Int. J. Environ. Res., 8(3):751-764,Summer 2014
ISSN: 1735-6865

Physicochemical Characteristics of Fine Ambient Aerosol from Quasi-Rural Area in Southern Poland

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Received 20 Oct. 2013; Revised 20 Dec. 2013; Accepted 27 Dec. 2013

ABSTRACT: 24-hour samples of PM_1 (submicron particles, aerodynamic diameters ≤ 1 μm) and $PM_{2.5}$ (fine particles, aerodynamic diameters ≤ 2.5 μm) were collected at a quasi-rural area in Racibórz (1 January-30 June 2011). The samples were analysed for carbon (organic and elemental), water-soluble ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) and concentrations of 21 elements with a carbon analyser (Sunset Laboratory Ltd.), an ion chromatograph (Herisau Metrohm AG) and an Epsilon 5 spectrometer (PANalitycal), respectively. To perform the monthly mass closure calculations for PM_1 and $PM_{2.5}$, chemical components were categorized into the organic matter (OM), elemental carbon (EC), secondary inorganic aerosol (SIA), crustal matter (CM), Na/K/Cl (sum of Na^+, K^+ and Cl^- concentrations), other elements (OE) and unidentified matter (UM). The results show that the particulate matter (PM) concentrations and its chemical composition are mainly influenced by the anthropogenic emissions (coal, waste and biomass combustion in home furnaces and energy production based on hard and brown coal combustion). On the other hand, the secondary organic and inorganic (to a lesser extent) aerosols constitute a considerable part of the PM mass. The findings indicate serious problems related to the possible reduction in the fine PM concentrations in southern Poland. Even though places such as Racibórz can be formally qualified as rural sites, such areas in southern Poland do not necessarily have low PM concentrations (lower than in cities) or chemical compositions of fine particles different from those in cities.

Key words:$PM_{2.5}$, PM_1, rural background, Organic matter, Crustal matter, Toxic metals,Chemical mass closure

INTRODUCTION

It is a well-known fact that fine ambient particles play a key role in the global climate changes. Their negative influence on human health is particularly evident (Englert, 2004; Pope and Dockery, 2006; Seinfeld and Pandis, 2006; Paasonen *et al.,* 2013). Obviously, their impact depends on their concentration levels in the air. The chemical composition of the particulate matter (PM) is another factor that directly influences the volatility, density, reactivity and toxicity of the atmospheric aerosol. It also has an indirect impact on the way the aerosol influences the environment, including human organisms. The knowledge of PM chemical compositions also facilitates the understanding of aspects such as time and space variations in ambient particle concentrations, source-receptor correlations and effectiveness of the emission reduction strategies. Thus, it is the basic information required for the identification of the PM emission sources.

The research into the PM chemical composition and the identification of its sources have been described in many studies over the last decade (such as Yin and Harrison, 2008; Canepari *et al.,* 2009; Putaud *et al.,* 2010; Spindler *et al.,* 2010; Shahsavani *et al.,* 2012; Choi *et al.,* 2013; Crippa *et al.,* 2013; Zhang *et al.,* 2013). The PM_1 fraction is the least known when it comes to the chemical composition and sources. The PM concentrations and chemical compositions can vary significantly, which depends on the main emission sources and chemical reactions occurring in the atmosphere. For that reason, it is necessary to conduct the research into the PM concentrations and chemical compositions in as many sites as possible. It is particularly important for Central and Eastern Europe as the knowledge of the PM chemical compositions is very limited in these regions (Putaud *et al.,* 2010). In Poland, the chemical compositions of $PM_{2.5}$ and PM_{10} were investigated in the city of Zabrze, which represents an urban area of southern Poland (Rogula-Kozłowska *et al.,* 2012). Moreover, the research into

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*Corresponding author E-mail:wioletta@ipis.zabrze.pl the concentrations of the PM_1 and $PM_{2.5}$ and their percentage in the total PM mass have also been conducted in Zabrze since 2005 (Klejnowski *et al.,* 2007 and 2012). The research shows that the percentage of PM_1 and $PM_{2.5}$ in the total PM can be very high in the urban areas of southern Poland. For example, PM_1 made 52% of the PM_{10} mass, whereas $PM_{2.5}$ constituted 68% of the PM_{10} mass in Zabrze in June. For the same measurement point in December, the fine dust ($PM_{2.5}$) made up 90% of the PM_{10} mass, while the submicron dust (PM_1) constituted 71% of the PM_{10} mass (Klejnowski *et al.,* 2012). Both this finding and the recognized chemical composition of $PM_{2.5}$ corroborate the fact that the fine dust in this area comes from anthropogenic sources. The studies also demonstrate that local sources, and particularly municipal emissions, are the main sources of fine dust in the Polish cities (Rogula-Kozłowska *et al.,* 2012; Rogula-Kozłowska *et al.,* 2013).

The aim of the following study was to understand concentrations and chemical compositions of PM_1 and $PM_{2.5}$ in the quasi-rural area in the south of Poland (Racibórz District, Commune of Racibórz). It also concerned the preliminary assessment of the PM_1 and $PM_{2.5}$ sources with the so-called chemical mass closure of ambient dust. The method compares sums of masses of the analysed dust components with the dust mass determined gravimetrically. Six classes of components were identified in this research, i.e. secondary inorganic aerosol (SIA), sum of sodium, chlorine and potassium (Na/K/Cl), organic matter (OM), elemental carbon (EC), crustal matter (CM) and other elements (OE). The difference between the sum of SIA, Na/K/Cl, OM, EC, CM, OE and the dust mass makes the so-called unidentified matter (UM). The classes were selected so that they could be compared with the data obtained at different European monitoring sites.

MATERIALS & METHODS

The 24-hour PM_1 and $PM_{2.5}$ samples were collected with the Partisol 2020 dust sampler (Ruprecht & Patashnick) and PNS sampler (Atmoservice), respectively. The sampling took place between 1st January and 30th June 2011 in the Commune of Racibórz in southern Poland (Fig. 1). Racibórz is located in the Racibórz District in the south-west part of the Silesia Province. It is close to the border with the Czech Republic. Its geographical coordinates are 50°52 N and 18°142 E. The Racibórz District is an agricultural region. Moreover, agriculture is one of the main fields of its economic development as the agrarian land makes 66.30% of the area. A few plants (chemical, energy and agro-food industries) and trade centres are located only in the centre of Racibórz (approx. 6 km away from the measurement point). The population density does not exceed 220 people per km^2 in the Racibórz District, whereas its level in the town of Racibórz is approx. 700 people per km^2. It is 3 to 5 times lower than in other cities of southern Poland. Most inhabitants live in the centre and its surrounding area. Low buildings with individual heating systems (biomass, coal, natural gas) dominate the landscape. The building development is compact in the centre and widely dispersed in the vicinity of the measurement point. The region of Racibórz is characterized by the following climatic data:

✓Air temperature: average annual temperature – +8 °C; average temperature in January – -2.1 °C; average temperature in July – +18.0 °C.

✓Number of freeze days: 100-110.

✓Number of days with precipitation: 170 (including 45 days with snow).

✓Winds along the Oder River (N-S): south winds dominate in autumn and winter, while north winds are more frequent in spring and summer; there is a large number of calm air periods.

PM_1 and $PM_{2.5}$ samples were collected on quartz fibre filters and Teflon membranes (Whatman Cat. No. 7592-104 and Whatman Cat. No. 1851-047, respectively) used in the alternate way every other day (the first filter was made of Teflon, then the quartz fibre one was used, and then the Teflon one was applied again, etc.). Before and after the exposition, all filters were conditioned in a weighing room (48 hours; relative air humidity 45±5%; air temperature 20±2 °C) and weighed twice, with a 24-h period between the weighings, on a Mettler Toledo microbalance (resolution 2 µg).

All 24-hour dust samples collected on the Teflon membranes underwent elemental composition analyses (Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Sb, Te, Ba, Pb). The elemental compositions of PM_1 and $PM_{2.5}$ were determined with energy dispersive X-ray fluorescence (EDXRF).

Two 1.5-cm^2 pieces were cut out from each of the quartz filters with dust. The first group underwent organic carbon (OC) and elemental carbon (EC) content analyses (Sunset Laboratories Inc.), whereas the other was examined for the contents of water-soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}). To determine these ions, combined samples from all pieces collected within each month were prepared. The combined monthly samples (separate for PM_1 and $PM_{2.5}$) were used to prepare water extracts. They were made through ultrasonizing the samples in 50 cm^3 of de-ionized water for 60 minutes at the temperature of 15°C. Then, they were shaken for approx. 12 hours (18°C, 60 r·min^{-1}). The ion content in extracts was determined with a Metrohm ion chromatograph (Herisau Metrohm AG, Switzerland).

Fig. 1. Location of the sampling point

The parameters of the equipment (Sunset Laboratory carbon analyser, Epsilon 5 EDXRF spectrometer, Herisau Metrohm AG ion chromatograph), the detailed descriptions of the analytical procedures, and the results of the validation of the method are given in the studies (Rogula-Kozłowska *et al.,* 2012; 2013; Rogula-Kozłowska and Klejnowski 2013).

Analytically determined 24-hour masses of each component (from the 24-hour samples) were summed for each month, with the exception of ions as their combined monthly samples were analysed. The monthly masses of dust components were divided by the dust mass from which they were determined (sum of sample masses analysed in a given month). In this way, the average monthly percentage of each component in the dust was determined. The average monthly concentration of a component was its percentage in the dust multiplied by the average monthly dust concentration (arithmetic mean calculated from the 24-hour concentrations obtained in a given month). For the mass reconstruction (chemical mass closure), the PM_1 and $PM_{2.5}$ components were categorized into organic matter (OM), elemental carbon (EC), secondary inorganic aerosol (SIA), crustal matter (CM), Na/K/Cl, other elements (OE), and the rest—unidentified matter (UM). The mass [OM] of OM was assumed to be 1.8 $[OC]_A$, where $[OC]_A$—the analytically determined masses of OC (Grosjean and Friedlander 1975; Turpin and Lim 2001). The mass [EC] of EC was $[EC]_A$. SIA included PM_1 or $PM_{2.5}$-bound SO_4^{2-}, NO_3^-, NH_4^+, so $[SIA]= [SO_4^{2-}]_A + [NO_3^-]_A + [NH_4^+]_A$.

The Na/K/Cl group included Na^+, K^+ and Cl^-, therefore $[Na/K/Cl]= [Na^+]_A+[K^+]_A+[Cl^-]_A$.

CM included CO_3^{2-}, SiO_2, Al_2O_3, Mg^{2+}, Ca^{2+}, FeO, Fe_2O_3 and TiO_2; $[CM]= [CO_3^{2-}]+ [SiO_2]+ [Al_2O_3]+ [Mg^{2+}]_A+ [Ca^{2+}]_A+[FeO]+[Fe_2O_3]+[TiO_2]$, where: [FeO] and $[Fe_2O_3]$ were calculated stoichiometrically from $[Fe]_A$ assuming a uniform Fe mass distribution between FeO and Fe_2O_3 and $[CO_3^{2-}]= 1.5[Ca^{2+}]_A+2.5[Mg^{2+}]_A$ (Marcazzan *et al.,* 2001); $[Al_2O_3]$, $[SiO_2]$ and $[TiO_2]$ were calculated stoichiometrically from the analytically determined $[Al]_A$, $[Si]_A$ and $[Ti]_A$; $[Ca^{2+}]_A$, $[Mg^{2+}]_A$ were determined analytically.

OE included V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Sb, Ba, Pb and $[OE] = [V]_A+ [Cr]_A+ [Mn]_A+ [Co]_A+[Ni]_A+[Cu]_A+[Zn]_A+[As]_A+[Se]_A+[Rb]_A+ [Sr]_A+ [Mo]_A+ [Cd]_A+ [Sb]_A+ [Ba]_A+ [Pb]_A$.

UM was PM-OM-EC-SIA-Na/K/Cl-CM-OE, and [UM]=[PM]-[OM]-[EC]-[SIA]-[Na/K/Cl]-[CM]-[OE], where [PM]—determined gravimetrically mass of PM_1 or $PM_{2.5}$.

The mass closure for PM_1 and $PM_{2.5}$ was examined separately for each month of the half-year research period in 2011.

RESULTS & DISCUSSION

In Racibórz, average monthly concentrations of PM_1 and $PM_{2.5}$ were 11.1-40.1 $\mu g \cdot m^{-3}$ and 12.0-75.0 $\mu g \cdot m^{-3}$, respectively (Table 1). The average concentrations of the analysed PM fractions obtained over the whole measurement period (arithmetic mean of average monthly concentrations) were 26.2 $\mu g\cdot m^{-3}$ (PM_1) and 37.9 $\mu g\cdot m^{-3}$ ($PM_{2.5}$). The average monthly concentrations were at least twice as high in the cold season (January-March) than in the warm season (April-June). The maximum 24-hour concentrations reached the level of 124.1 $\mu g\cdot m^{-3}$ (PM_1) and 152.3 $\mu g\cdot m^{-3}$ ($PM_{2.5}$). The highest concentrations were observed in January and February. High PM concentrations are normally observed in the Silesia Province in this period. It is related to the occurrence of the lowest yearly temperatures and the impact of the emission from fossil fuel combustion (Pastuszka *et al.,* 2010; Juda-Rezler *et al.,* 2011). Higher 24-hour and average PM concentrations in the cold season (heating season) are observed in most Polish and European regions (Putaud *et al.,* 2010; Spindler *et al.,* 2010; Majewski *et al.,* 2011; Zwoździak *et al.,* 2012).

The results obtained in this study were compared with the results from other rural or quasi-rural sites in Europe (Table 2). Dissimilar geographical and meteorological conditions as well as types and activity of the emission sources have influence on the differences in the PM concentrations in the compared locations. Nonetheless, it is clearly visible that the PM_1 and $PM_{2.5}$ concentrations observed in Racibórz are significantly higher than those in other European regions. It is likely that specific emissions of ambient dust and its precursors, characteristic particularly for southern Poland, are responsible for such a situation. The emissions originate from fossil fuel (mainly low-quality coal and fine coal), biomass, waste and rubbish combustion in home furnaces. The question of low emissions has already been partially solved in some Polish regions. The problem still exists in the south of Poland, particularly in the less well-off areas, such as the Racibórz District. Local inhabitants have virtually unlimited access to cheap, low-quality fuel that can be used in home furnaces. Importantly, the problem seems to have been gaining importance in recent years, in the era of the financial crisis. The location of Racibórz also influences the air quality. It lies in a close distance from the most highly urbanized and industrialized Polish region (Upper Silesia urban area) and highly industrialized Czech area (Moravia-Silesia).

Fine and submicron dust in Racibórz, similarly to other locations, is formed mainly from the carbonaceous matter (OC and EC) and secondary species (NO_3^-, SO_4^{2-}, NH_4^+) – Tables 2 and 3.

The average PM_1- and $PM_{2.5}$-related concentrations of OC (obtained over the whole measurement period) were high and equalled to 8.46 $\mu g\cdot m^{-3}$ and 11.84 $\mu g\cdot m^{-3}$ (arithmetic mean from all monthly concentrations), respectively. The EC concentration was lower, but still relatively high in comparison with other chemical components. It was 1.89 $\mu g\cdot m^{-3}$ (PM_1) and 2.72 $\mu g\cdot m^{-3}$ ($PM_{2.5}$) for the whole

Table 1. Statistics on the 24-hour PM_1 and $PM_{2.5}$ concentrations in Racibórz, in particular months of the half-year research period in 2011

	January	February	March	April	May	June
PM_1						
Number of 24-hour concentrations[a)]	31	16	25	30	31	30
Minimum [$\mu g\cdot m^{-3}$]	11.6	5.6	12.7	5.3	1.9	3.1
Minimum date	15-Jan	06-Feb	19-March	08-April	24-May	19-June
Maximum [$\mu g\cdot m^{-3}$]	124.1	71.8	73.7	46.7	24.1	20.7
Maximum date	31-Jan	16-Feb	04-March	10-April	09-May	08-June
Arithmetic mean [$\mu g\cdot m^{-3}$]	40.1	34.3	37.3	20.5	13.8	11.1
Standard deviation [$\mu g\cdot m^{-3}$]	25.5	19.0	16.8	8.3	5.2	4.5
$PM_{2.5}$						
Number of 24-hour concentrations[a)]	6	24	30	30	31	29
Minimum [$\mu g\cdot m^{-3}$]	32.6	6.9	13.2	5.5	6.6	4.8
Minimum date	06- Jan	05-Feb	06-March	13-April	25-May	24-June
Maximum [$\mu g\cdot m^{-3}$]	69.2	152.3	100.5	42.5	30.0	21.0
Maximum date	08- Jan	17-Feb	04-March	28-April	03-May	13-June
Arithmetic mean [$\mu g\cdot m^{-3}$]	50.9	75.0	47.3	25.5	16.6	12.0
Standard deviation [$\mu g\cdot m^{-3}$]	19.7	43.8	24.1	10.4	6.1	4.9

[a)] measurement time – at least 75% of the 24-hour period measurement period. The cold-season concentrations of OC and EC were higher than the warm-season ones. It suggests that fossil fuel combustion was the main source of carbon compounds in Racibórz. The highest average monthly values of the OC/EC concentration ratio were observed in June. They ranged between 3.75 and 7.51 (PM_1) and between 3.47 and 5.54 ($PM_{2.5}$), which indicates the clear dominance of the organic carbon compounds over EC. This result can also suggest a significant influence of the secondary organic carbon (SOC) formation processes in the air on the concentrations and chemical composition of the fine dust in the examined area (Pio *et al.,* 2011).

SOC is formed as a result of the gaseous precursors reactions taking place in the atmosphere, which are described by over 500 different chemical reactions. The products of the gaseous precursors transformations condense on the inorganic salt particles and take part in the processes of cloud droplets formation (Grosjean and Friedlander, 1975; Seinfeld and Pandis, 2006). Indirect methods are most frequently used to estimate the SOC and primary organic carbon (POC) contents in the OC concentration (Castro, 1999).

The 24-hour $PM_{2.5}$-related SOC and POC concentrations ($[SOC]_{24\text{-hour}}$ and $[POC]_{24\text{-hour}}$) in Racibórz (Fig. 2) were computed from the formula:

$$[SOC]_{24\text{-hour}} = [OC]_{24\text{-hour}} - [(OC/EC)_{min}]_{24\text{-hour}} \times [EC]_{24\text{-hour}};\ [\mu g \cdot m^{-3}]$$

$$[POC]_{24\text{-hour}} = [OC]_{24\text{-hour}} - [SOC]_{24\text{-hour}};\ [\mu g \cdot m^{-3}]$$

where:

$[OC]_{24\text{-hour}}$ and $[EC]_{24\text{-hour}}$ are the 24-hour $PM_{2.5}$-related OC and EC concentrations determined analytically;

$[(OC/EC)_{min}]_{24\text{-hour}}$ is the lowest 24-hour OC/EC ratio in the whole measurement period; $[(OC/EC)_{min}]_{24\text{-hour}} = 3.58$.

In Racibórz, the SOC percentage in the $PM_{2.5}$-related OC was significant. It was slightly higher in the warm season when the insolation was stronger and the EC concentrations, absorbing the solar radiation, were lower. The high emission of organic gaseous precursors in the cold season influenced significantly the presence of the SOC fraction in the OC even though the conditions for the SOC formation were less favourable than in the warm season.

The following PM-related anions had the highest concentrations in the air: SO_4^{2-} (1.04-2.88 $\mu g \cdot m^{-3}$ for PM_1 and 2.01-6.12 $\mu g \cdot m^{-3}$ for $PM_{2.5}$) NO_3^- (0.37-2.92 $\mu g \cdot m^{-3}$ for PM_1 and 0.61-5.54 $\mu g \cdot m^{-3}$ for $PM_{2.5}$) and Cl^- (0.01-1.81 $\mu g \cdot m^{-3}$ for PM_1 and 0.05-2.56 $\mu g \cdot m^{-3}$ for $PM_{2.5}$). On the other hand, for cations, NH_4^+ ambient concentrations were the highest. They were 0.17-1.16 $\mu g \cdot m^{-3}$ and 0.52-4.16 $\mu g \cdot m^{-3}$ for PM_1 and $PM_{2.5}$, respectively. Apart from Ca^{2+} and Mg^{2+}, the concentrations of water-soluble ions were higher in the cold season. They gradually decreased with each month passed. The most visible decrease in the average monthly concentrations concerned NO_3^- (between January and June). The average monthly concentrations of Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+ and K^+ were visibly correlated with the average monthly concentrations of EC (Table 4, linear correlation coefficient r, calculated at $p<0.5$). In conclusion, the above-mentioned ions probably originated from the combustion processes (particularly fossil fuel and biomass burning), similarly to EC (Terzi *et al.,* 2010; Đordević *et al.,* 2012).

Significant correlations between the average monthly concentrations of virtually all ions (except for NO_3^- and Na^+ as well as NO_3^- and K^+) were observed. Consequently, compounds such as KCl, NaCl, NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$ and K_2SO_4 were most likely the main compounds in which the given ions occurred.

NH_4NO_3 and $(NH_4)_2SO_4$ are the main inorganic products from transformations of gaseous precursors (SO_2, NO_x and NH_3). In the air, SO_2 oxidizes to gaseous SO_3 or liquid H_2SO_4. Afterwards, it is neutralized to ammonium sulphate ($(NH_4)_2SO_4$) or ammonium bisulphate (NH_4HSO_4). NO_x photochemically oxidises to HNO_3. Then, it is neutralized to ammonium nitrate (NH_4NO_3). The ability to form these compounds and the speed of transformations depend on meteorological conditions and the proportion of the concentration of gaseous precursors of PM to the concentration of neutralizing compounds (Seinfeld and Pandis, 2006).

In Racibórz, the neutralization ratio NR (normal equivalent, ratio of NH_4^+ and $SO_4^{2-}+NO_3^-$ concentrations) was generally lower for PM_1 than for $PM_{2.5}$. Its values (calculated from average monthly concentrations) ranged from 0.34 (June, PM_1) to 1.67 (January, $PM_{2.5}$). The six-month means were 0.56 (PM_1) and 1.26 ($PM_{2.5}$). For PM_1, the amount of ambient NH_4^+ was not sufficient to fully neutralize ambient H_2SO_4 and HNO_3 ($NR<1$). Consequently, it can be assumed that NH_4^+ did not form NH_4NO_3 (at first, NH_4^+ neutralizes sulphates). It suggests the existence of PM_1 components other than $(NH_4)_2SO_4$ and NH_4NO_3 in Racibórz, such as K_2SO_4 in the cold season (biomass combustion). The low value of NR indicates that the aerosol pH could be acidic. In general, the PM acidity cannot be excluded at any month in Racibórz. It is a common assumption that if $NH_4^+/SO_4^{2-} \geq 1.5$ (molar ratio), then sulphuric acid is totally neutralized (Seinfeld and Pandis, 2006), but some authors report the $PM_{2.5}$ acidity even when $NH_4^+/SO_4^{2-} \geq 2$ (Pathak *et al.,* 2009; Huang *et al.,* 2011).

Table 2. Mass concentrations of fine dust and percentages of selected components in the fine dust mass in the selected rural and quasi-rural areas in Europe

Site, PM_x(source of data)	PM mass concentration [$\mu g \cdot m^{-3}$]	Crustal Matter (%)	Sea Salt (%)	Trace Elements (%)	Elemental Carbon (%)	Organic Matter (%)	SO_4^{2-} (%)	NO_3^- (%)	NH_4^+ (%)	Unidentified Matter (%)
Thüringer Wald (Germany), $PM_{0.42\text{-}1.2}$ (Gnauk et al., 2005)	*9.6*	-	-	-	*5*	*19*	*22*	*16*	*8*	*38*
Basel (Switzerland), $PM_{2.5}$ (Hueglin et al., 2005)	18.9	6.6	-	3.6	8.5	23.7	21.8	16.6	10.8	3.8
Chaumont (Switzerland), $PM_{2.5}$ (Hueglin et al., 2005)	7.7	8.8	-	3.6	5.2	20.8	30.0	7.4	10.8	13.4
Hyytiälä (Finland), PM_1(Saarikoski, 2008)	4.4	-	-	-	4	48	41[a]			7
20 km away Birmingham (UK); $PM_1/PM_{2.5}$(Yin and Harrison, 2008)	11.7/14.3	*3.4/4.9*	*3.4/2.8*	-	*6.8/7.7*	*29.9/32.9*	*55.6/59.4*			*0.9/-7.7*
Villar Arzobispo (Spain); $PM_{2.5}$ (Pey et al., 2009)	18.0	28.9	2.2	-	15.6		13.9	7.2	6.7	25.5
Montseny (Spain); $PM_{2.5}$ (Pey et al., 2009)	13.6	9.6	1.5	-	27.2		20.1	8.8	8.1	24.7
Melpitz (Germany), PM_1 [b][d] (Spindler et al., 2010)	10/11	-	-	-	*10/9*	*10/9*	*20/18*	*<5/23*	*10/14*	*45/27*
Melpitz (Germany), PM_1 [c][d] (Spindler et al., 2010)	17/22	-	-	-	*12/9*	*15/16*	*21/18*	*<2/14*	*9/9*	*41/27*
Bologna (Italy), PM_1 [d][e] (Carbone et al., 2010)	*8.5/20.6*	2/0 [f]	2/0	-	48/43 [g]		27/8	8/34	13/14	-
Rome (Italy), PM_1 [d][e] (Carbone et al., 2010)	*7.7/6.7*	6/3 [f]	5/2	-	62/67 [g]		19/17	1/1	7/10	-
Rotterdam (Netherlands), $PM_{2.5}$ (Keuken et al., 2012)	15.8	4	4	4	11	20	33			24
Tourlos (Greece), $PM_1/PM_{2.5}$ (Pateraki *et al.*, 2012)	14.2/19.2	-	-	-	2.7/2.3	20.2/17.4	29.0/27.0	2.0/4.0	8.1/6.3	-
Salento (Italy), $PM_1/PM_{2.5}$ (Perrone et al., 2013)	15/25	0.9/0.8 [h]	0.5/0.9	<0.5/<0.5	10/8.4	33.6/32.5	15.3/16.8	1.5/2.1	5/4.8	-
Valverde del Camino (Spain), $PM_{2.5}$(Milford et al., 2013)	21.56	20	4	-	2 [i]	22	12	3	3	22
Racibórz (Poland), PM_1 [j](this study)	37.2/15.1	1.6/4.1	5.6/3.7 [k]	0.3/0.5	7.7/5.7	59.9/52.6	7.0/11.6	6.9/8.4	3.0/3.4	21.8/26.3
Racibórz (Poland), $PM_{2.5}$ [j](this study)	57.7/18.0	1.8/6.1	6.4/3.6 [k]	0.3/0.6	7.9/5.5	58.3/48.2	8.0/12.3	7.6/6.0	6.5/8.2	18.2/21.2

italics – data extracted from a chart

[a] sum of water-soluble ions; [b] air inflow from western sector; [c] air inflow from eastern sector; [d] summer/winter; [e] samples taken during daytime; [f] sum: (dust rich with Fe + Ca salts); [g] sum of WSOM (*water-soluble organic matter*) and WINCM (*water-insoluble carbonaceous matter);* [h] sum of Al and Fe; [i] as black carbon (BC); [j] cold season/warm season; [k] Na/K/Cl

Table 3. Ambient concentrations of OC, EC, water-soluble ions [μg·m^{-3}], and the remaining components [ng·m^{-3}] bound to PM$_1$ and PM$_{2.5}$ in Racibórz (Poland)

	Jan 2011		Feb 2011		March 2011		April 2011		May 2011		June 2011	
	PM$_{2.5}$	PM$_1$	PM$_{2.5}$	PM$_1$	PM$_{2.5}$	PM$_1$	PM$_{2.5}$	PM$_1$	PM$_{2.5}$	PM$_1$	PM$_{2.5}$	PM$_1$
OC	16.45	15.74	25.45	9.68	14.62	12.04	7.07	6.25	4.04	3.68	3.39	3.38
EC	4.74	3.47	4.59	2.58	3.92	2.61	1.55	1.38	0.88	0.86	0.63	0.45
Cl^-	2.23	1.81	2.56	1.4	1.93	1.14	0.42	0.28	0.16	0.15	0.05	0.01
NO_3^-	2.83	2.09	5.54	2.92	4.76	2.68	1.78	2.69	0.86	0.77	0.61	0.37
SO_4^{2-}	4.47	2.88	6.12	2.73	3.34	2.22	2.59	2.41	2.03	1.81	2.01	1.04
Na^+	1.14	0.51	0.45	0.34	0.39	0.26	0.36	0.35	0.28	0.27	0.28	0.18
NH_4^+	4.16	1.14	3.62	1.07	3.50	1.16	2.6	0.94	1.33	0.43	0.52	0.17
K^+	1.19	0.33	0.39	0.25	0.34	0.29	0.1	0.28	0.19	0.13	0.08	0.1
Ca^{2+}	0.09	0.06	0.38	0.04	0.08	0.07	0.09	0.02	0.03	0.07	0.06	0.04
Mg^{2+}	0.09	0.06	0.08	0.01	0.09	0.01	0.05	0	0.08	0.01	0.13	0.01
Al	50.37	35.7	42.65	30.91	56.67	28.58	29.88	23.77	41.45	32.45	66.26	34.06
Si	95.05	61.25	115.23	70.57	97.32	114.11	161.45	63	137.03	117.31	165.49	142.38
Ti	0.5	1.44	2.83	0.48	2.41	1.64	3.24	1.27	2.77	1.02	2.86	1.58
V	0.25	0.16	1.31	0.6	0.42	0.55	0.31	0.28	0.21	0.15	0.4	0.39
Cr	10.98	7.25	4.87	3.47	12.6	9.16	11.92	2.67	11.83	4.81	6.02	6.2
Mn	9.7	8.01	6.66	6.23	6.91	6.47	6.96	4.13	6.06	5.59	4.14	3.35
Fe	150.54	113.12	148.99	63.98	169.98	105.91	173.8	41.86	144.81	77.62	121.6	85.95
Co	0.91	0.28	0.1	0.1	0.15	0.13	0.17	0.14	0.34	0.24	0.01	0.01
Ni	7.44	6.47	8.09	3.47	20.52	13.3	21.8	2.25	18.22	3.32	8.73	4.92
Cu	8.47	7.39	7.37	5.03	5.60	4.96	4.56	2.86	5.01	4.61	6.65	5.02
Zn	56.3	59.19	105.91	54.04	65.74	53.82	49.82	19.92	34.05	28.38	19.42	18.9
As	6.97	6.16	13.12	5.75	6.71	5.53	5.89	2.3	3.85	3.7	2.44	2.15
Se	0.27	0.1	0.1	0	0.15	0.09	0.14	0.14	0.14	0.14	0.18	0.1
Rb	2.48	2.27	4.36	2.04	1.89	1.51	1.23	0.98	1.45	1.42	1.5	1.28
Sr	3.98	2.98	2.32	2.02	2.42	1.22	1.95	1.45	3.35	2.35	2.54	1.84
Mo	5.00	2.94	2.28	1.73	6.05	2.17	3.23	1.73	3.73	1.39	6.1	1.31
Cd	4.48	3.12	3.94	3.82	3.54	3.24	2.82	1.83	2.42	1.67	2.36	1.9
Sb	5.25	4.45	9.48	4.19	4.57	2.01	3.94	3.03	2.94	2.15	1.67	1.19
Te	1.98	1.23	1.49	0.71	1.71	1.33	1.9	1.13	0.81	0.63	0.57	0.84
Ba	8.93	7.45	4.54	3.99	5.66	3.03	4.97	3.84	5.05	3.26	4.68	4.47
Pb	19.13	18.09	41.31	19.05	22.35	17.88	19.47	7.64	13.37	12.49	8.98	7.44
$(NH_4)_2SO_4$ [a)	6.2	4.2	8.4	3.9	4.6	4.3	3.6	3.4	2.8	1.6	1.9	0.6
NH_4NO_3 [b)	11.1	-	5.9	-	10.0	-	7.3	-	2.5	-	-	-

[a) ambient concentration $[(NH_4)_2SO_4]$ of $(NH_4)_2SO_4$ [μg·m^{-3}] calculated as: $[(NH_4)_2SO_4]=1.38[SO_4^{2-}]_A$ if NR<1 and $[(NH_4)_2SO_4]=3.67\ [NH_4^+]_A$ if NR<1

[b) ambient concentration $[NH_4NO_3]$ of NH_4NO_3 [μg·m^{-3}] calculated as: $[NH_4NO_3]=4.44[ex\text{-}NH_4^+]$; $[ex\text{-}NH_4^+]=[NH_4^+]_A - 0.27[(NH_4)_2SO_4]$ if NR≥1

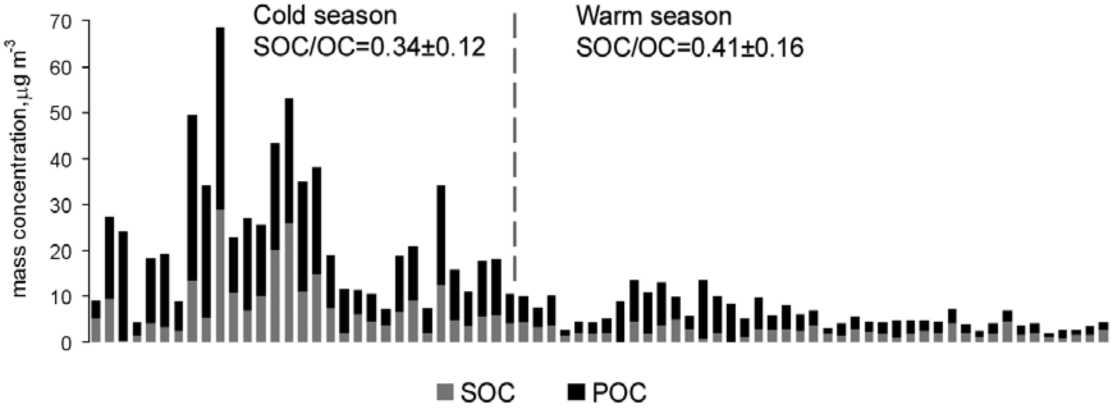

Fig. 2. 24-hour concentrations of the PM$_{2.5}$-related SOC and POC in Racibórz in the first half of 2011

Table 4. Linear correlation matrix ($p<0.5$) for average monthly concentrations of water-soluble ions and EC bound to PM_1 and $PM_{2.5}$ in Racibórz (Poland)

	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	EC
Cl^-	1.00	0.84	0.86	0.63	0.77	0.66	0.99
NO_3^-	0.84	1.00	0.83	0.32	0.74	0.39	0.84
SO_4^{2-}	0.86	0.83	1.00	0.60	0.84	0.60	0.86
Na^+	0.63	0.32	0.60	1.00	0.70	0.96	0.70
NH_4^+	0.77	0.74	0.84	0.70	1.00	0.69	0.82
K^+	0.66	0.39	0.60	0.96	0.69	1.00	0.73
EC	0.99	0.84	0.86	0.70	0.82	0.73	1.00

For $PM_{2.5}$, the NR was smaller than 1 only in June; in the remaining months, the NR was ≥1. It shows the occurrence of NO_3^-, SO_4^{2-} and NH_4^+ in the form of $(NH_4)_2SO_4$ and NH_4NO_3. For $PM_{2.5}$, the NH_4NO_3 concentrations were significantly higher than the $(NH_4)_2SO_4$ ones between January and April (Table 3). So, in Racibórz, ammonium nitrate occurred in the particles in the range of 1-2.5 μm. In the warm season, the weather conditions were not favourable to the formation of NH_4NO_3 in the air. Even though a certain amount of NH_4NO_3 might have evaporated, especially from the samples collected in summer, it is believed that the artefacts related to the semi-volatility of NH_4NO_3 can be important only for the samples very rich in ammonium (Pathak *et al.,* 2009). Generally, it may be expected that NO_3^- compounds with Ca^{2+} or Na^+ will occur in the summer period. For the whole measurement period (January-June) the linear dependence between average monthly concentrations of the PM_1- and $PM_{2.5}$-related NO_3^- and Na^+ was weak ($r=0.32$, Table 4). For the warm season (April-June), however, the dependence was strong and characterized by the linear correlation coefficient $r = 0.83$.

The average concentrations of elements were highly diverse in Racibórz (Table 3). Generally, the highest concentration values were found for crustal elements (such as Al, Si and Fe). Low trace elements concentrations, bound to both PM_1 and $PM_{2.5}$, were observed at the Racibórz measurement point. They were a few times lower than those measured in the cities of southern Poland in the previous years (Pastuszka *et al.,* 2010; Rogula-Kozłowska *et al.,* 2013). The Zn concentration was the highest (18.9-59.19 ng’”m^{-3} and 19.42-105.91 ng·m^{-3} for PM_1 and $PM_{2.5}$, respectively). The values of the Pb, Cr and Mn concentrations were lower (Table 3). Crustal elements were observed mainly in $PM_{2.5}$, whereas PM_1 was enriched with trace metals (such as Zn, Pb, Cr, Mn, Cu, Cd, Ni, As, Ba, V, Co) related to combustion and industrial processes (Querol *et al.,* 2007; Rajšić *et al.,* 2008). Obvious spatial variations were also observed in the ambient concentrations of elements. Most PM_1- and $PM_{2.5}$-related elements had lower ambient concentrations in the warm period, except for crustal elements (such as Al, Si).

The total mass of the identified ambient dust components (OM, EC, SIA, Na/K/Cl, CM and OE) made 68–93% and 74–90% of the PM_1 and $PM_{2.5}$ masses, respectively (Fig.3). The percentage of the unidentified matter (UM) in the PM mass was generally higher in the warm season and practically did not depend on the particle size.

The lack of the complete chemical mass closure (reconstruction of the total mass determined gravimetrically) may be caused by many factors. Systematic errors committed during the sampling and gravimetric or chemical analyses can be one of the possible reasons for the discrepancy between the PM mass and the sum of its component masses. Moreover, it is possible that compounds that do not undergo chemical analysis are present in the ambient dust (Almeida *et al.,* 2006). The lack of the complete mass closure is often assigned to the evaporation of the organic compounds and nitrates in the transport and PM sample storage processes (Rees *et al.,* 2004). The observed differences can also result from uncertainties that arise from the assessment of the percentage of the chemical compounds that are not measured directly, particularly organic and crustal matter (Turpin and Lim, 2001; Rees *et al.,* 2004; Almeida *et al.,* 2006; Ho *et al.,* 2006). The presence of water bound to PM particles is another important factor that influences the chemical balance of the ambient dust mass. Many studies prove that the water content in the total PM mass can be high (Tsyro, 2005; Canepari *et al.,* 2012). For example, Tsyro (2005) observe that according to the model calculations the water percentage in PM (in the 50% RH conditions) is different in various European regions. It can range between 20 and 30% of the $PM_{2.5}$ mass. The percentage of water bound to the ambient aerosol depends on the content of hygroscopic compounds in the PM samples and is usually higher in the fine dust fractions (Ho *et al.,* 2006).

OM was the most abundant compound, both in PM_1 and $PM_{2.5}$; the OM percentage in PM was in the range of 48-71% and 44-61% for PM_1 and $PM_{2.5}$, respectively. The OM content was significantly higher for both fractions in the cold season (particularly in January; Fig. 3). The higher OM content in the PM mass over the cold season resulted from high emissions of the organic carbon compounds, including the hydrocarbon emission from fuel combustion. The relatively high content of these components in the PM mass observed in the warm season results from the higher intensity of the SOC formation in the air in Racibórz (Fig. 2). It was also caused by the presence of the biological matter in the dust (Zhang *et al.,* 2009; Terzi *et al.,* 2010).

The EC percentage in the ambient dust mass was much lower (6 to 13 times) than the OM percentage. On average, it made approx. 7% of both PM_1 and $PM_{2.5}$ masses in the whole measurement period. Thus, the whole EC mass was accumulated in the submicron particles. Generally, the EC percentage in the dust mass and the EC concentrations in the air (Fig. 3) were higher in the cold season. It was related to the fact that there was an additional EC source in winter, namely fuel combustion in home furnaces. The highest EC percentage in PM (9%) was observed in January.

The secondary inorganic aerosol (SIA) made another important component of the fine PM in Racibórz. Its percentage was 2-11% and 5-16% for PM_1 and $PM_{2.5}$ masses, respectively. The highest SIA content was measured in May and June, when the meteorological conditions were favourable to the high intensity of transformations of aerosol gaseous precursors (Spindler *et al.,* 2010). The secondary aerosol formation could be the possible explanation for increased concentrations of SO_4^{2-}, NO_3^- and NH_4^+ in the warm period (Mkoma *et al.,* 2009). On the other hand, fossil fuel combustion combined with the unfavourable meteorological conditions and the movement of air masses from more polluted areas contributed to high ambient concentrations of water-soluble ions in the cold season (Fig. 3, Table 3; Ho *et al.,* 2006; Mkoma *et al.,* 2009).

The percentage of the chloride, potassium and sodium (Na/K/Cl) masses in the fine dust mass was significant. The Na/K/Cl percentage was 2.4-7% and 3.5-9% for PM_1 and $PM_{2.5}$, respectively (Fig. 3). The highest Na/K/Cl percentages in the PM_1 and $PM_{2.5}$ masses were observed in January. Most of this mass was accumulated in the submicron particles.

As the sampling point in Racibórz was an inland site located far from the traffic sources, it was assumed that fuel combustion was the main source of the Na/K/Cl compounds. The above-mentioned analysis of the correlations between Na^+, K^+, Cl^- and EC corroborated this finding. As Racibórz is a quasi-rural location, the high percentage of the Na/K/Cl compounds in the fine dust mass could also be brought about by additional sources of the alkaline dust, such as grass burning and grass and plant waste combustion in the surrounding meadows, fields and gardens.

The CM percentage in the PM_1 and $PM_{2.5}$ depended largely on the season. It was low in the cold season and did not exceed 2%. The CM content started to rise gradually in April and reached its highest level in June (6% in PM_1 and 9% in $PM_{2.5}$). The literature examples show that CM is usually a mixture of the road (from the abrasion of tyres, linings, brake pads and surface, etc.) and soil dust that is moved by the mixing air masses. Its chemical composition and dust particle sizes change under the influence of various transformations and processes (Sillanpää *et al.,* 2006; Orza *et al.,* 2011). Both the measurement point distance from the traffic sources and considerable seasonal variations in the CM concentrations indicate that the intensity of the soil dust resuspension influenced the CM percentage in the fine dust in Racibórz. The resuspension influence was particularly visible in the spring and summer months (Rogula-Kozłowska *et al.,* 2011). The higher CM percentage in the dust mass observed in the warm season is also related to the fact that the dust concentration was lower then, even though the CM concentration in the air was the same in both seasons.

The average percentage of other elements (OE) in the PM_1 and $PM_{2.5}$ masses at the quasi-rural site in Racibórz did not exceed 1% in the cold and warm seasons (Fig. 3). The OE mass was mainly concentrated in PM_1. The OE mass percentage in PM_1 and $PM_{2.5}$ was usually the same. April was an exception as the OE percentage in $PM_{2.5}$ was twice as high as in PM_1.

Elements such as V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Sb, Ba, Pb usually make a small percentage of the PM mass (e.g. Querol *et al.,* 2007; Rajšić *et al.,* 2008; Rogula-Kozłowska *et al.,* 2013; Table 2). Nevertheless, they were also important for the analysis because of their great environmental importance due to their toxicity and anthropogenic origin (Almeida *et al.,* 2006). These elements are usually associated with various sources, namely coal combustion, incineration and traffic (Sternbeck *et al.,* 2002; Querol *et al.,* 2007; Ragosta *et al.,* 2008; Rajšić *et al.,* 2008; Rogula-Kozłowska et al. 2013). In Racibórz, the element group is probably related to the local municipal sources. Nonetheless, it is mainly composed of the elements emitted together with other pollutants from distant sources (such as those located in the

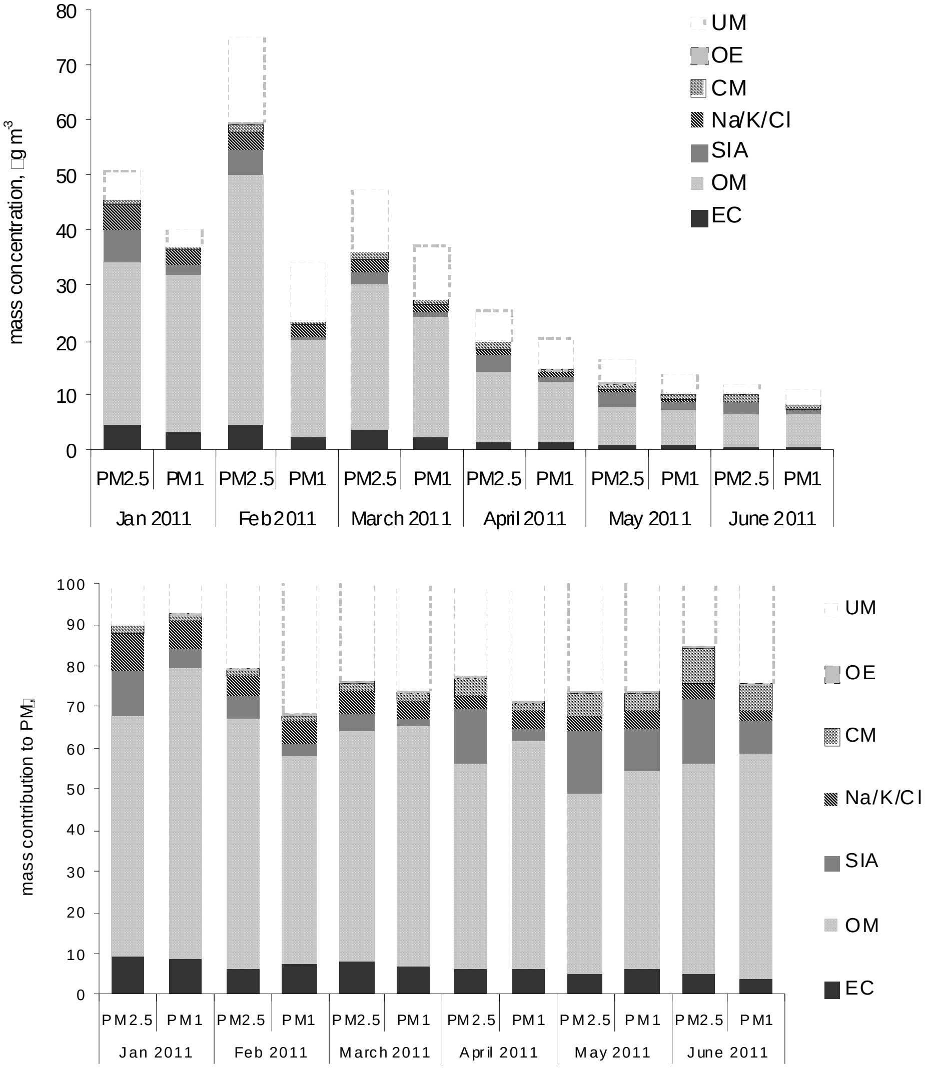

Fig. 3. Average monthly concentrations (a) and percentage in PM mass (b) of organic matter (OM), elemental carbon (EC), secondary inorganic aerosol (SIA), crustal matter (CM), Na/K/Cl, other elements (OE), and of the rest—unidentified matter (UM) related to PM_1 or $PM_{2.5}$ in Racibórz

Upper Silesia urban area). They can move with the air masses into the Racibórz region. Small variations in the OE mass percentage observed in the fine dust mass in the area support this fact.

In the quasi-rural area in Racibórz, the carbonaceous matter (EC+OM) percentage in the PM_1 and $PM_{2.5}$ samples was significantly higher than in other European regions (Table 2). On the other hand, the SIA content was visibly lower in the PM samples from Racibórz. The percentages of CM and Na/K/Cl compounds were lower or comparable to those obtained in the locations listed in Table 2. It is worth mentioning that the Na/K/Cl group created for this study was not usually included in the findings from other locations. Instead, the percentage of sea or road salt in the dust was estimated. The specific emission situation in southern Poland requires separating and discussing the fine dust components directly related to coal and biomass combustion. The results listed in Table 2 suggest that PM concentrations and compositions in Racibórz were mainly influenced by anthropogenic emissions.

CONCLUSION

The fine dust concentrations can be high in a quasi-rural area in southern Poland. For Racibórz, their mean values were 26.2 $\mu g \cdot m^{-3}$ (PM_1) and 37.9 $\mu g \cdot m^{-3}$ ($PM_{2.5}$) in the first half of 2011. They were significantly higher than those observed in similar European areas. Both PM_1 and $PM_{2.5}$ concentrations demonstrated high seasonal variations.The average monthly concentrations in the cold season were at least twice as high as those observed in the warm season. The maximum 24-h concentrations were 124.1 $\mu g \cdot m^{-3}$ (PM_1) and 152.3 $\mu g \cdot m^{-3}$ ($PM_{2.5}$) in the cold season. The average percentage of PM_1 in $PM_{2.5}$ was 69%. The maximum value was found for June (93%). In Racibórz, the OM percentage in the dust mass was 44-61% ($PM_{2.5}$) and 48-71% (PM_1). It was significantly higher for both fractions in the cold season (increased emissions from fuel combustion). The relatively high OM percentage in the PM mass observed in the warm season mainly resulted from the intensity of the SOC formation in the air, which was higher in the warm season. The highest SIA contents in the PM mass were also observed in the warm season (particularly in May and June). However, the elemental carbon percentage in the dust mass was higher in the cold season. The average EC percentage, observed over the whole measurement period, was ~7% for both PM_1 and $PM_{2.5}$ masses. Additionally, the sum of chloride, potassium and sodium (Na/K/Cl) masses made a significant part of the fine dust mass. It was 3.5-9 % for $PM_{2.5}$ and 2.4-7% for PM_1. The CM percentage in the PM_1 and $PM_{2.5}$ masses did not exceed 2% in the cold season. The highest CM values were observed in June (9% for $PM_{2.5}$ and 6% for PM_1). The average OE percentage did not exceed 1% in the PM_1 and $PM_{2.5}$ masses in the cold and warm seasons. Even though places such as Racibórz can be formally qualified as rural sites, such areas in southern Poland do not necessarily have low PM concentrations (lower than in cities) or chemical compositions of fine particles different from those in more urbanized areas. The obtained results demonstrate that the fine dust concentrations and compositions in Racibórz in the cold seasons are under the enormous influence of anthropogenic emissions (carbon, waste and biomass combustion in home furnaces and energy production based on hard and brown coal combustion). On the other hand, the researched area is under the influence of the emission from the entire region (including the polluted Upper Silesia and Ostrava areas) in the warm seasons. At that time, the SOC constitutes an important part of the PM mass. The SIA percentage is also significant, but to a lesser extent. The findings indicate serious problems related to the possible reduction in the fine dust concentrations in Racibórz and other areas whose characteristics are similar in the entire southern Poland.

ACKNOWLEDGEMENTS

The work was carried out within the projects of "An air quality monitoring system for the Polish-Czech borderland in Silesia and Moravia No. CZ.3.22/1.2.00/09.01610 (AIR SILESIA)" and "Chemical mass closure and the origin of fine PM in urban agglomerations differing in the amount and structure of emission of particulate matter and its precursors (No 2012/07/D/ST10/02895)", the former financed by the European Union from the European Cross-Border Fund, the latter—by the National Science Centre Poland (NCN).

REFERENCES

Almeida, S. M., Pio, C. A., Freitas, M. C., Reis, M. A. and Trancoso, M. A. (2006). Approaching $PM_{2.5}$ and $PM_{2.5-10}$ source apportionment by mass balance analysis, principal component analysis and particle size distribution. Science of the Total Environment, **368**, 663–674.

Caggiano, R., Macchiato, M. and Trippetta, S. (2010). Levels, chemical composition and sources of fine aerosol particles (PM_1) in an area of the Mediterranean basin. Science of the Total Environment, 408, 884–895.

Canepari, S., Farao, C., Marconi, E., Giovanelli, C. and Perrino, C. (2012). Qualitative and quantitative determination of water in airborne particulate matter. Atmospheric Chemistry and Physics, **12**, 27367–27393.

Canepari, S., Pietrodangelo, A., Perrino, C., Astolfi, M. L. and Marzo, M. L. (2009). Enhancement of source traceability of atmospheric PM by elemental chemical fractionation. Atmospheric Environment, **43**, 4754–4765.

Carbone, C., Decesari, S., Mircea, M., Giulianelli, L., Finessi, E., Rinaldi, M., Fuzzi, S., Marinoni, A., Duchi, R., Perrino, C., Sargolini, T., Vardè, M., Sprovieri, F., Gobbi, G.P., Angelini, F. and Facchini, M. C. (2010). Size-resolved aerosol chemical composition over the Italian Peninsula during typical summer and winter conditions. Atmospheric Environment, **44**, 5269–5278.

Castro, L. M., Pio, C. A., Harrison, R. M. and Smith, D. J. T. (1999). Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations. Atmospheric Environment, **33**, 2771-2781.

Choi, J. K., Heo, J. B., Ban, S. J., Yi, S. M. and Zoh, K. D. (2013). Source apportionment of PM2.5 at the coastal area in Korea Science of the Total Environment, **447**, 370-80.

Crippa, M., DeCarlo, P. F., Slowik, J. G., Mohr, C., Heringa, M. F., Chirico, R., Poulain, L., Freutel, F., Sciare, J., Cozic, J., Di Marco, C. F., Elsasser, M., Nicolas, J.B., Marchand, N., Abidi, E., Wiedensohler, A., Drewnick, F., Schneider, J., Borrmann, S., Nemitz, E., Zimmermann, R., Jaffrezo, J.-L., Prévôt, A.S. H. and Baltensperger, U. (2013). Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris. Atmospheric Chemistry and Physics, **13**, 961-981.

Đordević, D., Mihajlidi-Zelić, A., Relić, D., Ignjatović, L., Huremović, J., Stortini, A.M. and Gambaro, A. (2012). Size-segregated mass concentration and water soluble inorganic ions in an urban aerosol of the Central Balkans (Belgrade). Atmospheric Environment, **46**, 309–317.

Englert, N. (2004). Fine particles and human health – a review of epidemiological studies. Toxicology Letters, **149**, 235–242.

Gnauk, T., Brüggemann, E., Müller, K., Chemnitzer, R., Rüd, C., Galgon, D., Wiedensohler, A., Acker, K., Auel, R., Wieprecht, W., Möller, D., Jeaschke, W. and Herrmann, H. (2005). Aerosol characterization at the FEBUKO upwind station Goldlauter (1): Particle mass, main ionic components, OC/EC, and mass closure. Atmospheric Environment, **39**, 4209–4218.

Grosjean, D. and Friedlander, S. K. (1975). Gas-particle distribution factors for organic and other pollutants in the Los Angeles atmosphere. Journal of the Air Pollution Control Association, **25**, 1038.

Ho, K. F., Lee, S. C., Cao, J. J., Chow, J. C., Watson, J. G. and Chan, C. K. (2006). Seasonal variations and mass closure analysis of particulate matter in Hong Kong. Science of the Total Environment, **355**, 276–287.

Huang, X., Qiu, R., Chak, K. Chan., Pathak, R. K. (2011). Evidence of high PM2.5 strong acidity in ammonia-rich atmosphere of Guangzhou, China: Transition in pathways of ambient ammonia to form aerosol ammonium at $[NH_4^+]/[SO_4^{2-}]$ = 1.5. Atmospheric Research, **99**, 488–495.

Hueglin, C., Gehrig, R., Baltensperger, U., Gysel, M., Monn, C. and Vonmont, H. (2005). Chemical characterization of $PM_{2.5}$, PM_{10} and coarse particles at urban, near-city and rural sites in Switzerland. Atmospheric Environment, **39**, 637–651.

Juda-Rezler, K., Reizer, M., Oudinet, J. P. (2011). Determination and analysis of PM_{10} source apportionment during episodes of air pollution in Central Eastern European urban areas: The case of wintertime 2006. Atmospheric Environment, **45**, 6557-6566.

Keuken, M., van der Gon, H. D. and van der Valk, K. (2012). Non-exhaust emissions of PM and the efficiency of emission reduction by road sweeping and washing in the Netherlands. Science of the Total Environment, **408**, 4591–4599.

Klejnowski, K., Krasa, A. and Rogula, W. (2007). Seasonal variability of concentrations of total suspended particles (TSP) as well as PM10, PM2.5 and PM1 modes in Zabrze, Poland. Archives of Environmental Protection, **33 (3)**, 15–29.

Klejnowski, K., Pastuszka, J. S., Rogula-Kozłowska, W., Talik, E. and Krasa A. (2012) Mass size distribution and chemical composition of the surface layer of summer and winter airborne particles in Zabrze, Poland. Bulletin of Environmental Contamination and Toxicology, **88 (2)**, 255-259.

Majewski, G., Kleniewska, M. and Brandyk, A. (2011). Seasonal Variation of Particulate Matter Mass Concentration and Content of Metals. Polish Journal of Environmental Studies, **20 (2)**, 417-427.

Marcazzan, G. M., Vaccaro, S., Valli, G. and Vecchi, R. (2001) Characterisation of PM10 and PM2.5 particulate matter in the ambient air of Milan (Italy), Atmospheric Environment, **35**, 4639 4650.

Milford, C., Castell, N., Marrero, C., Rodríguez, S., Sánchez de la Campa, A. M., Fernández-Camacho, R., de la Rosa, J., and Stein, A. F. (2013). Measurements and simulation of speciated $PM_{2.5}$ in south-west Europe. Atmospheric Environment, **77**, 36–50.

Mkoma, S.L., Wang, W. and Maenhaut, W. (2009). Seasonal variation of water-soluble inorganic species in the coarse and fine atmospheric aerosols at Dar es Salaam, Tanzania. Nuclear Instruments and Methods in Physics Research, **267**, 2897–2902.

Orza, J. A. G., Cabello, M., Lidón, V. and Martínez, J. (2011). Contribution of resuspension to particulate matter inmission levels in SE Spain. Journal of Arid Environments, **75**, 545–554.

Paasonen, P., Asmi, A., Petäjä, T., Kajos, M. K., Äijälä, M., Junninen, H., Holst, T., Abbatt, J. P. D., Arneth, A., Birmili, W., van der Gon, H.D., Hamed, A., Hoffer, A., Laakso, L., Laaksonen, A., Leaitch, W.R., Plass-Dülmer, Ch., Pryor, S.C., Räisänen, P., Swietlicki, E., Wiedensohler, A., and Douglas, R. Worsnop, Veli-Matti Kerminenand Markku Kulmala. (2013). Warming-induced increase in aerosol number concentration likely to moderate climate change. Nature Geoscience, **6**, 438–442.

Pastuszka, J.S., Rogula-Kozłowska, W. and Zajusz-Zubek, E. (2010). Characterization of PM10 and PM2.5 and associated heavy metals at the crossroads and urban background site in Zabrze, Upper Silesia, Poland, during the smog episodes. Environmental Monitoring and Assessment, **168**, 613–627.

Pateraki, S., Assimakopoulos, V. D., Bougiatioti, A., Kouvarakis, G., Mihalopoulos, N. and Vasilakos, Ch. (2012). Carbonaceous and ionic compositional patterns of fine particles over an urban Mediterranean area. Science of the Total Environment, **424**, 251–263.

Pathak, R. K., Wu, W. S., Wang, T. (2009). Summertime PM2.5 ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere. Atmospheric Chemistry and Physics, **9**, 1711-1722.

Pérez, N., Pey, J., Querol, X., Alastuey, A., López, J. M. and Viana, M. (2008). Partitioning of major and trace components in PM_{10}-$PM_{2.5}$-PM_1 at an urban site in Southern Europe. Atmospheric Environment, **42**, 1677–1691.

Perrone, M. R., Becagli, S., Garcia Orza, J. A., Vecchi, R., Dinoi, A., Udisti, R. and Cabello, M. (2013). The impact of long-range-transport on PM_1 and $PM_{2.5}$ at a Central Mediterranean site. Atmospheric Environment, **71**, 176–186.

Pey, J., Pérez, N., Castillo, S., Viana, M., Moreno, T., Pandolfi, M., López-Sebastián, J. M., Alastuey, A. and

Querol, X. (2009). Geochemistry of regional background aerosols in the Western Mediterranean. Atmospheric Research, **94**, 422–435.

Pio, C., Cerqueira, M., Harrison, R. M., Nunes, T., Mirante, F., Alves, C., Oliveira, C., de la Campa, A. S., Artíñano, B. and Matos, M. (2011). OC/EC ratio observations in Europe: Re-thinking the approach for apportionment between primary and secondary organic carbon. Atmospheric Environment, **45**, 6121–6132.

Pope, C. A. and Dockery, D. W. (2006). Health effects of fine particulate air pollution: lines that connect. Journal of the Air & Waste Management Association, **56**, 709–742.

Putaud, J.-P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R., Hansson, H.C., Harrison, R. M., Herrmann, H., Hitzenberger, R., Hüglin, C., Jones, A. M., Kasper-Giebl, A., Kiss, G., Kousa, A., Kuhlbush, T. A. J., Löschau, G., Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J., Perrino, C., Pitz, M., Puxbaum, H., Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J., Spindler, G., ten Brink, H., Tursic, J., Viana, M., Wiedensohler, A., and Raes, F. (2010). A European aerosol phenomenology – 3: Physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. Atmospheric Environment, **44,** 1308–1320.

Querol, X., Viana, M., Alastuey, A., Amato, F., Moreno, T., Castillo, S., Pey, J., de la Rosa, J., Sánchez de la Campa, A., Artíñano, B., Salvador, P., García Dos Santos, S., Fernández-Patier, R., Moreno-Grau, S., Negral, L., Minguillón, M.C., Monfort, E., Gil, J.I., Inza, A., Ortega, L.A., Santamaria, J.M. and Zabalza, J. (2007). Source origin of trace elements in PM from regional background, urban and industrial sites of Spain. Atmospheric Environment, **41**, 7219–7231.

Ragosta, M., Caggiano, R., Macchiato, M., Sabia, S. and Trippetta, S. (2008). Trace elements in daily collected aerosol: Level characterization and source identification in a four-year study. Atmospheric Research, **89**, 206–217.

Rajšić, S., Mijić, Z., Tasić, M., Radenković, M. and Joksić, J. (2008). Evaluation of the levels and sources of trace elements in urban particulate matter. Environmental Chemistry Letters, **6**, 95–100.

Rees, S.L., Robinson, A.L., Khlystov, A., Stanier, C.O. and Pandis, S.N. (2004). Mass balance closure and the Federal Reference Method for $PM_{2.5}$ in Pittsburgh, Pennsylvania. Atmospheric Environment, **38**, 3305–3318.

Rogula-Kozłowska, W., Błaszczak, B., Szopa, S., Klejnowski, K., Sówka, I., Zwoździak, A., Jabłońska, M. and Mathews, B. (2013). PM2.5 in the central part of Upper Silesia, Poland: concentrations, elemental composition, and mobility of components. Environmental Monitoring and Assessment, **185**, 581-601.

Rogula-Kozłowska, W., Błaszczak, B., Klejnowski, K., Krasa, A. and Szopa, S. (2011). Concentrations of PM2.5, PM2.5-10 and PM-related elements at two heights in an urban background area in Zabrze (Poland), Archives of Environmental Protection, **37**, 31–47.

Rogula-Kozłowska, W. and Klejnowski, K. (2013). Submicrometer Aerosol in Rural and Urban Backgrounds in Southern Poland: Primary and Secondary Components of PM1, Bulletin of Environmental Contamination and Toxicology, **90 (1)**, 103-109.

Rogula-Kozłowska, W., Klejnowski, K., Rogula-Kopiec, P., Mathews, B. and Szopa, S. (2012). A study on the seasonal mass closure of ambient fine and coarse dusts in Zabrze, Poland, Bulletin of Environmental Contamination and Toxicology, **88**, 722–729.

Saarikoski, S. (2008). Chemical mass closure and source-specific composition of atmospheric particles. Academic Dissertation. Finnish Meteorological Institute, Contributions, No. 74.

Seinfeld, J. H. and Pandis, S. N. (2006). Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. John Wiley & Sons.

Shahsavani, A., Naddafi, K., Haghighfard, N. J., Mesdaghinia, A., Yunesian, M., Nabizadeh, R., Arahami, M., Sowlat, M. H., Yarahmadi, M., Saki, H., Alimohamadi, M., Nazmara, S., Motevalian, S.A. and Goudarzi, G. (2012). The evaluation of PM_{10}, $PM_{2.5}$, and PM_1 during the Middle Eastern Dust (MED) events in Ahvaz, Iran, from April through September (2010). Journal of Arid Environment, **77**, 72–83.

Sillanpää, M., Hillamo, R., Saarikoski, S., Frey, A., Pennanen, A., Makkonen, U., Spolnik, Z., Van Grieken, R., Braniš, M., Brunekreef, B., Chalbot, M.-C., Kuhlbusch, T., Sunyer, J., Kerminen, V.-M., Kulmala, M. and Salonen, R.O. (2006). Chemical composition and mass closure of particulate matter at six urban sites in Europe. Atmospheric Environment, **40**, 212–223.

Spindler, G., Brüggemann, E., Gnauk, T., Grüner, A., Müller, K. and Herrmann, H. (2010). A four-year size-segregated characterization study of particles PM_{10}, $PM_{2.5}$ and PM_1 depending on air mass origin at Melpitz. Atmospheric Environment, **44**, 164–173.

Sternbeck, J., Åke, S. and Kenth, A. (2002). Metal emission from road traffic and the influence of resuspension-results from two tunnel studies. Atmospheric Environment, **36**, 4735–44.

Terzi, E., Argyropoulos, G., Bougiatioti, A., Mihalopoulos, N., Nikolaou, K. and Samara, C. (2010). Chemical composition and mass closure of ambient PM10 at urban sites. Atmospheric Environment, **44**, 2231–2339.

Tsyro, S.G. (2005). To what extent can aerosol water explain the discrepancy between model calculated and gravimetric PM10 and PM2.5. Atmospheric Chemistry and Physics, 5, 515–32.

Turpin, B. and Lim, H. (2001). Species contributions to PM2.5 mass concentrations: revisiting common assumptions for estimating organic mass. Aerosol Science and Technology, **35**, 602–610.

Wagener, S., Langner, M., Hansen, U., Moriske, H. -J. and Endlicher, W. R. (2012). Spatial and seasonal variations of biogenic tracer compounds in ambient PM_{10} and PM_1 samples in Berlin, Germany. Atmospheric Environment, **47**, 33–47.

Yin, J. and Harrison, R. M. (2008). Pragmatic mass closure study for $PM_{1.0}$, $PM_{2.5}$ and PM_{10} at roadside, urban background and rural sites. Atmospheric Environment, **42**, 980–988.

Zhang, R., Jing, J., Tao, J., Hsu, S. -C., Wang, G., Cao, J., Lee, C. S. L., Zhu, L., Chen, Z., Zhao, Y. and Shen, Z. (2013). Chemical characterization and source apportionment of $PM_{2.5}$ in Beijing: seasonal perspective. Atmospheric Chemistry and Physics, **13**, 7053-7074.

Zhang, Y. X., Sheesley, R.J., Schauer, J. J., Lewandowski, M., Jaoui, M., Offenberg, J. H., Kleindienst, T. E. and Edney, E. O. (2009). Source apportionment of primary and secondary organic aerosols using positive matrix factorization (PMF) of molecular markers. Atmospheric Environment, **43**, 5567–5574.

Zwozdziak, A., Samek, L., Sowka, I., Furman, L. and Skrętowicz M. (2012). Aerosol Pollution from Small Combustors in a Village. ScientificWorld Journal, 2012, 956401.