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CHEMICAL COMPOSITION AND MASS CLOSURE OF AMBIENT PARTICULATE MATTER AT A CROSSROADS AND A HIGHWAY IN KATOWICE, POLAND

The concentration, chemical composition, and mass closure of various fractions of ambient particulate matter (PM) were analyzed at crossroads and at a highway in Katowice (Poland). It was shown that at both sites organic carbon can constitute even 57% of the fine PM mass, about 20% of the fine PM mass can originate from the photochemical transformations of inorganic gaseous precursors, and that the coarse PM was mainly the organic matter (up to 39%) and crustal matter (up to 24%). Traffic emissions in Katowice can affect the formation of secondary aerosol (organic and inorganic), the contributions to PM and ambient concentrations of soil matter, NaCl, and trace elements. At the highway, the greatest impact on the concentrations and chemical composition of fine particles was probably due to exhaust emissions. At the crossroads, in the center of the city, the non-exhaust traffic emissions probably affected the coarse PM.

1. INTRODUCTION

It is quite obvious that the growth of the road traffic causes the growth of the concentrations of ambient particulate matter (PM) and increases the health hazard from it [1, 2]. Within urbanized regions, at trafficked sites, the effects of the traffic-related PM and PM precursors are reflected in the specific size distribution of the particles and the chemical composition of PM [3].

The chemical composition of PM has been studied worldwide for many years, in general to assess the PM effects on human health and on the environment, and to establish methods for tracing the PM origin [4–7]. The origin of PM can be determined quite accurately by apportioning the gravimetrically determined PM mass between the groups of the analytically found PM components (PM mass closure) [e.g. 8–12]. The

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PM components are most often grouped into elemental carbon (EC), organic matter (OM), secondary inorganic aerosol (SIA), crustal or mineral matter (CM or MM), sea salt or sodium chloride (SS or NaCl), trace or other elements (TE or OE), and the possibly small rest-unidentified matter (UM).

The first investigations of the chemical composition and mass closure of the particular PM fractions in Poland suggest that in a typical Upper Silesian city (Zabrze) over 80% of $PM_{2.5}$ (throughout the whole paper, $x - y$ in PM_{x-y} denotes the interval of the aerodynamic diameters [µm] of the particles in PM_{x-y}; PM_x stands for $PM_{0.03-x}$ and 50% of $PM_{2.5-10}$ may be directly or indirectly linked to combustion of fuels, and that almost 50% of PM_1 may be secondary (inorganic or organic) aerosol from transformations of gaseous precursors [11, 12].

The goal of the presented work was to analyze the concentration, chemical composition, and mass closure of each of PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$ and PM_{10-40} at two sites strongly affected by traffic emissions and located within a typical urban area in the Upper Silesia Agglomeration. There is a need for the investigations of the effects of traffic emissions on the air quality in Poland, and it stems from the outdated road infrastructure and the dynamic vehicle fleet development during the last two decades.

2. METHOD

PM was sampled at two sites in Katowice (Poland). One of the measuring points (HW) was located close to the A4 highway, about 1.5 km south of the city center. The other point (CR) was located close to two busy crossroads and the greatest traffic circle in Katowice (Fig. 1).

Fig. 1. Location of sampling sites

At HW, PM was sampled from 13.03.2012 to 19.06.2012; at CR-from 20.06.22012 to 03.09.2012. There were 9 samplings at each sampling point; a single sampling lasted about one week (142 to 173 h at HW, 123 to 145 h at CR).

PM was sampled with a thirteen-stage DEKATI low pressure impactor (DLPI, flow rate 30 dm^3/min). The impactor takes samples of 13 PM fractions (onto substrate filters): $PM_{0.03-0.06}$, $PM_{0.06-0.108}$, $PM_{0.108-0.17}$, $PM_{0.17-0.26}$, $PM_{0.26-0.4}$, $PM_{0.4-0.65}$, $PM_{0.65-1}$, $PM_{1-1.6}$, $PM_{1.6-2.5}$, $PM_{2.5-4.4}$, $PM_{4.4-6.8}$, $PM_{6.8-10}$, PM_{10-40}. The samples of the fractions PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$ and PM_{10-40} were the summed samples of all their sub-fractions, their ambient concentrations were the sums of their sub-fraction concentrations.

The PM samples were taken onto quartz filters (Whatman, QMA, $\varnothing$25 mm, CAT No. 1851-025) and nylon filters (Whatman, nylon membrane filters 0.2 μm, $\varnothing$25 mm, Cat No. 7402-002), alternating between samplings. Before and after exposing, all the filters were conditioned in a weighing room (48 h, relative air humidity 45±5%, air temperature 20±2 °C) and weighed twice, with 24 h period between, on a RADWAG microbalance (resolution 1 μg).

The PM sampled onto quartz filters (4 one-week samples at each point) was analyzed for organic (OC) and elemental (EC) carbon. PM on the nylon filters (5 one-week samples at each point) was analyzed first for its elemental composition (Al, Si, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Ag, Cd, Sb, Te, Ba and Pb) by means of a nondestructive method based on energy dispersive X-ray fluorescence (EDXRF), then the samples were extracted with water and the concentrations of main water-soluble ions (Cl^-, SO_4^{2-}, NO_3^-, Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+}) were determined in the extracts.

The parameters of the equipment (Sunset Laboratory carbon analyzer, 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 have been described elsewhere [11, 12]. The arithmetic averages of the weakly concentrations of PM and its components were assumed as the average ambient concentrations in the sampling periods (Table 1).

The PM mass reconstruction (mass closure) based on the PM component division into elemental carbon (EC), organic matter (OM), secondary inorganic aerosol (SIA), the group comprising Cl^- and Na^+ (NaCl), crustal matter (CM), trace elements (TE), and unidentified matter (UM). The collective masses of the groups were computed from the analytically determined or calculated masses of their components. The sum of the masses of EC, OM, SIA, NaCl, CM, and TE was compared with the gravimetrically determined mass of PM. The mass closure was checked for each of PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$ and PM_{10-40} and each sampling site.

The mass of EC was assumed to be the analytically determined mass $[EC]_A$ of elemental carbon: $[EC] = [EC]_A$. The mass of OM (OM, all PM bound organic compounds) was assumed to be 1.4 of the analytically determined mass $[OC]_A$ of OC:

$[OM] = 1.4[OC]_A$. SIA consisted of SO_4^{2-}, NO_3^-, and NH_4^+ and $[SIA] = [SO_4^{2-}]_A$ $+ [NO_3^-]_A + [NH_4^+]_A$; $[NaCl] = [Cl^-]_A + [Na^+]_A$.

CM and TE consisted of the elements listed in Table 1; the contents of CM and TE depended on the PM fraction and the measuring point. The elements were divided into two parts based on the analysis of their enrichment factors (EF, Table 2). The method for computing the enrichment factors is given in [12, 13]. For any element, EF is not lower than 0; the closer its value to 1, the smaller the anthropogenic effect on the element amount in the air.

The elements with EF ≤ 20 were considered crustal (bolds in Table 2), and CM was assumed to include CO_3^{2-}, SiO_2, Al_2O_3, Mg^{2+}, Ca^{2+}, K_2O, FeO and Fe_2O_3 (without FeO and Fe_2O_3 for $PM_{1-2.5}$ at HW and PM_1 at CR), Rb and Sr (except Sr in PM_1 at both HW and CR) and Ba, (only in $PM_{2.5-10}$ and PM_{10-40} at CR). The masses of the CM components were computed stoichiometrically from the analytically determined masses of their component elements assuming that Fe is equally distributed between FeO and Fe_2O_3 and; the CO_3^{2-} mass was calculated from the masses of Ca^{2+} and Mg^{2+} [14].

The elements with EF > 20 were in TE: Sc, Ti, V, Cr, Mn, Fe (Fe only in $PM_{1-2.5}$ at HW and in PM_1 at CR), Co, Ni, Cu, Zn, As, Se, Br, Rb and Sr (Rb and Sr only in PM_1 at both HW and CR), Mo, Ag, Cd, Sb, Te, Ba (except Ba in $PM_{2.5-10}$ and PM_{10-40} at CR). The PM bound compounds of these elements were not identified. Thus, the mass [TE] of TE was assumed to be the sum of all the analytically determined masses of the elements from TE.

The mass of unidentified matter [UM] was the deficient mass; it was the difference between the gravimetrically determined mass of PM and [SIA] + [EC] + [OM] + [NaCl] + [CM] + [TE].

3. RESULTS AND DISCUSSION

3.1. CONCENTRATIONS OF PM AT THE SAMPLING POINTS

The concentration[2] of total PM (summed concentrations of PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$, and PM_{10-40}) at HW was higher than at CR (Table 1). The PM_1 and $PM_{1-2.5}$ concentrations at HW were very different from those at CR. The concentrations of $PM_{2.5-10}$ and PM_{10-40} were a bit higher at CR than at HW. The mass shares (percentages) of fine particles (PM_1 and $PM_{1-2.5}$) in total PM were lower at CR than at HW (the former by 5 the latter by 8%).

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[2]In the paper, concentration, or ambient concentration denote the average concentrations in the measuring period; the averaging periods for both sampling points are given in Sect. 2 and in Table 1.

Sampling period averages of concentrations of PM, OC, EC [$\mu g/m^3$],
water soluble ions, and the remaining components [ng/m^3] of PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$
and PM_{10-40} at the highway (HW) and the crossroads (CR) in Katowice

Species	HW (13.03.2012–19.06.2012)				CR (20.06.2012–03.09.2012)			
	PM_1	$PM_{1-2.5}$	$PM_{2.5-10}$	PM_{10-40}	PM_1	$PM_{1-2.5}$	$PM_{2.5-10}$	PM_{10-40}
PM	18.75	5.20	4.72	1.21	12.14	3.25	4.98	1.67
OC	5.57	1.77	1.29	0.25	4.93	1.22	1.39	0.36
EC	0.89	0.24	0.46	0.07	0.52	0.13	0.29	0.10
Na^+	38.33	29.48	71.63	16.17	50.63	31.93	41.58	7.79
NH_4^+	938.63	234.66	39.22	7.51	608.12	67.60	30.95	8.43
K^+	56.31	17.40	46.23	11.78	67.57	9.71	11.58	2.27
Ca^{2+}	24.16	2.76	45.28	10.92	35.28	17.63	71.07	41.19
Mg^{2+}	2.57	< DL	< DL	< DL	1.41	1.71	7.03	1.53
Cl^-	459.97	125.63	177.01	50.80	223.58	66.36	125.68	37.02
NO_3^-	1113.63	362.12	206.46	32.95	458.16	172.51	254.96	54.16
SO_4^{2-}	1437.18	360.41	166.67	46.01	1481.14	236.17	172.46	59.20
Al	12.41	17.20	43.75	11.05	8.94	34.11	61.49	15.20
Si	22.98	72.82	167.01	46.39	52.12	124.23	229.97	63.12
Sc	3.67	6.76	15.73	4.77	4.30	7.90	23.84	7.24
Ti	92.67	33.50	48.66	14.97	104.66	32.98	52.26	15.74
V	12.26	4.94	6.91	1.99	13.79	4.55	7.17	2.13
Cr	4.48	1.87	2.39	0.75	6.73	2.05	2.86	0.88
Mn	28.56	12.72	18.96	5.19	33.80	11.88	20.09	6.44
Fe	91.08	223.72	264.52	42.74	100.84	157.69	256.52	55.52
Co	2.14	1.10	1.34	0.35	1.66	0.47	0.66	0.19
Ni	0.50	0.29	0.36	0.07	0.52	0.21	0.33	0.08
Cu	7.08	7.33	6.72	0.84	7.61	3.40	4.08	0.86
Zn	38.42	24.96	14.52	3.84	35.86	34.34	28.35	6.51
As	6.62	3.97	1.60	0.42	6.71	4.57	2.87	0.65
Se	0.39	0.13	0.00	0.01	0.27	0.05	*<DL*	*<DL*
Br	6.46	1.41	0.51	0.16	3.51	0.23	0.18	0.08
Rb	0.77	0.20	0.11	0.02	0.49	0.09	0.15	0.03
Sr	1.75	1.03	1.55	0.42	2.07	0.86	1.28	0.32
Mo	1.04	0.56	0.77	0.21	1.31	0.69	0.85	0.28
Ag	1.98	0.48	0.76	0.28	2.18	0.54	0.84	0.20
Cd	2.98	1.16	1.16	0.35	3.19	0.92	1.22	0.38
Sb	51.23	17.05	22.26	6.97	55.90	14.71	22.59	7.15
Te	1.64	0.44	0.52	0.14	1.82	0.57	0.93	0.27
Ba	12.55	8.04	9.83	2.11	13.04	6.24	8.41	2.52
Pb	18.45	11.68	4.60	1.19	18.76	13.86	8.56	1.95

< DL – below limit of detection.

Almost all primary particles (mainly soot) from combustion of oil derivatives in car engines are fine PM; the majority have aerodynamic diameters not greater than 0.5 μm [16, 17]. Thus, the greatest impact on the fine particles concentrations at HW was probably due to exhaust emissions. At CR in the Katowice center, the re-suspended PM lifted by vehicles and pedestrians, an important PM source in the periods of low precipitation, probably affected the PM concentrations. Also the particles, mainly coarse [3, 18], from corrosion or abrasive wear of vehicles and road surface (braking, stopping, moving off) might have a stronger effect on PM at CR than at HW.

Table 2

Sampling period averages of the enrichment factors (EF[a]) of the elements from PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$ and PM_{10-40}, at a crossroads (CR) and a highway (HW) in Katowice

Species	UC [ppm]	HW (13.03.2012–19.06.2012)				CR (20.06.2012–03.09.2012)			
		PM_1	$PM_{1-2.5}$	$PM_{2.5-10}$	PM_{10-40}	PM_1	$PM_{1-2.5}$	$PM_{2.5-10}$	PM_{10-40}
Mg^{2+}	13510	**1**	**0**	**0**	**0**	**1**	**0**	**1**	**1**
Al	77440	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**
Si	303480	**1**	**1**	**1**	**1**	**2**	**1**	**1**	**1**
K^+	28650	**12**	**3**	**3**	**3**	**20**	**1**	**1**	**0**
Ca^{2+}	29450	**5**	**0**	**3**	**3**	**10**	**1**	**3**	**7**
Sc	7	3273	4345	3978	4775	5325	2562	4289	5270
Ti	3117	186	48	28	34	291	24	21	26
V	53	1444	420	231	264	2254	195	170	205
Cr	35	798	241	121	149	1666	133	103	128
Mn	527	338	109	64	69	556	51	48	62
Fe	30890	**18**	33	**15**	**10**	28	**12**	**11**	**9**
Co	11.6	1153	428	204	213	1237	92	72	84
Ni	18.6	167	70	34	25	241	26	23	22
Cu	14.3	3092	2307	832	410	4607	540	359	307
Zn	52	4612	2161	494	517	5974	1499	687	638
As	2	20654	8946	1417	1457	29059	5190	1807	1650
Se	0.1	29609	6888	72	572	28169	1366	0	0
Br	1.6	25182	3961	566	680	18999	331	140	246
Rb	110	43	**8**	**2**	**1**	39	**2**	**2**	**2**
Sr	316	35	**15**	**9**	**9**	57	**6**	**5**	**5**
Mo	1.4	4619	1804	968	1030	8098	1122	763	1021
Ag	0.1	224325	39581	24560	35260	343123	22186	19121	18894
Cd	0.1	182216	51288	20191	24363	271235	20489	15017	19180
Sb	0.3	1031550	247525	127084	157726	1562017	107699	91768	117502
Te	–	–	–	–	–	–	–	–	–
Ba	668	117	54	26	22	169	21	**16**	**19**
Pb	17	6776	3093	479	492	9559	1851	634	583

[a]EF are computed relative to the concentration of Al, a marker element for the Earth crust ($EF_{Al} = 1$). The chemical characterization of the Earth upper continental crust (UC, ppm) is taken from [15].

The differences in the PM concentrations between CR and HW reflect the differences in the emissions of the PM and PM precursors between the two measuring periods in Katowice. The monthly concentrations of $PM_{2.5}$ and PM_{10} taken from the State Environmental Monitoring Program station in Katowice (urban background) in 2012 are presented in Fig. 2 (http://stacje.katowice.pios.gov.pl/monitoring/).
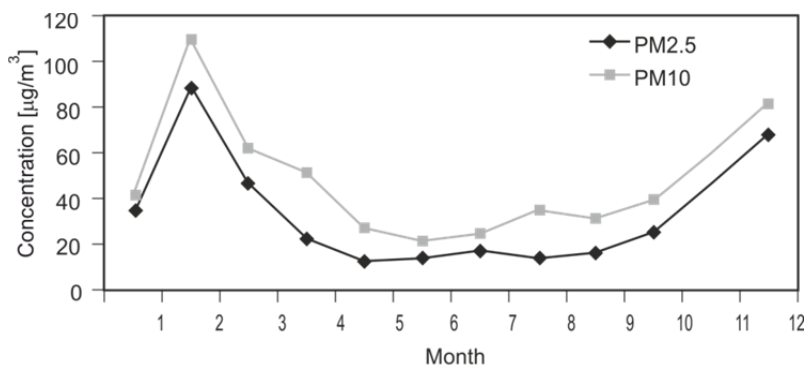

Fig. 2. Monthly concentrations of $PM_{2.5}$ and PM_{10} at the urban background point in Katowice in 2012 (http://stacje.katowice.pios.gov.pl/monitoring/)

In the holiday period (July–August), they were lower than in the rest of the year, especially those of $PM_{2.5}$ that are kept high by municipal and power plant emissions all over Poland not only in winter but also in March–June, the measuring period at HW. In the summer holiday period, vehicle and pedestrian traffic decreases, also municipal emissions decrease because of lower household demands for energy and fuels. The average $PM_{2.5}$ concentration (arithmetic mean of the monthly June, July, and August concentrations) at the urban background point in Katowice was equal to the average $PM_{2.5}$ concentration at CR (15 μg/m^3); the average PM_{10} concentration at the urban background point (40 μg/m^3) was even higher than at CR.

3.2. CHEMICAL COMPOSITION AND MASS CLOSURE OF PM_1, $PM_{1–2.5}$, $PM_{2.5–10}$ AND $PM_{10–40}$

At both sampling points, most of the mass of each PM fraction was in carbonaceous matter (OM and EC, Table 3, Fig. 3). The ambient OC concentrations at HW and at CR resembled the concentrations in other regions of Upper Silesia or traffic affected sites in Europe [11, 19]. The EC concentrations were much lower in Katowice, especially at CR (summer). In urban, and sometimes in rural regions of southern Poland, the winter EC concentrations are significantly higher than elsewhere in Europe, sometimes even than at traffic affected sites [11, 12, 19]. In Katowice, the EC concentrations are affected more by municipal emissions than by road traffic – unlike elsewhere in Europe [6]; it is confirmed by the EC distribution among the fractions: in Katowice, EC did not concentrate only in fine PM. Except for almost 10% EC contri-

bution to $PM_{2.5-10}$ at HW, all other fractional mass contributions were about 5% (Table 3). The mass of EC in the coarsest PM, PM_{10-40}, was 5.5% at HW and 5.8% at CR; in PM_1 – 4.8% and 4%. Thus, the coarse particles ($PM_{2.5-10}$ and PM_{10-40}) were very rich in EC.
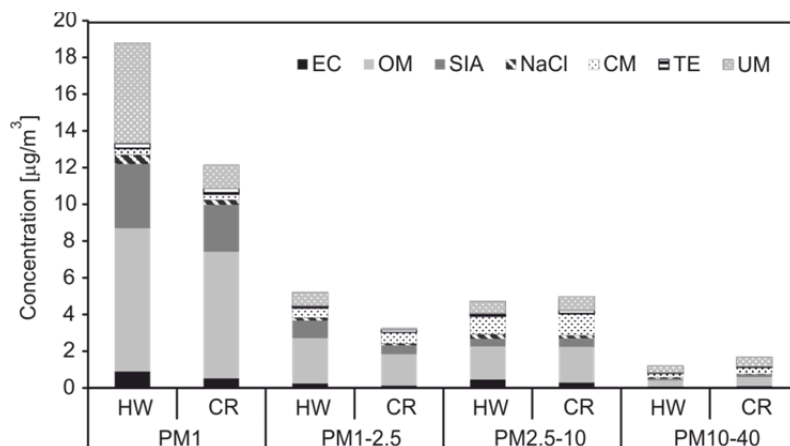

Fig. 3. Concentrations of organic matter (OM), elemental carbon (EC),
secondary inorganic aerosol (SIA), sum of sodium and chlorides (NaCl), crustal matter (CM),
trace elements (TE), and unidentified matter (UM) related to PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$ and PM_{10-40}
at the highway (HW) and at the crossroads (CR) in Katowice

Table 3

Chemical mass closure of PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$ and PM_{10-40}
at the highway (HW) and at the crossroads (CR) in Katowice [%]

Species	HW (13.03.2012–19.06.2012)				CR (20.06.2012–03.09.2012)			
	PM_1	$PM_{1-2.5}$	$PM_{2.5-10}$	PM_{10-40}	PM_1	$PM_{1-2.5}$	$PM_{2.5-10}$	PM_{10-40}
EC	4.8	4.6	9.7	5.5	4.3	4.0	5.8	5.8
OM	41.6	47.6	38.3	28.6	56.8	52.7	39.1	30.0
SIA	18.6	18.4	8.7	7.2	21.0	14.7	9.2	7.3
NaCl	2.7	3.0	5.3	5.6	2.3	3.0	3.4	2.7
CM	1.8	10.0	20.6	18.3	2.5	18.7	23.6	21.0
TE	1.6	2.7	3.3	3.7	2.6	4.3	3.7	3.2
UM	29.0	13.7	14.1	31.2	10.6	2.6	15.1	30.1

OM – organic matter, EC – elemental carbon, SIA – secondary inorganic aerosol, NaCl – sum of sodium and chlorides, CM – crustal matter, TE – trace elements, UM – unidentified matter.

In Katowice, in summer, the municipal emissions can contribute much to ambient EC. All over Silesia, inefficient coal-fired stoves or boilers emit big agglomerates of soot from incomplete combustion of coal during the whole year [19]; also the Polish

vehicle fleet, in general obsolete cars with ineffective exhaust control systems, emits agglomerated soot. In general, at both sites, OM contributed more to fine than to coarse PM; at CR the OM mass contribution to PM_1 was 56.8%. In each fraction, the OM mass was greater at CR than at HW (Table 3); the differences amounted from 0.8% ($PM_{2.5-10}$) to 15.2% (PM_1). It was due to the PM concentrations, lower at CR than at HW, because the OC ambient concentrations at CR were lower than at HW (Table 1).

The mass contributions of secondary (OC_{sec}) and primary (OC_{prim}) organic carbon to organic carbon in PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$ and PM_{10-40} at both sampling points are presented in Fig. 4.
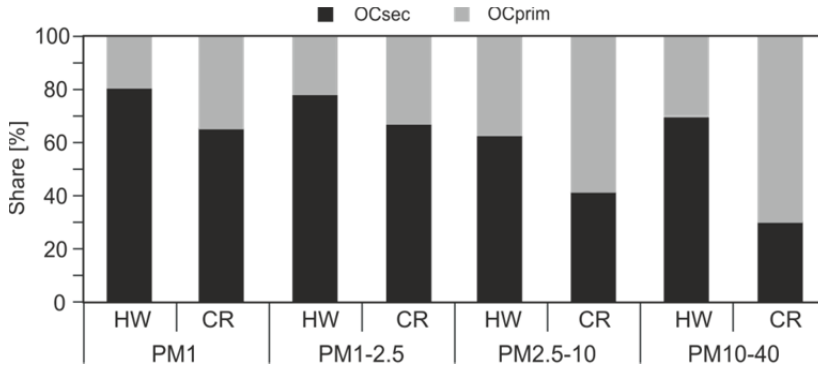

Fig. 4. Shares [%] of secondary organic carbon (OC_{sec}) and primary organic carbon (OC_{prim}) in organic carbon (OC) bound to PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$, PM_{10-40}, and TSP at the highway (HW) and at the crossroads (CR)

For the fraction *f* at the point *p*, they were computed from the following formulas [20]:

$$\left[OC_{sec}\right]_p^f = \left(\left[OC\right]_{pA}^f - \left(\frac{\left[OC\right]_A^s}{\left[EC\right]_A^s} \right)_{min}^p \left[EC\right]_A \right) \times 100\% \tag{1}$$

$$\left[OC_{prim}\right]_p^f = 100 - \left[OC_{sec}\right]_p^f \tag{2}$$

where:

$\left[OC_{sec}\right]_p^f$ is the mass contribution of OC_{sec} to the fraction *f* bound OC at the point *p*,

$\left[OC_{prim}\right]_p^f$ is the mass contribution of OC_{prim} to the fraction *f* bound OC at the point *p*,

$[OC]^f_{pA}$ is the analytically determined mass of the fraction f bound OC at the point p,

$[EC]^f_{pA}$ is the analytically determined mass of the fraction f bound EC at the point p,

$[OC]^s_A$ is the analytically determined mass of OC from the sample s,

$[EC]^s_A$ is the analytically determined mass of EC from the sample s,

$\left([OC]^s_A / [EC]^s_A\right)^p_{min}$ is the minimum $[OC]^s_A / [EC]^s_A$ over all the samples at the point p,

$\left([OC]^s_A / [EC]^s_A\right)^{HW}_{min} = 1.034$, $\left([OC]^s_A / [EC]^s_A\right)^{CR}_{min} = 2.793$.

OC$_{sec}$ (and secondary OM) arises from condensation of gaseous organic compounds and photochemical transformations of volatile organic compounds [20, 21]. Both sampling points were within the effect of road traffic causing high concentrations of nitric oxides, ozone, and hydrocarbons favorable for the formation of OC$_{sec}$. The insolation was also high at both sites (more intense during measurements at CR, (http://stacje.katowice.pios.gov.pl/monitoring/). Consequently, at both sampling points, OC$_{sec}$ prevailed in PM$_1$ and PM$_{1-2.5}$ bound OC. The share of OC$_{sec}$ in PM$_{2.5-10}$ and PM$_{10-40}$ bound OC was not greater than 40% at CR and was almost 70% at HW (Fig. 4). At HW, it might be due to the high percent of EC in coarse PM (condensation of gaseous organic compounds on the vast surfaces of EC particles); also the share of biological matter in OC (plant debris from lawn, pollen) was greater at CR than at HW.

Secondary inorganic aerosol (SIA), the PM part coming from the photochemical transformations of inorganic gaseous precursors, was about 16.5% of the total PM mass at both sites; it was 18.6% of the PM$_1$ mass at HW and 21% at CR; its parts in PM$_{2.5-10}$ and PM$_{10-40}$ were small.

Table 4

Ambient concentrations [μg/m^3] of ammonium sulfate and ammonium nitrate bound to PM$_1$, PM$_{1-2.5}$, PM$_{2.5-10}$ and PM$_{10-40}$, and neutralization ratios (NR) for these fractions at the highway (HW) and at the crossroads (CR) in Katowice

Species	HW (13.03.2012–19.06.2012)				CR (20.06.2012–03.09.2012)			
	PM$_1$	PM$_{1-2.5}$	PM$_{2.5-10}$	PM$_{10-40}$	PM$_1$	PM$_{1-2.5}$	PM$_{2.5-10}$	PM$_{10-40}$
NR	1.08	0.96	0.32	0.28	0.88	0.48	0.22	0.22
(NH$_4$)$_2$SO$_4$	1.98	0.50	0.14	0.03	2.23	0.25	0.11	0.03
ex-NH$_4^+$	0.40	0.10	0.00	0.00	0.00	0.00	0.00	0.00
NH$_4$NO$_3$	1.79	0.45	0.00	0.00	0.00	0.00	0.00	0.00

The capability of ambient ammonium (NH_4^+) to neutralize ambient sulfates (SO_4^{2-}) and nitrates (NO_3^-) can be expressed as the neutralization ratio *NR*, i.e. the proportion of the concentration of NH_4^+ [neq/m^3] to the collective concentration of SO_4^{2-} and NO_3^- [neq/m^3] (Table 4). *NR* was computed for each PM fraction and each sampling point.

The amount of NH_4^+ in a fraction with $NR \geq 1$ suffices for the total neutralization of the sulfuric (H_2SO_4) and nitric (HNO_3) acids from this fraction. The mass $[(NH_4)_2SO_4]$ of $(NH_4)_2SO_4$ in a fraction can be computed from the equation:

$$[(NH_4)_2SO_4] = 1.38[SO_4^{2-}]_A \qquad (3)$$

The mass $[ex-NH_4^+]$ of the fraction bound NH_4^+ left after its reaction with SO_4^{2-} and the mass $[NH_4NO_3]$ of the fraction bound NH_4NO_3 were computed from:

$$[ex-NH_4^+] = [NH_4^+]_A - 0.27[(NH_4)_2SO_4] \qquad (4)$$

$$[NH_4NO_3] = 4.44[ex-NH_4^+] \qquad (5)$$

NH_4^+ in the fraction with $NR < 1$ can neutralize only a part of SO_4^{2-} from this fraction. It is, $(NH_4)_2SO_4$ arises and there is too little NH_4^+ for NH_4NO_3 to be formed. The mass of $(NH_4)_2SO_4$ from these fractions was computed from:

$$[(NH_4)_2SO_4] = 3.67[NH_4^+]_A \qquad (6)$$

Table 4 presents the results of stoichiometric computations applied to the ambient concentrations of sulfates (SO_4^{2-}), nitrates (NO_3^-), and ammonium (NH_4^+). The computations, despite their simplicity, reveal clearly some regularity: NH_4NO_3 did not occur in SIA in any PM fraction at CR. At HW, the ambient concentrations of nitrates, much greater than at CR, could be neutralized by NH_4^+. So, at HW, ammonium sulfate $((NH_4)_2SO_4)$ and ammonium nitrate (NH_4NO_3) were present in fine PM bound SIA. Because the highway is the only pollution source that could cause high ambient concentrations of nitric oxides or ammonia, the precursors of NH_4NO_3, at HW, the composition of PM_1 and $PM_{1-2.5}$ bound SIA must have been formed by traffic. In the holiday season, the traffic effects at CR were weaker – the concentrations of PM_1 and $PM_{1-2.5}$ bound NO_3^- and NH_4^+ were much lower than at HW (Table 1).

Small NR for $PM_{2.5-10}$ and PM_{10-40} at both HW and CR mean the lack of NH_4NO_3 in these fractions; probably, at both the sites, sulfates and nitrates occurred as $CaSO_4$, $NaNO_3$, or $(Na)_2SO_4$ in coarse PM.

The CM and NaCl mass shares in PM fractions were noticeable at both HW and CR (Table 3, Fig. 3). The CM shares in $PM_{2.5-10}$ and PM_{10-40} were about 20% at both points; the share in $PM_{1-2.5}$ at CR was equally high. The CM shares in PM_1, the frac-

tion coming mainly from combustion (high OM + EC) and from the transformations of gaseous PM precursors (SIA) did not exceed 2.5% at both points. The shares of NaCl in fine PM did not exceed 3% at both points, in coarse PM at HW it was almost 5.6%.

At HW, the salt from winter road deicing, accumulated during winter on the road-sides, can be re-suspended and together with mineral particles (of CM) and traffic-related big non-exhaust particles (tire and brake lining wear, particles from corroded car parts, road surface particles, etc.) may be caught by the impactor, especially in spring, the sampling period at HW. In summer, at CR in the city center, roads and pavements are daily cleaned and sprinkled with water to limit the dust re-suspension. The winter deicing salt had been removed long before the sampling at CR started. Probably, the majority of big particles in CM at CR did not come from re-suspension, but they were brought by the wind from lawns and green belts.

Besides the winter road deicing, the most probable sources of PM_1 and $PM_{1-2.5}$ bound Na^+ and Cl^- in Katowice are domestic stoves (burning low quality coal and household wastes [11–13]). The high contribution of NaCl to PM at CR in summer, due to high concentrations of Na^+ (Table 1), may also be related with biomass burning in the CR neighborhood [4, 6, 8].

The mass of TE in PM was also significant at the two sites. At CR, its contributions to PM_1 and to $PM_{1-2.5}$ were twice the contributions at HW. The TE contributions to coarse PM were similar at both sites (Table 3). The greater at CR than at HW amount of fine PM bound metals (probably from oxides) in TE is probably caused by municipal emissions – in the holiday season the traffic density decreased significantly at CR. At HW, far from the city core, the TE probable basic source was road traffic. At both sites, the coarse PM bound TE probably came from non-exhaust emissions: tire wear, brake lining, car part corrosion, road surface abrasion, etc. Also, the measuring points might be affected by non-ferrous metal smelters, cokeries, lead and cadmium refineries, cement factories, etc., releasing some of the TE components to the air [11–13].

The best fit of the reconstructed mass was received for PM_1 at CR. At both sites, the greatest UM share was in PM_{10-40}. Water may account for up to 30% of the PM mass in some periods of the year [22]. It seems that the water content in PM was greater at HW because of higher air humidity and lower air temperatures at this point. Such conditions favor condensation of water on the airborne particles. Moreover, the composition of PM differs between the sites, the presence of ammonium nitrate, or great amounts of chlorides (calcium chloride and its hydrates from maintaining of roads in winter) might make PM more hygroscopic at HW. UM comprises also uni-dentified elements chemically bound to the elements from TE (e.g. oxygen from the oxides of elements from TE). Moreover, PM was not analyzed for all possible compounds and elements. The observable contributions to the near-road TE may have the platinoids, or to CM—the lanthanides, neither considered in the work. And, of course, it should always be kept in mind that the sample taking, sampling campaign duration,

artifacts arising in the transport, weighing, chemical analyses, and many others, affect the difference between the gravimetrically and the analytically found masses of TSP.

4. CONCLUSIONS

The mass reconstruction of selected PM fractions at HW (highway) and CR (crossroads) revealed no significant differences in the PM composition between these sites and earlier investigated urban areas in Poland. At urban background sites in Poland, at HW, and at CR alike, fine PM ($PM_{2.5}$) consists mainly of carbonaceous matter (organic matter and elemental carbon), being 46 and 52% of the PM_1 and $PM_{1-2.5}$ masses at HW and 61 and 57% of the PM_1 and $PM_{1-2.5}$ masses at CR, respectively. Another significant component of $PM_{2.5}$ is secondary inorganic aerosol (sulfates, nitrates, ammonium), being 19 and 18% of the PM_1 and $PM_{1-2.5}$ masses at HW and 21 and 15% of the PM_1 and $PM_{1-2.5}$ masses at CR. Coarse dust ($PM_{2.5-40}$), at both sites, consists mainly of carbonaceous matter (48 and 45% of $PM_{2.5-10}$ and PM_{10-40} masses at HW, 34 and 36% of $PM_{2.5-10}$ and PM_{10-40} masses at CR) and mineral/crustal matter (21 and 18% of $PM_{2.5-10}$ and PM_{10-40} masses at HW, 45 and 36% of $PM_{2.5-10}$ and PM_{10-40} masses at CR).

The chemical composition of PM at both HW and CR differs from the PM composition at other traffic affected sites in Europe. Elemental carbon contributes less to $PM_{2.5}$ and more to $PM_{2.5-40}$, $PM_{2.5}$ contains more organic carbon and significantly less secondary inorganic aerosol in Katowice than elsewhere in Europe. It is hard to explain what these differences are due to because the results of any investigation depend strongly on the sapling and analytical methods, equipment, averaging of results, calculations for chemical mass closure checking, etc. However, the specificity of the chemical composition of PM and the PM components in southern Poland, compared to the PM composition in other European regions, seems to be beyond doubt. A very important in Poland, negligible in the majority of other European countries, source of PM and PM bound elemental carbon is the municipal emissions (combustion of low-quality coal, coal dust, biomass, and household waste in domestic ovens, combustion of hard coal in local heating plants). Therefore, although it was shown here that traffic affects the formation of the secondary aerosol in $PM_{2.5}$ and the shares of soil matter and NaCl in $PM_{2.5-40}$ in Katowice, the traffic effect on the concentrations and chemical composition of PM may be significantly lower in southern Poland than elsewhere in Europe.

REFERENCES

[1] Künzli N., Kaiser R., Medina S., Studnicka M., Chanel O., Filliger P., Herry M., Horak Jr F., Puybonnieux-Texier V., Quénel P., Schneider J., Seethaler R., Vergnaud J.-C., Sommer H., *Public-health impact of outdoor and traffic-related air pollution: a European assessment*, Lancet, 2000, 356, 795.

[2] Levy J.I., Buonocore J.J., Von Stackelberg K., *Evaluation of the public health impacts of traffic congestion: a health risk assessment*, Environ. Health, 2010, 9.

[3] Pant P., Harrison R.M., *Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: A review*, Atmos. Environ., 2013, 77, 78.

[4] Putaud J.-P., Raes F., Van Dingen R., Brüggemann R., Facchini M.-C., Decesari S., Fruzzi S., Gehrig R., Hüglin R., Laj P., Lorbeer G., Maenhaut W., Mihalopoulos N., Müller K., Querol X., Rodriguez S., Schneider J., Spindler G., Brink H., Tørseth K., Wiedensohler A., *European aerosol phenomenology . 2. Chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe*, Atmos. Environ., 2004, 38, 2579.

[5] Perez L., Medina-Ramón M., Künzli N., Alastuey A., Pey J., Perez N., Garcia R., Tobias A., Querol X., Sunyer J., *Size fractionate particulate matter, vehicular traffic, and case-specific daily mortality in Barcelona (Spain)*, Environ. Sci. Technol., 2009, 43, 4707.

[6] Viana M., Kuhlbusch T.A.J., Querol X., Alastuey A., Harrison R.M., Hopke P.K., Winiwarter W., Vallius W., Szidat S., Prévôt A.S.H., Hueglin C., Bloemen H., Wåhlin P., Vecchi R., Miranda A., Kasper-Giebl A., Maenhaut W., Hitzenberger R., *Source apportionment of particulate matter in Europe: A review of methods and results*, Aerosol Sci., 2008, 39, 827.

[7] Kong S., Ji Y., Lu B., Bai Z., Chen L., Han B., Li Z., *Chemical compositions and sources of atmospheric PM_{10} in heating, non-heating and sand periods at a coal-based city in northeastern China*, J. Environ. Monitor., 2012, 14, 852.

[8] Sillanpää M., Hillamo R., Saarikoski S., Frey A., Pennanen A., Makkonen U., Spolnik Z., Van Grieken R., Braniš M., Brunekreef B., Chalbot M., Kuhlbusch T., Sunyer J., Kerminen V.M., Kulmala M., Salonen R.O., *Chemical composition and mass closure of particulate matter at six urban sites in Europe*, Atmos. Environ., 2006, 40, 212.

[9] Yin J., Harrison R.M., *Pragmatic mass closure study for $PM_{1.0}$, $PM_{2.5}$ and PM_{10} at roadside, urban background and rural sites*, Atmos. Environ., 2008, 42, 980.

[10] Theodosi C., Grivas G., Zarmpas P., Chaloulakou A., Mihalopoulos N., *Mass and chemical composition of size-segregated aerosols (PM1, PM2.5, PM10) over Athens, Greece: local versus regional sources*, Atmos. Chem. Phys., 2011, 11, 11895.

[11] Rogula-Kozłowska W., Klejnowski K., *Submicrometer aerosol in rural and urban backgrounds in Southern Poland: Primary and secondary components of PM1*, B. Environ. Contam. Tox., 2013, 90, 103.

[12] Rogula-Kozłowska W., Klejnowski K., Rogula-Kopiec P., Mathews B., Szopa S., *A study on the seasonal mass closure of ambient fine and coarse dusts in Zabrze, Poland*, B. Environ. Contam. Tox., 2012, 88, 722.

[13] Rogula-Kozłowska W., Błaszczak B., Szopa S., Klejnowski K., Sówka I., Zwoździak A., Jabłońska M., Mathews B., *PM2.5 in the central part of Upper Silesia, Poland: concentrations, elemental composition, and mobility of components*, Environ. Monit. Assess., 2013, 185, 581.

[14] Marcazzan G.M., Vaccaro S., Valli G., Vecchi R., *Characterisation of PM10 and PM2.5 particulate matter in the ambient air of Milan (Italy)*, Atmos. Environ., 2001, 35, 4639.

[15] Wedepohl K.H., *The composition of the continental crust*, Geochim. Cosmochim. Acta, 1995, 59, 1217.

[16] Maricq M.M., *Chemical characterization of particulate emission from diesel engines: a review*, Aerosol Sci., 2007, 38, 1079.

[17] Geller M.D., Ntziachristos L., Mamakos A., Samaras Z., Schmitz D.A., Froines J.R., Sioutas C., *Physicochemical and redox characteristics of particulate matter (PM) emitted from gasoline and diesel passenger cars*, Atmos. Environ., 2006, 40, 6988.

[18] Thorpe A., Harrison R.M., *Sources and properties of non-exhaust particulate matter from road traffic: a review*, Sci. Total Environ., 2008, 400, 270.

[19] Rogula-Kozlowska W., Rogula-Kopiec P., Klejnowski K., Blaszczyk J., *Influence of vehicular traffic on concentration and mass size distribution of two fractions of carbon in an urban area atmospheric aerosol*, Rocz. Ochr. Środ., 2013, 15, 1623.

[20] Castro L.M., Pio C.A., Harrison R.M., Smith D.J.T., *Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations*, Atmos. Environ., 1999, 33, 2771.

[21] Grosjean D., Friedlander S.K., *Gas-particle distribution factors for organic and other pollutants in the Los Angeles atmosphere*, JAPCA, 1975, 25, 1038.

[22] Tsyro S.G., *To what extent can aerosol water explain the discrepancy between model calculated and gravimetric PM10 and PM2.5?*, Atmos. Chem. Phys., 2005, 5, 515.