Bull Environ Contam Toxicol (2013) 90:103–109
DOI 10.1007/s00128-012-0868-4

Submicrometer Aerosol in Rural and Urban Backgrounds in Southern Poland: Primary and Secondary Components of PM_1

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Received: 5 July 2012 / Accepted: 16 October 2012 / Published online: 27 October 2012

Abstract Diurnal samples of PM_1 (submicrometer particles, having aerodynamic diameters not greater than 1 μm) were collected at an urban background site in Zabrze (from 01.08. to 31.12.2009) and a rural background site in Racibórz (from 01.08. to 31.12.2010). The samples were analyzed 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 by using, respectively, a Sunset Laboratory carbon analyzer, a Herisau Metrohm AG ion chromatograph, a PANalitycal Epsilon 5 spectrometer. To perform the monthly mass closure calculations for PM_1, the chemical components were categorized into organic matter (OM), elemental carbon (EC), secondary inorganic aerosol (SIA), crustal matter (CM), marine components (MC), other elements (OE) and unidentified matter (UM). The mass contributions of secondary (SOM) and primary (POM) organic matter to PM_1 were also estimated. In average, 50 % of PM_1 in Zabrze and 40 % in Racibórz were secondary aerosol coming from the transformations of its gaseous precursors. High concentrations and mass contributions of EC and OM to PM, and probable PM acidic nature in Zabrze, indicate particularly high hazard from the ambient submicrometer particles to the inhabitants of southern Poland.

Keywords PM_1 · Fine particles · Organic matter · Elemental carbon · SIA · SOA · POA · Chemical mass closure

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The size, usually in terms of equivalent (most often aerodynamic) diameter, is a key characteristic of an atmospheric aerosol particle (Hinds 1998). All the particle properties, also these deciding the particle-human body interactions, depend on its size (López-Villarrubia et al. 2012). The strong epidemiological evidence suggests growth of the health hazard from ambient particles with the particle decreasing aerodynamic diameter—the finest particles are most harmful (Oberdörster et al. 1995; Pope and Dockery 2006; Dockery and Stone 2007; Kappos 2011). Usually, there are considerable amounts of submicrometer particles in the air (Makkonen et al. 2010; Kumar et al. 2010; Ham and Kleeman 2011; Massey et al. 2012; Aas et al. 2012). Examinations of the air quality in such cities as Wroclaw and Zabrze confirm predominance of PM_1 in the urbanized areas of southern Poland (Zwoździak et al. 2011; Klejnowski et al. 2012).

The second important characteristic of atmospheric aerosol, the chemical composition of its particles, depends on the particle size, defines the volatility, density, reactivity and toxicity of the dust and affects the human health as well (Englert 2004). In Southern Poland, the airborne hazardous compounds accumulate mainly in the finest particles (Zwoździak et al. 2011; Rogula-Kozłowska et al. 2012). However, analyzing the data concerning the physical and chemical properties of atmospheric aerosol from over whole Europe (e.g. Putaud et al. 2010; EMEP 2011) one can notice evident lack of chemical characteristics of the fine dust fractions, including PM_1.

The goal of the presented work was to measure concentrations, determine chemical composition and primary and secondary pollutant shares in PM_1 at two sites in southern Poland: urban Zabrze and rural Racibórz.

Materials and Methods

Diurnal samples of PM_1 were taken in Zabrze (01.08–31.12.2009) and in Racibórz (01.08–31.12.2010), southern Poland (Fig. 1), with the use of a Ruprecht&Patashnik Partisol 2020. They were collected on quartz and Teflon filters, the same kind every other day. Before and after exposing, 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 dust on the Teflon filters was analyzed for elemental composition (Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Sb, Te, Ba, Pb). From each exposed quartz filter two equal segments (1.5 cm^2 each) were cut, one was analyzed for OC and elemental carbon (EC), the second one entered a combined monthly sample for the month the filter came from. The monthly samples were analyzed for water soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}).

The OC and EC contents of dust were determined with the use of a Sunset Laboratories Inc. thermal–optical instrument (NIOSH-like protocol, quartz). The instrument corrects the measurements of the products of pyrolysis of carbon compounds by measuring light absorbance of EC (CEN/TR 16243:2011). The detection limit (for TC = OC + EC), equal to 0.52 $\mu g/m^2$, was determined by analyzing blank samples (clean filters, CEN/TR 16243:2011). To control its performance, the apparatus was systematically calibrated within the range of measured concentrations, blanks (several clean filters from each lot) were analyzed on a regular basis, the NIST standards (RM 8785 NIST and RM 8786 NIST, certified carbon content) were analyzed. The recovery of OC was 98 %–132 %, of EC 95 %–116 %.

The applications of a Herisau Metrohm AG ion chromatograph to examine water extracts of dust for ions and of a PANalytical Epsilon 5 EDXRF spectrometer to determine elemental composition of dust on Teflon filters are described in (Rogula-Kozłowska et al. 2012).

The mass closure computations were done for each month and site separately. The concentrations of the categories were computed from the concentrations of the dust components (Table 1). The concentration of the secondary inorganic aerosol (SIA) was the sum of the concentrations of PM_1-related SO_4^{2-}, NO_3^- and NH_4^+. The concentration of the marine components (MC) was the sum of PM_1-related Na^+ and Cl^-. The concentration of organic matter (OM) was 1.4 times the concentration of PM_1-related organic carbon (OC) (Turpin and Lim 2001). The

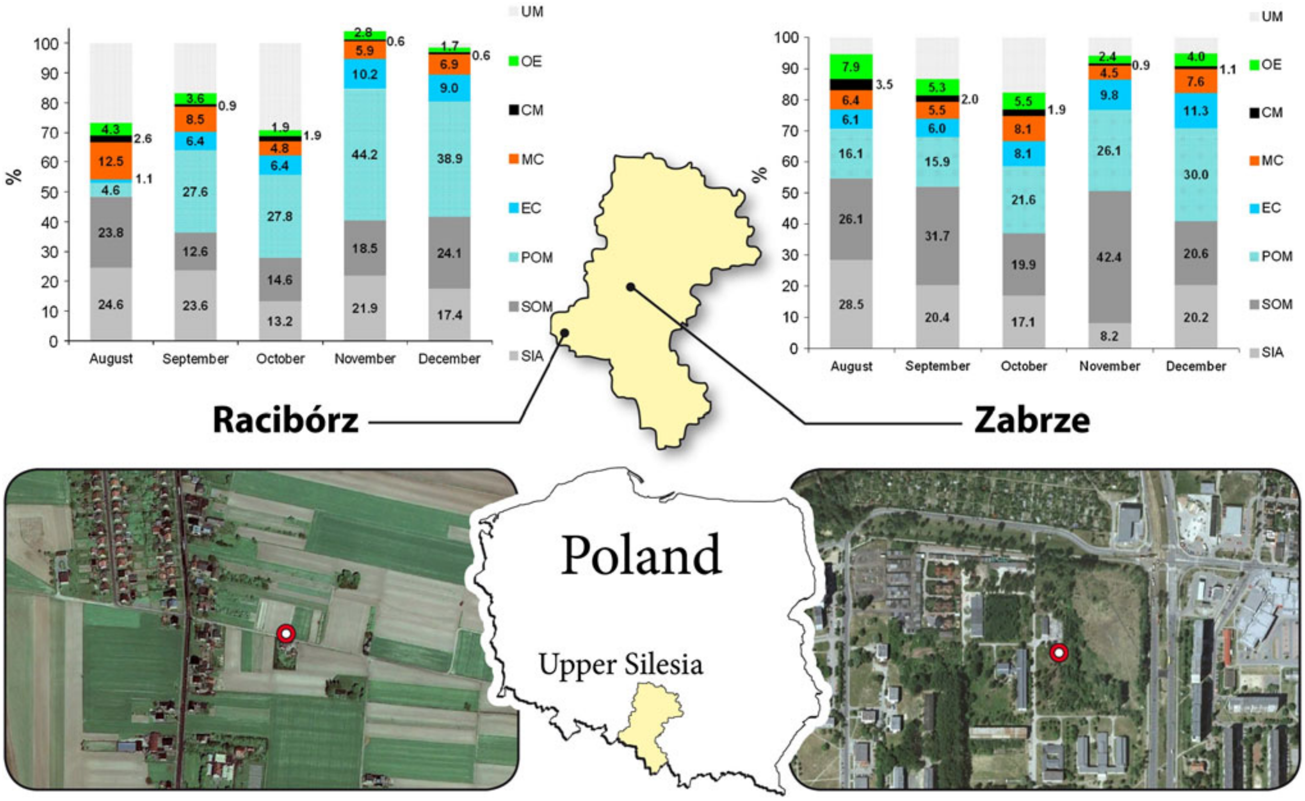

Fig. 1 Location of sampling points and monthly chemical mass closure of PM_1 in Zabrze and Racibórz, Poland

Table 1 Concentrations of PM$_1$ and its components in Zabrze and Racibórz

	Zabrze (01.08–31.12.2009)					Racibórz (01.08–31.12.2010)				
	August	September	October	November	December	August	September	October	November	December
PM$_1$, μg/m^3	16.66	24.55	27.93	60.17	50.03	13.32	17.61	40.39	31.93	57.27
OC, μg/m^3	5.02	8.34	8.29	29.44	18.09	2.70	5.06	12.25	14.29	25.76
OC$_{sec}$, μg/m^3	3.10	5.55	3.98	18.21	7.37	2.26	1.58	4.22	4.22	9.86
EC, μg/m^3	1.01	1.47	2.27	5.91	5.64	0.14	1.12	2.59	3.25	5.13
Cl$^-$, μg/m^3	0.62	0.49	1.00	0.86	1.56	1.08	0.57	1.29	1.12	3.15
NO$_3$$^-$, μg/m^3	1.14	1.45	1.68	1.69	2.65	0.84	1.37	2.34	2.58	3.20
SO$_4$$^{2-}$, μg/m^3	3.27	3.26	2.90	2.98	6.79	1.80	2.22	2.18	2.94	4.07
Na$^+$, μg/m^3	0.45	0.85	1.27	1.82	2.26	0.58	0.93	0.66	0.76	0.82
NH$_4$$^+$, μg/m^3	0.34	0.29	0.19	0.25	0.69	0.63	0.57	0.83	1.48	2.72
K$^+$, μg/m^3	0.47	0.38	0.26	0.35	1.03	0.38	0.36	0.45	0.58	0.47
Ca^{2+}, μg/m^3	0.54	0.50	1.07	0.84	0.71	0.14	0.20	0.18	0.07	0.09
Mg^{2+}, μg/m^3	0.26	0.18	0.09	0.09	0.09	0.08	0.03	0.14	0.02	0.02
Al, ng/m^3	52.59	41.06	74.57	54.69	47.32	60.30	22.97	72.54	18.45	16.70
Si, ng/m^3	22.47	49.32	46.54	49.17	74.76	3.08	*bld*	130.64	58.94	118.27
Ti, ng/m^3	1.35	0.41	0.26	0.62	1.23	1.20	0.22	0.15	0.70	1.96
V, ng/m^3	0.56	0.41	0.90	0.94	0.45	0.67	0.61	0.80	0.41	0.71
Cr, ng/m^3	0.92	2.87	5.56	5.31	5.15	5.07	3.20	5.66	14.88	26.47
Mn, ng/m^3	11.19	18.06	19.74	8.97	7.47	4.94	5.67	9.74	5.88	8.67
Fe, ng/m^3	196.00	236.32	104.67	108.76	96.07	61.97	43.87	79.35	128.15	211.25
Co, ng/m^3	*bld*	2.74	0.32	0.04	9.26	*bld*	*bld*	0.59	*bld*	0.03
Ni, ng/m^3	0.87	1.25	2.29	1.37	1.22	1.36	1.52	2.00	2.08	4.54
Cu, ng/m^3	5.06	13.63	8.06	9.85	6.45	2.36	4.07	5.41	4.73	8.25
Zn, ng/m^3	56.37	80.23	96.28	171.92	131.59	12.94	32.53	76.51	61.65	91.70
As, ng/m^3	3.71	2.63	3.99	10.07	14.19	1.23	3.32	5.51	3.70	11.02
Se, ng/m^3	*bld*	3.67	9.69	3.97	1.02	*bld*	*bld*	0.01	*bld*	*bld*
Rb, ng/m^3	1.12	0.90	2.27	1.92	3.37	0.82	1.35	2.47	1.56	3.21
Sr, ng/m^3	2.82	3.69	3.33	6.64	7.13	2.40	4.22	2.40	2.59	5.07
Mo, ng/m^3	2.93	1.88	2.19	2.37	4.29	2.79	2.13	4.95	2.22	3.63
Cd, ng/m^3	1.75	1.36	1.32	5.27	4.58	1.15	1.66	2.81	2.60	5.23
Sb, ng/m^3	2.27	1.09	3.50	7.46	5.68	1.29	3.19	6.27	3.70	4.46
Te, ng/m^3	1.96	0.77	2.52	2.08	3.57	1.60	1.83	2.45	0.37	1.61
Ba, ng/m^3	3.71	4.87	6.89	3.78	6.79	3.69	1.70	3.63	3.43	7.07
Pb, ng/m^3	15.51	48.70	23.22	33.99	42.03	2.04	11.81	18.34	23.84	35.24

bld below limit of detection

concentration of crustal matter (CM) was the sum of the stoichiometrically computed concentrations of oxides of Mg^{2+}, Fe (except for August and September in Zabrze and November and December in Racibórz), Al, Si and Ti (Querol et al. 2001; Rogula-Kozłowska et al. 2012). The concentration of the other elements (OE) is the sum of the concentrations of PM$_1$-related K$^+$, Ca^{2+}, V, Cr, Mn, Fe (only for August and September in Zabrze and November and December in Racibórz), Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Sb, Ba, Pb. The PM$_1$-related elements were included into CM and OE by analyzing their enrichment coefficients (EF, Table 2). The elements with EF greater than 5 (Table 2, bolded) were in OE, the rest was in CM. The concentration of the unidentified matter (UM) was received by subtracting the sum of the SIA, MC, OM, EC, CM, OE concentrations from the PM$_1$ concentration.

The monthly PM$_1$ concentrations were computed by dividing the mass of the dust collected during the month by the volume of the air the dust was taken from. The monthly mass shares (percentages) of PM$_1$ components were computed by dividing the mass of the component collected during the month by the mass of PM$_1$ from this month. The average monthly concentration of a component is its percentage in PM$_1$ multiplied by the monthly PM$_1$

Table 2 Enrichment factors for PM_1 related elements in Zabrze and Racibórz, Poland

	Zabrze					Racibórz				
	August	September	October	November	December	August	September	October	November	December
K^+	21.1	44.7	9.7	51.3	166.7	17.0	42.4	16.8	85.0	76.1
Ca^{2+}	23.55	57.24	38.78	119.69	111.78	6.11	22.90	6.52	9.97	14.17
Al	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Si	0.1	0.3	0.2	0.2	0.4	<0.1	–	0.5	0.8	1.8
Ti	0.6	0.2	0.1	0.3	0.6	0.5	0.2	0.1	0.9	2.9
V	15.5	14.7	17.6	25.0	13.9	16.2	38.5	16.1	32.5	61.8
Cr	38.7	154.7	164.9	214.7	240.6	186.1	308.1	172.8	1783.9	3506.1
Mn	31.3	64.6	38.9	24.1	23.2	12.0	36.2	19.7	46.8	76.3
Fe	9.3	14.4	3.5	5.0	5.0	2.6	4.8	2.7	17.4	31.7
Co	–	445.5	28.8	4.8	1306.8	–	–	54.3	–	12.8
Ni	69.0	127.1	128.1	104.2	107.4	93.8	275.6	114.9	143.9	823.3
Cu	520.7	1797.8	585.3	975.2	737.8	212.3	959.8	403.5	1387.0	2676.4
Zn	1596.4	2909.8	1922.9	4681.2	4141.6	319.6	2109.4	1570.6	4975.2	8176.4
As	2382.4	4433.5	2129.6	21128.9	32895.7	789.8	5596.7	2940.9	7763.3	25546.9
Se	–	83366.9	121295.0	67666.5	20140.4	–	–	188.7	–	–
Rb	15.0	15.4	21.4	24.7	50.1	9.6	41.3	24.0	59.6	135.4
Sr	11.4	39.4	11.2	88.2	104.6	9.8	45.0	8.1	34.4	74.4
Mo	3082.5	2533.6	1621.2	2394.5	5010.8	2555.2	5139.3	3772.1	6652.5	12020.2
Cd	22034.5	44953.5	13814.4	216814.0	208186.1	14479.8	54869.7	29407.9	106967.1	237732.2
Sb	9404.4	11854.7	12052.2	100984.3	84951.9	5344.3	34693.9	21590.6	50086.1	66705.2
Ba	7.1	24.6	11.0	23.7	47.1	7.1	8.6	5.8	21.5	49.1
Pb	1343.5	5402.5	1418.5	2830.6	4045.9	154.4	2342.2	1151.7	5884.3	9609.9

Elements with $EF > 5$ are in bold

The definition of the enrichment factor EF_x may be found in (Rogula-Kozłowska et al. 2012)

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)

concentration. The average seasonal (summer: August, September; winter: October–December) PM_1 concentrations and the percentages of the component categories in the PM_1 mass were computed as arithmetical means of the respective monthly concentrations and percentages (Table 3).

Results and Discussion

The PM_1 concentrations were high, especially in winter, at both the rural background station in Racibórz and the urban background station in Zabrze. In winter, the concentration were higher than elsewhere in Europe during several recent years (Table 3).

The chemical compositions of PM_1 in Zabrze and Racibórz were similar (Table 1). At both sites, PM_1 was mainly composed of carbon, sodium, calcium and potassium, as well as sulfates, nitrates, and chlorides. The concentrations of PM_1, PM_1-related carbon compounds and the components of SIA were higher in winter, in November and December especially high, and much higher in Zabrze than in Racibórz. They were higher in winter because the emission of dust and its precursors grows in a heating season over whole Poland (characteristic elevated EC and SIA concentrations at both sites in December), their higher values in Zabrze were due to the character and location of the station. In Zabrze, in densely built-up and populated Silesian Agglomeration with well developed transport network, the fine dust sources are numerous and concentrated. The station in Racibórz is located in clean, typical rural area, where the emission of fine dust from traffic-related and industrial sources is low and the main fine dust sources are domestic stoves, heating boilers and, brought by south-western winds, air pollutants from Ostrava and farther regions of the Czech Republic and central Germany.

At both sites, MC (chlorides and sodium) had high, higher than in other regions of Europe, mass contributions to PM_1 (Tables 1, 3). In summer, the ambient MC concentrations and MC mass contributions to PM_1 were higher in Racibórz than in Zabrze—it may be a result of the combustion of biomass (leaves, grass, wood in domestic

Table 3 Concentrations of PM_1 ($\mu g/m^3$) and mass contributions to PM_1 of selected PM_1 component classes (%) in some European urban and rural areas

	PM_1	CM	MC[j]	EC	OM	SIA	UM
Zabrze (Poland), urban background	20.6/46[d]	3/1	6/7	6/10	45/54	24/15	9/10
Racibórz (Poland), rural background	15.5/43.2	2/1	10/6	4/9	34/56	24/18	22/9
Hyytiälä (Finland), regional background[1]	4.4[e]	–	–	4	48	41[m]	7
Helsinki (Finland), urban[1]	21[f]	–	–	8	40	23[m]	29
Barcelona (Spain), urban background[2]	19[f]	5	1		45[k]	31	18
Melpitz (Germany), rural background[a,3]	10/11[d]	–	–	10/9	10/9	<35/55	45/27
Melpitz (Germany), rural background[b,3]	17/22[d]	–	–	12/9	15/16	<32/41	41/27
Birmingham (UK), urban background[4]	12.6[g]	5/8[h,i]	1/2	8/16	23/33	55/41[n]	8/0
Bologna (Italy), rural[c,5]	8.5/20.6[d]	2/0[h,i]	2/0		48/43[l]	48/56	–
Rome (Italy), suburb[c,5]	7.7/6.7[d]	6/3[h,i]	5/2		62/67[l]	27/28	–

[1] Saarikoski (2008); [2] Pérez et al. (2008); [3] Spindler et al. (2010); [4] Yin and Harrison (2008); [5] Carbone et al. (2010)

[a] Measured during inflow of air masses from the west; [b] Measured during inflow of air masses from the east; [c] Sampled in daytime; [d] Summer/winter; [e] Summer; [f] Year; [g] Whole measuring period average concentration; [h] Spring/winter; [i] Sum: dust rich in Fe + salts of Ca; [j] Or sea salt; [k] Sum: EC + OM; [l] Sum: water-soluble OM + water insoluble carbonaceous matter; [m] Sum of water soluble ions; [n] Sum: $(NH_4)_2SO_4 + (NH_4NO_3/NaNO_3)$

stoves) more common in neighborhood of the station in Racibórz than in Zabrze. In winter, at both sites, ambient chlorides and sodium may come from domestic boilers (combustion of low quality coal and domestic waste)—the distance to the nearest see (Baltic sea) and the size of the PM_1 particles preclude any marine effects on PM_1-related MC concentrations.

At both sites, like elsewhere in Europe (Tables 1, 3; Fig. 1), the concentrations of CM (oxides of Al, Si, Mg, Fe, Ti) were slightly higher in winter than in summer; the CM contributions—in summer than in winter. In summer, the average contribution of CM to PM_1 was slightly greater in Zabrze than in Racibórz and it may be related with density of traffic.

Trace elements (OE) had relatively high, higher in summer than in winter, mass contributions to PM_1 at both sites (Fig. 1, from 1.7 % in Racibórz, December, to 7.9 % in Zabrze, August). The ambient OE concentrations were similar at both sites in winter, in Zabrze they were higher in summer.

As, Cd, Co, Cr, Mn, Ni and Pb present in suspended dust (especially respirable) should be considered a direct threat to human health. The concentrations Ni, As and Pb were high at both sites. Similar or higher ambient concentrations of these elements, but in $PM_{2.5}$, occur in other cities of southern Poland (Rogula-Kozłowska et al., in press), nevertheless the concentrations in Zabrze and Racibórz were sometimes more than ten times the concentrations in other urban regions in Europe (e.g. Vasilakos et al. 2007; Pérez et al. 2008; Vecchi et al. 2004). Pb and other metals are present in hard and brown coal, the principal sources of energy in Poland. In Zabrze, road traffic (admixtures in gasoline, oils, lubricants), industry—lead refinery, aluminum and iron foundries, galvanizing plants, cokery plants, tile factory, bituminous mass factory, and other located in Zabrze or in the neighbor cities, are additional sources of these elements.

At both sites and seasons, the main components of dust, OM and SIA, were related with fuel combustion in car engines, industrial energy production, and domestic stoves.

The SIA mass contributions to PM_1 at the two sites were similar in seasons, the OM contributions too. The SIA contributions to PM_1 at other European sites are rather higher, the OM contributions—lower (Table 3). In both Zabrze and Racibórz, the SIA contributions to PM_1 in winter were lower than in summer—quite uncommon in Europe.

SIA arises from transformations of gaseous precursors, such as SO_2 and NO_x. In the air, SO_2 oxidizes to gaseous SO_3 or liquid H_2SO_4, then is neutralized to ammonium sulfate [$(NH_4)_2SO_4$] or ammonium bisulfate (NH_4HSO_4). NO_x photochemically oxidises to HNO_3, then is neutralized to ammonium nitrate (NH_4NO_3). In Racibórz, the monthly concentrations of SO_2 and SO_4^{2-} were highly linearly correlated, so were the NO_x and NO_3^- concentrations—both R^2 are equal to 0.92. The correlation coefficients for the SO_2 and SO_4^{2-} concentrations and the NO_x and NO_3^- concentrations in Zabrze are 0.66 and 0.36, respectively. The correlation coefficients for the SO_2 and SIA concentrations and the NO_x and SIA concentrations are 0.77 and 0.12 in Zabrze and 0.97 and 0.88 in Racibórz, respectively.

In Racibórz, the neutralization ratio NR (normal equivalent, ratio of NH_4^+ and $SO_4^{2-} + NO_3^-$ concentrations) was from 0.46 (September) to 1.1 (December), the five-month average is 0.73. Hence, in September (also in August and October) the amount of ambient NH_4^+ was not sufficient to fully neutralize ambient H_2SO_4 and HNO_3. NR close to 1 occurred in Racibórz in November and December suggesting alkaline character of PM_1. In Racibórz, the ratio NH_4^+/SO_4^{2-} (0.37 for $(NH_4)_2SO_4$) was between 0.6 and 1.5 from June to December. So, in Racibórz, ambient NH_4^+ could neutralize whole ambient SO_4^{2-}; in some periods (especially in hot ones) it might not be able to neutralize total ambient HNO_3. This and better correlation of SO_2 with SIA than NO_x with SIA mean that SIA in Racibórz mainly consisted of ammonium sulfate and ammonium bisulfate. Ammonium nitrate contributed to SIA less in August-October than in winter.

In Zabrze NR was very low: from 0.12 in October to 0.21 in August, its five-month average is 0.17. The proportion NH_4^+/SO_4^{2-} was from 0.17 in October to 0.28 in August. So, there was not enough ambient NH_4^+ to neutralize ambient H_2SO_4 in Zabrze, the atmospheric aerosol might have acidic reaction—it may be confirmed by acidity of precipitations in Silesia (Hławiczka et al. 2003). In summer, the weather conditions are not favorable for the formation of NH_4NO_3 in the air. At first, NH_4^+ neutralizes sulfates (confirmed by higher proportion NH_4^+/SO_4^{2-} in Zabrze in August). It accounts for no correlation between NO_x and SIA.

It does not mean that PM_1-related SO_4^{2-} and NO_3^- could not be totally neutralized (cation/anion equivalent ratio ~1). Instead, it suggests the existence of other than $(NH_4)_2SO_4$ and NH_4NO_3 components of PM_1 in Zabrze, such as $NaNO_3$ and $Ca(NO_3)_2$ in summer and K_2SO_4 in winter (biomass combustion). At both sites, EF for Ca^{2+} and K^+ in PM_1 were high, suggesting their anthropogenic (combustion) origin instead of usually attributed to them relation with PM_1 through oxides occurring in soil.

The OC and EC contents of PM_1 presented here were determined with the use of a thermal-optical analyzer. It yields other OC/EC in PM_1 than the thermal method applied by the authors in 2009 to $PM_{2.5}$ (Rogula-Kozłowska et al. 2012). Organic carbon is a major form of carbon in PM_1. Its mass contribution to PM_1 is much greater than the EC contribution. In Zabrze in 2009, the concentrations of PM_1- and $PM_{2.5}$-related OC + EC were close, therefore both methods are supposed to measure them correctly (Table 1, Rogula-Kozłowska et al. 2012). But in the present paper, the actual (correct) OC/EC in fine dust in southern Poland is presented for the first time.

The monthly OC/EC in summer (August, September) are higher than in winter in both Zabrze and Racibórz. They were higher in Racibórz than in Zabrze for particular months. It may be due to the absence of traffic-related fine dust sources in Racibórz (submicrometer particles of soot, Japar et al. 1986). The higher summer than winter and rural than urban OC/EC were also observed in England in 2004–2005 (Harrison and Yin 2008), but OC/EC in southern Poland is in average two times greater than in England; it is also greater than OC/EC in Barcelona in 2005–2006 (Pérez et al. 2008).

Oxidizing organic vapors may be a source of low-volatile organic compounds, which condense to form particles in the air, therefore a source of secondary organic aerosol (SOA) (Grosjean and Seinfeld 1989). SOA may have greater contribution to dust than primary organic aerosol (POA).

Because there is no simple method for separation of secondary (OC_{sec}) and primary carbon in dust-related OC the PM_1-related OC_{sec} concentrations in Zabrze and Racibórz were computed from the formula:

$$OC_{sec} = OC - (OC/EC)_{min} \times EC \qquad (1)$$

where OC and EC are monthly OC and EC concentrations in Zabrze or Racibórz $(OC/EC)_{min}$ is the lowest OC/EC[1] between the 1st of August and 31st December in Zabrze or Racibórz.

The OC_{sec} concentrations, presented in Table 1, were computed using monthly concentrations and as such they are only approximate values giving only a rough idea about monthly mass contributions of OC_{sec} to PM_1.

Figure 1 summarizes all the presented results. The secondary aerosol, SIA + SOM (secondary OM, SOM = $1.4{*}OC_{sec}$) may be more than 50 % of the PM_1 mass in the cities of southern Poland (Zabrze). At a rural background sites it is in average by about 10 % lower because of lower SOM contribution to PM_1 (worse conditions for SOA formation in Racibórz—probably lower ambient LZO and O_3 concentrations). At both sites, SIA contributed to the PM_1 mass more in summer, SOM—in winter. In general, the primary components of aerosol, EC + POM (primary organic aerosol, POM = $1.4{*}(OC - OC_{sec})$) had greater mass contributions to PM_1 in Racibórz. At both sites, the greatest POM and EC mass contributions to PM_1 occurred in November and December.

In Zabrze and Racibórz, the greatest mass contributions of MC + CM + OE to PM_1 occur in August (almost 20 %). In winter this contribution is lower by almost half.

All, the high ambient concentrations of SOM, POM and EC, high mass contributions of carbon compounds (equally, primary and secondary) to PM_1 and relatively small differences in the PM_1 chemical composition between rural and urban environments confirm the influence of combustion of fossil fuels on the concentrations and chemical composition of PM_1 in southern Poland. In cities, besides combustion of wood and coal in heating or power plants and domestic stoves, also road traffic and industry discharge coal compounds into the atmosphere (Juda-Rezler et al. 2011; Sówka et al. 2012)—this accounts for the difference between SOM and POM distribution in urban and rural dust.

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[1] The Sunset Laboratory software computes OC/EC for each sample; from among all OC/EC, the lowest ones were selected: 1.9 for Zabrze and 3.1 for Racibórz.

The products of the transformations of air pollutants in the cities of southern Poland, where NR is very low and urban aerosol may be acidic, cause serious environmental and health risks.

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