarizes the basic descriptive statistics for concentrations of PM2.5 measured at the urban background station. The PM2.5 levels varied between 12 and 100 µg/m^3, with the mean value of 36±21 µg/m^3. There is no the 24h PM2.5 EU target

value, only the annual one for protection of health of 25 µg/m^3 (from 1.1.2010). The World Health Organization (WHO) Air Quality Guidelines (AQG) value for 24 h PM2.5 is more restrictive and equals the annual EU target value [12]. According to the WHO statement, meeting the guideline value for 24h mean will protect against short-term high pollution that would lead to the substantial health risk.

Table 1

Basic descriptive statistics calculated for 24 h PM2.5 [µg/m^3]
concentrations for the sampling period January/March/April 2009

Value	PM2.5 (19.01–6.02)	PM2.5(2.03–29.03)	PM2.5 (6.04–27.04)
Minimum	18	12	12
Maximum	100	85	52
Average	50	32	24
Standard deviation	24	18	12

The measured concentrations of PM2.5 were very high, particularly in January/February, well above the AQG. The samples containing above 25 µg/m^3 of PM2.5 constituted 52% (Fig. 1). The scenario may be worst because only 3 months were analyzed in Wrocław, and the highest concentrations were monitored during wintertime which is six month long or even longer.
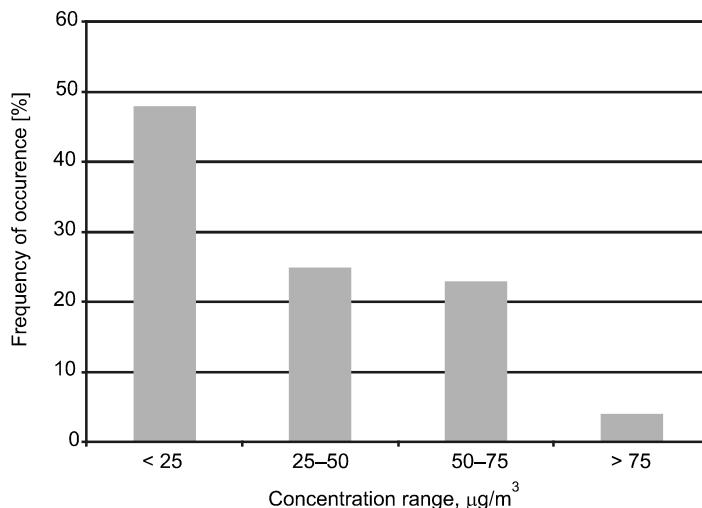

Fig. 1. Histogram of 24 h PM2.5 concentrations
for the sampling period (January/March/April 2009)

Four principal components were identified with eigenvalues higher than 1.0. The loading extent (≥ 0.7 in this study) of the correlations between the principal compo-

nents and the original variables was used to assign source identity to each one of the PCs. It can be seen from Table 2 that four components accounted for approximately 81 % of the total variance in the dataset. The identified major sources included: road dust, combustion of liquid fuels, soil/mineral material; As/Mn industrial emission.

Table 2

Results of analyses of elemental components of PM2.5 aerosol in Wroclaw
from January to April 2009 (bold marked factor loadings ≥ 0.70)

Component	PC1	PC2	PC3	PC4
Eigenvalues	10.53	2.99	2.27	1.22
Cum. eigenvalues	10.53	13.52	15.79	17.01
% Variance	50.14	14.22	10.82	5.82
Cum. % variance	50.14	64.36	75.18	81.00
Variable				
H	**0.81**	0.25	0.24	0.41
Al.	–0.16	**0.90**	–0.20	–0.01
Si	0.10	0.91	0.27	0.08
S	0.32	0.49	0.62	0.35
Cl	**0.91**	–0.02	0.11	0.28
K	**0.86**	0.20	0.11	0.38
Ca	**0.75**	0.52	–0.11	0.05
Ti	0.47	**0.70**	0.06	0.08
V	–0.17	–0.06	**0.82**	–0.19
Cr	0.36	0.11	0.28	**0.74**
Mn	0.41	0.30	0.026	**0.74**
Fe	0.51	0.20	–0.29	0.57
Ni	0.10	0.01	**0.94**	0.05
Cu	**0.82**	0.01	–0.16	0.42
Zn	**0.83**	–0.13	–0.074	0.44
As	0.17	–0.17	–0.15	**0.86**
Pb	0.61	–0.08	–0.06	**0.73**
Se	0.42	0.39	0.07	0.69
Br	**0.70**	0.04	0.19	0.61
Rb	**0.70**	0.22	0.43	0.24
Sr	–0.035	–0.02	–0.31	–0.00

Source 1 represents a complex mixture of compounds with high concentrations of H, Cl, K, Ca, Cu, Zn, Br, Rb. Hydrogen originates mainly from organic substances (OC) and possibly ammonium sulfate (water evaporates during the analysis). Wood burning and vehicle emissions (gasoline) are both associated with OC and Ca, however wood burning is also associated with K and Rb. Road dust and vehicle resuspension are characterized by OC, Ca, Cl, Zn, Cu, Br, Road salt may be distinguished by high levels of Cl, Na (not measured), and Ca. At low temperatures sodium

chloride mixed with calcium chloride is often used. It may also contain small amounts of K and Br. Bromine correlates greatly with Cl. The correlation coefficient $r = 0.84$ is calculated. Cu may be released from brake pads, Zn from tires and brake wear.

The presence of Al, Si and Ti is associated with mineral material or soil dust (factor 2) while V and Ni characterize heavy oil combustion (factor 3). As and Mn, Cr, Pb present a high correlation with the factor 4. Metal smelting and burning of fossil fuels (including waste wood) are the major industrial processes that may contribute to contamination of air with these metals.

Multilinear regression analysis (MLRA) was applied to the experimental data, using as dependent variables PM2.5 total mass concentrations and as independent variables the principal component factor scores [10, 11]. The relative source contributions to each sample are shown in Fig. 2.
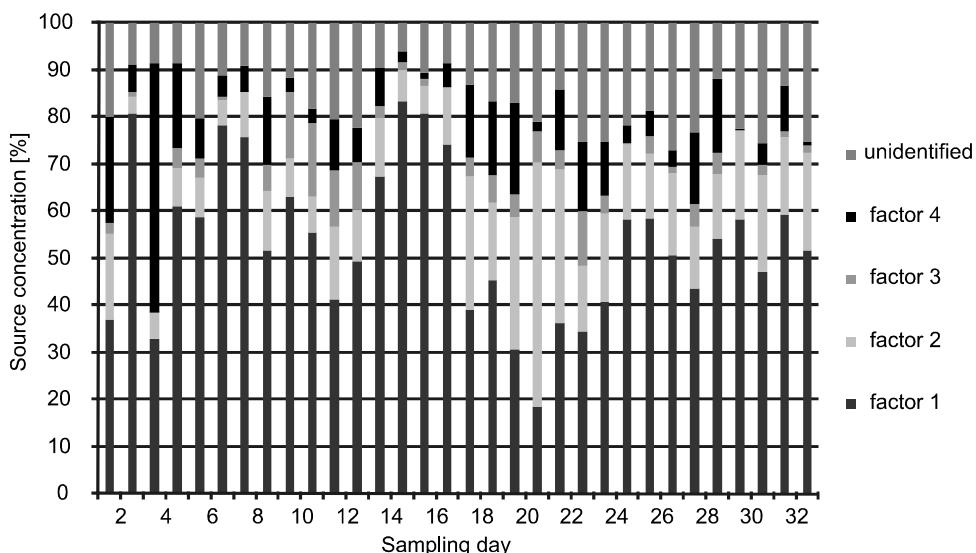

Fig. 2. Daily relative contribution of the identified sources to the PM2.5 mass
for the sampling period (January/March/April 2009)

The average relative contributions of the identified sources to the PM2.5 mass for the whole sampling period, January/March/April, 2009 are given in Fig. 3. The figure shows that the average contribution of source 1 which was loosely identified as road dust was 54%. The daily contribution changed from 18% to 82% during the sampling period (Fig. 4). An interesting feature of this solution is the existence of two main components that have been identified as wood combustion products and road salts.

Source 2 represents soil with high concentrations of Al, Si and Ti, and contributes 15% to the total PM2.5 mass at this site. The average ratio of Al to Si concentrations is 0.22, very close to the typical ratio observed in soils, 0.29 [13]. Source 3 appears to

be heavy oil combustion with the presence of Ni and V mixed with S. This source contributes 4% to the total PM2.5 mass. Source 4 with high concentrations of As and Mn, Cr, Pb is assigned as industrial sources and contributes 10% to the total PM2.5 mass. An unexplained portion averaged 17% of PM2.5 mass. Some of the unexplained mass may be due to additional sources of elemental carbon, however, more work needs to be done to resolve this problem.
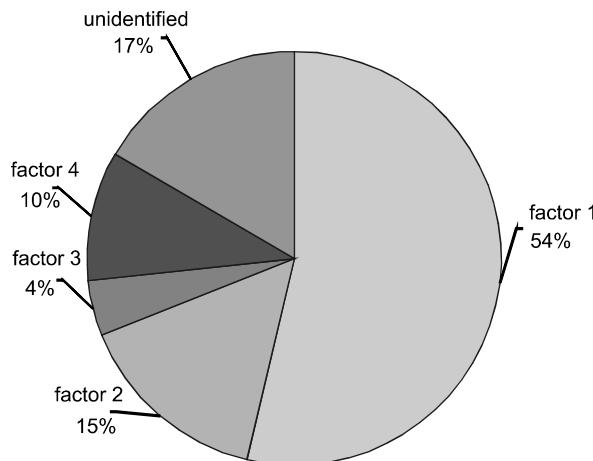

Fig. 3. Average relative contributions of the identified sources to the PM2.5 mass
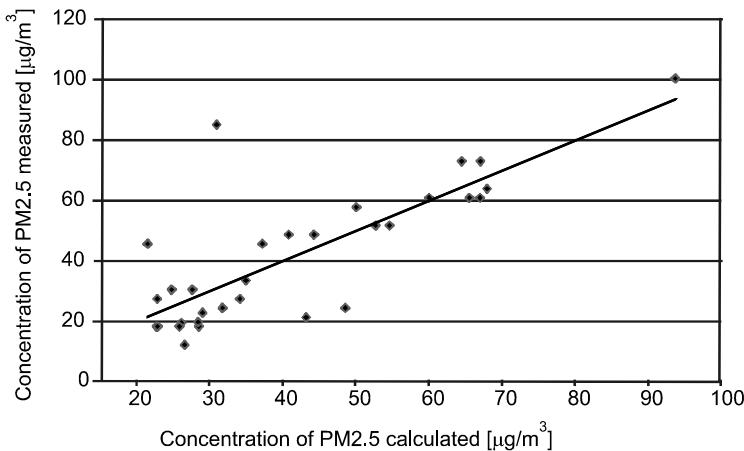

Fig. 4. Comparison of the predicted total PM2.5 mass from MLR analysis
with the measured PM2.5 mass concentrations

The test of the effectiveness of PCA together with MLRA is the comparison of the predicted PM2.5 mass versus the measured one. The results are presented in Fig. 4. The squared correlation coefficient R^2 is 0.64.

4. CONCLUSIONS

The elemental composition data of the ambient aerosol collected at the residential site of Wrocław was studied to identify possible emission sources using PCA and MLRA. The results can be summarized as four sources: road dust, combustion of liquid fuels, soil/mineral material; As/Mn industrial emission were identified, road dust was the major source for the ambient aerosols. There is a strong evidence for a significant role of wood burning and road salt, the contribution of As emission source was observed, however, the industrial process was not recognized. It is likely that the main contributors are stationary combustion sources (boilers, furnaces, stoves, and fireplaces) in the residential and industrial use sectors. Other sources of variation in the concentration that might aid the separation of the emission sources should be incorporated, as wind direction and speed, time of year.

The compatibility of the predicted PM2.5 mass versus the measured one shows that the applied mathematical methods PCA and MLRA seem to be promising in determining the sources of atmospheric aerosol particles.

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