

The elemental composition and origin of fine ambient particles in the largest Polish conurbation: first results from the short-term winter campaign

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Abstract Diurnal (24-h) samples of fine particulate matter (PM_{2.5}, ambient particles with an aerodynamic diameter not greater than 2.5 μm) and soil samples were collected in an urban area in Warsaw, in winter. The samples were analysed for 24 elements with an Epsilon 5 spectrometer (PANalytical). The results were then arranged and compared with the results of research conducted earlier in Poland and other parts of the world. Afterwards, sources of ambient PM_{2.5} were identified and the share of each in the concentration of PM_{2.5} was evaluated by means of enrichment factor (EF) analysis, principal component analysis (PCA) and multi-linear regression analysis (MLRA). The results were interpreted using a detailed analysis of correlations between diurnal concentrations of PM_{2.5}, PM_{2.5}-elements, and of changes in meteorological conditions. The winter average ambient concentration of PM_{2.5} in Warsaw, was 10.7±7.5 μg/m³ and was much lower than in the other sites in Poland. In Warsaw, regardless of the concentration of PM_{2.5}, the concentrations of certain PM_{2.5}-bound elements, mainly toxic, were high, e.g. the average ambient concentrations of PM_{2.5}-bound Se, As, Co, V, Cd and Ni were 12.7±30.5, 10.6±34.4, 9.4±13.7, 15.1±32.7, 9.6±22.2 and 3.5±5.0 ng/m³, respectively. The elemental composition and concentrations of PM_{2.5} appeared to be influenced mainly by the anthropogenic emissions (energy production based on coal

and biomass combustion, whose mean contribution to the concentration of PM_{2.5} was 18.4 %, and energy production based on oil combustion with a contribution of 9.9 % in PM_{2.5}). A mixture of soil matter and road dust was also identified in PM_{2.5} (8 %). The mean contribution of traffic (exhaust) emissions to the concentration of PM_{2.5} in an urban area, selected as representative of the Warsaw conurbation, was assessed at 15.4 %.

1 Introduction

In recent years, particular attention in air-quality research has been paid to the chemical characteristics of particulate matter (PM) and principally to its fine particle fraction PM_{2.5} (ambient particles with an aerodynamic diameter not greater than 2.5 μm). There are two main reasons for the interest in PM_{2.5} compositions. One is the adverse health effect that PM_{2.5} exerts (Englert 2004; Pope and Dockery 2006; Kennedy 2007; Viana et al. 2008a, b; Belis et al. 2013; Cheng et al. 2014; Daher et al. 2014). The other is the possibility of using such knowledge to manage air quality (assessment of PM emission source percentages, elaboration of actions that will limit the PM concentrations in the researched areas).

The elemental analysis of PM partly characterizes the PM chemical composition; it usually suffices for understanding the temporal and spatial relationship between the source and the receptors of PM and for the assessment of the efficiency of emission abatement methods (Chow 1995; Viana et al. 2008a; Sówka et al. 2012; Zhang et al. 2011). It also provides some information on potential PM health and environmental effects (Swaine 2000; Duvall et al. 2008; Wiseman and Zereini 2009; Lettino et al. 2012; Baxter et al. 2013).

Some elements in PM, including all heavy metals, are considered toxic (Costa and Dreher 1997; Swaine 2000). Even

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though concentrations of toxic elements, such as As, Cd, Pb, and Ni, in the air do not normally exceed permissible levels, chronic contact with such pollutants contributes to many adverse health effects, as they accumulate in the body tissues (bones, kidneys, brain; Costa and Dreher 1997; Swaine 2000; WHO 2000; EC 2004). Exposure to their salts or oxides can cause acute or chronic poisonings, tumours, diseases of the cardiovascular and nervous systems, and of the kidneys (Lippmann 2008), and some elements can weaken the immune system in humans (Goyer 1986). The adverse effects of lead are well known (Chow 1995). Some elements are not bioavailable in their elemental forms; although recent studies show that PM_{2.5}-bound heavy metals are bioavailable, the majority occur in well water-soluble compounds (Wiseman and Zereini 2009; Na and Cocker 2009; Rogula-Kozłowska et al. 2013a, b).

The influence on health is determined by the concentration of the elements in the air, their chemical form and the PM fraction type to which they are bound. In PM coming from industrialized and highly urbanized regions, in which non-industrial combustion (municipal and residential sectors) and traffic are also dominant emission sources, large concentrations of toxic heavy metals are observed (including Cd, Pb or Cr; Table 1). The elemental composition of natural PM forms in a completely different way, particularly when considering PM from the seaside and desert areas (Viana et al. 2008a; Campos-Ramos et al. 2011; Bozlaker et al. 2013). In such locations, elements bound to the crustal fraction dominate (Si, Al, Ca, K and Fe). The biggest differences in the levels of the harmful elements in the air are observed in areas that differ in the degree of anthropopressure, such as urban and background areas and in regions characterized by different emission structure types.

The elemental composition of PM_{2.5} and the identification of their sources have been the subject of numerous studies (Table 1). Nevertheless, such information and details are still unavailable for the area of Eastern Europe (Viana et al. 2008a; Putaud et al. 2010; Calvo et al. 2013; Rogula-Kozłowska et al. 2014). The available works on PM-bound metal mass size distribution confirm the tendency of PM-bound heavy metals to accumulate in the finest PM particles (e.g. Fernandez et al. 2001; Daher et al. 2012; Rogula-Kozłowska et al. 2012, 2013b; Daher et al. 2014).

Studies of the elemental composition of PM_{2.5} carried out in Poland have hardly gone beyond the south of the country (Table 2). However, in central Poland, where the population density in the Warsaw conurbation reaches 632 people per square kilometre, the emission conditions are completely different than in the south; the traffic structure and intensity are totally different and so is the density of built-up areas and meteorological conditions that affect the atmospheric dispersion of pollutants (Majewski et al. 2011; Badyda et al. 2015).

This paper presents and discusses results of the elemental composition of PM_{2.5} obtained in winter from the largest Polish conurbation, situated in the central part of the country. In the heating season (winter) in most urban areas, the combustion of various fuels for heating keeps the PM concentrations high (Table 1). In Poland, episodes of smog and extremely high PM concentrations are frequent, occurring most often at the end of the year (December/January). These are due to municipal emissions and specific weather conditions (Pastuszka et al. 2010; Juda-Rezler et al. 2011; Lewandowska and Falkowska 2013; Czarnecka and Nidzgorska-Lencewicz 2014). For the purposes of this study, PM was sampled in winter (November–December of 2013), when all possible emission sources were active. Emissions from traffic, industry and re-suspended dust are present in Warsaw, throughout the whole year, and municipal emissions (fossil fuel and biomass combustion) grow significantly in late autumn and early winter, but in November–December, the smog episodes and very high municipal emissions, capable of overshadowing the contributions of other sources to PM elemental composition and concentrations, almost certainly do not occur (Rogula-Kozłowska et al. 2014; <http://powietrze.gios.gov.pl/gios/>). This selection of the sampling period favoured determination of the elemental composition and identification of all possible sources of PM_{2.5}.

2 Materials and methods

2.1 Samples collection and preparation

The observations were conducted in Warsaw ($\lambda E=21^{\circ} 02'$, $\varphi N=52^{\circ} 09'$) at a measurement site located in the district of Ursynów, and selected to satisfy the criteria of being an urban background location, as specified in Directive 2008/50/EC (Fig. 1). The topographical, meteorological conditions and the structure and amount of emissions from PM and gas pollution sources (the share of local emissions—from boiler houses and rooms, stoves, industrial facilities and traffic—in the concentration of particulate matter) at the sampling point are typical of the whole agglomeration (Majewski et al. 2011; Majewski et al. 2014).

From 26 November 2013 to 25 December 2013, 30 diurnal samples of PM_{2.5} were collected by means of an MVS6D PM sampler (provided by ATMOSERVICE; Poznań, Poland). The sampler is equipped with a sampling head that aspires PM_{2.5} at a flow of 2.3 m³/h (according to EN14907). The PM_{2.5} was collected using PTFE filters (PM_{2.5} Air Monitoring Membrane, PTFE, 46.2 mm with support ring, CAT. No. 7592-104; GE Healthcare Bio-Sciences Corp.; Piscataway, NJ, USA). The mass of the PM_{2.5} was determined by weighing the filters before and after exposure; MYA 5.3Y.F micro balance (RADWAG; Radom, Poland) was used

Table 1 Concentrations of the twelve trace elements (ng/m³) associated with PM_{2.5} in various regions across the world; results from urban sites in the last decade (or earlier if the averaging period and the decade overlap)

Reference	City (country)	Averaging period	PM µg/m ³	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Ba	Pb
(Schleicher et al. 2011)	Beijing (China)	VI 2005–V 2008	63	1.3	1.9	33	55	0.4	1.6	16	336	13	2.5	–	32
(Wang et al. 2013)	Shanghai (China)	VI 2009–IX 2010	62.25	–	9	66	1328	–	9	15	236	–	1	–	59
(Friend et al. 2011)	Hong Kong (China)	XI 2004–X 2005	–	0.02	0.002	0.02	0.19	0.0003	0.01	0.01	0.22	0.01	–	–	0.05
(Xu et al. 2012)	Fuzhou (China)	IV 2007–I 2008 S	23.58	2.6	5.0	16.9	219.0	–	3.2	73.8	151.1	7.2	–	–	23.1
(Yang et al. 2012)	Fuzhou (China)	IV 2007–I 2008 W	59.81	3.7	10.1	47.6	563.2	–	3.4	164.9	232.6	16.8	–	–	46.6
(Mansha et al. 2012)	Jinan (China)	III 2006–II 2007 S	129.04	0.01	0.02	0.05	0.99	0.01	0.01	0.02	0.56	0.03	0.01	0.04	0.28
(Singh et al. 2011)	Jinan (China)	III 2006–II 2007 W	204.89	–	0.03	0.16	2.02	0.02	0.01	0.05	0.99	0.03	–	0.07	0.43
(Alolayan et al. 2013)	Karachi (Pakistan)	I 2006–I 2008 W	98.44	–	0.015	0.053	3.706	–	–	0.039	2.31	0.05	–	0.136	0.13
(Lestari and Mauliadi 2009)	Karachi (Pakistan)	I 2006–I 2008 S	55.89	–	0.031	0.053	3.36	–	–	0.056	2.89	0.071	–	0.707	0.119
(Halek et al. 2010)	Delhi (India)	IV–VI 2008 S	39.4	1.8	74.1	33.7	612.7	–	29.5	65.2	477.2	–	2.4	–	500.2
(Cohen et al. 2010)	Delhi (India)	XI 2007–II 2008 W	61.8	5.6	80.5	25.6	2446	–	15.3	125.3	825.1	–	12.6	–	630.8
(Murrillo et al. 2012)	Kuwait City (Kuwait)	II 2004–X 2005 W	29	0.01	–	0.03	1.5	–	0.00	0.02	0.08	–	–	–	0.03
(Osornio-Vargas et al. 2011)	Kuwait City (Kuwait)	II 2004–X 2005 S	57	0.01	–	0.04	2.1	–	0.01	0.01	0.05	–	–	–	0.02
(Chiou et al. 2009)	Bandung City (Indonesia)	2001–2007 DS	48	–	0.06	0.01	0.33	–	0.01	0.02	0.46	–	–	–	0.03
(Pancras et al. 2013)	Bandung City (Indonesia)	2001–2007 WS	39	–	0.02	0.02	0.51	–	0.03	0.01	0.36	–	–	–	0.03
(Davis et al. 2011)	Tehran (Iran)	2007 W	210.5	–	0.30	0.32	3.73	–	–	1.37	24.26	0.20	–	–	0.58
(Halek et al. 2010)	Hanoi (Vietnam)	IV 2001–XII 2008	54.2	0.003	0.005	0.061	0.394	0.002	0.004	0.010	0.487	–	–	–	0.236
(Cohen et al. 2010)	Salamanca (Mexico)	XI 2006–XI 2007	45	0.15	0.018	–	1.01	–	0.012	0.044	0.430	–	–	–	0.123
(Osornio-Vargas et al. 2011)	Mexicali (USA)	X 2005–III 2006	–	0.13	0.09	0.04	1.94	–	0.01	0.04	0.05	–	–	–	–
(Chiou et al. 2009)	Mexicali (USA)	X 2005–III 2006	–	0.10	0.07	0.05	1.57	–	0.01	0.08	0.16	–	–	–	–
(Pancras et al. 2013)	Hamshire (USA)	VII 2003–VIII 2005	10.986	3.3	0.95	1.4	64	–	0.92	1.33	8.4	0.90	–	10.5	2.4
(Davis et al. 2011)	Dearborn (USA)	VII–VIII 2007	15.66	1.03	–	6.70	37.55	–	0.36	3.08	34.53	0.94	0.30	3.45	4.04
(Davis et al. 2011)	Atlanta (USA)	2005–2007	–	1.2	0.9	1.4	88.2	–	0.5	9.0	10.1	1.5	–	–	3.0
(Davis et al. 2011)	Chicago (USA)	2005–2007	–	1.4	2.0	3.2	105.2	–	1.0	5.6	24.6	1.0	–	–	5.0
(Davis et al. 2011)	Cleveland (USA)	2005–2007	–	2.7	4.0	10.5	336.5	–	2.7	9.0	52.1	2.8	–	–	11.7
(Davis et al. 2011)	Dallas (USA)	2005–2007	–	1.3	0.6	2.7	120.0	–	0.4	3.7	9.9	0.4	–	–	2.7
(Davis et al. 2011)	Detroit (USA)	2005–2007	–	3.1	3.2	9.1	241.8	–	1.7	9.4	54.0	1.6	–	–	6.7
(Davis et al. 2011)	Houston (USA)	2005–2007	–	5.1	0.8	3.0	106.9	–	1.6	5.5	14.0	1.2	–	–	2.3
(Davis et al. 2011)	Los Angeles (USA)	2005–2007	–	4.8	1.4	3.4	168.6	–	2.5	10.2	13.6	0.6	–	–	3.4
(Davis et al. 2011)	Miami (USA)	2005–2007	–	5.8	7.5	2.5	150.2	–	3.4	4.4	9.2	0.6	–	–	2.0
(Davis et al. 2011)	Minneapolis (USA)	2005–2007	–	3.3	1.8	1.7	56.2	–	1.7	3.6	9.7	0.9	–	–	2.7
(Davis et al. 2011)	New York (USA)	2005–2007	–	7.1	1.8	3.8	124.6	–	11.7	5.1	31.8	0.8	–	–	4.6
(Davis et al. 2011)	Philadelphia (USA)	2005–2007	–	4.5	3.0	2.2	93.3	–	4.3	7.3	15.1	1.0	–	–	4.2
(Davis et al. 2011)	Phoenix (USA)	2005–2007	–	3.2	2.8	4.0	196.1	–	1.2	6.5	10.3	0.6	–	–	2.8
(Davis et al. 2011)	Pittsburgh (USA)	2005–2007	–	1.7	3.7	5.4	142.3	–	2.0	6.8	35.4	3.1	–	–	12.5

Table 1 (continued)

Reference	City (country)	Averaging period	PM $\mu\text{g}/\text{m}^3$	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Ba	Pb
	Raleigh (USA)	2005–2007	–	1.9	2.7	0.9	74.3	–	1.4	4.3	7.6	0.8	–	–	2.5
	Riverside (USA)	2005–2007	–	6.2	4.1	3.5	181.9	–	2.3	8.8	18.5	0.8	–	–	4.3
	San Diego (USA)	2005–2007	–	3.6	2.7	2.1	97.2	–	1.9	9.3	7.4	0.8	–	–	2.9
	San Jose (USA)	2005–2007	–	2.2	2.0	1.1	79.6	–	1.3	4.7	6.8	0.6	–	–	2.4
	Seattle (USA)	2005–2007	–	5.9	2.3	7.6	99.4	–	2.6	5.1	15.2	1.0	–	–	3.8
(Murillo et al. 2013)	San Jose (Costa Rica)	VI 2010–VII 2011	26	2.9	7.0	61	257	–	3.86	43	–	–	–	–	7.6
	Moravia (Costa Rica)		18	0.9	5.1	44	141	–	2.94	57	–	–	–	–	7.29
(Jorquera and Barraza 2012)	Santiago (Chile)	2004	32.3	0.5	1.7	11.9	244	–	0.4	19.3	46	10.3	–	7.9	18.9
(Jorquera and Barraza 2013)	Antofagasta (Chile)	XII 2007–I 2008	42	0.007	–	0.010	0.354	–	0.002	0.068	0.060	0.050	–	–	0.014
(Lemos et al. 2012)	Rio Grande (Brazil)	I 2010	41.17	0.70	bid	–	4.18	–	1.39	4.18	bid	bid	bid	–	bid
	Rio Grande (Brazil)	X 2009	8.15	0.86	bid	–	0.86	–	0.86	0.86	35.14	bid	bid	–	bid
(Dieme et al. 2012)	Dakar (Senegal)	VII–IX 2009	75.1	0.002	0.002	0.027	3.027	bid	0.001	0.005	0.024	bid	–	0.026	0.007
	Dakar (Senegal)	VII–IX 2009	105.4	0.004	0.003	0.036	4.567	0.001	0.002	0.006	0.054	bid	–	0.040	0.019
(von Schneidmeyer et al. 2010)	Zonguldak (Turkey)	XII 2004–X 2005	29.6	–	3.8	8.0	130.0	–	3.0	61.0	58.0	–	–	–	11.9
(Cuccia et al. 2013)	Genoa (Italy)	V 2009–V 2010	15.0	12.0	3.0	4.0	135.0	–	7.0	5.0	17.0	–	–	17.0	8.0
(Lettino et al. 2012)	Tito Scalo (Italy)	IV 2010	9.0	–	47.0	9.0	195.0	3.0	16.0	8.0	420.0	–	2.0	–	34.0
(Szoboszlai et al. 2012)	Debrecen (Hungary)	X 2008	13.7	–	–	11.1	655.4	–	–	34.6	16.9	–	–	–	6.8
	Debrecen (Hungary)	X 2008	11.4	–	–	7.9	353.8	–	–	15.5	38.4	–	–	–	30.2
	Debrecen (Hungary)	V 2009	7.5	–	–	2.1	111.6	–	–	8.0	5.3	–	–	–	2.4
(Aldabe et al. 2011)	Navarra (Spain)	I–XII 2008	15.38	–	2.39	2.57	–	0.99	1.31	11.98	17.98	0.16	0.05	12.08	2.29
(Fernández-Camacho et al. 2012)	Huelva (Spain)	IV 2008–XII 2009	19.3	3.4	1.6	4.0	200.0	0.2	2.3	31.2	37.3	5.1	0.6	19.7	10.8

The symbols for the measuring periods, decimal places in the numbers (concentrations of PM and PM-bound elements), and units are all reproduced here as they appear in the source texts. Entries in italics are data in $\mu\text{g}/\text{m}^3$

W winter, *S* summer, *A* autumn, *DS* dry season, *WS* wet season, *bid* below detection limit

Table 2 Average concentration at the time of measurement and its standard deviation of the diurnal concentration calculated for PM_{2.5} (µg/m³), PM_{2.5}-bound elements (ng/m³; ppm) and elements (ppm) or their oxides (%) in the soil at the urban background location in Warsaw

Published mass concentrations of PM _{2.5} and the elemental composition of PM _{2.5} in Poland									
	² Zabrze; year	² Katowice; year	³ Zabrze; winter	³ Zabrze; summer	⁴ Gdańsk; year	^{5,6} Łódź; year	^{7,8} Wrocław; winter	^{7,8} Wrocław; summer	PM _{2.5} (n=30)
									Mass conc.
¹ Mass conc.	22.0	31.0	66.85	18.44	24.0	—	49.1	16.0	10.7
Na	62.3	107.4	450.0	240.0	—	—	—	—	131.2
Mg	6.1	7.4	14.0	n/d	—	—	—	—	45.0
Al	147.6	136.5	n/d	120.0	113.0	—	48.0	32.0	217.2
Si	503.2	443.3	110.0	310.0	—	—	259.0	193.0	226.6
S	816.3	1355.5	3350.0	1650.0	—	—	1946.0	727.0	497.0
Cl	684.6	787.1	3450.0	40.0	—	—	1589.0	118.0	42.3
K	180.4	227.2	340.0	170.0	—	—	528.0	110.0	64.6
Ca	26.7	30.7	10.0	80.0	—	699.10	159.0	89.0	93.0
Sc	—	—	—	—	—	—	—	—	5.5
Ti	3.6	4.2	0.54	2.01	—	—	11.0	7.0	1.7
V	0.2	0.5	—	—	1.13	—	—	—	15.1
Cr	1.7	1.8	1.32	0.23	3.30	—	4.3	1.6	1.2
Mn	16.1	8.8	21.6	16.71	5.0	—	23.0	9.0	5.7
Fe	160.8	157.0	180.0	150.0	—	—	215.0	78.0	84.6
Co	0.3	0.4	—	—	0.12	—	—	—	9.4
Ni	0.8	0.4	0.36	0.21	3.82	—	4.0	0.7	3.5
Cu	6.5	8.2	8.88	8.14	—	—	40.0	20.0	13.2
Zn	72.5	90.3	184.49	65.99	—	48.13	227.0	43.0	16.5
As	1.5	2.1	9.59	n/d	0.7	—	4.9	1.2	10.6
Se	0.9	1.0	0.45	0.46	—	—	—	—	12.7
Br	6.6	9.1	25.1	1.61	—	—	—	—	6.4
Sr	3.9	3.0	1.25	1.61	—	—	2.2	0.7	4.1
Cd	1.2	2.3	1.14	1.23	0.9	0.53	—	—	9.6
Pb	24.8	35.1	49.71	23.74	22.3	14.16	81.0	27.0	21.9

PM _{2.5} -bound elements (ng/m ³) and elemental composition of PM _{2.5} (ng/m ³) in Poland									
	⁹ Avg	¹⁰ Std dev.	Avg	Std dev.	Soil (n=6)	Avg	Std dev.	¹¹ ppm	Std dev.
¹² Na	10.7	7.5	—	—	—	—	—	—	—
K ₂ O	131.2	162.6	29209.6	63491.4	K ₂ O	0.68	0.54	0.68	0.54
Mg	45.0	87.4	8124.9	18704.5	CaO	0.37	0.77	0.37	0.77
Al	217.2	182.5	32391.5	42295.0	TiO ₂	0.38	0.10	0.38	0.10
Si	226.6	241.2	33625.4	44786.3	V	53.21	8.40	53.21	8.40
S	497.0	471.0	50993.7	50993.2	Cr	40.33	30.14	40.33	30.14
Cl	42.3	69.8	7945.3	13611.3	Mn	334.05	292.91	334.05	292.91
K	64.6	70.5	6967.6	8135.5	Fe ₂ O ₃	1.45	0.27	1.45	0.27
Ca	93.0	138.9	14557.8	32579.8	Ni	2.62	1.05	2.62	1.05
Sc	5.5	7.5	996.8	1852.4	Cu	25.63	1.73	25.63	1.73
Ti	1.7	2.9	197.2	317.9	Zn	51.07	22.36	51.07	22.36
V	15.1	32.7	2241.4	6162.6	As	3.01	0.74	3.01	0.74
Cr	1.2	1.4	174.7	273.3	Se	1.00	0.55	1.00	0.55
Mn	5.7	11.7	826.2	1774.3	Rb	38.66	7.95	38.66	7.95
Fe	84.6	142.1	13280.7	26074.7	Sr	47.29	6.77	47.29	6.77
Co	9.4	13.7	1025.5	1522.4	Zr	204.73	64.93	204.73	64.93
Ni	3.5	5.0	615.7	892.9	Mo	1.13	0.33	1.13	0.33
Cu	13.2	26.6	2189.6	6862.6	Ag	0.48	0.35	0.48	0.35
Zn	16.5	20.2	2575.6	3494.4	Cd	0.31	0.10	0.31	0.10
As	10.6	34.4	1568.7	4254.4	Sb	0.83	0.36	0.83	0.36
Se	12.7	30.5	1723.7	4067.0	Cs	3.50	0.42	3.50	0.42
Br	6.4	9.6	1456.6	3356.7	Ba	285.49	56.00	285.49	56.00
Sr	4.1	3.5	758.0	1313.6	Pb	12.58	3.07	12.58	3.07
Cd	9.6	22.2	3592.0	15868.9	Sc	8.32	1.33	8.32	1.33
Pb	21.9	26.1	4248.3	6894.3	Sn	1.72	0.87	1.72	0.87

The results are listed alongside available published data on mass concentration of PM_{2.5} (µg/m³) and elemental composition of PM_{2.5} (ng/m³) in Poland

¹ Average ambient mass concentration of PM_{2.5} in µg/m³

² Rogula-Kozłowska et al. 2013a

³ Rogula-Kozłowska et al. 2012

⁴ Rogula-Kozłowska et al. 2014

⁵ Krzemińska-Flowers et al. 2006

⁶ Average of the concentrations from the three sites (Kilińskiego, Szkolna, Wróblewskiego)

⁷ Zwoździak et al. 2013

⁸ Average of the seasonal outdoor concentrations

⁹ Arithmetic mean

¹⁰ Standard deviation

¹¹ Content of elements in the mass of PM_{2.5} (µg element per 1 g PM_{2.5}; ppm)

¹² Symbols in bold denote the elements with EF_x>5

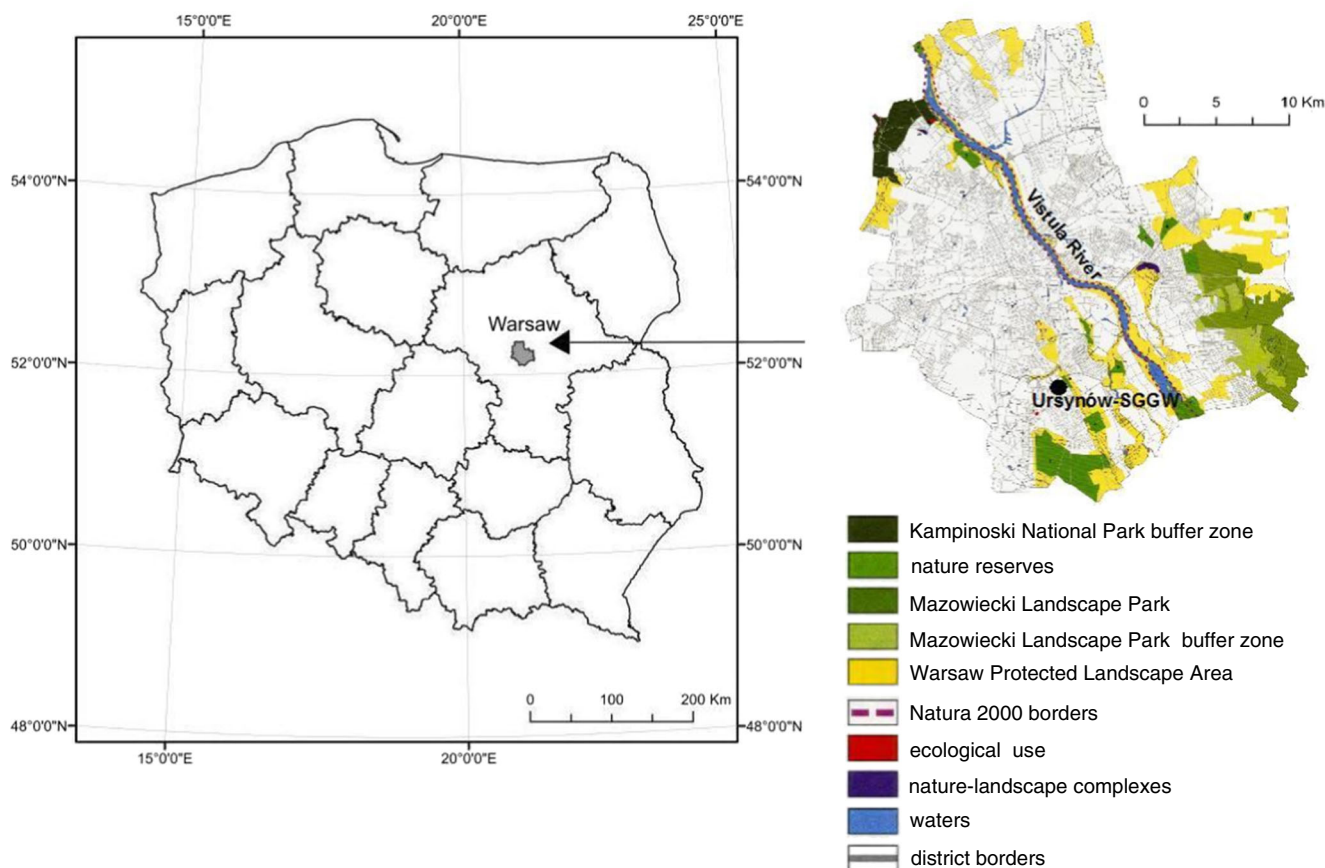


Fig. 1 Location of the sampling point in Warsaw (Poland)

(1- μg resolution). Before each weighing, the filters were conditioned for 48 h in the weighing room (relative air humidity $45 \pm 5\%$, air temperature $20 \pm 2\text{ }^\circ\text{C}$).

In the course of the observations, values of basic meteorological parameters were measured at the Ursynów Meteorological Station of the Warsaw University of Life Sciences (Ursynów-SGGW) according to instructions for the network of state weather stations operated by the Institute of Meteorology and Water Management (IMWM). Hourly results of the measurements were averaged for 24-h intervals from 00:00 to 00:00 h; diurnal samples of $\text{PM}_{2.5}$ were taken at the same times.

The Warsaw location was also used to obtain soil samples (approx. 0.5 kg each) from six places selected in the area around the PM sampler. Three of these were situated within the prevailing wind direction, at a few to a dozen metres from the sampler, whereas in the other three places, the flow direction of air masses was the opposite. The soil samples were collected at a depth of 10 to 20 cm using a plastic shovel and cloth bags which were then transported to a laboratory. At the laboratory, the samples were first dried in an electric dryer at $105\text{ }^\circ\text{C}$ and then sieved using a nylon screen with a mesh size of 2 mm in order to remove leaves, twigs and stones, to obtain a

homogeneous material for subsequent analysis. Then, the soil samples were dried again until a constant weight was obtained and then ground for 3 min in a vibrating corundum bowl mill (Testchem, Radlin, Poland). The ground samples were processed mechanically to form pellets. To this end, a carefully weighed amount of soil was mixed with an appropriate amount of binder (synthetic wax—STW wax batch 64; PANalytical B.V.; Almelo, The Netherlands). The mixture was then pressed for 2 min using a manual hydraulic press (20 t).

2.2 Chemical analyses

The diurnal samples of $\text{PM}_{2.5}$ and the soil samples were analysed to find their elemental composition. The elemental composition of $\text{PM}_{2.5}$ was determined by means of energy dispersive X-ray fluorescence (EDXRF). An Epsilon 5 (PANalytical B.V.; Almelo, The Netherlands) calibrated with the use of thin-layer single-element standards (Micromatter; Vancouver, Canada) was used to measure the total concentrations of the elements. To control the performance of the analytical procedure, the NIST SRM2873 samples were measured weekly (the recoveries were between 79 and 124 % of the certified value, except 54 % recovery of Co) and X-ray

tube and detector drift monthly. The detection limits were from 0.3 ng/cm² (Pb) to 14.2 ng/cm² (Mg).

The same method was used to measure the content of elements in the soil pellets. Calibration lines were prepared using 46 certified reference materials, whereas two other materials (SRM2709, SRM2711; NIST) were used to verify the measurement correctness of the calibration (standard sample recovery ranged from 90 % for V to 114 % for Ni). Certified standards and reference materials were prepared in the same way as the soil samples collected in the field. During the calibration, an analytical programme was developed to include specific parameters (settings and X-ray tube and detector parameters, and the type of secondary anode for individual excitation conditions) in which the soil samples were analysed.

Results of the analyses of the elemental composition of the PM_{2.5} and soil were averaged and collected in Table 2.

2.3 Results analyses

Enrichment factors (EF) allow for assessment of the anthropogenic effect on the concentrations of the PM_{2.5}-related elements. The enrichment factor EF_{*x*} is defined for the element *x* as:

$$EF_x = \frac{(C_x/C_{ref})_{PM}}{(C_x/C_{ref})_{soil}} \quad (1)$$

where *C_x* and *C_{ref}* designate the concentrations of the element *x* and the reference element, respectively, and $(C_x/C_{ref})_{PM}$ and $(C_x/C_{ref})_{soil}$ are the proportions of these concentrations in PM and in the soil, respectively. In the paper, the observed concentrations *C_x* are related to the concentration *C_{Ti}* of Ti. Ti was the only element among typical soil markers that was identified in the Warsaw soil samples. Consequently, EF_{Ti}=1.

The soil concentrations of those elements that were not identified in the Warsaw soil samples, but were identified in the samples of PM_{2.5}, were taken from data of the chemical characterization of the Earth's upper continental crust (Wedepohl 1995).

EF_{*x*} up to 5 indicates the crustal origin of the element *x*, while higher EF_{*x*} suggests a strong anthropogenic effect on the concentrations of *x*. In Table 2, the symbols of the elements *x* with EF_{*x*}>5 are given in bold. Out of 24 analysed elements, only Mg, Al, Si, Ti and Fe demonstrated a crustal origin.

Further analysis of data consisted in the application and the methodology are described by Thurston and Spengler (Thurston and Spengler 1985). This method combines a factor analysis (FA) to identify the possible sources with a multilinear regression analysis (MLRA) to quantify their contribution to PM levels.

The first step in this stage was the principal component analysis (PCA) to the 24×30 data matrix of the element

concentrations representing the diurnal PM_{2.5}-bound element concentrations. Subsequently, the values of new variables—principal components (only principal components with eigenvalues >1.0 were considered according to Kaiser criterion)—were used in an MLRA. All the computations were performed using Statistica 8.0.

3 Results and discussion

The average concentration of PM_{2.5} in Warsaw, was definitely lower than recorded earlier in other parts of the country (Table 2). It was also lower than the PM_{2.5} concentrations observed in Asian cities but did not really differ from the concentrations recorded in Europe (Table 1). Apart from the amount of emissions, the parameters that proved to have the greatest influence on the pattern of concentrations in Warsaw, in the measurement period were air temperature, precipitation and wind speed. The values of these parameters were exceptionally favourable at the time in terms of the intensity of exchange of air masses and washing away of atmospheric pollutants. The mean monthly temperature of air in November and December 2013 was approximately 2 °C higher than its corresponding typical mean values recorded throughout the years. At the time of the measurements, the diurnal temperature of air ranged from −2.1 to 6.6 °C. The wind blew mostly from the WSW and SW, which accounted for 50 and 16 %, respectively, of all observed directions. The mean diurnal wind speed ranged from 1.6 to 9.4 m/s. The precipitation total in the analysed period reached 17.5 mm, and days with a precipitation of at least 0.1 mm made as much as 37 % of the whole period.

Fluctuations of air temperature, precipitation and wind speed clearly affected the concentrations of PM_{2.5}. The average concentration of PM_{2.5} calculated for days when the diurnal air temperature fell below 0 °C was approximately 25 % higher than the value of its average concentration on days with temperatures above 0 °C (Table 3). The average concentration of PM_{2.5} on days without precipitation was also 25 % higher than when it occurred.

The average concentrations of PM_{2.5} calculated for days on which the mean diurnal wind speed was lower than 5 m/s were over two times higher than the average concentrations on days when the wind speed was equal to or higher than 5 m/s.

On days when the wind speed was low, the atmospheric pressure was observed to exceed 1005 hPa, which—by generating downward movement of air—indirectly contributed to increased PM_{2.5} concentrations in the air.

Diurnal concentrations of all PM_{2.5}-bound elements were not as clearly correlated with temperature, precipitation or wind speed as in the case of PM_{2.5} alone. Nevertheless, on days with sub-zero temperatures, the concentrations of certain elements, e.g. Na, Al, Si, Ca, Ti, Mn, Cu, Br or Pb, were on

Table 3 Average concentration of PM_{2.5} (μg/m³) and PM_{2.5}-bound elements (ng/m³) in different averaging periods selected because of prevailing atmospheric conditions during the observations

	¹ Precipitation		² Air temperature		³ Wind speed		⁴ Air pressure		⁵ Wind direction					
	+	–	>0	<0	<5	>5	>1005	<1005	ESE	SE	SSW	SW	WNW	WSW
PM _{2.5}	8.8	11.7	10.0	13.2	11.7	5.7	12.2	7.6	4	8.2	17.7	11.4	7.3	11.3
Na	111.1	142.9	112.4	206.4	131.0	132.4	154.1	85.6	344.3	64.5	87.5	88.5	106.1	169.2
Mg	27.6	55.1	48.0	33.0	50.4	18.0	57.6	19.8	131.2	25.5	30	22.4	27.1	28.3
Al	198.6	227.9	183.5	351.8	226.7	169.5	247.4	156.7	197.9	136.8	596.6	188.7	82.2	188.4
Si	174.1	257.0	215.2	272.1	218.7	266.2	257.6	164.7	103.1	49.9	384.8	207.8	382	231.6
S	543.1	470.3	572.5	195.1	511.6	424.1	512.9	465.1	615.1	287.9	569.1	588.7	382.7	531.9
Cl	49.3	38.3	43.6	37.4	45.3	27.7	47.1	32.8	9	10.7	9	46.5	9	35.3
K	68.8	62.3	72.1	34.7	74.8	14.0	78.7	36.4	47.1	57	133.9	132.7	37.6	42.8
Ca	116.6	79.3	71.6	178.3	91.7	99.2	98.3	82.4	17.8	23.7	83	160.4	27.3	107.4
Sc	8.3	3.9	6.3	2.5	4.3	11.6	4.3	7.9	1.6	6.1	7.3	1.9	6.8	6.8
Ti	1.5	1.8	1.5	2.3	1.4	3.2	1.5	2.2	2.1	2.2	2.7	0.3	0.2	2.2
V	3.7	21.6	18.3	2.3	16.4	8.3	13.4	18.3	102.6	42.3	3.2	21.8	0.8	6.9
Cr	0.8	1.5	1.3	0.9	1.4	0.5	1.6	0.6	2.3	1.2	2.2	0.6	0.2	1.4
Mn	5.9	5.6	4.8	9.3	6.7	0.8	5.8	5.6	8.1	0.8	0.8	2.4	0.8	4.6
Fe	81.3	86.6	98.0	31.3	94.9	33.4	102.6	48.6	194.6	94.8	105.3	32.8	1	86.3
Co	7.7	10.4	10.3	5.8	10.2	5.3	9.6	9.1	2.7	5.5	0.4	8.5	6.2	9.8
Ni	3.0	3.9	3.8	2.4	4.0	1.1	4.3	1.9	0.4	10.3	0.4	4.8	0.4	2.9
Cu	3.9	18.7	12.2	17.3	15.4	2.7	18.0	3.7	3.7	3.9	3.4	24.9	1.4	15.9
Zn	12.7	18.7	18.7	7.9	18.5	6.9	16.7	16.1	33.5	28.4	22	9.7	3.3	13.1
As	20.6	4.9	12.5	3.1	4.2	42.6	4.4	23.1	9.5	6	6.8	2.7	0.4	15.3
Se	22.6	7.0	13.9	8.0	6.5	43.8	7.8	22.6	12.2	1.9	1.1	3.3	0.6	19.9
Br	7.8	5.6	6.0	8.1	4.4	16.2	5.2	8.8	3.7	2.3	1.4	3	0.2	10.5
Sr	4.0	4.1	4.7	1.8	3.9	4.9	3.2	5.8	0.6	4.7	2.4	5	2.3	4.1
Cd	16.0	5.8	11.3	2.6	5.9	28.0	5.2	18.2	1.6	5.9	3.6	6.3	6.2	14.4
Pb	24.9	20.2	18.1	37.2	20.1	31.1	22.3	21.3	62.8	22.9	55.2	16.4	2.9	21.2

¹ Average concentrations determined separately for precipitation days (+) and no precipitation days (–)

² Average concentrations determined separately for days when mean diurnal air temperature was below 0 °C (<0) and for days when it was 0 °C or higher (>0)

³ Average concentrations determined separately for days when mean diurnal wind speed was below 5 m/s (<5) and for days when it was 5 m/s or higher (>5)

⁴ Average concentrations determined separately for days when mean diurnal air pressure was below 1005 hPa (<1005) and for days when it was 1005 hPa or higher (>1005)

⁵ Average concentrations determined separately for days when the frequency of occurrence of each of the selected wind directions (ESE, SE, SSW, SW, WNW, WSW) exceeded 60 % within 24 h

average about 40 % higher than on days with positive temperatures. This correlation should suggest a connection with the source of PM_{2.5} and PM_{2.5}-bound elements within the analysed area. Such elements as Na, Mn, Ca, Cu and Br have an evidently anthropogenic origin in the air of the area (EF_x>5; Table 2) and most likely come from the combustion of solid fuels (coal and/or biomass) in household stoves or local house boilers. Some may also come from the combustion of liquid fuels in motor vehicle engines (Chow 1995; Sówka et al. 2012; Sanderson et al. 2014; Kumar et al. 2013). These elements were strongly correlated with PC1–PC5 (Table 4).

Other elements that were correlated with the same components included Cl, K, Se, Fe, Sc, As, Zn and Cd. Depending on the value of correlation between the concentrations of specific elements and subsequent principal components (factor loadings for the elements in PC1–PC5), and based on elemental profiles of PM_{2.5} from various sources (Table 5), it was established that the primary source of PM_{2.5} and most of elements it carried was—within the analysed area—the combustion of coal and biomass (Tables 4 and 5). The mean contribution of this source to the concentrations of PM_{2.5} at the time of the observations was 18.4 %. Its

Table 4 Results from principal components analysis (PCA) and from a multi-linear regression analysis (MLRA) performed for PM_{2.5} and PM_{2.5}-bound element concentrations

Component	Element factor loading	Source/% variance	Average source contributions (%) to PM _{2.5} concentrations in sampling period (results from MLRA)*
PC1	Sc _{-0.79} , Se _{-0.77} , As _{-0.77} , Br _{-0.73} , Cl _{0.46} , Al _{0.44} , Mn _{0.40} , Mg _{0.37} , Si _{0.36} , Ca _{0.32} , Cd _{-0.31}	Coal combustion/15.4	1.1 Coal and biomass combustion (A)/18.4
PC2	Mg _{0.69} , Zn _{0.65} , Fe _{0.63} , Cl _{0.58} , As _{0.42} , Se _{0.41} , Sc _{0.39} , Cu _{-0.39} , Al _{0.33} , Mn _{0.32}	Coal combustion/11.4	4.5
PC3	Ca _{-0.55} , Co _{-0.53} , Fe _{0.44} , Mn _{-0.43} , Sr _{0.42} , Si _{-0.41} , Cl _{-0.40} , Br _{-0.40} , Cr _{0.39} , Cu _{-0.37} , As _{-0.34} , Zn _{0.33} , Cd _{0.31}	Biomass or/and coal combustion/9.8	1.6
PC4	Pb _{0.77} , Na _{0.57} , Sr _{-0.51} , Co _{-0.45} , K _{-0.38}	Biomass or/and coal combustion/8.4	9.1
PC5	K _{-0.67} , S _{-0.59} , Cu _{-0.40} , Cl _{0.37} , Cd _{0.34} , Ni _{0.31} , Fe _{-0.30}	Biomass combustion/7.6	2.1
PC6	V _{0.54} , Ca _{-0.45} , Cu _{0.41} , Cr _{0.36} , Si _{0.34} , Co _{-0.32} , Mg _{0.31} , Sr _{-0.31}	Oil-fired power plant/6.8	3.6 Oil-fired power plant (B)/9.9
PC7	Ni _{0.58} , Mn _{-0.46} , Si _{0.43} , Ti _{-0.41} , Co _{0.32} , Na _{0.30} , V _{-0.30}	Oil-fired power plant/6.3	6.3
PC8	Cr _{0.62} , Sr _{-0.38} , S _{0.37} , Na _{-0.35} , V _{-0.31}	Motor vehicles/5.7	15.7 Motor vehicles (C)/15.7
PC9	Ti _{-0.60} , Ni _{-0.44} , Al _{0.42} , Cd _{0.38}	Soil and road dust/5.2	2.5 Soil and road dust (D)/8.0
PC10	Ti _{-0.43} , Si _{-0.38} , Ni _{0.33} , Mn _{0.31}	Soil and road dust/4.6	5.5
Total variance	81.3 %		52.0 %

Elements with factor loadings <0.30 are not included. Elements presented in descending order of their factor loads, with factor loadings indicated as subscript

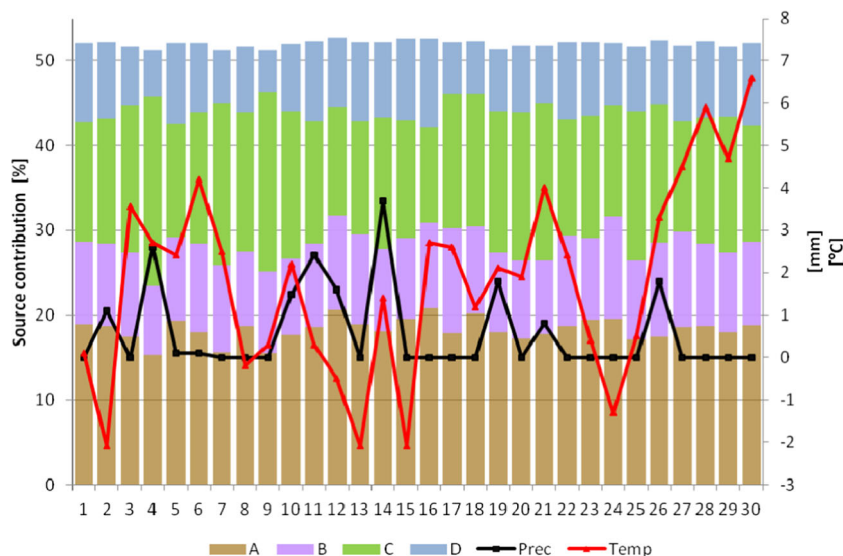
*The sets of measured PM_{2.5} diurnal concentrations and the concentrations computed for each day from MLRA-determined contributions were substantially correlated ($R^2=0.54$)

diurnal contribution to the concentrations of PM_{2.5} ranged from 15.3 to 20.9 % (Fig. 2) and was negatively correlated with air temperature ($R^2=-0.22$).

It was difficult to clearly assign one of the two identified sources (coal or biomass combustion) to the principal components PC1–PC5. In the case of PC3 and PC4, there were no grounds to make a final choice. The decision to connect PC1 and PC2 with the combustion of coal was based on high correlations with Se, As and Br and an analysis of the connection between diurnal concentrations of Se, As and Br with the wind

speed and direction. PM_{2.5}-bound Se, As and Br originate from coal combustion mainly at large power-generation facilities (power plants and combined heat and power plants (Czarnecka and Nidzgorska-Lencewicz 2014; Kumar et al. 2013; Juda-Rezler and Kowalczyk 2013)). The average concentrations of these elements were definitely higher in the periods when the air temperature dropped below zero than in above-zero conditions (Table 3). At wind speeds exceeding 5 m/s, the concentrations of Se, As and Br were—on average—400 % higher than on days when the wind speeds were

Fig. 2 Diurnal contributions (%) of identified sources of PM_{2.5} (A—coal and biomass combustion, B—oil-fired power plant, C—motor vehicles, D—soil and road dust) to the concentrations of PM_{2.5} in Warsaw in winter against the diurnal air temperature (*Temp*) and precipitation (*Prec*)



lower than 5 m/s. Therefore, it is quite possible that at higher wind speeds, $PM_{2.5}$ -bound Se, As and Br came from areas where coal-fired power plants and combined heat and power (CHP) plants are situated. It is understandable that facilities like these, and CHP plants in particular, produce larger amounts of pollution on colder days when the demand for heat and power increases. On days when the concentrations of Se, As and Br were high—much higher than average—the air was predominantly coming from the WSW (Table 3). This is the direction of large coal-fired boiler houses, a coal-fired power plant (burning coal with biomass) and—further to the south—Silesia, an area heavily polluted with $PM_{2.5}$, the source of which is mainly coal combustion in winter (Rogula-Kozłowska et al. 2012, 2013 b; 2014).

High correlation values of K, S and Cl with PC5 imply a share of biomass combustion in the concentrations of $PM_{2.5}$ (the contribution of this source to the concentrations of $PM_{2.5}$ averaged at 2.1 %, Table 4). High concentrations of K, S, Cl, but also Ca, Co, Sr and Cd were recorded on days when the air masses came from the SW and SSW, which are the directions of scattered sources of $PM_{2.5}$ —small local boiler houses and individual domestic cookers and stoves. It is worth mentioning here that the contribution of coal and biomass combustion to the concentrations of $PM_{2.5}$ in Warsaw, seems to be relatively small in winter, considering the results of earlier research carried out in the south of Poland (Juda-Rezler et al. 2011; Sówka et al. 2012; Rogula-Kozłowska et al. 2012, 2013a, 2014). To some extent, this could be blamed on the limited quantity of data used to perform PCA and MLRA and the ensuing error of estimation. Although such an error could not have been completely avoided, looking at the list of concentrations in Table 2, we can clearly see that the obtained result is sensible. The concentrations of K, S and Cl in Warsaw, were outstandingly lower than in south Poland. However, these low values did not result from a low concentration of $PM_{2.5}$, which can be proven by high (higher than in the south part of the country) concentrations of other elements. It seems that the number of buildings provided with heat by central heating systems is a few times greater in Warsaw, than in the south, where a lot more houses have independent heating. Moreover, in Warsaw—the most developed and one of the richest places in Poland—residential houses and buildings with independent heating systems more often use natural gas as heating fuel. Biomass is used only in houses with fireplaces, small local boiler houses and large coal-fired CHP plants as an additive. Coal, on the other hand, is hardly used in households as a heat source, whereas in the south of Poland, it is commonly burned in obsolete, low-efficiency stoves from early autumn until late spring, often with household waste, including plastics and other materials. Therefore, it can be claimed that in winter, Warsaw demonstrates an actual contribution of coal and biomass power generation to the concentrations of $PM_{2.5}$. The contribution is largely determined by

emissions from CHP plants, power plants and local boiler houses. Home stoves in Warsaw, are most likely mainly accountable for the emissions of PM from biomass combustion.

The concentrations of certain elements, particularly V, Co, Ni, Sr and Cd, were evidently higher (up to a few times) than their respective concentrations recorded in other parts of the country. This is puzzling in the context of low—much lower than in other regions—concentrations of $PM_{2.5}$ in Warsaw, in winter. Exceptionally high concentrations of V, Co, Ni, Sr and Cd were observed when air masses were flowing from the ESE and SW directions, where residential buildings with individual stoves and oil-and-gas-fired boilers prevail. An analysis of elemental profiles of the sources of $PM_{2.5}$ (Table 5) indicates that the source of these elements must be an oil-fired power plant, and high correlation values of V, Ni, Co and Cr with PC6 and PC7 confirm this (Table 4). The contribution of emissions from oil-fired power plants to the concentrations of $PM_{2.5}$ in Warsaw, reached 9.9 %; its diurnal values ranged from 8.1 to 12.3 % and were negatively correlated with the air temperature ($R^2=-0.27$). In other parts of Poland, such a clear influence of heating oil combustion on PM concentrations had not been observed before. It is obvious that the reason for this is the small number of modern oil-and-gas boiler houses in other parts of the country, especially in the south, where most of the data published on the chemical composition of $PM_{2.5}$ originates. In European cities and in the USA, the situation is like in Warsaw, as partially suggested by the concentrations of Ni and V there (Table 1).

In the SW, as well as the WSW, there is a dense network of streets and roads with a substantial traffic load. The minimum distance of a busy road from a measurement site is 500 m in the SW and 1000 m in the WSW. On days with the wind coming from the SW and WSW, high concentrations of S, V, Cr, Mn, Fe, Zn and Pb were observed. Some of these elements were strongly correlated with PC8 (Table 4). An analysis of the elemental profiles of $PM_{2.5}$ from Table 5 allowed for the assumption that PC8 must have implied another source of $PM_{2.5}$, i.e. motor vehicles. The mean contribution of emissions from the engines of motor vehicles to the concentrations of $PM_{2.5}$ at the time of the observations was 15.7 %, which had changed from 11.4 to 22.3 % on individual days. This value was positively correlated with the air temperature ($R^2=0.19$). Of course, at higher temperatures, when the contribution of domestic stoves and other power-generation sources (boiler houses and CHP plants) to the concentrations of $PM_{2.5}$ decreased, the role of traffic emissions in the shaping of air pollution by fine PM increased. The values of diurnal contribution of emissions from motor vehicles to the concentrations of $PM_{2.5}$ were also positively correlated with precipitation ($R^2=0.30$; Fig. 2), which means that at the time of rain or snowfall, the contribution of this source to the concentrations of $PM_{2.5}$ increased. Most probably, very small (nano- and ultrafine) particles emitted with car exhausts were not

Table 5 Compounds in PM_{2.5} from various sources and in ambient PM_{2.5} in winter in Warsaw

	<0,1%	0,1-1%	1-10%	>10%
	Source	*PM _{2.5}	Source	PM _{2.5}
Motor vehicles	^a Cr, Ni, Y, Sr, Ba		Si, Cl, Al, P, Ca, Mn, Fe, Zn, Br, Pb	SO ₄ ⁼ , NH ₄ ⁺ S, Cl ⁻ , NO ₃
Biomass combustion	Ca, Fe, Mn, Zn Br, Rb, Pb		NO ₃ ⁻ , SO ₄ ⁼ , NH ₄ ⁺ Na ⁺ , S	Cl ⁻ , K ⁺ , Cl, K
Coal-fired boiler	Cl, Cr, Mn, Ga, As Se, Br, Rb, Zr	Sc, Ti, Cr, Mn, Co, Ni, Sr,	NH ₄ ⁺ , P, K, Ti, V Ni, Zn, Sr, Ba, Pb	Mg, Cl, K, V, Cu, Zn, As, Se, Br, Cd, Pb
Oil-fired power plant	V, Ni, Se, As, Br Ba		Al, Si, P, K, Zn	SO ₄ ⁼ , OC, EC Al, S, Ca, Fe
Antimony roaster	V, Cl, Ni, Mn		SO ₄ ⁼ , Sb, Pb	NH ₄ ⁺ , OC, EC Na, Ca, Pb
				S
				Na, Al, Si, S, Ca, Fe, Si
				S, SO ₄ ⁼
				—

Reference: (Chow 1995)

*The arithmetic mean of the diurnal element contributions to the PM_{2.5} mass was the criterion for the elements to be included into a proper group (<0.1 %, 0.1–1 %, 1–10 %)

^a Symbols in red denote the elements occurring in Warsaw PM_{2.5} in amounts equal to amounts in the emission profiles from Chow 1995, blue symbols denote the elements occurring in amounts greater than amounts assigned to the sources by Chow, and green symbols denote the elements whose amount in Warsaw PM_{2.5} is too low to classify them into the proper Chow group and they belong to the preceding one

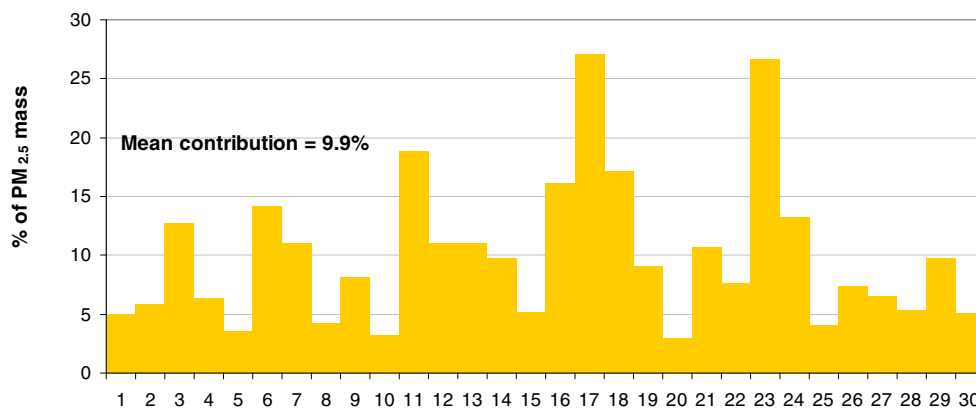
washed away by short-term precipitation. Larger particles, on the other hand, coming from other sources and/or particles that are suspended in the air long enough to form clusters and/or agglomerates when transported and transformed (Hinds 1999; Seinfeld and Pandis 2012) are easily and quickly washed away from the atmosphere (Seinfeld and Pandis 2012). Thus, it can be assumed that when the share of particles emitted from other sources in the concentrations of PM_{2.5} decreases, the share of motor vehicle engine emissions indirectly increases.

The last identified source of PM_{2.5} in Warsaw, was soil and road dust (PC9 and PC10, whose mean contribution to the concentrations of PM_{2.5} at the time of observations was 8 %). This source was identified mainly owing to the high

correlations of crustal elements, Ti, Al and Si (Table 1) with the principal components (Table 4). Since Ni, Mn and Cd, the source of which was friction of vehicle components (car bodies, brake pads and discs, exhaust pipes etc.) (Thorpe and Harrison 2008), which also correlated with PC9 and PC10. It was determined that they did not come only from soil matter, but from a combination of soil matter and road dust (mechanical processes—non-exhaust emissions). The diurnal contributions of this source to the concentrations of PM_{2.5} ranged from 5.0 to 10.3 % and were positively correlated with the wind speed ($R^2=0.17$).

The exclusive contribution of soil matter (SM) to PM_{2.5} (without road dust) can be easily estimated. The elements that were viewed as of crustal/soil origin in Warsaw, (i.e. whose

Fig. 3 Diurnal contributions (%) of PM_{2.5}-bound soil matter (SM) to PM_{2.5} mass



EF_x was up to 5: Mg, Al, Si, Ti and Fe—Table 2) occurred in soil mainly in the form of oxides and carbonates. Their most common compounds are SiO_2 , Al_2O_3 , Fe_2O_3 and TiO_2 .

Therefore, the mass concentration of soil matter [SM] was determined using the following formula:

$$[SM] = [SiO_2] + [Al_2O_3] + [Fe_2O_3] + [TiO_2] + [CO_3^{2-}] \quad (2)$$

where $[SiO_2]$, $[Al_2O_3]$, $[Fe_2O_3]$, and $[TiO_2]$ were calculated stoichiometrically from the analytically determined $[Si]$, $[Al]$, $[Fe]$ and $[Ti]$; $[CO_3^{2-}] = 1.5[Ca^{2+}]_A + 2.5[Mg^{2+}]_A$ (Marcazzan et al. 2001). In this paper, the quantities of Ca and Mg in water-soluble compounds (Ca^{2+} and Mg^{2+}) were not determined, but they were calculated using the values of analytically determined mass concentrations of Ca and Mg ($[Ca]$ and $[Mg]$), as well as the conclusions of the research described in Rogula-Kozłowska et al. (2013a) which demonstrate that more than 50 % of the mass of $PM_{2.5}$ -bound Ca and Mg in an urban area in Poland occurs in water-soluble compounds. Therefore, it was assumed that $[Ca^{2+}] = 0.5[Ca]$ and $[Mg^{2+}] = 0.5[Mg]$.

The average concentration of soil matter in air at the time of the observations was $1.14 \mu g/m^3$. The mean contribution of SM to the mass of $PM_{2.5}$ was estimated at nearly 10 % (Fig. 3). Therefore, the estimated contribution corresponds well to the contribution of soil and road dust to $PM_{2.5}$, calculated using MLRA. Even if the contribution of SM to $PM_{2.5}$, calculated in a simplified way, is largely overestimated, it is still evident that soil matter makes the principal component of PM in Warsaw, from the source identified herein as ‘soil and road dust’ or—in other words—a component of PM from soil and road surface erosion processes and re-suspension of dust.

4 Conclusions

In winter, the concentrations of $PM_{2.5}$ in Warsaw, are low, in comparison to the values recorded in other parts of Poland and in most urban areas worldwide. Nevertheless, concentrations of some $PM_{2.5}$ -elements, mainly toxic (Se, Ar, Co, V, Cd, Ni), may reach high values. This suggests that despite low concentrations of $PM_{2.5}$ in the air, there exists substantial exposure of the residents to the negative impact of the toxic components of PM. This is highly probable, because the measurements were taken in an urban background area where generally observed levels should be lower than in areas located in the vicinity of the major sources of $PM_{2.5}$.

In Warsaw, $PM_{2.5}$ and $PM_{2.5}$ -elements come from four sources of emissions. Coal and biomass combustion accounts for nearly 18.4 % of fine PM in the air. The contributions of oil-fired power plants, motor vehicles and soil/road dust to the concentrations of $PM_{2.5}$ amount to 9.9, 15.7 and 8.0 %, respectively. The total share of identified sources of emissions in

the concentrations of $PM_{2.5}$ is a little over 50 %, which means that nearly 50 % of $PM_{2.5}$ in the analysed area may be so-called background concentration. Results of earlier studies of the concentrations of $PM_{2.5}$ in an area where the country-specific background concentration was measured for $PM_{2.5}$ (Diabla Góra) support this conclusion (Rogula-Kozłowska et al. 2014).

It can also be expected that some PM from unidentified sources is secondary aerosol, originating from the transformations of organic and inorganic gaseous precursors of PM. In order to validate this conclusion, it is necessary to determine the content of water-soluble ions and carbonaceous matter in $PM_{2.5}$.

The results obtained in this paper come from the first series of observations conducted in the area of the Warsaw conurbation; however, the series was short and covered winter only. Therefore, they should be interpreted with a degree of caution and the conclusions must not be applied to areas of central Poland outside the Warsaw conurbation. Yet the research evidently demonstrates that the concentrations of both $PM_{2.5}$ and $PM_{2.5}$ -bound elements follow similar patterns in the central part of the country and in other urban areas of Europe, but not in the south of Poland. Due to the prevailing western and south-western winds, it seems that the area of central Poland may be substantially affected by pollution carried from the south of the country.

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