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Mass Size Distribution and Chemical Composition of the Surface Layer of Summer and Winter Airborne Particles in Zabrze, Poland

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Abstract Mass size distributions of ambient aerosol were measured in Zabrze, a heavily industrialized city of Poland, during a summer and a winter season. The chemical analyses of the surface layer of PM₁₀, PM_{2.5} and PM₁ in this area were also performed by X-ray photoelectron spectroscopy (XPS). Results suggested that the influence of an atmospheric aerosol on the health condition of Zabrze residents can be distinctly stronger in winter than in summer because of both: higher concentration level of particulate matter (PM) and higher contribution of fine particles in winter season compared to summer. In Zabrze in June (summer) PM₁₀ and PM_{2.5} reached about 20 and 14 µg/m³, respectively, while in December (winter) 57 and 51 µg/m³, respectively. The XPS analysis showed that elemental carbon is the major surface component of studied airborne particles representing about 78%–80% (atomic mass) of all detected elements.

Keywords Atmospheric aerosol · Mass size distribution · Surface composition

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Exposure to aerosol particles is related with a number of adverse health effects. Long term exposure to high concentrations of particulate matter (PM) increases the risk of lung cancer, respiratory diseases and arteriosclerosis, whereas short-term exposure peaks can cause exacerbation of several forms of respiratory diseases, including bronchitis and asthma, as well as changes in heart rate variability (Samet et al. 2000; Sorensen et al. 2003; Zhang et al. 2011).

Evidence suggests that the toxicological and carcinogenic properties of aerosol particles depend on their sizes and chemical composition (Diociaiuti et al. 2001; Cho et al. 2009). Therefore, it is important to measure the size distribution of airborne particles or, at least, the concentration of some selected fraction of total suspended particles (TSP) and their chemical composition. Most researchers agree that the following aerosol fractions should be monitored: particles with aerodynamic diameter ≤10 µm (PM₁₀), particles with aerodynamic diameter ≤2.5 µm (PM_{2.5})—so called fine or respirable particles, and particles with aerodynamic diameter ≤1 µm (PM₁). PM₁₀ represents the upper size range of particles that can pass the nose and the mouth (Pope and Dockery 1999), PM_{2.5} represents the upper size range of particles that can all enter into the respiratory tract and reach deeper parts of the lungs (Wichmann 2004), and PM₁ is the upper size for the particle fraction that includes appreciable amounts of even smaller particles that can penetrate into the bloodstream (Wichmann and Peters 2000; Spindler et al. 2010).

Although knowledge on the chemical composition of aerosol particles causing the adverse health effects has been extending, the particle surface composition is analyzed very rarely. During the last 40 years only few studies have addressed the surface chemistry of urban air particulates (Craig et al. 1974; Hutton and Williams 2000; Zhu

et al. 2001; Wawros et al. 2001; Pastuszka et al. 2003; Qi et al. 2006; Rogula-Kozłowska et al. 2008). On the other hand, the surface chemistry of airborne particles is crucial in determining health effects, because the surface is directly accessible to biological fluids after inhalation (Kendall et al. 2001).

In Poland some studies on the surface of aerosol particles were carried out during the last decade (Wawros et al. 2001; Wawroś et al. 2003; Pastuszka et al. 2003; Rogula-Kozłowska et al. 2008) but the relationship between the mass-size-distribution of airborne particles and their surface composition is still unknown. This work aimed to make the first step in this direction.

This paper presents results of the study of mass size distribution of ambient aerosol in the urban background site of the heavy industrialized city of Poland, and the chemical analyses of the surface layer of PM_{10} , $PM_{2.5}$ and PM_1 in this area.

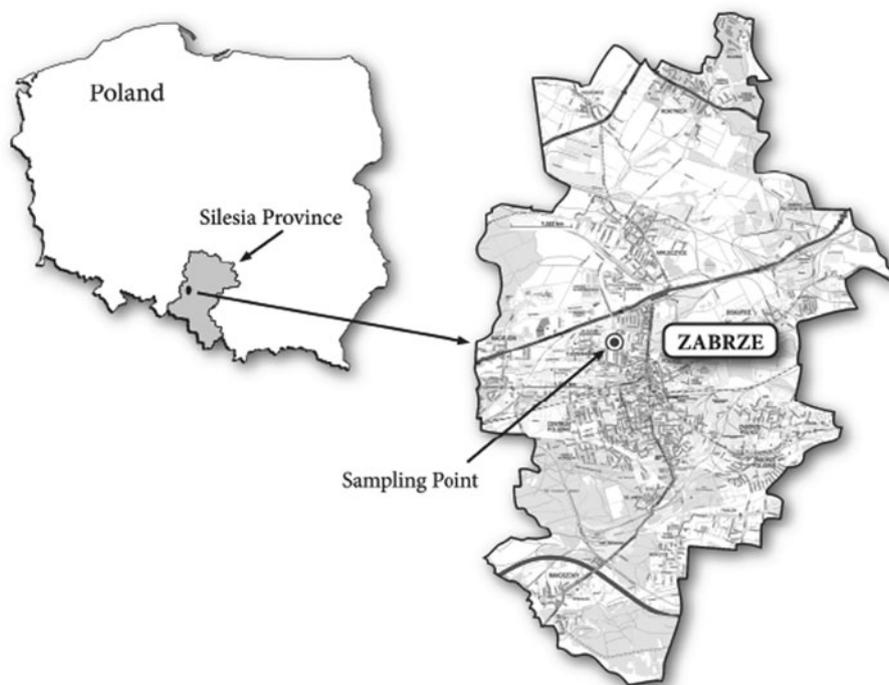
Materials and Methods

Ambient aerosols were sampled in Zabrze, Upper Silesia, Poland, from June 2007 to August 2007 and from October 2007 to January 2008. Like other cities in this region Zabrze is still greatly polluted by municipal and industrial sources while in most Western European countries vehicular emission is dominant. The sampling point ($50^{\circ}18'58''N$, $18^{\circ}46'18''E$) was located in the central part of Zabrze, in the Institute of Environmental Engineering of

the Polish Academy of Science (Fig. 1), near the air quality monitoring station belonging to the regional network. The site is surrounded by blocks of flats, detached houses and a few supermarkets. In winter they are heated by domestic heating systems burning hard coal or by the central heating system. About 500 m north and west there are moderately busy roads. This point is an official urban background site of the regional network.

During two study campaigns 19 measurements were carried out. Each measurement consisted in passing atmospheric air, at 30 L/h, through the 13-stage low-pressure cascade impactor DLPI (DEKATI, Finland) that split the sucked in dust into 13 fractions of particles in the range of aerodynamic diameters from 0.03 to 10 μm (0.03–0.06, 0.06–0.108, 0.108–0.17, 0.17–0.26, 0.26–0.4, 0.4–0.65, 0.65–1.0, 1.0–1.6, 1.6–2.5, 2.5–4.4, 4.4–6.8, 6.8–10.0 and $>10 \mu m$). The particles with diameters less than 0.03 μm were not collected; and the mass of the particles with diameters greater than 20 μm was assumed to be negligible. The airborne particles were collected onto polycarbonate or aluminum substrates, and the concentrations of particular dust fractions were determined by using the gravimetric method. Sampling time was mostly 1 week but sometimes 9–10 days, therefore 3 sets of 13 impactor samples were typically collected monthly. The substrates were conditioned for 48 h in the weighing room (air humidity $45 \pm 5\%$, air temperature $20 \pm 2^{\circ}C$) before weighing. Each substrate was weighed twice with a 24 h period between the weighing, before and after exposure, on a Mettler Toledo microbalance (resolution 2 μg). A clean

Fig. 1 Location of the sampling point



substrate was rejected if its two weights differed more than 5 μg . Before chemical analyses, substrates were stored in tight containers in a refrigerator.

Two 13-item sample sets (one set of samples from June and one from December collected on polycarbonate substrates) were analyzed by applying the X-ray photoelectron spectroscopy (XPS) to determine the surface elemental composition of all collected particle fractions. The PHI 5700/660 Photoelectron Spectrophotometer (Physical Electronics, USA) was used. In the selected samples the elements in the collected particles' surface were identified and relative amounts of the detected elements were determined from the XPS spectra in the energy range 0–1400 eV. The results were developed with the use of the Multipak computer program. Binding energies of particular elements were referred to C1s (284.6 eV) level. The detection limit for every element is 0.01% (atomic mass) in this method.

Combining the particles collected on some, appropriate impactor stages, the concentration levels of PM_{10} , $\text{PM}_{2.5}$ and PM_1 , as well as their surface composition have been determined.

Results and Discussion

The size distribution data obtained during the summer and heating season campaigns are presented in Fig. 2a, b, respectively, while Fig. 2c shows the averaged seasonal results.

Analyzing Fig. 2 it can be seen that in summer season the two-modal mass-size distribution, typical for the urban areas, has appeared. In winter, however, the size-distribution curve has been changed significantly. First of all, the peak for the fine particles is much higher in winter than in summer, indicating the increase of the emission level of fine particles in winter, certainly due to the heating, based in Poland on the coal combustion. It should also be noted that the second peak of the size-distribution, obtained in summer for the coarse particles—disappeared in winter. Such result can be related with the decay of the resuspension of the roadside dust in winter because the settled particles are covered by snow.

Significantly elevation of the concentration level of airborne particles in winter can also be seen from Table 1. Besides, Table 1 shows the increasing contribution of fine particles in PM_{10} in winter compared to summer. The ratio of $\text{PM}_1/\text{PM}_{10}$ was equal to 52 and 71% in June and in December, respectively. It should also be noted that the concentration levels of PM_{10} and $\text{PM}_{2.5}$ in Zabrze reaching in June (summer season) about 20 and 14 $\mu\text{g}/\text{m}^3$, respectively, are similar to the data obtained in other urban areas in Europe but the December PM_{10} and $\text{PM}_{2.5}$ levels (57 and 51 $\mu\text{g}/\text{m}^3$) are distinctly higher compared to another sites.

For example, in Melpitz, located in the east of the German lowlands, from 1999 until 2008 the PM_{10} mass concentration shows an inter-annual spread between 17 and 24 $\mu\text{g}/\text{m}^3$ in summer, and 21 and 34 $\mu\text{g}/\text{m}^3$ in winter (Spindler et al. 2010). Besides, the average contribution of $\text{PM}_{2.5}$ in PM_{10} in Melpitz was 72% in summer and 82% in winter

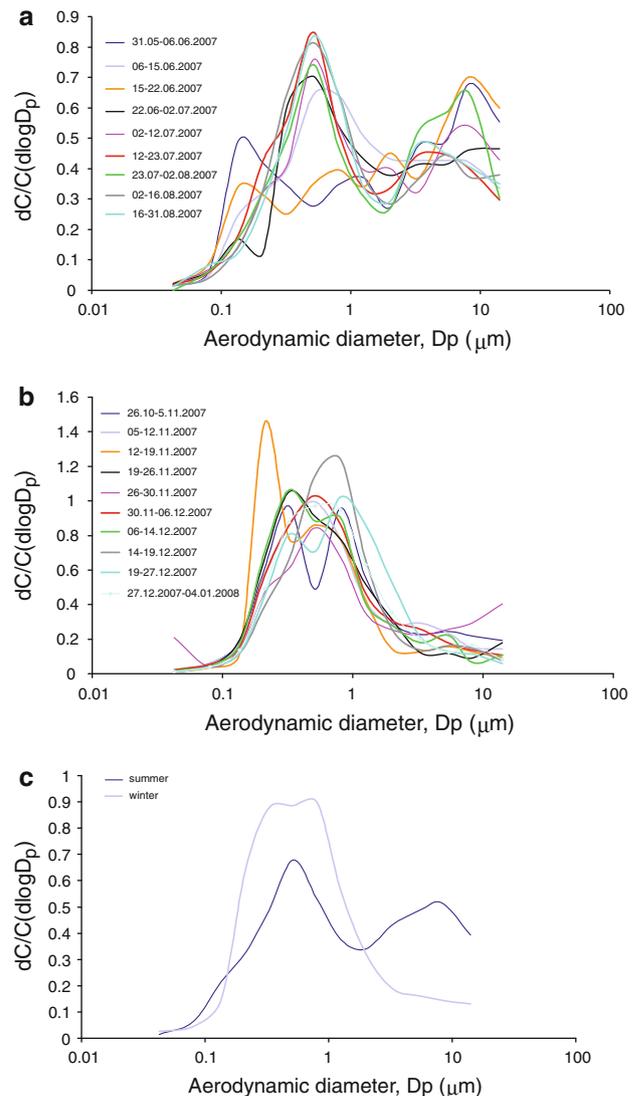


Fig. 2 Seasonal mass-size distribution of urban aerosol in Zabrze (a and b—original sampling data, c—averaged seasonal results)

Table 1 Mean levels of PM_1 , $\text{PM}_{2.5}$, PM_{10} in June (summer season) and in December (winter season) in Zabrze, Upper Silesia, Poland

| | Concentration ($\mu\text{g}/\text{m}^3$) | |
|-------------------|--|----------|
| | June | December |
| PM_1 | 10.39 | 40.73 |
| $\text{PM}_{2.5}$ | 13.64 | 51.27 |
| PM_{10} | 20.16 | 57.27 |

(Spindler et al. 2010) i.e. significantly higher compared to Zabrze. In Palermo, Italy, the mean concentration of PM₁₀ was between 33 and 41 µg/m³ in summer and 34–46 µg/m³ in winter while PM_{2.5} mean levels ranged from 24 to 32 µg/m³ in summer and from 23 to 34 µg/m³ in winter (Dongarra et al. 2010).

The relative content of the elements determined from XPS analysis is presented in Table 2.

It can be seen that the particulate surface was clearly dominated by carbon and oxygen. The average distributions of the detected elements were ranked as follows: carbon represented about 78%–80% (atomic mass) of all detected elements, oxygen: 13%–16%, silicon and aluminum: 2%–4%, nitrogen and sulfur: 0.4%–1.1%, calcium and chloride: 0.1%–0.4%.

It should be noted that the surface layer of PM₁₀, PM_{2.5} and PM₁ sampled in December contains slightly more carbon, nitrogen and chlorine than the airborne particles collected in June which might be explained by the intensive coal combustion in both, industrial heating plants and in the individual home stoves in winter. It has been previously

Table 2 Relative concentration of elements detected in the surface layer of PM₁, PM_{2.5} and PM₁₀ in June (summer season) and in December (winter season) in Zabrze, Upper Silesia, Poland

| Element | Fraction | Relative concentration (%) | |
|---------|-------------------|----------------------------|----------|
| | | June | December |
| C1s | PM ₁ | 77.67 | 79.46 |
| | PM _{2.5} | 78.11 | 80.60 |
| | PM ₁₀ | 79.83 | 80.34 |
| O1s | PM ₁ | 16.01 | 14.20 |
| | PM _{2.5} | 15.61 | 13.45 |
| | PM ₁₀ | 14.24 | 13.29 |
| Si2p | PM ₁ | 2.99 | 1.95 |
| | PM _{2.5} | 2.96 | 1.84 |
| | PM ₁₀ | 3.20 | 2.72 |
| Al2p | PM ₁ | 1.56 | 4.07 |
| | PM _{2.5} | 1.50 | 4.07 |
| | PM ₁₀ | 1.19 | 3.40 |
| N1s | PM ₁ | 0.81 | 0.96 |
| | PM _{2.5} | 0.84 | 0.97 |
| | PM ₁₀ | 0.79 | 1.11 |
| S2p | PM ₁ | 0.46 | 0.47 |
| | PM _{2.5} | 0.50 | 0.45 |
| | PM ₁₀ | 0.44 | 0.44 |
| Ca2p | PM ₁ | 0.31 | 0.12 |
| | PM _{2.5} | 0.31 | 0.14 |
| | PM ₁₀ | 0.31 | 0.13 |
| Cl2p | PM ₁ | 0.21 | 0.31 |
| | PM _{2.5} | 0.18 | 0.30 |
| | PM ₁₀ | 0.17 | 0.39 |

documented that this process is related with the high emission of carbon, mainly soot, as well as significant emission of N and Cl elevating the relative concentration of these elements in the surface layer of airborne particles (Rogula-Kozłowska et al. 2008). Previous chemical and morphological analysis of the atmospheric aerosol in Upper Silesia region showed that aerosol particles there, originated from both natural environment and anthropogenic activity (Wawroś et al. 2003). Certainly, the contribution of the second group of the emission sources (anthropogenic sources) distinctly increases in winter elevating the relative concentration of these, mentioned above, elements as well as some others, for example aluminum. It is known that fly ash, produced during coal combustion, is composed of metal oxides such as aluminium oxides and iron oxides (Grassian 2009). On the other hand, the relative concentration of elements of probably crustal origin like silicon and calcium significantly decreases during the heating season.

Summarising the obtained results it can be stated that in the studied area the winter atmospheric aerosol seems to be more dangerous than the summer aerosol because of both: higher concentration level of PM and higher contribution of fine particles in winter season compared to summer. The slightly higher content of carbon in the surface layer of airborne particles in winter than in summer can also magnify the toxicity of these winter particles.

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