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Winter Mass Concentrations of Carbon Species in PM_{10}, $PM_{2.5}$ and PM_1 in Zagreb Air, Croatia

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Abstract The purpose of our investigation was to examine the mass concentrations of EC, OC and TC (EC + OC) in PM_{10}, $PM_{2.5}$ and PM_1 particle fractions. Daily PM_{10}, $PM_{2.5}$ and PM_1 samples were collected at an urban background monitoring site in Zagreb during winter 2009. Average OC and EC mass concentrations were 11.9 and 1.8 µg m^{-3} in PM_{10}, 9.0 and 1.4 µg m^{-3} in $PM_{2.5}$, and 5.5 and 1.1 µg m^{-3} in PM_1. Average OC/EC ratios in PM_{10}, $PM_{2.5}$, and PM_1 were 7.4, 6.9 and 5.4, respectively.

Keywords EC · OC · TC · OC/EC mass ratio

Airborne particulate matter (PM) is considered to be one of the major environmental pollutants in urban areas. Particulate matter in atmosphere originates either from the direct emission or from the chemical transformation of gaseous pollutants (Ho et al. 2006). It is well known that these particulates may cause serious health problems, especially those associated with respiratory and cardiovascular diseases affecting the morbidity and mortality rates (Husain et al. 2007).

Total carbon (TC) is one of the major components of the atmospheric aerosol and consists mainly of elemental carbon (EC), organic carbon (OC) and carbonate carbon (CC) (Na et al. 2004). Elemental carbon (EC) is emitted directly in the particulate form during incomplete combustion of carbon-containing fuels and can also be called soot, black carbon and light adsorbing carbon (Chen et al. 2004; Na et al. 2004). Particulate organic carbon (OC), which contains a wide range of molecular forms and volatilities, can be emitted directly or formed through photochemical reactions from its gaseous precursors in the atmosphere (Turpin et al. 2000). Some of the organic carbon particles, such as volatile and semi-volatile organics can act like irritants and allergens (Sillanpää et al. 2005), while aromatic organic compounds like polycyclic aromatic hydrocarbon (PAHs), oxy-PAHs, and nitro-PAHs are potential mutagens and carcinogens, and may cause serious health problems (Ho et al. 2006), and can also affect the climate change (Turpin et al. 2000). Elemental carbon has a significant effect on the global climate change, global warming and reduced visibility (Lonati et al. 2007).

The purpose of our investigation was to examine the mass concentrations of EC, OC and TC (EC + OC) in PM_{10}, $PM_{2.5}$ and PM_1 particle fractions, to see their relationships and correlation in and between PM_{10}, $PM_{2.5}$ and PM_1 particle fractions, and to estimate OC/EC mass ratio. This is the first report on EC and OC in Zagreb air.

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Materials and Methods

PM_{10}, $PM_{2.5}$ and PM_1 particle fractions (particle with the aerodynamic diameter less than 10, 2.5 and 1 µm) were collected during 24-h periods at the sampling site situated in Zagreb during winter (January–March) 2009. The sampling site was located in a northern residential part of the town, approximately 1.5 m above the ground and 15 m away from the road. The samples were collected on quartz fibre filters (Pall Tissuequartz 2500QAT-UP) 90 mm in diameter. The nominal flow rate was 72 L min^{-1}. The possible main sources of carbon species and particulate matter in most cases are natural gas burning for space heating and food preparation, as well as from the moderate traffic at the nearby road. Quartz fibre filters were chosen because a high temperature is needed for the filter preparation and analysis of the samples. Before sampling, filters were prefired for 3 h at 900°C in a furnace, in order to reduce the blank level of carbon in the filter (Birch and Cary 1996; Lin and Tai 2001). After sampling and weighing, filters were stored in the freezer until the analysis to prevent the loss of volatile OC.

Mass concentrations of PM_{10}, $PM_{2.5}$ and PM_1 particle fractions were determined gravimetrically. Before and after the sampling, filters were conditioned at the constant temperature (20 ± 1°C) and relative air humidity (50 ± 5 % RH) for 48 h, prior to the first weighing and reweighing after the next 24 h. Microbalance Mettler TOLEDO MX5 with the resolution of 1 µg was used.

A portion of each sample (1.5 cm^2) was used to determine OC and EC with thermal/optical transmittance (TOT) method. Analyses were made on Carbon Aerosol Analyser (Sunset Laboratory Inc., USA) with a FID flame ionization detector (Birch and Cary 1996).

To ensure QA/QC so as to prove the consistent operation of the instrument, inner standard, external sucrose aqueous solution and cross method procedure were used. For the evaluation of the efficiency of the method recovery, two sets of filters (blank samples and real samples) were analyzed after being spiked with known concentration of carbon. The results of recovery were 96.26 %–104.24 % with relative standard deviation RSD < 5 %.

The detection limits were determined and calculated on the basis of an average ($\gamma \pm 3\sigma$) taken from ten repeated measurements of blank samples (unexposed filters). The detection limits were: 0.02 µg cm^{-2} for EC, 0.52 µg cm^{-2} for OC, and 0.53 µg cm^{-2} for TC. The detection limits expressed in µg m^{-3} were 0.01 µg m^{-3} for EC, 0.32 µg m^{-3} for OC and 0.33 µg m^{-3} for TC.

Results and Discussion

Table 1 shows statistical parameters of mass concentrations of measured pollutants, carbon species mass contribution to the overall PM mass, as well as OC/EC mass ratio in PM_{10}, $PM_{2.5}$ and PM_1 particle fractions.

Average mass concentrations of PM_{10}, $PM_{2.5}$ and PM_1 were 47.2, 37.4 and 27.3 µg m^{-3}, respectively. Average OC, EC and TC mass concentrations were 11.88, 1.76 and 13.64 µg m^{-3} in PM_{10}, respectively and contributed 24.15 %, 4.29 % and 28.44 % to the total PM_{10} mass, respectively. In $PM_{2.5}$ the average OC, EC and TC mass concentrations were 9.03, 1.40 and 10.43 µg m^{-3}, respectively and contributed 23.76 %, 4.42 % and 28.18 % to the total $PM_{2.5}$ mass, respectively. In PM_1 the average OC, EC

Table 1 Statistical parameters of measured pollutants

Statistical parameters	Mass concentrations (µg m^{-3})				Mass contribution to the overall PM mass (%)			Mass ratio
	PM	EC	OC	TC	EC	OC	TC	OC/EC
PM_{10}								
n	85	85	85	85	85	85	85	85
Avg	47.2	1.76	11.88	13.64	4.29	24.15	28.44	7.39
SD	26.4	0.85	8.13	8.51	2.08	5.06	5.46	4.71
Min	16.0	0.42	2.52	2.94	0.79	12.50	14.76	1.91
Max	146.7	4.31	43.83	46.92	12.30	37.79	40.46	23.52
Median	38.2	1.58	9.37	11.25	4.07	23.59	27.92	5.62
$PM_{2.5}$								
n	83	83	83	83	83	83	83	83
Avg	37.4	1.40	9.03	10.43	4.42	23.76	28.18	6.95
SD	20.1	0.66	5.63	5.91	2.33	5.32	6.53	3.92
Min	13.3	0.41	2.00	2.41	0.86	10.88	13.09	2.11
Max	106.6	3.77	30.96	33.30	11.27	38.32	46.44	19.45
Median	30.9	1.32	7.17	8.71	3.69	23.59	27.39	5.54
PM_1								
n	63	63	63	63	63	63	63	63
Avg	27.3	1.09	5.48	6.58	4.28	19.88	24.17	5.35
SD	9.4	0.44	2.36	2.57	1.91	4.48	5.43	2.29
Min	13.3	0.30	0.96	1.28	1.37	4.09	5.46	1.73
Max	54.4	2.67	11.71	13.60	11.77	31.64	37.01	11.56
Median	24.3	1.02	5.03	6.45	3.99	20.38	24.32	5.04

PM particulate matter, *EC* elemental carbon, *OC* organic carbon, *TC* total carbon, *OC/EC* mass concentration ratio, *n* number of samples, *Avg* average value, *SD* standard deviation, *Min* minimum value, *Max* maximum value and TC mass concentrations were, 5.48, 1.09 and 6.58 µg m^{-3}, respectively and contributed 19.88 %, 4.28 % and 24.17 % to the total PM_1 mass, respectively. Mass concentrations of measured pollutants were comparable with results measured in other cities (Viana et al. 2006, 2007; Vecchi et al. 2004; Lonati et al. 2007; Sillanpää et al. 2005; Schwartz et al. 2008).

The OC/EC mass ratio has been used to identify the presence of secondary organic aerosols (Ho et al. 2003). The OC/EC ratio value <2 suggests that OC measured in urban areas may be formed from direct emissions of particles as a primary pollutant, while the OC/EC ratio value >3 indicates the presence of secondary organic aerosols. Average OC/EC mass ratio in our research was, 7.39 in PM_{10}, 6.95 in $PM_{2.5}$, and 5.35 in PM_1 (Table 1). This indicates that the atmospheric formation of secondary organic compounds was the main source of OC in the researched area during winter period.

Table 2 Correlation between mass concentrations of OC, EC and TC in PM_{10}, $PM_{2.5}$ and PM_1 particle fractions

Correlated components	OC	EC	TC
PM_{10}	0.884**	0.348**	0.868**
OC		0.412**	
$PM_{2.5}$	0.869**	0.204	0.823**
OC		0.421**	
PM_1	0.866**	0.224	0.834**
OC		0.401**	

PM particulate matter, *EC* elemental carbon, *OC* organic carbon, *TC* total carbon

** $p < 0.01$

Table 2 shows the correlation between mass concentrations of all carbon species (OC, EC and TC) in PM_{10}, $PM_{2.5}$ and PM_1 particle fractions. Good correlation for PM and OC (r = 0.884 for PM_{10}; r = 0.869 for $PM_{2.5}$ and r = 0.866 for PM_1) was observed, while the correlation between OC and EC in PM was poor (r = 0.412 for PM_{10}; r = 0.421 for $PM_{2.5}$ and r = 0.401 for PM_1), it confirmed the assumption given above, that the atmospheric transport and transformation of secondary organic species was the dominant source of OC.

Weekly distributions of PM_{10}, $PM_{2.5}$ and PM_1 mass concentration, OC and EC mass concentration and OC/EC mass ratio in PM_{10}, $PM_{2.5}$ and PM_1 are shown in Fig. 1. Results show that no statistical difference ($p < 0.01$) between particular days was found. OC/EC mass ratios were higher during the weekend days compared to working days so it can be more attributed to low EC level than to elevated OC concentrations. It can be assumed that minimization of EC levels during weekend days was caused by the reduced traffic density during weekend days.

Table 3 shows the relations between measured pollutant in PM_{10}, $PM_{2.5}$ and PM_1 particle fractions. The regression analysis shows that the 73 % and 64 % of PM_{10} mass were present in $PM_{2.5}$ and PM_1 particle fraction respectively, as well as 68 % and 65 % of OC in PM_{10} were present in $PM_{2.5}$ and PM_1 particle fraction respectively. For EC it was 73 % and 57 % and for TC it was 68 % and 64 %, respectively.

Mass contribution of carbon species to the overall PM mass is shown in Fig. 2. Results show that OC contribution to each particle fraction mass followed this order: $PM_{10} > PM_{2.5} > PM_1$, EC mass contribution was: $PM_{2.5} > PM_{10} > PM_1$ and TC contribution was: $PM_{10} > PM_{2.5} > PM_1$.

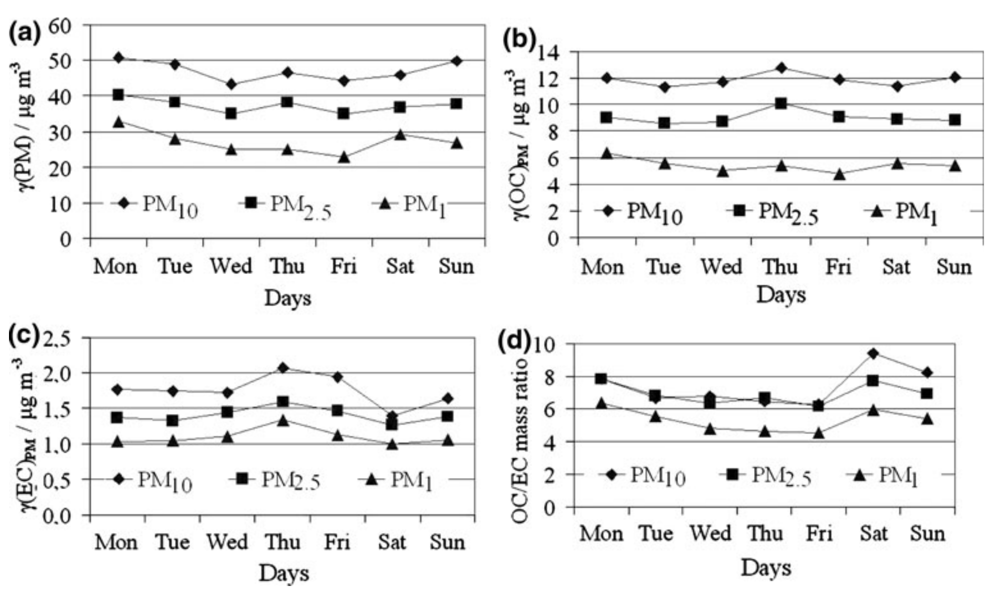

Fig. 1 Weekly mass concentrations distribution of **a** PM_{10}, $PM_{2.5}$ and PM_1, **b** OC, **c** EC and **d** OC/EC in PM_{10}, $PM_{2.5}$ and PM_1 particle fractions

Table 3 Relations between pollutants mass concentrations in PM_{10}, $PM_{2.5}$ and PM_1 particle fractions

Measured pollutants	n	r	*p*	y = ax + b
PM	83	0.967	**	$PM_{2,5} = 0.73 \times PM_{10} + 2.67$
	63	0.845	**	$PM_1 = 0.64 \times PM_{10} + 4.24$
OC	83	0.994	**	$OC_{(PM2.5)} = 0.68 \times OC_{(PM10)} + 0.85$
	63	0.972	**	$OC_{(PM1)} = 0.65 \times OC_{(PM10)} + 0.08$
EC	83	0.944	**	$EC_{(PM2.5)} = 0.73 \times EC_{(PM10)} + 0.11$
	63	0.957	**	$EC_{(PM1)} = 0.57 \times EC_{(PM10)} + 0.16$
TC	83	0.993	**	$TC_{(PM2.5)} = 0.68 \times TC_{(PM10)} + 1.01$
	63	0.974	**	$TC_{(PM1)} = 0.64 \times TC_{(PM10)} + 0.19$

PM particulate matter, *EC* elemental carbon, *OC* organic carbon, *TC* total carbon, *n* number of samples, *r* correlation coefficient

y = ax + b: linear regression

** $p < 0.01$

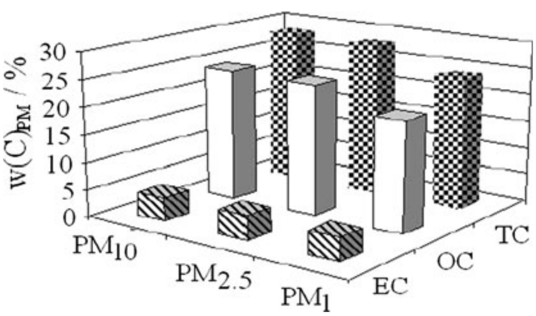

Fig. 2 EC, OC and TC mass contribution to total PM_{10}, $PM_{2.5}$ and PM_1 mass

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