

PM_{2.5} in the central part of Upper Silesia, Poland: concentrations, elemental composition, and mobility of components

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Abstract The paper discusses ambient concentrations of PM_{2.5} (ambient fine particles) and of 29 PM_{2.5}-related elements in Zabrze and Katowice, Poland, in 2007. The elemental composition of PM_{2.5} was determined using energy dispersive X-ray fluorescence (EDXRF). The mobility (cumulative percentage of the water-soluble and exchangeable fractions of an element in its total concentration) of 18 PM_{2.5}-related elements in Zabrze and Katowice was computed by using sequential extraction and EDXRF combined into a simple method. The samples were extracted twice: in deionized water and in ammonium acetate. In general, the mobility and the concentrations of the majority of the elements were the same in both cities. S, Cl, K, Ca, Zn, Br, Ba, and Pb in both cities, Ti and Se in Katowice, and Sr in Zabrze had the mobility greater than 70%. Mobility of typical crustal elements, Al, Si, and Ti, because of high proportion of their exchangeable fractions in PM, was from 40 to 66%. Mobility of Fe and Cu was lower than 30%. Probable

sources of PM_{2.5} were determined by applying principal component analysis and multiple regression analysis and computing enrichment factors. Great part of PM_{2.5} (78% in Katowice and 36% in Zabrze) originated from combustion of fuels in domestic furnaces (fossil fuels, biomass and wastes, etc.) and liquid fuels in car engines. Other identified sources were: power plants, soil, and roads in Zabrze and in Katowice an industrial source, probably a non-ferrous smelter or/and a steelwork, and power plants.

Keywords Fine particles · Water-soluble fraction · EDXRF · Mobility · Enrichment factor · Source apportionment

Introduction

Recent years have brought numerous papers concerning chemical composition of PM_{2.5} (Dutkiewicz et al. 2006; Viana et al. 2007; Zhang et al. 2007). These papers, in general, are important to the air quality management and add to the knowledge on the effects of particulate matter (PM) on human health (Marmur et al. 2006). The knowledge on the elemental composition of PM_{2.5} helps to assess the environmental effects of PM_{2.5} (Braga et al. 2005; Suzuki 2006) and to identify the dust sources (Canepari et al. 2009; Koltay et al. 2006; Quiterio et al. 2005; Rajšić et al. 2008; Yadav and Rajamani 2006). However, the elemental composition of PM, which conventional methods are usually able to yield, is insufficient

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for assessment of the PM health effects. The health effects of PM_{2.5} depend more on the bioavailability than on the total concentrations of the PM_{2.5} components (Costa and Dreher 1997; Dellinger et al. 2001; Valavanidis et al. 2000; Van Maanen et al. 1999). The bioavailability of elements is identified with their mobility, which is defined as the water solubility of their compounds. So, the bioavailability of a PM-related element may be expressed as the amount of the water-soluble compounds of this element in the water extract of a PM sample. It is crucial to the element migration from the atmosphere to water and soil.

Some authors (Caussy et al. 2003) claim that the metal bioavailability cannot be properly understood until new, simpler and universal, analytical methods are developed. To analyze PM_{2.5} for its elemental composition, the authors of the paper use energy dispersive X-ray fluorescence (EDXRF), a technique widely applied in determinations of elemental composition of PM (Chow 1995; US EPA 1999). They also used EDXRF to determine the mobility of selected elements.

Speciation analyses (e.g., analyses of solid samples for bioavailability of their components) base on sequential chemical extraction. Filgueiras et al. (2002) gave a detailed description of a number of such procedures. They point out that only a few out of several hundreds of applications of the sequential extraction to solid environmental samples concern the ambient particles. Many papers concerning the sequential extraction and elemental fractionation of PM have appeared since the Filgueiras' paper. However, the number of works concerning the sequential extraction of soil, bottom sediments, wastes, etc. is incomparably greater. In the total number of the publications concerning the elemental composition of PM, the papers on elemental fractionation of PM are only a small percent. In Table 1, the authors list all the papers on elemental fractionation of PM, dated after 2002, they were able to find. The solvent most often used in determinations of the mobility of PM-related elements is water. Only a few of the papers mention the application of a second reagent (MgCl₂, NH₄OAc, and KNO₃).

The mobility of a PM-related element strongly depends on the element distribution among the compounds of the PM matrix (Dabek-Zlotorzynska et al. 2005; Fernández Espinoza et al. 2002; Jarvis et al. 1995); therefore, it depends on the PM origin. For example, the amount of water-soluble compounds of Pb in total ambient PM₁₀-related Pb decreased greatly

after the combustion of gasoline had ceased to be the main source of ambient Pb in Santiago de Chile. Despite this, the share of the mobile forms of Pb (water-soluble + exchangeable fractions) in its total concentration did not decrease significantly (Richter et al. 2007)—this also proves that not always the mobility of an element (metal) may be identified with the proportion of its water-extractable mass in its total concentration.

The goal of this work was to analyze the ambient concentrations of PM_{2.5} and the concentrations and mobility of some PM_{2.5}-related elements in two Polish cities. Except for data published by Krzemińska-Flowers et al. (2006) and Pastuszka et al. (2010), the authors have not found works on the elemental composition of PM_{2.5} in Poland. Neither were data on mobility of the PM-related elements available. PM was sampled in Zabrze and Katowice, two cities in Upper Silesia (population density 1,693/km²), Poland, in 2007. From the air pollution point of view, it is the most interesting region of Poland. The two recent decades of economical changes forced the greatest drop of industrial air pollution in Poland (in Zabrze, yearly dust fall exceeded 2,100 g/m² in the 1970s, oscillated between 700 and 800 g/m² in the 1980s, and was less than 350 g/m² after 1995). However, still functioning ancient steel works and cokeries together with road traffic and combustion of fossil fuels for energy production maintain high concentrations of ambient dust in the region (Pastuszka et al. 2003, 2010).

Materials and methods

The paper presents an application of the two-stage extraction (in water and ammonium acetate, NH₄OAc) to determination of the mobility of the PM_{2.5}-related elements. The water-soluble fraction of PM contains water-soluble species and, leached into water, consists of free ions and ions complexed with soluble organic matter and other constituents. It comprises the most mobile and potentially available metal and metalloid species, easily washable out from the PM matrix by water or releasable by some living organisms (Kyotani and Iwatsuki 2002).

The NH₄OAc-soluble (exchangeable) fraction includes weakly adsorbed metals retained on solid surface (Al-Masri et al. 2006) by relatively weak electrostatic interaction, metals that can be released through ion exchange, and metals that can be coprecipitated with

Table 1 Concentrations and mobility of PM-related elements in various locations in the world

Sampling site	Techniques applied	Reagent ^a	Extracted fraction ^a	Dust fraction: element/concentration (ng/m ³)/mobility (%)
Tartous (Syria), coastal city with industrial emissions ^b	DPASV at the SMDE	1. Distilled water (pH=6.5) 2. MgCl ₂ (pH=7)	1. Water-soluble 2. Exchangeable	TSP: Cu/4283 ^g ; Zn/133/0.2; Pb/193/<1 TSP: Cu/2504 ^g ; Zn/134/0; Pb/284/<1
Darya (Syria), city with industrial emissions ^b	ICP-MS	1. Deionized water 2. NH ₄ OAc (pH=7)	1. Water-soluble 2. Exchangeable	PM ₁₀ : Mg ^p /1929 ^g ; Al ^p /3030 ^g ; Ca/784 ^g ; Ti/807 ^g ; V/681 ^g ; Cr/553 ^g ; Mn/81 ^g ; Ni/272 ^g ; Cu/176 ^g ; Zn/756 ^g ; As/110 ^g ; Mo/56 ^g ; Ba/426 ^g ; Pb/394 ^g
Metropolitan Region of Chile (Santiago) ^e	AAS	1. Distilled water	1. Water-soluble	PM ₁₀ : Mg ^p /1929 ^g ; Al ^p /3030 ^g ; Ca/784 ^g ; Ti/807 ^g ; V/681 ^g ; Cr/553 ^g ; Mn/81 ^g ; Ni/272 ^g ; Cu/176 ^g ; Zn/756 ^g ; As/110 ^g ; Mo/56 ^g ; Ba/426 ^g ; Pb/394 ^g
Near highway in Canada (British Columbia) ^d	ICP-MS	2. KNO ₃	2. Exchangeable	TSP: Mn/18/43; Fe/602/1; Cu/106/42; Zn/32/56; Pb/4/13
National University of Singapore (research station) ^e	ICP-MS	1. Ultrapure water + microwave energy	1. Water-soluble	PM ₁₀ : V/60 ^g ; Cr/59 ^g ; Mn/10/17; Fe/265/11; Co/1/13; Ni/13/22; Cu/754; Zn/41/44; As/8/18; Cd/2/7; Pb/16/25
Helsinki, traffic, sea ^f				PM _{2.5} : V/55 ^g ; Cr/19/38; Mn/10/11; Fe/172/11; Co/1/6; Ni/13/45; Cu/4/31; Zn/37/92; As/7/17; Cd/2/11; Pb/13/15
Amsterdam, traffic, sea ^f				PM _{2.5} : Al ^f /57 ^g ; S/215/100; Cl/18/100; K/71/83; Ca/51/51; V/5.7/100; Cr/0.35/40; Mn/1.3/100; Fe/72/44; Ni/2.6/85; Cu/1.6/94; Zn/12/100; Pb/5.7/56
Duisburg, traffic, metal industry ^f	EDXRF	1. Deionized water	1. Water-soluble	PM _{2.5} : Al ^f /42 ^g ; S/396/100; Cl/220/100; K/130/61; Ca/42/81; V/5.5/82; Cr/0.31/100; Mn/3.4/94; Fe/140/41; Ni/1.9/79; Cu/4.2/100; Zn/36/89; Pb/17/76
Prague, traffic, residential heating with solid fuels ^f	ICP-MS			PM _{2.5} : Al ^f /44 ^g ; S/36; Si/270.6/100; Cl/210/52; K/110/100; Ca/53/87; V/1.1/100; Cr/3.7/25; Mn/14/71; Fe/270/36; Ni/1.9/58; Cu/6.3/100; Zn/84/90; Pb/27/85
Barcelona, traffic, metal industry, harbor, sea ^f	IC			PM _{2.5} : Al ^f /65 ^g ; S/22; Si/462/100; Cl/43/100; K/230/100; Ca/27/85; V/1.6/100; Cr/0.2/90; Mn/3.2/97; Fe/88/65; Ni/0.74/100; Cu/4/98; Zn/70/84; Pb/36/61
Athens, traffic ^f				PM _{2.5} : Al ^f /55 ^g ; S/22; Si/462/100; Cl/44/100; K/110/100; Ca/140/93; V/18/100; Cr/0.95/48; Mn/3.1/100; Fe/140/31; Ni/6.6/76; Cu/6.3/92; Zn/58/100; Pb/19/84
Edinburgh (UK), urban background ^g	ICP-MS	1. Ultrapure water	1. Water-soluble	PM _{2.5} : Al ^f /62 ^g ; S/32; Si/429/100; Cl/16/100; K/94/100; Ca/390/100; V/7.2/100; Cr/0.18/100; Mn/5.3/87; Fe/200/36; Ni/2.3/100; Cu/7.5/100; Zn/33/94; Pb/19/84
The Kofu City (Japan), urban ^h	ICP-AES	1. Distilled water	1. Water-soluble	PM _{2.5} (summer): Ti ^f /0.4 ^g ; V/0.4 ^g ; Cr/0.5/27; Mn/0.7/45; Fe/27.6/12; Ni/1.0/45; Cu/1.4/50; Zn/7.5/74; As/0.3/63; Cd/0.4/75; Pb/13.6/49
				PM ₁₀ : Ti ^f /3.66 ^g ; V/1.14/67; Cr/1.60/13; Mn/2.94/40; Fe/183/6; Ni/3.43/11; Cu/4.93/45; Zn/13.3/58; As/0.37/60; Cd/0.34/74; Pb/14.1/33

Table 1 (continued)

Sampling site	Techniques applied	Reagent ^a	Extracted fraction ^b	Dust fraction: element/concentration (ng/m ³)/mobility (%)
	EDXRF			Na/5 ⁶ , ⁹⁰ ; Mg/40/63; Al/60/0; Si/200/0; S/1750/100; Cl/360/100; K/270/96; Ca/230/48; Ti/3/0; V/0.8/0; Cr/1.2/100; Mn/3.2/63; Fe/50/40; Cu/9.5/95; Zn/80/75; Br/11/100; Pb/70/100
				PM _{2.5} (winter): Na/100 ⁶ , ⁹⁸ ; Mg/35/57; Al/140/14; Si/500/0; S/1000/100; Cl/640/100; K/370/95; Ca/110/91; Ti/7/0; V/5/80; Cr/6/0; Mn/4.7/43; Fe/120/17; Cu/6/0; Zn/40/88; Br/7.5/100; Pb/65/23
				PM _{2.5-10} (summer): Na/300 ⁶ , ⁹³ ; Mg/80/50; Al/280/14; Si/11500/0; S/125/100; K/280/79; Ca/290/86; Ti/18/0; V/2.1/100; Cr/0.3/0; Mn/5/76; Fe/170/18; Cu/1/0; Zn/10/100; Pb/80/100
				PM _{2.5-10} (winter): Na/70 ⁶ , ⁹² ; Mg/140/25; Al/660/6; Si/2250/0; S/240/100; K/90/0; Ca/470/74; Ti/40/0; V/3.3/85; Cr/5.2/0; Mn/7.8/69; Fe/330/6; Cu/2.5/0; Zn/15/100; Br/1.0/100; Pb/15/93
Seville (Spain), urban ⁱ	ICP-AES	1. Milli-Q-grade water (pH=7.4)	1. Soluble and exchangeable metals	PM _{0.61} : Mg/173.1/10; Ca/954/27; Ti/3.17/8; V/4.08/50; Mn/7.43/33; Fe/260.8/4; Co/0.293/35; Ni/1.44/40; Cu/9.57/27; Cd/0.210/25; Pb/43.7/4
Calgary, high traffic, commercial ^j	CE	1. Deionized water	1. Water-soluble	PM _{2.5} : Mn/25 ⁹⁴ /42; Fe/335/2; Cu/7/5; Zn/21/47
Winnipeg, high traffic, commercial ^j	EDXRF	1. Deionized water	1. Water-soluble	PM _{2.5} : Mn/15 ⁹⁵ /40; Fe/293/3; Cu/6/3; Zn/20/56
Quebec City, industrial ^j	CE	1. Deionized water	1. Water-soluble	PM _{2.5} : Mn/31 ⁹⁵ /4; Fe/257/15; Cu/7/35; Zn/74/53
Toronto, industrial ^j	CE	1. Deionized water	1. Water-soluble	PM _{2.5} : Mn/44 ⁹⁶ /5; Fe/480/9; Cu/21/9; Zn/95/66
Toronto-2, cleaner residential air ^j	CE	1. Deionized water	1. Water-soluble	PM _{2.5} : Mn/14 ⁹⁷ /2; Fe/173/26; Cu/5/54; Zn/39/29
Montreal, cleaner residential air ^j	EDXRF	1. Deionized water	1. Water-soluble	PM _{2.5} : Mn/17 ⁹⁵ /5; Fe/158/7; Cu/5/10; Zn/26/13; Cd/10/81
Montreal-2, cleaner residential air ^j	CE	1. Deionized water	1. Water-soluble	PM _{2.5} : Mn/16 ⁹³ /3; Fe/161/11; Cu/108/57; Zn/51/34
Baltimore, personal exposure samples ^k	EDXRF	1. Ultrapure water	1. Water-extractable	PM _{2.5} : Mg/33.62 ⁹⁷ /8; Al/32.02 ⁷⁷ /7; Ti/0.89/48; Mn/0.71/78; Co/0.13/25; Ni/1.02/88; Cu/6.38/64; Zn/25.82/91; Rb/0.055/100; Sr/0.20/76; Cd/0.07/100; Sb/0.12/76; Ba/0.68/62; Pb/2.81/62
Baltimore, indoor aerosols samples ^k	EDXRF	1. Ultrapure water	1. Water-extractable	PM _{2.5} : Mg/20.97 ⁹⁷ /8; Al/19.40/63; Ti/0.67/77; Mn/0.45/84; Co/0.29/19; Ni/1.71/84; Cu/4.01/68; Zn/26.86/86; Rb/0.033/100; Sr/0.18/81; Cd/0.041/100; Sb/0.071/94; Ba/0.33/60; Pb/2.36/70
Guangzhou (China), urban; ground ^l	ICP-MS	1. H ₂ O (pH=7.4)	1. Soluble and exchangeable	PM _{2.5} : Al/2081 ⁹¹ ; Cr/7.693/7; Mn/62.49/30; Fe/1457/2; Co/0.943/26; Ni/6.454/28; Cu/57.32/21; Zn/504.8/46; As/24.28/33; Mo/2.046/44; Cd/4.431/39; Pb/201.6/12
Guangzhou (China), urban; roof ^l	ICP-MS	1. H ₂ O (pH=7.4)	1. Soluble and exchangeable	PM _{2.5} : As/24.28/33; Mo/2.046/44; Cd/4.431/39; Pb/201.6/12

Table 1 (continued)

Sampling site	Techniques applied	Reagent ^a	Extracted fraction ^b	Dust fraction: element/concentration (ng/m ³)/mobility (%)
New York (USA), downtown ^m	ICP-MS	1. Distilled water	1. Water-soluble	Al/2724 ^{q1} ; Cr/9.764/5; Mn/72.19/32; Fe/1908/2; Co/0.816/18; Ni/6.345/23; Cu/53.55/22; Zn/570.3/51; As/25.64/36; Mo/2.185/51; Cd/4.732/43; Pb/212.3/13
				PM _{2.5}
Poland, Zabrze, urban background (residential heating with hard coal) ⁿ	EDXRF	1. Deionized water (Milli-Q-Gradient purity)	1. Water-soluble	Mg ^o /988; Al/11; Ca/47; V/88; Cr/5; Mn/84; Fe/62; Co/73; Ni/64; Zn/90; As/84; Se/70; Cd/12; Sb/71; Pb/88
		2. NH ₄ OA (pH~7)	2. Exchangeable	PM _{2.5} Al ^r /40; Si/66; S/85; Cl/94; K/92; Ca/96; Ti/58; Cr/53; Mn/42; Fe/20; Cu/22; Zn/81; Se/67; Br/85; Sr/74; Sb/63; Ba/94; Pb/77
Poland, Katowice, urban background (residential heating with hard coal) ⁿ				PM _{2.5} Al ^r /45; Si/53; S/88; Cl/94; K/93; Ca/96; Ti/64; Cr/56; Mn/45; Fe/28; Cu/23; Zn/83; Se/90; Br/88; Sr/67; Sb/61; Ba/93; Pb/79

DPASV differential pulse anodic stripping voltammetry, *SMDE* static mercury drop electrode, *AAS* atomic absorption spectroscopy, *CE* capillary electrophoresis

^a Reagents and extracted fractions are named after the cited papers

^b Al-Masri et al. (2006)

^c Richter et al. (2007)

^d Preciado and Li (2006)

^e Karthikeyan et al. (2006)

^f Sillanpää (2006)

^g Heal et al. (2005)

^h Kyotani and Iwatsuki (2002)

ⁱ Fernández Espinoza et al. (2002)

^j Dabek-Zlotorzynska et al. (2005)

^k Graney et al. (2004)

^l Feng et al. (2009)

^m Qureshi et al. (2006)

ⁿ This study

^o Values taken from charts

^p Averages of element concentrations in 1997–2003

^q Mobility as the contribution of the water-soluble fraction

^r Mass of sulfur in the IC-measured mass of SO₄²⁻ was determined stoichiometrically

^s Assumed 100% for the elements whose concentrations of water-soluble fraction were higher than the total concentrations (*italics*)

^t Median values

^u Only mobility of elements; no concentrations were given in the source paper

^v Only mobility of elements; the concentrations are in Table 2

carbonates. Changes in the ionic composition, influencing adsorption–desorption reactions, or lowering of pH can cause remobilization of metals from this fraction. Exchangeable metal ions are the measure of those trace metals which are released most readily into the environment.

The main steps of the method are presented on the scheme in Fig. 1. Figure 1 (the step-by-step scheme of the experiment), the equipment, and the analytical techniques are described in “Sampling sites and sampling method” and “Elemental analysis and mobility of elements”.

Sampling sites and sampling method

In 2007, alternately, each odd month in Zabrze and each even month in Katowice, diurnal samples of $PM_{2.5}$ were taken in 6- or 7-day campaigns, except for February (8 days), March (3 days), and December (4 days). The numbers of samples taken at each site in winter (heating season, January–March and October–December) and in summer (non-heating season, April–September) are given in Table 2.

The sampling points (Fig. 2) were located at urban background sites (sites in urban areas where levels of

Fig. 1 Scheme of the method

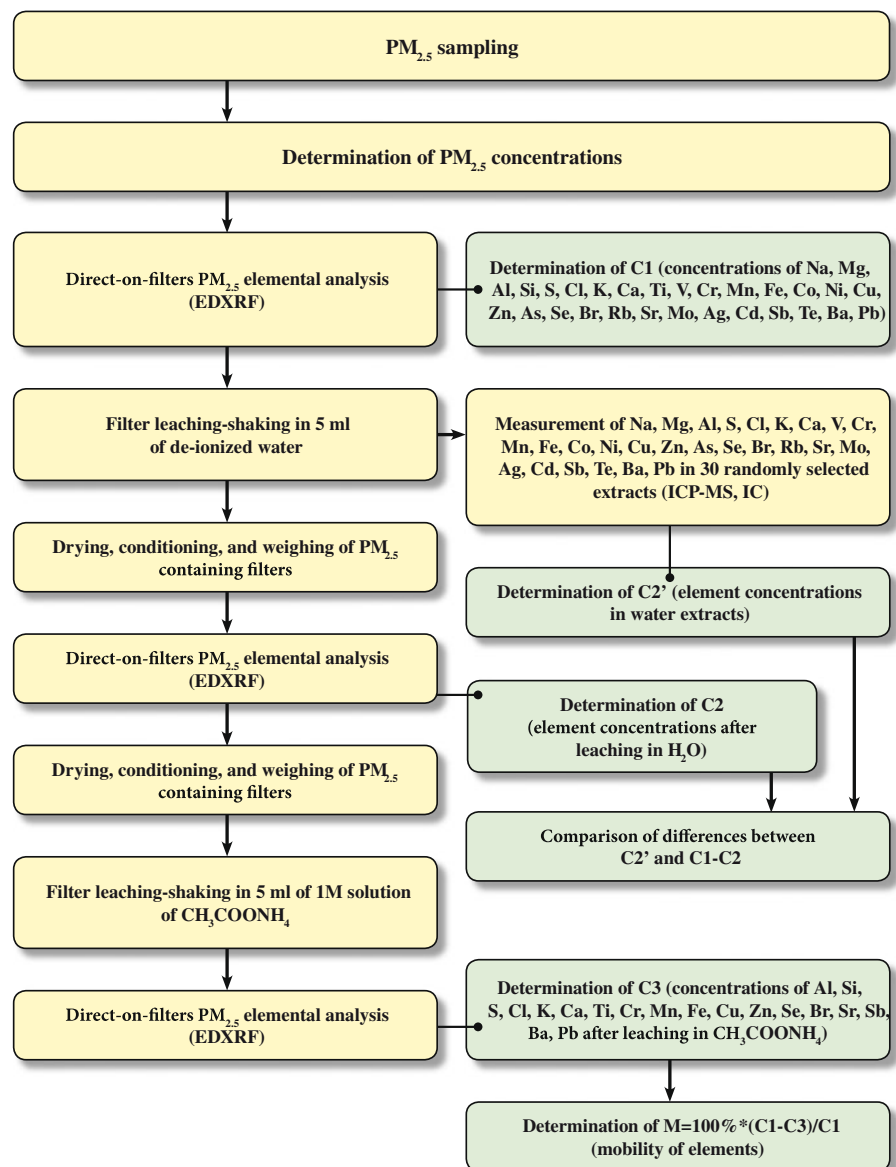


Table 2 Average concentrations of PM_{2.5} (in micrograms per cubic meter) and of PM_{2.5}-related elements ($\overline{C1}$ —total, $\overline{C2}$ —after extraction in water, and $\overline{C3}$ —after extraction in ammonium acetate, in nanograms per cubic meter) in Zabrze and Katowice in 2007

Zabrze, n=36 (16 W; 20 S)						Katowice, n=39 (18 W; 21 S)					
$\overline{C1}$						$\overline{C2}$					
$\overline{C3}$						$\overline{C3}$					
PM _{2.5} 22.0 (29.9 W; 16.8 S)						PM _{2.5} 31.0 (45.7 W; 17.7 S)					
	DL	N	A±SD	A	A		N	A±SD	A	A	
Na	2.7	15	62.3±121.2	95.8 ^a	–	Na	20	107.4±166.6	149.0 ^a	–	
Mg	41.8	3	6.1±24.1	25.2 ^a	–	Mg	3	7.4±26.7	22.2 ^a	–	
Al	16.6	35	147.6±108.8	127.8	88.1	Al	38	136.5±81.6	119.1	74.9	
Si	21.3	30	503.2±602.8	458.9	172.7	Si	33	443.3±401.7	397.2	208.1	
S	1.5	36	816.3±448.9	158.7	122.5	S	39	1,355.5±725.5	170.9	160.5	
Cl	1.3	36	684.6±1,041.0	68.6	44.1	Cl	39	787.1±1,005.5	70.9	48.0	
K	1.1	36	180.4±194.2	19.6	15.0	K	39	227.2±120.0	19.3	16.0	
Ca	1.2	36	26.7±22.2	6.9	1.1	Ca	39	30.7±19.8	7.4	1.3	
Ti	0.8	36	3.6±2.6	2.5	1.5	Ti	39	4.2±5.6	2.5	1.5	
V	0.3	10	0.2±0.3	0.3 ^a	–	V	19	0.5±0.8	0.4 ^a	–	
Cr	0.9	33	1.7±1.9	1.0	0.8	Cr	36	1.8±1.3	1.1	0.8	
Mn	3	31	16.1±41.4	10.7	9.4	Mn	39	8.8±6.9	6.0	4.8	
Fe	0.7	36	160.8±303.1	135.4	128.1	Fe	39	157.0±69.1	131.1	113.1	
Co	0.4	11	0.3±0.8	0.2 ^a	–	Co	22	0.4±0.4	0.1 ^a	–	
Ni	0.6	18	0.8±1.9	1.0 ^a	–	Ni	26	0.4±0.9	0.5 ^a	–	
Cu	1.4	35	6.5±6.8	5.4	5.1	Cu	39	8.2±3.6	6.8	6.3	
Zn	0.9	36	72.5±64.5	17.1	13.5	Zn	39	90.3±49.9	19.0	14.9	
As	11.6	7	1.5±3.5	1.1 ^a	–	As	9	2.1±4.0	1.2 ^a	–	
Se	0.2	22	0.9±1.1	0.6	0.3	Se	30	1.0±1.2	0.4	0.1	
Br	0.4	36	6.6±7.6	2.1	1.0	Br	37	9.1±8.1	2.6	1.1	
Rb	0.7	10	0.2±0.3	0.4 ^a	–	Rb	17	0.3±0.5	0.4 ^a	–	
Sr	1.0	33	3.9±3.1	2.5	1.0	Sr	33	3.0±2.5	1.8	1.0	
Mo	4.9	20	2.5±2.7	0.7 ^a	–	Mo	26	2.9±2.5	0.4 ^a	–	
Ag	3.3	22	2.3±2.2	2.4 ^a	–	Ag	28	2.8±2.1	2.3 ^a	–	
Cd	4.5	12	1.2±1.7	0.9 ^a	–	Cd	23	2.3±2.2	1.3 ^a	–	
Sb	5.7	24	5.1±6.9	3.9	1.9	Sb	31	5.6±3.8	4.4	2.2	
Te	5.1	11	1.4±2.3	0.9 ^a	–	Te	14	1.6±2.4	1.3 ^a	–	
Ba	7.6	28	6.4±10.6	0.9	0.4	Ba	23	4.2±4.3	0.3	0.3	
Pb	0.3	36	24.8±20.6	12.2	5.7	Pb	39	35.1±21.0	19.7	7.2	

The detection limits for the procedure were determined by using two blanks—PTFE filters. Each of the blanks underwent the entire EDXRF procedure, like the regular samples, 30 times. The detection limit for each element was computed as the standard deviation from the 60 results received for this element by measuring the blanks)

n number of samples, W winter, S summer, $\overline{C1}$ total average concentration, $\overline{C2}$ average concentration after extraction in water, $\overline{C3}$ average concentration after leaching in ammonium acetate, DL detection limit, in nanograms per square centimeter, *N* number of results greater than DL; *A*±SD average±standard deviation

^a Average concentrations in 15 water extracts measured with ICP-MS or IC

pollutants are representative of exposure of the urban population to pollutants; EC 2008). Each sampling site was representative of an area of a few square kilometers.

The nearby blocks of flats were heated from the central network, while the detached houses by combusting fossil fuels, biomass, and household garbage in domestic

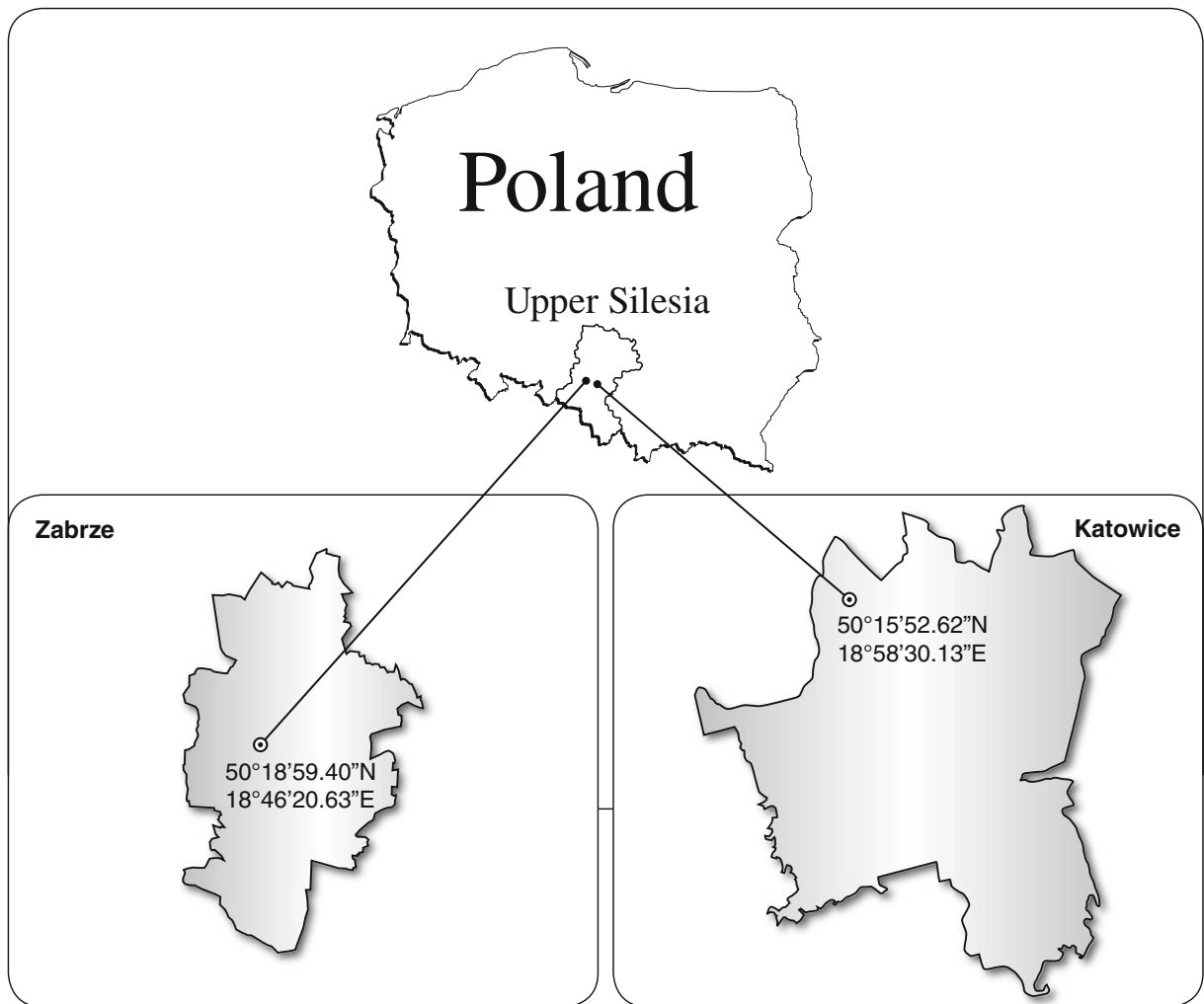


Fig. 2 Location of sampling sites

stoves. Each site was within about 200 m from a busy road, which might also be a source of PM.

A Rupprecht & Patashnick Dichotomous Partisol® Plus model 2025 was used to sample PM_{2.5}. PM_{2.5} was collected on Whatman PTFE filters. Its concentrations were determined gravimetrically (Mettler Toledo microbalance, resolution 2 µg, electric charge neutralizer). The air humidity and temperature in the weighing room were kept at 50 (±5)% and 20 (±1)°C. The filter conditioning time in the weighing room was 48 h.

Elemental analysis and mobility of elements

The elemental composition of PM_{2.5} was determined by the application of EDXRF (Bertin 1975; Jenkins 1999). A PANalytical Epsilon 5, calibrated with the

thin-layer single-element Micromatter calibration standards (US EPA 1999), was used. The element concentrations were received by comparing the results with the calibration curves. The NIST standard reference material (SRM2873) was measured weekly (except for Na, V, and Co, whose recovery coefficients were 73, 52, and 39%, respectively; recovery of each element was between 85 and 120% of the certified value). The detection limits for the elements are shown in Table 2. The daily ambient concentrations C₁ of Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Ag, Cd, Sb, Te, Ba, and Pb were determined (Table 2) and the average ambient concentrations $\overline{C_1}$ (arithmetic mean of C₁) of each element were computed separately for Katowice and Zabrze at this stage.

The elemental analysis of PM_{2.5}, direct on the substrate filters, was followed by two-stage extraction of the samples: in water (deionized water, Milli-Q-Gradient purity, Millipore, USA) and in 1 M solution of ammonium acetate (CH₃COONH₄, pH=7). The samples were extracted in 5 ml of the water and then in 5 ml of the ammonium acetate solution, in polyethylene containers (Roth). Each time, they were being shaken (150 rpm) for 1 h at the temperature 20°C. After each extraction, the samples were washed with the water (the after-washing water was put into the container with the extract), dried to constant weight, and analyzed for elemental composition with Epsilon 5 (EDXRF).

The EDXRF elemental analysis of PM on the water-washed filters allowed to determine C2—the diurnal ambient concentration of the water-insoluble fraction of an element. Each C2 was lower than the respective C1 by the value of the concentration of the water-soluble fraction. The daily ambient concentration of the water-soluble fraction of an element was C1–C2.

Thirty (15 from Zabrze and 15 from Katowice) randomly selected water extracts (acidified with supra-pure HNO₃ and kept at 4°C till analyzing) were analyzed for Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Se, Sr, Mo, Ag, Cd, Te, Sb, Ba, and Pb using ICP-MS (Elan 6100 DRC-e Perkin Elmer, the method validated with the NIST 1643e reference standard; recovery 95–115%, detection limits: 0.181 µg/l for Al, Fe, and Zn; 0.096 µg/l for V and As; 0.013 µg/l for Cr and Mo; 0.036 µg/l for Mn, Te, and Pb; 0.002 µg/l for Co and Ag; 0.024 µg/l for Ni; 0.064 µg/l for Cu; 0.003 µg/l for Rb; 0.041 µg/l for Se and Cd; 0.010 µg/l for Sr, Sb, and Ba). In thirty other similarly selected water extracts, the concentrations of Na⁺, Mg²⁺, Ca²⁺, K⁺, Cl⁻, SO₄²⁻, and Br⁻ were determined using ion chromatography (IC, Swiss Herisau Metrohm AG ion chromatograph, the method validated with the CRM Fluka product no. 89316 and no. 89886, standard recovery 92–109%, detection limits: 0.050 mg/l for Cl⁻, SO₄²⁻, and K⁺, 0.034 mg/l for Br⁻, 0.07 mg/l for Na⁺, and 0.12 mg/l for Ca²⁺ and Mg²⁺). The ICP-MS and IC analyses enabled comparison of the concentrations C2' of the elements in the water solution with the differences C1–C2.

The concentration C3 (after leaching in CH₃COONH₄) was determined for these 18 elements whose comparison of C1–C2 and C2' (Water-soluble fraction of PM_{2.5}-related elements: EDXRF vs. IC or ICP-MS) proved that the water concentrations of their soluble

fraction may be correctly determined by applying EDXRF alone. In the last step, the daily mobility *M* and the average mobility (arithmetic mean) \overline{M} in Zabrze and Katowice for each of these 18 elements were computed (Fig. 1).

Results and discussion

Water-soluble fraction of PM_{2.5}-related elements: EDXRF vs. IC or ICP-MS

The average ambient concentrations $\overline{C1}$ of PM_{2.5}-related elements in Zabrze and Katowice in 2007, standard deviations of data series, numbers *N* of the concentrations C1 higher than the detection limits DL of the elements are shown in Table 2. Because all the lower than DL diurnal concentrations entered the averages as zeros, $\overline{C1}$ lower than DL appear in Table 2 for both Zabrze and Katowice.

For each element and for each of the 30 samples, the relative difference ΔC between the EDXRF-determined C1–C2 and the IC- or ICP-MS-determined C2' was computed from the equation:

$$\Delta C = \frac{|(C1 - C2) - C2'|}{(C1 - C2)} \times 100\%. \quad (1)$$

For each element, $\overline{\Delta C}$ is the arithmetic average of its 30 ΔC . $\overline{\Delta C}$ were high for Na, Mg, V, Co, Ni, As, Rb, Mo, Ag, Cd, and Te (from 65 to 315%, Fig. 3). Moreover, the 30-element set of EDXRF-determined C1–C2 and the 30-element set of IC- or ICP-MS-determined C2' were not linearly correlated for each of these elements (*R* between 0.09 and 0.53).

Low $\overline{\Delta C} \leq 17\%$ for Co, As, Mo, and Ag were accidental—the coefficients *R* of linear correlation between their two concentrations were very low. It was probably due to the high detection limits for Mg, Ni, As, Rb, Mo, Ag, Cd, and Te and to the low recoveries for Na, V, and Co, which caused underestimation of the daily concentrations of these elements.

The two 30-element sets of the EDXRF- and IC-measured concentrations were well-correlated linearly for S, Cl, K, Ca, and Br (*R* between 0.78 and 0.93); the sets of the EDXRF- and ICP-MS-measured concentrations were well-correlated linearly for Al, Cr, Mn, Fe, Cu, Zn, Se, Sr, Sb, Ba, and Pb (*R* between 0.76 and 0.94). $\overline{\Delta C}$ for these 16 elements were between 7% (Ba) and 30% (Cu).

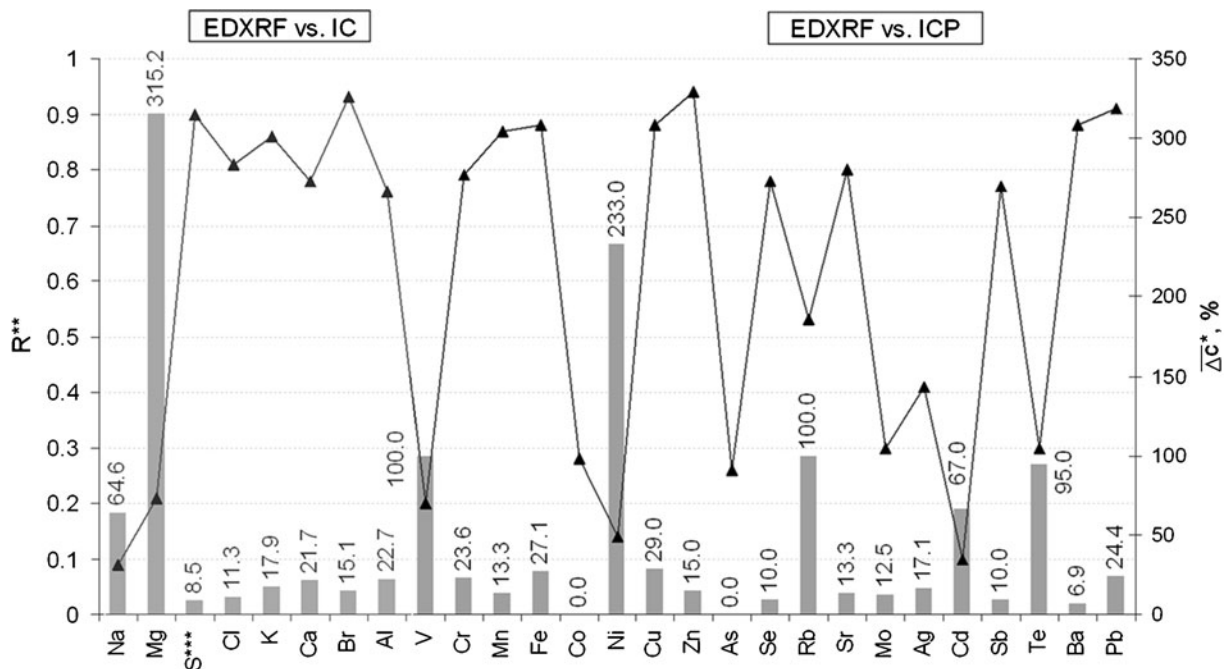


Fig. 3 Differences and correlations between EDXRF and IC (Na through Br) or ICP-MS (Al through Pb) measured element concentrations. The bars represent $\overline{\Delta C^*}$ —the arithmetic mean of 30

ΔC (asterisk). R —Pearson's correlation coefficient ($p < 0.01$) (double asterisks). Mass of sulfur in the IC-measured mass of SO_4^{2-} was determined stoichiometrically (triple asterisk)

EDXRF performed well with the elements with $N \geq 0.7n$ and $C1/DL > 9$ (except Cr, Sb, and Ba whose $C1/DL$ was between 1.6 and 3.8). Si and Ti satisfied these conditions too, and although $C1-C2$ for Si and Ti was not comparable with $C2'$ (too high DL in the water extracts), the concentrations of the water-soluble fractions of Si and Ti, and then their mobility, were, like those of Al, S, Cl, K, Ca, Cr, Mn, Fe, Cu, Zn, Se, Br, Sr, Sb, Ba, Pb, considered possible to be determined by using EDXRF alone.

It was not possible to determine the concentrations of the water-soluble fraction of Na, Mg, Ni, As, Rb, Mo, Ag, Cd, Te, V, and Co with EDXRF. They are given in Table 2 as the averages of the concentrations in 15 water extracts (15 for Zabrze and 15 for Katowice) measured by means of ICP-MS or IC (marked with 'a' in superscript).

The calibration of an X-ray fluorescence spectrometer with the most popular uniformly structured thin-layer standards (Micromatter Inc.), based on Compendium Method IO-3.3 (US EPA 1999), is widely applied in the analyses of the elemental composition of $\text{PM}_{2.5}$. The presented application of the proposed method in the determinations of the concentrations of water-soluble

fraction and/or mobility of some elements is universal. It simplifies the analyses (sample is analyzed directly on a filter) and, replacing the whole variety of techniques (some listed in Table 1), it may improve the comparability of the results from various sites. Besides, the direct-on-filter measurement of the mass of an element after extraction allows for avoiding problems with applications of solvents in sequential extraction. For example, although the extraction in water (the simplest solvent excluding uncontrolled behavior of metals and their extracts possible in other chemical solutions) allows for determination of the most mobile and potentially bioavailable metals and metalloids, suspensions may be formed in the extracts and the efficiency of the extraction of some elements is low (Filgueiras et al. 2002). Similarly, although ammonium acetate is widely recommended for extractions of exchangeable fractions, determinations of the mass of the extracted elements in its solution may be troublesome (Filgueiras et al. 2002).

Mobility of $\text{PM}_{2.5}$ -related elements

In this work, the environmental mobility M of a PM-related element is defined as the contribution of its two

fractions (water-soluble and exchangeable) to its total concentration (Tables 1 and 2 and Eq. 1).

$$M = \frac{C1 - C3}{C1} \times 100\% \quad (2)$$

Starting from the least mobility, the 18 elements may be listed in the order of their average mobility \bar{M} as follows:

Zabrze:

Fe<Cu<Al<Mn<Cr<Ti<Sb<Si<Se<Sr<Pb<Zn<S<Br<K<Ba<Cl<Ca

Katowice:

Cu<Fe<Al<Mn<Si<Cr<Sb<Ti<Sr<Pb<Zn<Se<Br<S<Ba<K<Cl<Ca

The 18 elements may be divided into three groups by their mobility (Table 1). The first group is the elements with the mobility greater than 70%: S, Cl, K, Ca, Ti, Zn, Se (Katowice), Br, Sr (Zabrze), Ba, and Pb. Probably, highly mobile Cl, K, Ca, Se, and Ba occurred in PM_{2.5} as sulfates, chlorides, and nitrates (Kyotani and Iwatsuki 2002). The second group comprises the elements with the mobility between 40 and 70%: typical crustal Al, Si, and Ti, but also Cr, Se (Zabrze), Mn, Sr (Katowice), and Sb. The third group comprises the elements with the mobility less than 30%: Fe and Cu.

The elements differed significantly with the contributions of their mobile fraction to their totals in PM_{2.5}. For most of them, a great part of this fraction was extracted in water (Table 2). Almost the whole mobile fraction of S, Cl, K, Zn, and Ba in PM_{2.5} from both sites was water-soluble (from 74% for Ca in Zabrze to 92% for K in Katowice). Great parts of Se (Katowice), Cr, Br, and Pb were in water-soluble forms (~40–70% of $\bar{C1}$). The water-soluble and exchangeable fractions of Se (Zabrze), Sr, Sb, and Pb had similar shares in $\bar{C1}$. The water-soluble fractions of Al, Si, Fe, and Cu gave no more than 25% of $\bar{C1}$ —the mobility of Al, Si, and Sb depended strongly on the exchangeable fraction (Table 2).

The environmental mobility of the PM_{2.5}-related elements in Zabrze and Katowice was comparable. The differences for particular elements, except Si (66%—Zabrze and 53%—Katowice), Ti (58 and 64%), Fe (20 and 28%), Se (67 and 90%), and Sr (74 and 67%), were not greater than 5% (Table 1).

The distribution of a PM-related element between the mobile and immobile phases depends on a sampling

site (Dabek-Zlotorzynska et al. 2005; Qureshi et al. 2006), i.e., the mobility of PM-related elements differs from place to place (Table 1). Kyotani and Iwatsuki (2002) observed high concentrations of water-soluble fractions of PM₁₀- and PM_{2.5}-related Pb and higher than in Zabrze and Katowice concentrations of mobile fractions of Zn and Mn in Kofu (Japan, Table 1). Like in Zabrze and Katowice, Ti, Fe, and Cr occurred in weakly water-soluble forms. Fernández Espinosa et al. (2002) examined PM_{<0.61} in Seville (urban station) for water-soluble and exchangeable fractions of selected metals. The mobility of Fe, Ti, Ca, Mn, and Pb was higher in Seville than in Upper Silesia. The differences may be due to different contributions of various PM sources, i.e., to different origin of PM in Silesia, Seville, and Kofu.

Besides the origin, the matrix of PM (aluminosilicate/carbonic matter) and pH of the reagent affect the mobility of PM-related elements (Colin et al. 1990; Desboeufs et al. 2001; Ebert and Baechmann 1998; Kyotani and Iwatsuki 2002). The solubility of the components of crustal aerosol is considered lower than that of the components of marine and anthropogenic aerosols (Giusti et al. 1993; Table 1). The presented results consist with it: the PM_{2.5}-related crustal elements, such as Fe and Al and (in a lower degree) Ti and Si, were immobile at both sites.

Except for Cu and Mn, all the remaining metals (and also Se and Sb) occurred mainly in water-soluble compounds. These may occur as bioavailable sulfates and chlorides (e.g. PbCl₂, ZnCl₂, SbCl₂, Qureshi et al. 2006). Chlorides in high concentrations occur, for instance, in gases from waste combustion (Schroeder et al. 1987). Copper, differently distributed in the Zabrze and Katowice samples from other metals, occurred probably as insoluble oxides, CuO or Cu₂O (Al-Masri et al. 2006; Dabek-Zlotorzynska et al. 2005). Also Pb and Zn might occur as, for example, insoluble PbSO₄, PbO, and ZnO in the Silesian PM_{2.5}.

High mobility of heavy metals¹ in Upper Silesia confirms their anthropogenic origin. Metals in anthropogenic particles are the metals from surface abrasion,

¹ There are numerous definitions of *heavy metals* in the available literature (IUPAC 2002). In the present work, the term heavy metal refers to “Element commonly used in industry and generically toxic to animals and to aerobic and anaerobic processes, but not every one is dense nor entirely metallic. Includes As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Zn” (Scott and Smith 1981, after IUPAC 2002).

hot vapor condensation, and metals condensed on surface of other particles—they are more susceptible to releasing than metals bound onto crustal matter (Heal et al. 2005). Consequently, they occur in the most available to ecosystems forms. Because they are weakly bound onto dust particles, they may be easily released to soil and plants through ion exchange (Dabek-Zlotorzynska et al. 2005).

Heavy metals in bioavailable forms usually prevail in the urban air, where most of PM_{2.5} originates from car exhaust and/or industry (Table 1). Mobility of heavy metals is much higher in Upper Silesia than, for example, in Edinburgh, Kofu, Seville, the majority of sites in Canada, and at two sites in Syria (in Syria—the coarse PM-related metals; Table 1).

Usually, the mobile fractions of PM-related elements are contained in PM_{2.5}. The serious hazard to human health from the fine particles consists in their easy way into the deep regions of lungs, where the mobile fractions of metals are bioactivated (Feng et al. 2009; Sun et al. 2001; Voutsas and Samara 2002).

Concentrations and sources of PM_{2.5} and PM_{2.5}-related elements

In Upper Silesia, the concentrations of PM_{2.5} decreased significantly during the last two decades. In the mid-1990s (1995–1996), the average concentration of PM_{2.5} in Świętochłowice (the city halfway between Katowice and Zabrze) was 58 µg/m³ (Houthuijs et al. 2001). The average PM_{2.5} concentration in Katowice and Zabrze in 2007 was 26.5 µg/m³ (Table 2). This 54% drop in PM_{2.5} concentration during a decade was due to restructuring of the industry and closing of many factories across whole Silesia. Although the industrial activity in Silesia was significantly limited, it remained high enough to be one of the highest in Europe and to maintain high concentrations of PM in the region. The Europeans exposed to high PM₁₀ concentrations, exceeding the yearly limit of 40 µg/m³, are more than 9% of the total population of the world. Among them, the most threatened people are people in the Balkans, then in Czech Republic, Hungary, and southern Poland (EEA Technical Report 2009).

The PM_{2.5} concentrations in Zabrze and Katowice are high, especially in winter (Table 2). In 2007, the yearly PM_{2.5} concentrations were much higher in these two cities than in some other big cities in the world, such as New York, USA (Qin et al. 2006), and higher or close

to the concentrations in some European cities such as Duisburg, Helsinki, Prague, and Amsterdam (Puustinen et al. 2007; Sillanpää 2006).

There is no definite threshold of the PM concentration beneath which PM does not exert adverse health effects (Monn 2001; WHO 2005). Gradually, with the progress of knowledge, the PM health effects, including mortality, are being linked to lower and lower PM concentrations (Bell et al. 2004; Vedal et al. 2003). Because the value of 25 µg/m³ is (after the World Health Organization) “the lowest level at which total, cardiopulmonary, and lung cancer mortality have been shown to increase with more than 95% confidence in response to long-term exposure to PM_{2.5}” the PM_{2.5} concentrations should be maintained lower than this value (WHO 2005). In the experimental period, the PM_{2.5} concentrations in Zabrze and Katowice were most frequently between 10 and 20 µg/m³ (almost 42 and 36% of all the observations in Zabrze and Katowice, respectively, Fig. 4). However, in Zabrze nine (25% of the total) and in Katowice sixteen (41% of the total), concentrations were greater than 30 µg/m³. High diurnal PM_{2.5} concentrations, between 50 and 110 µg/m³, occurred in both cities only in winter.

Starting from the lowest concentration, PM_{2.5}-related elements may be listed in the order of their growing total average concentrations \bar{C} as follows (Table 2):

Zabrze:

V=Rb<Co<Ni<Se<Cd<Te<As<Cr<Ag<Mo<Ti<Sr<Sb<Mg<Ba<Cu<Br<Mn<Pb<Ca<Na<Zn<Al<Fe<K<Si<Cl<S

Katowice:

Rb<Co=Ni<V<Se<Te<Cr<As<Cd<Ag<Mo<Sr<Ti=Ba<Sb<Mg<Cu<Mn<Br<Ca<Pb<Zn<Na<Al<Fe<K<Si<Cl<S

Al, Si, S, Cl, K, Ca, Fe, Zn, and Pb prevailed in the sampled PM.

The average concentrations \bar{C}_I of a particular element at both sampling sites were similar. The differences between them were small, within a factor of 2 (Table 2). However, the daily concentrations C_I of the elements varied, the standard deviations are high (Table 2). It is mainly due to varying weather conditions (especially wind direction; Seinfeld 1986; Somerville et al. 1996).

Enrichment factors allow for assessment of the anthropogenic effect on the concentrations of the PM-related elements (Cong et al. 2007; Morata et al.

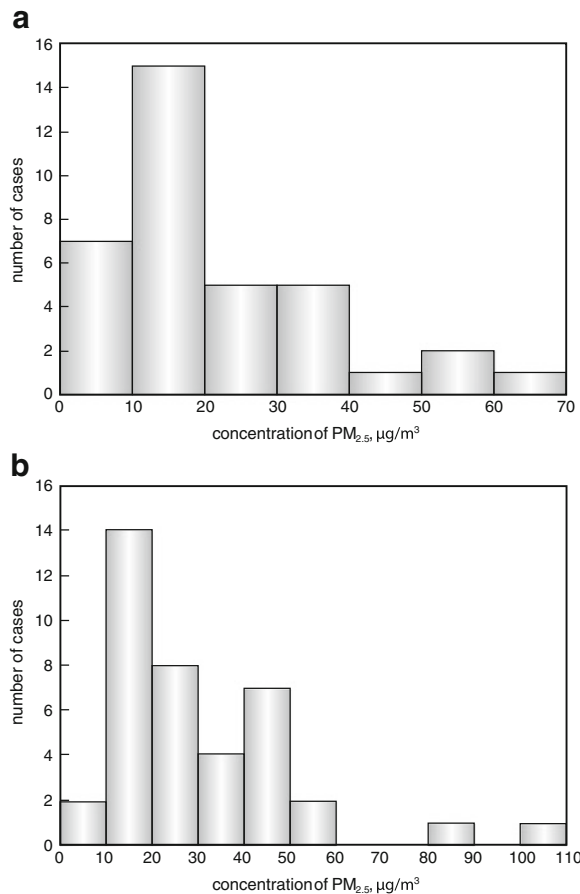


Fig. 4 Frequency of occurrence of the diurnal concentrations of $PM_{2.5}$ at the urban background stations in Zabrze (a) and Katowice (b) in 2007

2008; Rajšić et al. 2008). The enrichment factor EF_x is defined for the element x as:

$$EF_x = \frac{(C_x/C_{ref})_{PM}}{(C_x/C_{ref})_{crust}} \quad (3)$$

where, respectively, C_x and C_{ref} designate the concentrations of the element x and the reference element, $(C_x/C_{ref})_{PM}$ and $(C_x/C_{ref})_{crust}$ are the proportions of these concentrations in PM and in the Earth's crust. In the paper, the observed concentrations C_x are related to the concentration C_{Al} of Al, the marker element for the Earth's crust. Consequently, $EF_{Al}=1$. The chemical characterization of the Earth upper continental crust is taken from Wedepohl (1995). Because the chemical

composition (especially heavy metal content) of the soil at the investigated sites differs from the chemical composition of the upper continental crust, EF_x was also computed using the data on heavy metal content of the uppermost layer (1–6 cm) of the soil in the Zabrze and Katowice regions taken from Magiera et al. (2007). All EF_x are listed in Table 3.

EF_x close to 1 indicates the crustal origin of the element x , high EF_x suggests strong anthropogenic effect on the concentrations of x (Birmili et al. 2006; Jasan et al. 2009; Morata et al. 2008). In Table 3, the symbols of the elements x with $EF_x > 10$ are in bold.

The total concentrations of crustal $PM_{2.5}$ -related Fe, Ca, Al, Si, and Ti (López et al. 2005) were higher in Zabrze and Katowice than in the majority of other sites in the world (Tables 1 and 2).² They were lower than the concentrations of PM- and $PM_{2.5-10}$ -related Fe, Ca, Al, Si, and Ti in Syria (Al-Masri et al. 2006) and Japan (the Kofu City; Kyotani and Iwatsuki 2002)—fine and coarse PM have different origins (Finlayson-Pitts and Pitts 1986; Hinds 1998). The low enrichment factors suggest the natural (soil) origin of Fe, Ca, Si, and Ti in PM in Zabrze and Katowice (Table 3). In both cities, the low contribution of the water-soluble fraction of Fe, Al, and Si (Table 2) to their totals suggests stability of the compounds in which they occurred. Probably, their concentrations in Zabrze and Katowice were higher than elsewhere because the $PM_{2.5}$ concentrations were high themselves, not because of the existence of other than natural sources of these metals. The concentrations of $PM_{2.5}$ -related Ca, Ti, and probably Fe ($EF_{Fe} > 10$ relative to the Silesian soil Fe content, lower than the upper continental crust one, Table 3) might show the anthropogenic effect.

In general, the concentrations of the $PM_{2.5}$ -related heavy metals in Zabrze and Katowice were lower than in other cities affected by industrial emission, such as Tartous and Darya (Syria) and Guangzhou (China; Table 1). However, some metals, e.g., Pb and Zn, had concentrations higher (often several times) in Zabrze and Katowice than in other urbanized areas

² The methods of sampling, chemical analyses, sampling periods, and sampled dust fractions differ, so the results may not be comparable. Nevertheless, they may illustrate distribution of the levels of the ambient concentrations of elements in the world.

Table 3 Values of EFs for PM_{2.5}-related elements in Zabrze and Katowice

	Relative to upper continental crust (Wedepohl 1995)		Relative to soil from Zabrze and Katowice (Magiera et al. 2007)	
	Zabrze	Katowice	Zabrze	Katowice
Na	2	3	–	–
Mg	–	–	–	–
Al	1	1	–	–
Si	1	1	–	–
S	659	1,151	–	–
Cl	903	926	–	–
K	4	6	–	–
Ca	1	1	–	–
Ti	1	1	–	–
V	2	9	–	–
Cr	42	36	154	146
Mn	18	13	77	9
Fe	3	4	16	14
Co	15	25	–	–
Ni	33	22	150	52
Cu	335	440	235	159
Zn	1,079	1,298	481	143
As	694	977	–	–
Se	8,336	7,723	–	–
Br	3,303	4,253	–	–
Rb	1	3	–	–
Sr	9	7	–	–
Mo	1,298	1,602	–	–
Ag	29,780	30,286	–	–
Cd	8,079	20,288	414	231
Sb	11,317	14,132	–	–
Te	–	–	–	–
Ba	6	5	–	–
Pb	1,058	1,734	77	42

Symbols of elements x with EF_x> 10 are in bold

such as Singapore, Helsinki, Amsterdam, Athens, Edinburgh, or Baltimore (Table 1). Very high EFs (Table 3) and high mobility (except for Cu, Table 1) clearly indicate strong anthropogenic effect on ambient concentrations of the PM_{2.5}-related heavy metals.

The enrichment factors of Zn, Cd, and Pb in PM_{2.5} are much lower computed relative to the chemical composition of the Upper Silesian soil than relative to the composition of the upper continental crust (Table 3). The cause is the very high concentrations of these three metals in the Upper Silesian soil. The high heavy metal content of soil

in Silesia is the result of the long-term (almost 200 years) continual activity of industry (steelworks, cokeries, non-ferrous metal smelters, power stations, etc.).

Although the ambient air in Upper Silesia is of much better quality now than it used to be 20 years ago, when Silesia was among the most polluted regions of Europe and where the yearly dust fall was about 1 kg/m², the problem of its fine dust pollution remains still unsolved (EMEP 2009). The high anthropogenic heavy metal content of PM_{2.5} enhances the adverse effect PM_{2.5} has on the population of Upper

Silesia. The composition of the Silesian PM_{2.5} is due to the high use of fossil fuels for energy production and the concentration of industry in the region (big cokeries, steelworks, and non-ferrous metal smelters). The relatively high concentrations of As and Cd (indicating, when elevated, hard coal-fuelled power plants; López et al. 2005) and the concentrations of V and Ni (considered tracers of combustion of oil fuels in urban areas) in Zabrze and Katowice, lower than in almost all other sites (Table 1), fit this argumentation very well.

The concentrations of PM_{2.5}-related S and Cl in both cities were much higher than elsewhere (Table 1). Similarly, K, the biomass combustion indicator (Chen et al. 2001), generally had higher concentrations in Katowice and Zabrze. Because the distance from Katowice and Zabrze to the Baltic Sea (over 500 km) precludes the marine origin of Cl and S, and EF_S and EF_{Cl} are high, the two elements were probably anthropogenic in the greater part and originated from combustion of fossil fuels. They might be contained in fly ash, and some part of S (especially its water-soluble fraction) might originate from the transformations of SO₂ in the atmosphere (Alastuey et al. 2004; Gao and Chen 2006).

The probable sources of PM_{2.5} in Zabrze and Katowice were identified using principal component analysis (PCA). The average contributions of particular categories of sources of PM_{2.5} or of its precursors to the PM_{2.5} concentrations in Zabrze and Katowice were determined using multiple linear regression analysis (MLRA). All the computations followed the

procedure proposed by Thurston and Spengler (1985) and Almeida et al. (2005) and were done by using STATISICA 8.0. The results are presented in Table 4.

The first dominant factor, PM_{2.5}, had high loading (greater than 0.5) of almost the same elements in both cities. PM was typical urban and it was a mixture of traffic dust (Cu, Zn, Sb, and Pb) (Lammel et al. 2002; Laugh et al. 2005; Sternbeck et al. 2002) and products of combustion of hard coal and hard coal dust (S, Se, K, and Cl; Begun et al. 2005), wastes (Cu, Mn, Pb, Sb, Zn, Cl, and Br; Chueinta et al. 2000; Vallius et al. 2005), and biomass (S and K; Begun et al. 2005) in domestic furnaces. This source contributed 78% to the PM_{2.5} concentrations in Katowice and 36% in Zabrze. EF_K was high, so K in Katowice might originate from combustion.

In Katowice, factor 1 had lower contributions to the daily PM_{2.5} concentrations in summer than in winter (Fig. 5b). It reflects the combustion of fossil fuels and wastes in the local (domestic) heat-generating furnaces. Factor 1 had no seasonal effect on the daily PM_{2.5} concentrations in Zabrze (Fig. 5a). Probably they were strongly affected by the road, 200 m distant from the sampling site.

The application of the emission profiles of various processes (Chow 1995; Table 5) to the mass shares of the elements in PM in Zabrze and Katowice indicated the road traffic and combustion of hard coal, biomass, and wastes as the main sources of PM_{2.5} in Upper Silesia. The effects of the combustion and traffic were hard to separate. The elemental composition of PM_{2.5}

Table 4 Results of principal component analysis and multiple linear regression analysis for Zabrze and Katowice

	Factor 1	Factor 2	Factor 3
Zabrze			
Elements with PCA loadings ≥0.5	Cl, Mn, Fe, Cu, Zn, Br, Pb	S, Ca, Ti, Sb	Al, K, Sr
Variance, %	35.1	20.2	13.8
Average contribution to PM _{2.5} concentrations in sampling period (MLRA) ^a , %	35.6	10.7	23.7
Katowice			
Elements with PCA loadings ≥0.5	S, Cl, K, Cu, Zn, Br, Sb, Pb	Ti, Cr, Mn, Fe	S, Ca, Se
Variance, %	32.6	16.1	11.2
Average contribution to PM _{2.5} concentrations in sampling period (MLRA) ^a , %	77.7	14.8	3.7

PCA principal component analysis, MLRA multiple linear regression analysis

^a The sets of the measured PM_{2.5} diurnal concentrations and the concentrations computed for each day from the MLRA-determined contributions were substantially correlated ($R^2=0.88$ for Katowice and $R^2=0.79$ for Zabrze)

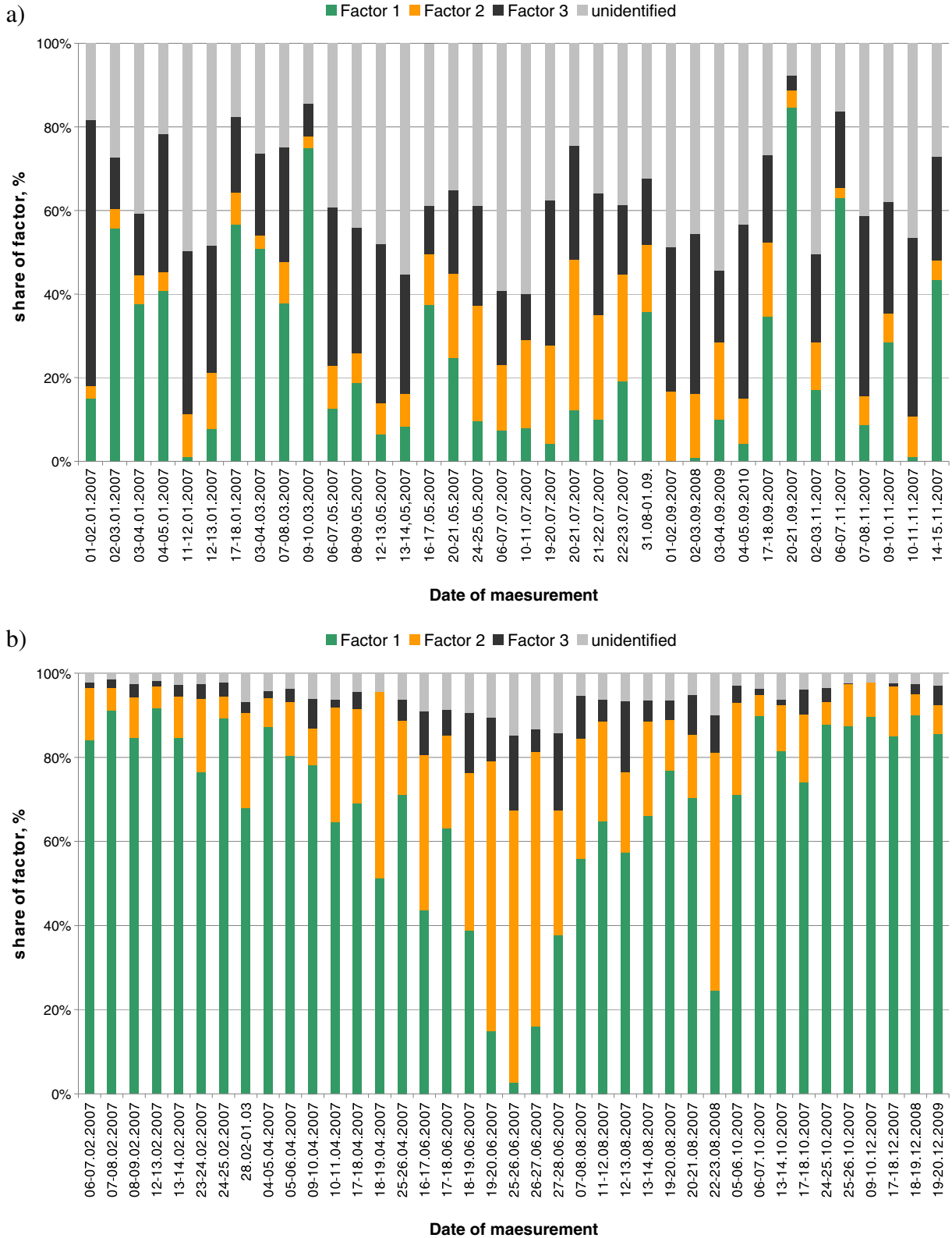


Fig. 5 Daily contributions of PM_{2,5} sources in Zabrze (a) and Katowice (b)

Table 5 Elements occurring in particles of PM_{2.5} from various sources

Source of particles ≤2.5 μm	Content of PM _{2.5} (percent mass)							
	<0.1% (Chow 1995)	This study ^a	0.1–1% (Chow 1995)	This study	1–10% (Chow 1995)	>10% (Chow 1995)	This study	This study
Motor vehicles	Cr, Ni, Y, Sr, Ba	V, Rb, Co, Ni, Se, Cd, Te, As, Cr, Mo, Ag, Ti, Br, Sr, Sb, Cu, Ba, Mn ^b	(Chow 1995) Si, Cl, Al, P, Ca, Mn, Fe, Zn, Br, Pb	This study Pb, Ca, Na, Mg, Zn, Fe, K, Al	(Chow 1995) SO ₄ ²⁻ , NH ₄ ⁺ , S, Cl ⁻ , NO ₃	OC, EC	Cl, Si, S	OC, EC
Combustion of biomass	Ca, Fe, Mn, Zn, Br, Rb, Pb		(Chow 1995) NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , Na ⁺ , S		(Chow 1995) Cl ⁻ , K ⁺ , Cl, K	OC, EC		OC, EC
Oil incineration	K ⁺ , OC, Cl, Ti, Cr, Co, Ga, Se		(Chow 1995) NH ₄ ⁺ , Na ⁺ , Zn, Fe, Si		(Chow 1995) V, OC, EC, Ni	S, SO ₄ ²⁻		
Waste incineration	V, Mn, Cu, Ag, Sn		(Chow 1995) K ⁺ , Al, Ti, Zn, Hg		(Chow 1995) NO ₃ ⁻ , Na ⁺ , EC, Si, S, Ca, Fe, Br, La, Pb	SO ₄ ²⁻ , NH ₄ ⁺ , OC, Cl		
Coal-fuelled boiler	Cl, Cr, Mn, Ga, As, Se, Br, Rb, Zr		(Chow 1995) NH ₄ ⁺ , P, K, Ti, V, Ni, Zn, Sr, Ba, Pb		(Chow 1995) SO ₄ ²⁻ , OC, EC, Al, S, Ca, Fe	Si		
Oil-fuelled power station	V, Ni, Se, As, Br, Ba		(Chow 1995) Al, Si, P, K, Zn		(Chow 1995) NH ₄ ⁺ , OC, EC, Na, Ca, Pb	S, SO ₄ ²⁻		
Melting furnace	V, Mn, Sb, Cr, Ti		(Chow 1995) Cd, Zn, Mg, Na, Ca, K, Se		(Chow 1995) Fe, Cu, As, Pb	S		
Antimony roaster	V, Cl, Ni, Mn		(Chow 1995) SO ₄ ²⁻ , Sb, Pb		(Chow 1995) S	–		

^a Daily mass shares of an element in PM_{2.5} were computed and then the mean was taken; the groups for Katowice comprised the same elements as the respective groups for Zabrze

^b Mass shares of Na, Mg, V, Co, Ni, As, Rb, Mo, Ag, Cd, and Te in PM_{2.5} were computed from C2' (average of 15 C2', Table 2)

For a particular source, symbols of elements whose PM_{2.5} mass shares in Katowice and Zabrze are in the same percentage ranges as in Chow 1995, are in bold

alone did not allow for the assessment of the combustion contributions to the PM_{2.5} concentrations.

The effect of an industrial process was indicated by PCA in Katowice. In average, factor 2, with Cr, Mn, Fe, and Ti, contributed 14.8% to the PM_{2.5} concentrations in Katowice (Table 4). This effect was clearer in summer, when the factor 1 effects weakened (Fig. 5). It might mean as well iron and steel metallurgy contribution (Querol et al. 2007) as a non-ferrous smelter activity (some characteristic elements were in factor 1).

Factor 3, comprising S, Ca, and Se in Katowice, indicated the contribution of coal-fired power plants to the PM_{2.5} concentrations (Begun et al. 2005; Biegalski and Hopke 2004; Ross 1985; Table 5). The daily contributions did not vary much (Fig. 5); the yearly one was not greater than 4% (Table 4). In Zabrze, this contribution was greater (about 10%)—factor 2 with S, Ca, Ti, and Sb (Table 4). But the sampling site in Zabrze lies within the effect of an iron foundry and a ceramic plant, and the traffic emission was significant in this area (secondary soil and road dust); therefore, the elements in factor 2 in Zabrze (especially Ti and Sb) might partially come from these sources. It agrees with the high contribution of factor 2 to the summer PM_{2.5} concentrations in Zabrze (Fig. 5). Factor 3 in Zabrze, with Al, K, and Sr (Table 4), might indicate combined contribution (24%) of natural sources (Begun et al. 2005) and biomass burning (Li and Shao 2010) to the PM_{2.5} concentrations.

Conclusions

With the use of an X-ray fluorescence spectrometer, calibrated for elemental analyses of PM_{2.5}, besides the standard analyses, the environmental mobility of PM_{2.5}-related elements can be determined. The technique for the determination of the concentrations of the water-soluble fraction and/or mobility of some elements, presented here, is universal. By avoiding the problems with solvents and allowing for direct-on-filter measurements, without the mineralization stage, it simplifies analyses; by replacing the variety of commonly used techniques, it may unify the results from various locations.

In Upper Silesia, the mobility of the PM_{2.5}-related elements may be expressed as the combined contribution of their water-soluble and exchangeable fractions to PM_{2.5}. The mobility of PM_{2.5}-related Al and Si

almost entirely depends on the exchangeable fraction. This fraction, to a great extent, also determines the mobility of Ti, Se, Sr, Sb, and Pb. The water-soluble fraction is responsible for the mobility of S, Cl, K, Ca, and of the majority of heavy metals.

In general, the mobility and the concentrations of the elements were almost the same in Zabrze and Katowice. PM_{2.5}-related Al, Si, S, Cl, K, Ca, Fe, Zn, and Pb had the greatest concentrations, and their mobility, in general, was greater than 70% in both cities. The mobility of crustal Al and Si was 40–66%. Fe and Cu had mobility lower than 30%. The average yearly concentration of PM_{2.5} in Upper Silesia, despite its 50% drop during the last two decades, was high in 2007 (22 µg/m³ in Zabrze and 31 µg/m³ in Katowice).

Combustion of various materials in domestic furnaces (hard coal, biomass, garbage, and oil) and of liquid fuels in car engines contributed 78% in Katowice and 36% in Zabrze to PM_{2.5} (traffic and municipal emissions). Other identified sources were coal-fuelled power plants (pollution characteristic of a coal-fuelled boiler) and soil and road dusts in Zabrze and an industrial source, probably a non-ferrous smelter or/and a steelwork, and power plants in Katowice.

The congruence of the measured diurnal PM_{2.5} concentrations and the concentrations determined by means of combined PCA and MLRA proves adequacy of the mathematical methods used for finding the sources of PM_{2.5} in Silesia. However, the identification of the PM_{2.5} source categories is questionable—it needs more precise both emission source profiles and PM_{2.5} chemical composition.

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