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# A Study on the Seasonal Mass Closure of Ambient Fine and Coarse Dusts in Zabrze, Poland

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**Abstract** Diurnal samples of $PM_{2.5}$ and $PM_{2.5–10}$ were taken in an urban background area in Zabrze (Upper Silesia in southern Poland) in the winter (January–March) and summer (July–September) of 2009. The samples were analyzed for carbon (organic and elemental), water soluble ions ($Na^+$, $NH_4{}^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $F^-$, $Cl^-$, $NO_3{}^-$, $PO_4{}^{3-}$, $SO_4{}^{2-}$) and concentrations of 27 elements by using, respectively, a Behr C50 IRF carbon analyzer, a Herisau Metrohm AG ion chromatograph, and a PANalitycal EPSILON 5 X-ray fluorescence spectrometer. To perform the mass closure calculations for both dust fractions in the two periods, the particulate matter (PM) chemical components were categorized into organic matter, elemental carbon, secondary inorganic aerosol, crustal matter, marine components and unidentified matter. The chemical composition of the two dust fractions and the element enrichment coefficients in the two seasons, referred to proper emission profiles, proved about 80% of $PM_{2.5}$ and more than 50% (in winter 65%) of $PM_{2.5–10}$ mass coming from anthropogenic sources, mainly from fuel combustion and specific municipal emission shaping the winter emission of ambient dust in the area.

**Keywords** $PM_{2.5}$ · $PM_{2.5–10}$ · OC · EC · SIA · EF · Chemical mass closure · Municipal emission

Ambient particulate matter (PM) combines constituents having whole variety of physicochemical properties (Chow 1995; Hinds 1998). The chemical composition of fine ($PM_{2.5}$) and coarse ($PM_{2.5–10}$) dusts and identification of their sources are the concern of many works (Perez et al. 2008; Viana et al. 2008; Pey et al. 2009; Putaud et al. 2010; Dabek-Zlotorzynska et al. 2011). In general, more attention is paid to $PM_{2.5}$ because of the health effects the inhaled fine dust exerts on humans (Englert 2004), nevertheless, in some areas, $PM_{2.5–10}$ appears equally important (Kim and Jo 2006; Amato et al. 2009).

Data on $PM_{2.5}$ and $PM_{2.5–10}$, on their concentrations and chemical composition, in Eastern Europe are not very abundant (EMEP 2009; Putaud et al. 2010). The data on the properties and chemical composition of PM in Poland are yet more incomplete (Houthuijs et al. 2001; Zwoździak et al. 2001; Pastuszka et al. 2003, 2010; Rogula-Kozłowska et al. 2008).

The paper presents results of the chemical analyses of $PM_{2.5}$ and $PM_{2.5–10}$ in Zabrze, in summer and winter, and indicates the probable sources of both dust fractions.

## Materials and Methods

The investigation took place in Zabrze, Upper Silesia (Fig. 1), the region of Poland where the recent two decades of economical changes forced the biggest drop in air pollution in Poland, and where ancient steel works, cokeries and coal mines, together with road traffic and combustion of fossil fuels for energy production still maintain high concentrations of ambient dust (Pastuszka et al. 2003, 2010; Rogula-Kozlowska et al. 2008). PM was sampled at an urban background sampling point (Directive 2008) with a two-channel Ruprecht & Patashnik Dichotomus Partisol

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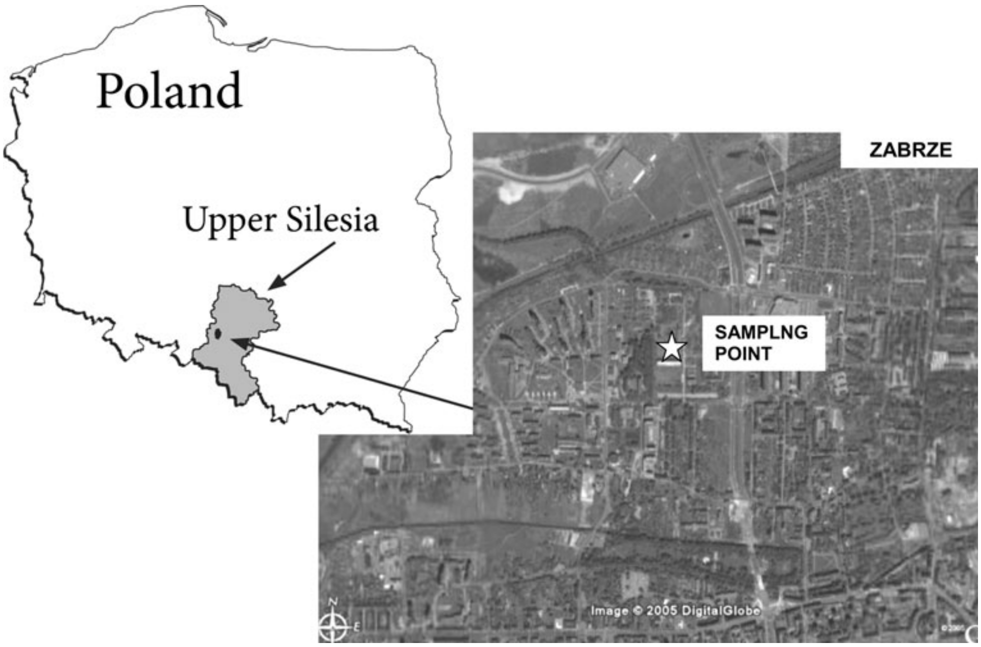

**Fig. 1** Location of the sampling point

2025 in winter (January–March, heating season) and summer (July–September, non-heating season). The PM concentrations were determined gravimetrically.

Two daily samples of each PM fraction from each week of the sampling period, taken on Teflon filters (22 winter and 26 summer samples of each $PM_{2.5}$ and $PM_{2.5–10}$), underwent a direct-on-filter elemental analysis followed by an analysis for ion content. Three daily samples of each PM fraction from each week, taken on quartz fiber filters (33 winter and 39 summer samples of each $PM_{2.5}$ and $PM_{2.5–10}$) were analyzed for OC and EC contents.

Before exposing, the quartz filters were pre-fired in a muffle furnace for 4 h at 900°C. Before and after exposing, all the filters were conditioned in a weighing room (48 h, relative air humidity 45 ± 5%, air temperature 20 ± 2°C) and weighed twice, with 24 h period between, on a Mettler Toledo microbalance (resolution 2 µg).

The elemental composition of $PM_{2.5}$ and $PM_{2.5–10}$ was determined by means of energy dispersive X-ray fluorescence (EDXRF). A PANalytical Epsilon 5, calibrated with the use of thin-layer single-element Micromatter standards (US EPA 1999), was used to measure the total concentrations of the elements. NIST SRM2873 samples were measured weekly (the recoveries were between 85% and 120% of the certified value, except 52% and 39% recoveries of V and Co) and the monitor monthly to control the performance of the analytical procedure. The detection limits were from 0.2 ng/cm$^2$ (Se) to 21.3 ng/cm$^2$ (Si).

The OC and EC contents were determined by using a Behr C50 IRF. A heated sample releases organic substances which is oxidized with copper (II) oxide (CuO) to carbon dioxide ($CO_2$). Combustion of the sample in pure oxide allows for determination of EC. The $CO_2$ content in the gas stream was determined by means of non-dispersive infrared spectrometry (NDIR, $\lambda = 4.26$ µm). The gas mixture with certified $CO_2$ content was used to calibrate the apparatus. The standard recovery (RM 8785 NIST and RM 8786 NIST) for this calibration was 119% for EC and 79% for OC.

Ion content in extracts was determined using a Metrohm ion chromatograph (Herisau Metrohm AG, Swiss). The method was validated by using the CRM Fluka products no. 89316 and no. 89886, the standard recovery was 92%–109% of the certified value, the detection limits were from 0.02 mg/L ($NH_4^+$) to 0.17 mg/L ($Mg^+$). The water extracts of $PM_{2.5}$ and $PM_{2.5–10}$ were made by ultrasonizing the sample on Teflon filters in 50 cm$^3$ of de-ionized water for 60 min at temperature 15°C, then shaking for about 12 h (18°C, 60 r/min). Before the extraction, the filter surface was moistened with 0.1 cm$^3$ of ethanol (96%, pure).

## Results and Discussion

The concentrations of $PM_{2.5}$ and $PM_{2.5–10}$ and the chemical composition of both fractions in the summer and winter of 2009 are presented in Table 1.

To determine the anthropogenic effect on the element concentrations in PM enrichment factors (*EF*) were analyzed. The enrichment factor $EF_x$ for the element $x$ is defined as:

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

**Table 1** Concentration of $PM_{2.5}$, $PM_{2.5-10}$ and of their components in summer and winter in Zabrze in 2009

| | Summer | | Winter | | Summer | Winter | | Summer | | Winter | | Summer | Winter |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $PM_{2.5}$ (µg/m$^3$) | $PM_{2.5-10}$ (µg/m$^3$) | $PM_{2.5}$ (µg/m$^3$) | $PM_{2.5-10}$ (µg/m$^3$) | $PM_{2.5}/PM_{10}$ | $PM_{2.5}/PM_{10}$ | | $PM_{2.5}$ (ng/m$^3$) | $PM_{2.5-10}$ (ng/m$^3$) | $PM_{2.5}$ (ng/m$^3$) | $PM_{2.5-10}$ (ng/m$^3$) | $PM_{2.5}/PM_{10}$ | $PM_{2.5}/PM_{10}$ |
| PM | 18.44 | 12.81 | 66.85 | 8.9 | 0.59 | 0.88 | Ti | 2.01 | 20.22 | 0.54 | 13.5 | 0.09 | 0.04 |
| OC | 4.21 | 1.54 | 9.9 | 1.46 | 0.73 | 0.87 | V | bld | bld | bld | bdl | – | – |
| EC | 4.12 | 1.53 | 19.34 | 1.75 | 0.73 | 0.92 | Cr | 0.23 | 0.08 | 1.32 | 0.68 | 0.74 | 0.66 |
| $Na^+$ | 0.24 | 0.18 | 0.45 | 0.21 | 0.57 | 0.68 | Mn | 16.71 | 17.7 | 21.6 | 7.9 | 0.49 | 0.73 |
| $NH_4^+$ | 0.53 | 0.07 | 2.01 | 0.07 | 0.88 | 0.97 | Co | bld | bld | bld | bdl | – | – |
| $K^+$ | 0.14 | bld | 0.4 | 0.12 | – | 0.77 | Ni | 0.21 | 0.17 | 0.36 | 0.84 | 0.55 | 0.30 |
| $Mg^{2+}$ | bld | bld | 0.14 | bld | – | – | Cu | 8.14 | 6.29 | 8.88 | 4.21 | 0.56 | 0.68 |
| $Ca^{2+}$ | bld | bld | 0.47 | bld | – | – | Zn | 65.99 | 32.84 | 184.49 | 17.83 | 0.67 | 0.91 |
| $F^-$ | 0.06 | 0.04 | 0.08 | 0.06 | 0.60 | 0.57 | As | bld | bld | 9.59 | bld | – | – |
| $Cl^-$ | 0.04 | 0.08 | 1.53 | 0.15 | 0.33 | 0.91 | Se | 0.46 | 0.01 | 0.45 | 0.02 | 0.98 | 0.96 |
| $NO_3^-$ | 0.51 | 0.82 | 3.12 | 0.65 | 0.38 | 0.83 | Br | 1.61 | 0.15 | 25.1 | bld | 0.91 | – |
| $PO_4^{3-}$ | bld | bld | 0.25 | 0.1 | – | 0.71 | Rb | 0.13 | 0.16 | 0.03 | 0.38 | 0.45 | 0.07 |
| $SO_4^{2-}$ | 3.23 | 1.06 | 5.51 | 0.91 | 0.75 | 0.86 | Sr | 1.61 | 3.5 | 1.25 | 2.58 | 0.32 | 0.33 |
| Al | 0.12 | 0.64 | 0 | 0.4 | 0.16 | 0.00 | Mo | 2.12 | 2.71 | 2.68 | 2.06 | 0.44 | 0.57 |
| Si | 0.31 | 1.52 | 0.11 | 0.67 | 0.17 | 0.14 | Ag | 1.44 | 2.3 | 0.97 | 2.22 | 0.39 | 0.30 |
| S | 1.65 | 0.15 | 3.35 | 0.27 | 0.92 | 0.93 | Cd | 1.23 | 0.35 | 1.14 | bld | 0.78 | – |
| Cl | 0.04 | 0.08 | 3.45 | 0.08 | 0.33 | 0.98 | Sb | 0.15 | bld | 3.66 | bld | – | – |
| K | 0.17 | 0.14 | 0.34 | 0.08 | 0.55 | 0.81 | Te | 0.52 | 1.04 | 0.48 | 0.34 | 0.33 | 0.59 |
| Ca | 0.08 | 0.33 | 0.01 | 0.13 | 0.20 | 0.07 | Ba | 0.15 | 1.67 | bld | 1.58 | 0.08 | – |
| Fe | 0.15 | 0.44 | 0.18 | 0.29 | 0.25 | 0.38 | Pb | 23.74 | 11.25 | 49.71 | 4.29 | 0.68 | 0.92 |

*bld* below limit detection

where $C_x$ and $C_{ref}$ are the concentrations of the element $x$ and the reference element, and $(C_x/C_{ref})_{PM}$ and $(C_x/C_{ref})_{crust}$ are the proportions of these concentrations in PM and in the Earth crust, respectively. The observed concentrations $C_x$ should have been related to the concentration $C_{si}$ of silicone, the marker element for the Earth crust, but because of lower detection limit and higher standard recovery Al was chosen to be the reference element. Consequently, $EF_{Al} = 1$.

The chemical composition of the upper continental crust was taken from Wedepohl (1995).

The low value of $EF_x$ indicates the crustal origin of the element $x$ and negligible anthropogenic effect on its concentrations. High $EF_x$ suggests the effect of anthropogenic sources. In Table 2, the symbols of the elements $x$ with high $EF_x$ are in underlined bolds. The symbols of the elements that have low summer *EFs* as the $PM_{2.5}$-related and low both summer and winter *EFs* as the $PM_{2.5-10}$-related are in bold; as $PM_{2.5}$-related, these elements have very high winter *EFs*.

On the basis of the chemical composition of the $PM_{2.5}$ and $PM_{2.5-10}$ samples (Table 1), the chemical mass closure was checked for each of $PM_{2.5}$ and $PM_{2.5-10}$ in the summer and winter of 2009. The chemical components in PM were divided into eight classes – Table 3, Fig. 2.

**Table 2** Enrichment factors for $PM_{2.5}$- and $PM_{2.5-10}$-related elements in Zabrze, Poland

| | Summer | | Winter | |
|---|---|---|---|---|
| | $PM_{2.5}$ | $PM_{2.5-10}$ | $PM_{2.5}$ | $PM_{2.5-10}$ |
| Al | 1 | 1 | 1 | 1 |
| **Si** | 0.66 | 0.61 | 35.66 | 0.42 |
| **S** | 1108.32 | 18.89 | 350854 | 53.76 |
| **Cl** | 44.01 | 15.52 | 539399 | 25.07 |
| **K** | 3.88 | 0.58 | 1179.79 | 0.52 |
| **Ca** | 1.83 | 1.36 | 22.79 | 0.87 |
| **Ti** | 0.41 | 0.79 | 17.22 | 0.83 |
| **Cr** | 4.2 | 0.28 | 3782.63 | 3.74 |
| **Mn** | 20.28 | 4.09 | 4095.63 | 2.89 |
| **Fe** | 3.09 | 1.73 | 574.39 | 1.8 |
| **Ni** | 7.24 | 1.11 | 1952.68 | 8.71 |
| **Cu** | 363.93 | 53.58 | 62051 | 56.59 |
| **Zn** | 811.76 | 76.91 | 354520 | 66 |
| **As** | – | – | 478971 | – |
| **Se** | 3539.34 | 8.42 | 543772 | 43.9 |
| **Br** | 642.75 | 11.65 | 1567737 | – |
| **Rb** | 0.78 | 0.18 | 25.11 | 0.67 |
| **Sr** | 3.26 | 1.35 | 396.16 | 1.57 |
| **Mo** | 970.47 | 235.51 | 191274 | 282.54 |
| **Ag** | 16707.9 | 5100.6 | 1756330 | 7760.68 |
| **Cd** | 7692.48 | 415.78 | 1118664 | – |
| **Sb** | 315.88 | – | 1180298 | – |
| Ba | 0.15 | 0.3 | – | 0.46 |
| **Pb** | 893.19 | 80.6 | 292157 | 48.55 |

The average of the $PM_{2.5}/PM_{10}$ proportions from 25 cities of Central and Western Europe was 0.68; the average for 4 southern Poland cities was 0.75 (Houthuijs et al. 2001). In Zabrze, in 2009, the average $PM_{2.5}/PM_{10}$ was 0.73 – it has not changed for a decade and has been slightly higher than in other European cities. The concentrations of $PM_{2.5}$ and the proportion $PM_{2.5}/PM_{10}$ (Table 1) in Zabrze in 2009, like in the preceding years (Klejnowski et al. 2007, 2009), were higher in winter than in summer. Such high winter $PM_{2.5}$ concentrations contribute to violating of the yearly standards for the $PM_{2.5}$ and $PM_{10}$ concentrations (25 and 40 µg/m$^3$, Directive 2008) in Zabrze. These high winter PM concentrations are caused by very low ambient temperature, shallow inversion layer, and intense municipal emission from combustion usually occurring in the beginning of a year. The meteorological conditions together with the high PM and $SO_2$ concentrations are favorable for occurrence of smog episodes in southern Poland (Mira-Salama et al. 2008; Pastuszka et al. 2010; Juda-Rezler et al. 2011).

The chemical compositions of $PM_{2.5}$ and $PM_{2.5-10}$ differ (Table 1, Fig. 2) – it is mainly due to different both origin and atmospheric lifetime of the two PM fractions. The composition of each fraction varies depending on a season (Tables 1, 3). $PM_{2.5}$ in Zabrze consists mainly of carbon compounds (yearly mean is 52% of the mass; 5% greater in winter than in summer) and of the secondary particles (in average 20% of the mass). Transformations of gas precursors are more intense in summer than in winter (Alastuey et al. 2004) and, consequently, the contribution of secondary inorganic aerosol (SIA) to $PM_{2.5}$ in Zabrze is higher in summer than in winter by 7%. Nevertheless, equally in winter and in summer, SIA content of $PM_{2.5}$ in Zabrze is much higher than in other European countries (Table 3).

$PM_{2.5-10}$ in Zabrze, in both seasons, consists mainly of crustal silicone, iron, calcium, and potassium oxides, carbon compounds, probably from organic debris (Hinds 1998) and fuel combustion (hydrocarbons adsorbed onto big particles and soot agglomerates, great, about 42.7%, contribution of carbon compounds to the $PM_{2.5-10}$ mass in winter). The contributions of SIA to $PM_{2.5-10}$ in winter and summer are similar and resemble the contributions in Zurich, Barcelona, Duisburg, Prague and Amsterdam (Table 3).

The ambient concentrations of EC (Table 1) and its contributions to $PM_{2.5}$ and $PM_{2.5-10}$ (Table 3) are very high in both seasons. The average EC mass contributions to the two fractions in 2009 are almost equal to, and to $PM_{2.5}$ in winter even higher than, the organic matter (OM) contributions. It had never occurred in other European cities (Table 3). The standard recoveries show that the method slightly overestimates the EC and underestimates the OC

**Table 3** The percentage shares of the chemical components in $PM_{2.5}$ and $PM_{2.5-10}$ in Zabrze and other European cities

| | Zabrze | | | | Zurich[1] | | Barcelona[2] | | Duisburg[3] | | Prague[3] | | Amsterdam[3] | | Helsinki[3] | | Athens[3] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Summer | | Winter | | Year | | Year | | Winter | | Winter | | Winter | | Summer | | Summer | |
| | f[4] | c[5] | f | c | f | c | f | c | f | c | f | c | f | c | f | c | f | c |
| OM | 32.0 | 16.8 | 20.7 | 23.0 | 23.7 | 9.6 | 34 | <1 | 31 | 24 | 54 | 27 | 23 | 15 | 46 | 15 | 35 | 18 |
| EC | 22.3 | 11.9 | 28.9 | 19.7 | 8.8 | 7.4 | | | 9.0 | 2.9 | 5.7 | 5.5 | 5.4 | 2.3 | 8.4 | 1.6 | 6.6 | 0.96 |
| $NH_4^+$ | 2.9 | 0.5 | 3.0 | 0.8 | 10.4 | 2.5 | 5 | 0 | 7.5 | 0.96 | 7.1 | 2.1 | 7.0 | 2.7 | 8.6 | 0.16 | 9.3 | 0.06 |
| $NO_3^-$ | 2.8 | 6.4 | 4.7 | 7.3 | 17.3 | 10.3 | 9 | 16 | 13 | 12 | 7.5 | 6.5 | 18 | 14 | 4.7 | 3.7 | 1.1 | 5.5 |
| $SO_4^{2-}$ | 17.5 | 8.3 | 8.2 | 10.2 | 17.3 | 6.7 | 16 | 4 | 19[6] | 3.4 | 20 | 6.8 | 14 | 5.3 | 26 | 0.78 | 31 | 1.3 |
| MC | 1.5 | 2.0 | 5.8 | 3.3 | – | – | 2 | 10 | 7.9[7] | 19 | 1.1 | 7.7 | 10 | 34 | 5.8 | 7.4 | 1.3 | 3.5 |
| CM | 10.6 | 55.9 | 0.1 | 41.3 | 7.4 | 19.9 | 16 | 63 | 5.6[8] | 27.9 | 2.5 | 39 | 2.6 | 22.1 | 6.4 | 47.6 | 5.1 | 65 |
| OE | 4.0 | 1.3 | 8.8 | 1.4 | 2.2 | 5.2 | – | – | 1.2 | 1.8 | 0.47 | 1.1 | 0.32 | 0.59 | 0.35 | 0.66 | 0.34 | 0.39 |
| OM + EC | 54.3 | 28.7 | 49.6 | 42.7 | 32.5 | 17 | 34 | <1 | 40 | 26.9 | 59.7 | 32.5 | 28.4 | 17.3 | 54.4 | 16.6 | 41.6 | 18.96 |
| SIA | 23.2 | 15.2 | 15.9 | 18.3 | 45 | 19.5 | 30 | 20 | 39.5 | 16.36 | 34.6 | 15.4 | 39 | 22 | 39.3 | 4.64 | 41.4 | 6.86 |
| CM | 10.6 | 55.9 | 0.1 | 41.3 | 7.4 | 19.9 | 16 | 63 | 5.6 | 27.9 | 2.5 | 39 | 2.6 | 22.1 | 6.4 | 47.6 | 5.1 | 65 |
| MC + OE | 5.5 | 3.3 | 14.6 | 4.7 | 2.2 | 5.2 | 2 | 10 | 9.1 | 20.8 | 1.57 | 8.8 | 10.32 | 34.59 | 6.15 | 8.06 | 1.64 | 3.89 |
| Σ | 93.6 | 103.1 | 80.2 | 107.0 | 87.1 | 61.6 | 82 | 93 | 94.2 | 91.96 | 98.37 | 95.7 | 80.32 | 95.99 | 106.25 | 76.9 | 89.74 | 94.71 |

[1] (Hüeglin et al. 2005); [2] (Perez et al. 2008); [3] (Sillanpää et al. 2006); [4] f – $PM_{2.5}$; [5] c – $PM_{2.5-10}$, [6] – Nss-$SO_4^{2-}$ (non sea salt-sulfate), [7] SS (sea salt), [8] WSS + WIS (water-soluble soil + water-insoluble soil)

*OM* organic matter = 1.4*[OC], *MC* marine components = $[Na^+]+[Cl^-]$, **CM* crustal matter = 2.2*[Al] + 2.49*[Si] + 1.63*[Ca] + 2.42*[Fe] + 1.94*[Ti] + 2.4*[K], after Malm et al. (1994) supplemented with 2.4*[K] due to stoichiometric concentration of $K_2O$, * *OE* other elements = sum of all trace elements (for *S* the concentration of water-soluble compounds was subtracted), without major crustal elements (Al, Si, Ca, Fe, Ti, K) and marine components (MC), *SIA* secondary inorganic aerosol = $[SO_4^{2-}] + [NO_3^-] + [NH_4^+]$

* High *EFs* suggest anthropogenic effect on the concentrations of $PM_{2.5}$-related Si, K, Ca, Ti and Fe in winter (Table 2). Consequently, it was assumed that the winter total concentrations of these elements in $PM_{2.5}$ cannot be used to estimate the contribution of CM. The concentrations 21.6, 3.0, 3.0, 0.27, 1.77 ng/m$^3$ of Si, K, Ca, Ti and Fe, respectively, yielded the *EFs* similar to the summer *EFs* of these elements. The difference between these concentrations and the concentrations of $PM_{2.5}$-related Si, K, Ca, Ti and Fe in winter is caused by the anthropogenic emission (it was included into OE for the winter $PM_{2.5}$)

Low *EFs* suggest no anthropogenic effect on $PM_{2.5}$-related Rb, Sr and Ba in summer and $PM_{2.5-10}$-releted Cr, Mn, Ni, Rb, Sr and Ba in summer and winter (Table 2), therefore their concentrations (Table 1) were added to the concentrations of CM for summer $PM_{2.5}$ and winter and summer $PM_{2.5-10}$ and excluded from OE. In the Silesian dust, these elements may occur in mixtures of variously configured and proportioned minerals: chromite, crocoite, manganite, pyrolusite, gamierite, pentlandite, celestite, lepidolite, barite, vaterite etc., so their compound-dependent concentrations were not computed and instead their total concentrations were added to CM

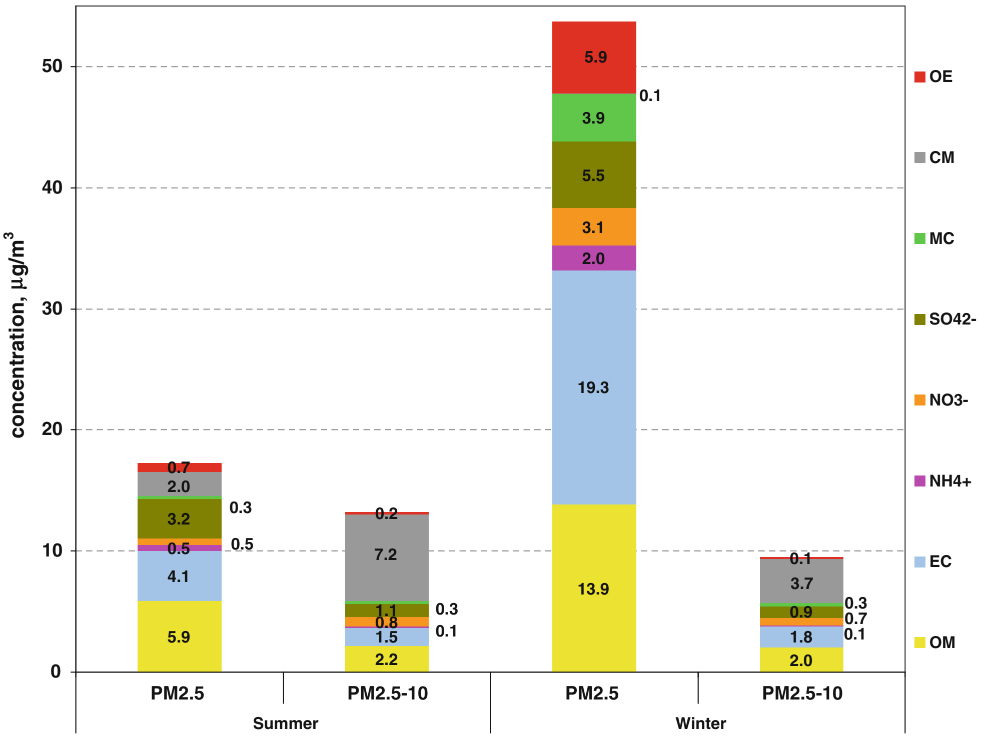

**Fig. 2** Concentrations (µg/m$^3$) of the components of PM$_{2.5}$ of PM$_{2.5–10}$ in the summer and winter of 2009 (symbols explained below Table 3)

concentrations, and other (e.g. thermo-optical) methods would probably give other relations between EC and OC in PM in Zabrze. However, the high concentrations of EC in the two dust fractions, compared to other parts of Europe, still confirm the specificity of the PM emission in southern Poland. The production of energy in Poland bases on combustion of hard and brown coals (94% of the total energy production). In winter, the emission from municipal sources, negligible in majority of other European countries, adds greatly to the emissions within Polish urbanized areas. The chemical composition of PM$_{2.5}$ in Zabrze fits to the profiles of the emissions from combustion of fuel in car engines, combustion of biomass and furnace oil, smelting, combustion of wastes in winter (municipal emission) and combustion of coal in power plants in summer (Table 4). In winter, the contribution of PM from coal combustion for energy production (mainly secondary particles from transformations of SO$_2$ and NO$_x$ from power stations) to the total PM$_{2.5}$ concentrations is small relative to the contribution of PM from combustion of low quality coal (soot, compounds of sulfur, chlorine and silicone, trace elements) and a wide spectrum of wastes (municipal and other: plastics, Styrofoam, rubber, lacquered materials) in inefficient ancient domestic furnaces.

Significant parts (10 and 4%) of PM$_{2.5}$ and PM$_{2.5–10}$ masses are MC + OE, i.e. combination of marine components (MC) and other elements (OE). In Zabrze, both, like the carbon compounds, probably come from combustion—their concentrations and contributions to the PM$_{2.5}$ mass, the proportions PM$_{2.5}$/PM$_{10}$ (e.g. for Cl, K, and Pb) are higher in winter (Tables 1 and 3), and they are anthropogenic (even the PM$_{2.5}$ related crustal elements in winter, Table 2). The mass concentration of the PM$_{2.5}$ related MC + OE in winter is almost 10 µg/m$^3$, while in summer it is not greater than 1 µg/m$^3$ (Fig. 2).

In many places, the concentrations of MC (especially of Na$^+$) allow for estimating sea salt content in PM (especially in PM$_{2.5–10}$, Sillanpää et al. 2006; Viana et al. 2008). The distance from Zabrze to the nearest sea (the Baltic Sea, about 500 km) precludes the effect of a sea. PM$_{2.5–10}$ in Zabrze (equally in winter and in summer) comes from three sources: paved and non-paved roads, and natural soil – Table 4.

In Zabrze, the mass of natural soil dust (CM) is in average 55% of the PM$_{2.5–10}$ mass in summer and 40% in winter. Some part of PM$_{2.5–10}$ may come from local traffic on two local roads, distant by about 100 m from the measuring point, and one greater, distant by about 500 m. The mix of road dust (particles from car bodies, tires, break shoes and pads, often absorbing fuel combustion products, Han et al. 2011), soil, and sand contributes greatly to PM$_{2.5–10}$. The relatively high concentrations of the PM$_{2.5–10}$ related MC (sodium and chlorine) in winter may be due to salt applied to icy roads in winter.

Concluding, in Zabrze, about 64% of the PM$_{2.5}$ mass in winter and 60% in summer are anthropogenic (OM + EC + MC + OE–mainly from combustion). SIA, whose concentrations depend mainly on emission of SO$_2$ and NO$_x$, but also on insolation, air humidity, neutralizing compounds, are 23% of the PM$_{2.5}$ mass in summer and 16% in winter.

**Table 4** Compounds in $PM_{2.5}$ and $PM_{2.5–10}$ from various sources (Chow 1995) and in $PM_{2.5}$ and $PM_{2.5–10}$ in winter and summer 2009 in Zabrze

| | <0.1% | | 0.1-1% | | 1-10% | | >10% | |
|---|---|---|---|---|---|---|---|---|
| | (Chow, 1995) | *Zabrze | (Chow, 1995) | Zabrze | (Chow, 1995) | Zabrze | (Chow, 1995) | Zabrze |
| | | | $PM_{2.5}$– summer | | | | | |
| Motor vehicles. | **Cr,Ni,Y,Sr,Ba | $Mg^{2+}$, $Ca^{2+}$, $PO_4^{3-}$, Ti, V, Cr, Co, Ni, Cu, As, Se, Br, Rb, Sr, Mo, Ag, Cd, Sb, Te, Ba | *Si*,Cl,Al,*P*,Ca,Mn,Fe,Zn,*Br*,Pb | K,$K^+$, $F^-$, Cl,$Cl^-$, Al, Ca, Fe, Zn, Mn, Pb | $SO_4^=$,$NH_4^\pm$ *S*,$Cl^-$,$NO_3$ | $Na^+$, $NH_4^+$, $NO_3^-$, Si | OC,EC | OC, EC, S,$SO_4^{2-}$ |
| Biomass combustion | Ca,*Fe*,*Mn*,*Zn* Br,Rb,*Pb* | | $NO_3^-$, $SO_4^=$, $NH_4^+$ $Na^+$,*S* | | $Cl^-$,$K^+$,*Cl*,*K* | | OC,EC | |
| Coal fired boiler | *Cl*,Cr,*Mn*,Ga, As Se,Br,Rb,Zr | | $NH_4^+$,P,K,*Ti*,*V* *Ni*,Zn,*Sr*,*Ba*,Pb | | $SO_4^=$,*OC*,*EC* *Al*,*S*,*Ca*,*Fe* | | *Si* | |
| Oil fired power plant | V,Ni,Se,As,Br Ba | | Al,*Si*,*P*,K,Zn | | $NH_4^+$,*OC*,*EC* Na,*Ca*,*Pb* | | S, $SO_4^=$ | |
| Antimony roaster | V,*Cl*,Ni,*Mn* | | $SO_4^=$,*Sb*,Pb | | *S* | | --- | |
| | | | $PM_{2.5}$– winter | | | | | |
| Motor vehicles. | Cr,Ni,Y,Sr,Ba | Al, Ti, V, Cr, Mn, Co, Ni, Cu, As, Se, Br, Rb, Sr, Mo, Ag, Cd, Sb, Te, Ba | Si,*Cl*,*Al*,P,Ca,*Mn*,Fe,Zn,*Br*,Pb | $Na^+$, K,$K^+$, $Mg^{2+}$, Ca, $Ca^{2+}$, $F^-$, $PO_4^{3-}$, Si, Fe, Zn, Pb | $SO_4^=$,$NH_4^+$ S,$Cl^-$,$NO_3$ | $NH_4^+$, Cl,$Cl^-$, $NO_3^-$, S,$SO_4^{2-}$ | OC,EC | OC, EC |
| Biomass combustion | *Ca*,*Fe*,Mn,*Zn* Br,Rb,*Pb* | | $NO_3^-$, $SO_4^=$, $NH_4^+$ $Na^+$,*S* | | $Cl^-$,$K^+$,Cl,*K* | | OC,EC | |
| Coal fired boiler | V,Mn,Cu,Ag Sn | | $K^+$,*Al*,*Ti* Zn,Hg | | $NO_3^-$,$Na^+$,*EC* *Si*,S,*Ca*,*Fe*, Br,La,*Pb* | | $SO_4^=$,$NH_4^\pm$ OC,*Cl* | |
| Oil fired power plant | V,Ni,Se,As,Br Ba | | *Al*,Si,P,K,Zn | | $NH_4^\pm$,*OC*,*EC* *Na*,*Ca*,*Pb* | | *S*, $SO_4^=$ | |
| Antimony roaster | V,*Cl*,Ni,Mn | | $SO_4^=$,*Sb*,Pb | | S | | --- | |
| | | | $PM_{2.5-10}$– summer | | | | | |
| Paved roads | Cr,Sr,*Pb*,Zr | $K^+$, $Mg^{2+}$, $Ca^{2+}$, $PO_4^{3-}$, V, Cr, Co, Ni, Cu, As, Se, Br, Rb, Sr, Mo, Ag, Cd, Sb, Te, Ba | $SO_4^=$,$Na^+$,$K^+$,*P*,*S*,Cl,Mn,Zn,*Ba*,Ti | $F^-$, Cl,$Cl^-$, $NH_4^+$, Zn, Ti, Mn, Pb | *EC*,Al,K,Ca,Fe | $Na^+$, $NO_3^-$, S,$SO_4^{2-}$, Al, K, Ca, Fe | OC,Si | OC, EC, Si |
| Non-paved roads | $NO_3^-$,$NH_4^+$,P,*Zn*, Sr,Ba | | $SO_4^=$,$Na^+$,$K^+$,*P*,*S*,Cl,Mn,Ti | | *OC*,Al,K,Ca,Fe | | Si | |
| Natural soil | Cr,*Mn*,*Zn*,Sr, Ba | | $Cl^-$,$Na^+$,*EC*,*P* *S*,Cl,Ti | | *OC*,Al,Mg K,Ca,Fe | | Si | |
| | | | $PM_{2.5-10}$– winter | | | | | |
| Paved roads | Cr,Sr,Pb,Zr | $Mg^{2+}$, $Ca^{2+}$, V, Cr, Co, Ni, Cu, As, Se, Br, Rb, Sr, Mo, Ag, Cd, Sb, Te, Ba, Pb | $SO_4^=$,$Na^+$,$K^+$,*P*,*S*,*Cl*,Mn,Zn,*Ba*,Ti | $NH_4^+$, $F^-$, Ti, Mn, Zn | *EC*,Al,K,Ca,Fe | $Na^+$, Cl,$Cl^-$, K,$K^+$, $NO_3^-$, $PO_4^{3-}$, Al, Si, Ca, Fe | OC,*Si* | OC, EC, S,$SO_4^{2-}$ |
| Non-paved roads | $NO_3^-$,$NH_4^+$,*P*,*Zn*, Sr,Ba | | $SO_4^=$,$Na^+$,$K^+$,*P*,*S*,*Cl*,Mn,Ti | | *OC*,Al,K,Ca,Fe | | *Si* | |
| Natural soil | Cr,*Mn*,*Zn*,Sr,Ba | | $Cl^-$,$Na^+$,*EC*,*P* *S*,*Cl*,Ti | | *OC*,Al,Mg K,Ca,Fe | | *Si* | |

* The arithmetic mean of the daily element contributions to the PM mass was the criterion for the elements to be included into a proper group (<0.1%, 0.1–1%, 1–10%); ** underlined symbols denote the elements occurring in Zabrze PM in amounts equal to amounts in the emission profiles from Chow 1995, *italic* symbols denote the elements occurring in amounts greater than amounts assigned to the sources by Chow, *underlined italic* symbols denote the elements whose amount in Zabrze PM is too low to classify them into the proper Chow group and they belong to the preceding one

Over 50% of the mass of $PM_{2.5-10}$ in summer and about 40% in winter come from natural sources (soil). The rest is the particles from road traffic, agglomerates of primary soot and hydrocarbons bound onto the surface of big particles. Within a typical urbanized area of southern Poland, over 80% of $PM_{2.5}$ and 50% of $PM_{2.5-10}$ may be directly or indirectly linked with combustion processes. High concentrations of carbon compounds, soot, and (in winter) of $PM_{2.5}$ related heavy metals (As over 9, Pb almost 50 ng/m$^3$), and also relatively high concentrations of probably wholly anthropogenic Se (coal combustion, $PM_{2.5}/PM_{10}$ for Se is close to 1), indicate that the production of almost entire heat and electric power from hard and brown coals, and the specific municipal emission in winter, are the causes of the low quality of ambient air in southern Poland during a whole year.

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