Organic and elemental carbon associated to PM_{10} and $PM_{2.5}$ at urban sites of northern Greece

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Abstract Organic carbon (OC) and elemental carbon (EC) concentrations, associated to PM_{10} and $PM_{2.5}$ particle fractions, were concurrently determined during the warm and the cold months of the year (July–September 2011 and February–April 2012, respectively) at two urban sites in the city of Thessaloniki, northern Greece, an urban-traffic site (UT) and an urban-background site (UB). Concentrations at the UT site (11.3±5.0 and 8.44±4.08 14 µg m^{-3} for OC_{10} and $OC_{2.5}$ vs. 6.56±2.14 and 5.29±1.54 µg m^{-3} for EC_{10} and $EC_{2.5}$) were among the highest values reported for urban sites in European cities. Significantly lower concentrations were found at the UB site for both carbonaceous species, particularly for EC (6.62±4.59 and 5.72±4.36 µg m^{-3} for OC_{10} and $OC_{2.5}$ vs. 0.93±0.61 and 0.69±0.39 µg m^{-3} for EC_{10} and $EC_{2.5}$). Despite that, a negative UT-UB increment was frequently evidenced for $OC_{2.5}$ and $PM_{2.5}$ in the cold months possibly indicative of emissions from residential wood burning at the urban-background site. At both sites, cconcentrations of OC fractions were significantly higher in the cold months; on the contrary, EC fractions at the UT site were prominent in the warm season suggesting some influence from maritime emissions in the nearby harbor area. Secondary organic carbon, being estimated using the EC tracer method and seasonally minimum OC/EC ratios, was found to be an appreciable component of particle mass particularly in the cold season. The calculated secondary contributions to OC ranged between 35 and 59 % in the PM_{10} fraction, with relatively higher values in the $PM_{2.5}$ fraction (39–61 %). The source origin of carbonaceous species was investigated by means of air parcel back trajectories, satellite fire maps, and concentration roses. A local origin was mainly concluded for OC and EC with limited possibility for long range transport of biomass (agricultural waste) burning aerosol.

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Introduction

Organic carbon (OC) and elemental carbon (EC) constitute major components of atmospheric particles with a sum contribution in European urban areas reaching up to 25–40 % and 30–50 % of total PM_{10} and $PM_{2.5}$ masses, respectively (Putaud et al. 2004), while their contribution to the ultrafine particle mass can reach up to almost 100 % (Sardar et al. 2005). Recent epidemiologic studies have demonstrated the risks of exposure to increased levels of urban carbonaceous aerosols, revealing notable associations with cardiovascular mortality and morbidity (Ostro et al. 2007; Ito et al. 2011). Moreover, the OC fraction may include compounds like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls, known for their potential to induce carcinogenic and mutagenic effects (WHO 2000). Diesel particles, in particular, apart from solid elemental carbonaceous material (EC), contain hundreds of different organic compounds (n-alkanes and n-carboxylic acids, PAHs, oxygenated-PAHs, benzoic acids, hopanes, steranes, etc.), most of which are still unidentified (Rogge et al. 1993).

EC is primarily produced by incomplete combustion. In contrast, OC, anthropogenic or biogenic, can be emitted directly into the air (primary organic carbon, POC) or formed in the atmosphere through reactions of organic precursors with oxidative species and subsequent gas-to-particle partitioning of the less volatile products (secondary organic carbon, SOC) (Jones and Harrison 2005; Saylor et al. 2006). Relative contributions of primary and secondary organic aerosol components are difficult to directly quantify by chemical analysis because OC is a complex mixture of hundreds of compounds with a variety of chemical and physical properties. Researchers have employed several indirect methods to estimate the amount of primary and secondary organic aerosol. The EC tracer method (Turpin and Huntzicker 1991) has been frequently applied due to its simplicity and reliance on ambient EC and OC measurements alone (Castro et al. 1999; Lim and Turpin 2002; Cabada et al. 2004; Harrison and Yin 2008; Pio et al. 2011).

It has been suggested that an important percentage of OC in Western Europe can have long- or regional-scale origin. According to Viana et al. (2007), 69, 67, and 44 % of the OC concentrations in Amsterdam, Ghent, and Barcelona, respectively, could have originated from long-range transport since continental episodes during the winter period were characterized by high OC/EC ratios resulting from high OC concentrations of secondary origin. Long-range transport of carbonaceous aerosols has also been evidenced in the eastern Mediterranean (Crete Island) attributable to agricultural waste burning in European countries surrounding the Black Sea in March–April and July–September. This transport was estimated to have a rather small contribution on an annual basis (14 and 20 % to the levels of OC and EC, respectively), which could be significant (>30 %) in August; Sciare et al. 2008). Long-range transport of biomass burning aerosols from countries bordering the Black Sea was also suggested for other locations in eastern Mediterranean, such as the Rhodes Island (Argyropoulos et al. 2011).

The aim of the current study was to provide new and additional data for carbonaceous species in the urban atmosphere. For this purpose, OC and EC associated to PM_{10} and $PM_{2.5}$ particle fractions were investigated over the warm and the cold period of the year at two typical urban sites in Thessaloniki, northern Greece: a kerbside site strongly impacted by vehicular traffic and an urban background site. The fractionation of carbonaceous species between fine and coarse particles and their spatiotemporal variations were evaluated. The contribution of SOC to organic carbon was calculated, and its potential formation processes were assumed. Furthermore, the possibility for long- or regional-scale origin of carbonaceous aerosols was assessed.

Materials and methods

Sampling sites description

Thessaloniki (40°62′ E, 22°95′ N) is the second largest city in Greece hosting more than 1 million inhabitants in an area of about 200 km^2. The city is located at the mouth of Thermaikos Gulf (Fig. 1) being surrounded by hills to the north and the mountain of Hortiatis (1,200 m) to the east. In the west, the area is flat allowing connection of the city with the rest of the Macedonian mainland. Several industrial islands are located to the north (cement and lime production and marble quarry facilities), northwest (oil refining, polypropylene production, metal scrap incineration, nonferrous metal smelting, iron and steel manufacturing, and electrolytic MnO_2 production), and west (oil hydroskimming, truck and auto painting, metal recovery facilities, and lubricating oil recovery facilities).

Thessaloniki experiences a rather Mediterranean climate with mean temperatures during winter and summer at 7 and 25.3 °C, respectively, and mean annual rainfall at 445 mm. The highest frequency of air pollution episodes is associated with the presence of anticyclonic conditions over northern Greece, being characterized by weak or very weak surface pressure gradient intensity, depending on the position and extension of the anticyclone (Flocas et al. 2009). Additionally, the terrain complexity and the pronounced terrain features of the Greater Thessaloniki Area lead to the formation of local atmospheric circulations, such as sea-land breezes and drainage flows that affect the development, evolution, and maintenance of air pollution levels (Helmis et al. 1997).

The main particle emission sources in the greater Thessaloniki area include industry and road transport with total estimated PM_{10} emissions around 9,000 and 600 t/year, respectively (Markakis et al. 2010). Nevertheless, source apportionment studies conducted at various sites of the city revealed small contribution from industry, obviously because the industrial sources are located outside the main urban structure, while indicating motor vehicles as the major source with contributions to the ambient levels of PM_{10} sometimes higher than 50 % (Samara et al. 2003; Argyropoulos et al. 2011). The absence of a contemporary public transportation system forces people to overuse private cars and consequently leads to high emission regimes at urban sites of the city. The vehicle fleet profile of the more than 500,000 automobiles registered in the area includes around 90 % gasoline-fueled passenger cars, 7 % diesel vehicles including mainly buses, trucks, and taxies not fitted with particle filters, given that, in contrast to other European cities, diesel passenger cars were not allowed in Thessaloniki until November 2011, and 1 % two-stroke engines. Central heating also plays a significant role during the cold period of the year (October–April) with estimated PM_{10} emissions around 1,200 t/year (Markakis et al.
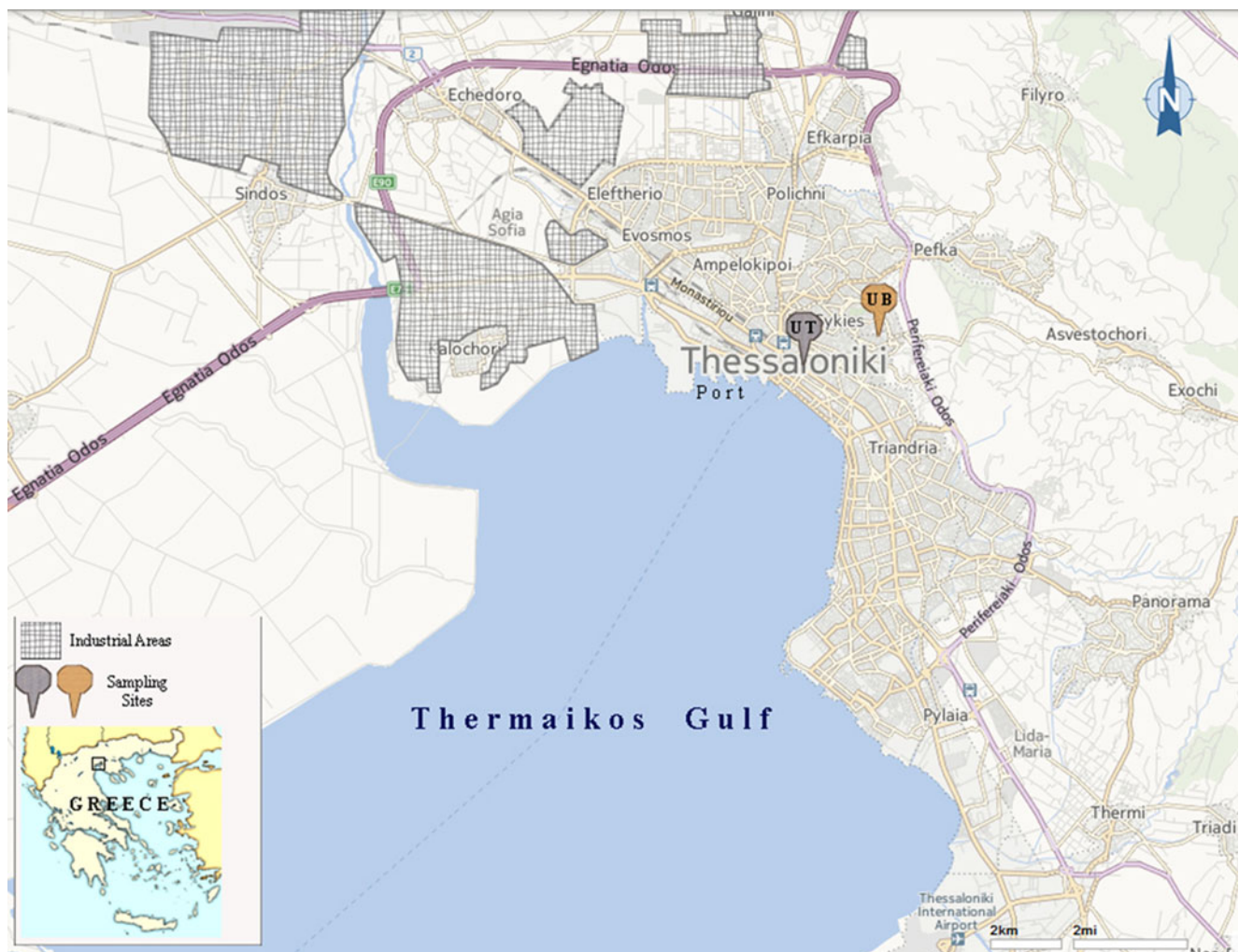
Fig. 1 Map of the study area with sampling sites (*UT* urban-traffic, *UB* urban background)

2010) and annual contribution to the ambient levels of PM_{10} at urban sites of the city in the range of 6–9 % (Samara et al. 2003; Argyropoulos et al. 2011). Diesel oil and natural gas have been regularly used as fuel for residential heating in most districts of the city; however, a distinct move of households towards wood and pellet burning was evidenced in the city and the surrounding residential communities in the cold months of 2011–2012 as a result of the economic crisis. Finally, the shipping activity in the Thessaloniki's harbor has been estimated to contribute with around 180 t/year to the total PM_{10} emissions (Markakis et al. 2010); however, its contribution to the ambient levels of PM_{10} is so far unidentified.

The present study was concurrently conducted at two of the air quality monitoring stations of the Municipality of Thessaloniki that, despite the short distance between them (only 2.5 km), usually exhibit the maximum and minimum levels of air pollutants in the urban agglomeration (Petrakakis et al. 2008). The urban-traffic site (UT) was located in the commercial city center (11.4 m asl), next to a busy road (~58,000 vehicles/day), while the urban background site

(UB) was located in the upper part of the city (174.0 m asl), in a residential area, around 800 m from the ring road. At both sites, the PM_{10} and $PM_{2.5}$ sampling devices were positioned on the roof of the monitoring stations (~3.0 m above ground level). Sampling was carried out during the warm and the cold months of the year (July–September 2011 and February–April 2012, respectively).

Gaseous pollutants (CO, SO_2, NO, NO_2, and O_3) and meteorological parameters (surface air temperature, relative humidity, and wind speed) were recorded at both sampling stations during the sampling campaigns using standard monitoring procedures (Kassomenos et al. 2011).

PM sampling and mass measurement

PM_{10} and $PM_{2.5}$ sampling was carried out according to European Standards EN-12341:1998 and EN14907:2005, respectively (http://www.cen.eu/cen). Low volume samplers (Ingenieur Derenda, Berlin) equipped with PM_{10} and $PM_{2.5}$ inlets were employed for this purpose operating at constant

flow rate of 2.3 m^3/h. PM_{10} and $PM_{2.5}$ fractions were collected on Φ 47 mm high purity quartz filters (Tissuquartz[TM], Pall) prefired at 500 °C for 4 h. Each sampling had a 24-h duration starting at 00:00. The PM_{10} and $PM_{2.5}$ masses were gravimetrically determined according to EN-12341 and EN14907, respectively. Loaded and unloaded filters were conditioned for 48 h at 20±1 °C and 50±5 % relative humidity before weighing in a Sartorius CP2P-F filter balance (d=0.001–0. 005 mg). Filter samples were stored in a cool and dark place until analyses (for <2 weeks).

OC and EC analysis

OC and EC concentrations were determined on quartz filter sections (1.5 cm^2) by the thermal optical transmission method in a Sunset Laboratory OC/EC analyzer. Briefly, samples were heated in a completely oxygen-free helium atmosphere, through four increasing temperature steps, to remove all organic carbon on the filter. The transition from the third temperature to the fourth (from 500 to 700 °C) also decomposes carbonate carbon. Then, the pure helium eluent is switched to a 2 % oxygen/helium mixture in the sample oven and the temperature is stepped up to 850 °C for EC determination. Organic and elemental carbons were detected by a flame ionization detector after oxidation to carbon dioxide that is finally reduced to methane. The detection limit of analysis was 0.5 $\mu g\ cm^{-2}$ for both OC and EC, and the uncertainty was better than 10 % (the average analytical error was ±2.7 and ±1.1 $\mu g\ cm^{-2}$ for OC and EC, respectively).

Data validation

Routine calibration procedures (use of standard masses, field and laboratory blank filters, and flow rate calibration) were employed to validate the determination of the PM_{10} mass concentration. Positive sampling artifacts of OC related to the adsorption of volatile gases on the particle collector (Matsumoto et al. 2003) were examined using field-filter blanks in each sampling site and season. The OC concentration in field-filter blanks averaging 4.4±2.0 $\mu g\ cm^{-2}$ (n=8) was subtracted from that of the sample filters. Negative artifacts related to desorption of volatile organic compounds from particles collected on the filter was checked by the tandem filter method (two quartz fibre filters from the same lot in series). The back/front ratio of OC in tandem filters averaged 0.20±0.12 (n=8); however, no corrections for negative sampling artifacts were made to the data presented in this study. Laboratory blank filters were also analyzed for about 10 % of all PM samples, and their concentration was subtracted from real samples.

Air parcel backward trajectories

Seventy-two-hour air parcel backward trajectories ending at Thessaloniki on each sampling date were calculated using the HYbrid Single Particle Lagrangian Integrated Trajectory model of the National Oceanic and Atmospheric Administration (http://www.arl.noaa.gov/ready/hysplit4.html).

Statistical analysis

The IBM SPSS Statistics 20 program was used for statistical analysis of experimental data. Spatial and temporal differences were investigated with the nonparametric median test. Correlations between determined parameters were investigated by calculating Pearson correlation coefficients.

Results and discussion

OC and EC concentrations

Summary statistics for OC and EC concentrations associated with the PM_{10} and $PM_{2.5}$ particle fractions are given in Table 1 along with corresponding particle mass concentrations.

The concentrations of the PM_{10} fractions of OC and EC (OC_{10} and EC_{10}, respectively) found at the UT site (11.3±5.0 and 6.56±2.14 $\mu g\ m^{-3}$, respectively) are among the highest values reported for urban locations influenced by traffic

Table 1 Concentrations of OC and EC associated to PM_{10} and $PM_{2.5}$ particle fractions ($\mu g\ m^{-3}$)

	Mean	SD	Median	Min	Max
Urban-traffic site, UT (N=57)					
PM_{10}	51.1	14.0	50.0	27.9	93.1
OC_{10}	11.3	5.03	9.82	4.33	22.7
EC_{10}	6.56	2.14	6.41	2.51	11.2
OC_{10}/EC_{10}	1.96	1.16	1.48	0.65	4.72
$PM_{2.5}$	31.2	11.4	29.1	15.9	68.4
$OC_{2.5}$	8.44	4.08	7.47	2.98	23.1
$EC_{2.5}$	5.29	1.54	4.91	2.54	9.17
$OC_{2.5}/EC_{2.5}$	1.86	1.38	1.32	0.56	6.48
Urban-Background site, UB (N=54)					
PM_{10}	33.7	15.2	30.7	14.9	73.8
OC_{10}	6.62	4.59	5.63	1.71	23.9
EC_{10}	0.93	0.61	0.79	0.14	3.33
OC_{10}/EC_{10}	7.52	2.81	6.91	3.25	16.1
$PM_{2.5}$	23.5	12.3	19.3	9.93	65.5
$OC_{2.5}$	5.72	4.36	4.47	1.23	21.9
$EC_{2.5}$	0.69	0.39	0.59	0.19	1.87
$OC_{2.5}/EC_{2.5}$	8.08	2.64	7.79	3.40	16.7

emissions in large European cities (Viana et al. 2006; Grivas et al. 2012). These concentrations are also relatively higher than those previously found at another, less trafficked, site within urban Thessaloniki (Flarountzou et al. 2008; Chrysikou et al. 2009; Terzi et al. 2010) as a result of the stronger intensity of primary sources at UT with a large number of vehicles and extremely aggravated traffic conditions.

The UB site exhibited significantly lower concentrations than UT for both carbonaceous species with $OC_{2.5}$ and $EC_{2.5}$ levels (5.7 ± 4.4 μg m^{-3} and 0.69 ± 0.39 μg m^{-3}, respectively) towards the lowest values found at urban background sites in other European cities (3.8–15.7 μg m^{-3} and 0.68–1.6 μg m^{-3}, Sillanpää et al. 2005; 9.2 and 1.4 μg m^{-3}, Lonati et al. 2007), as well as in other urban background sites in Europe (Viana et al. 2006 and references herein; Reche et al. 2012), concentrations. The OC and EC levels at this site were reasonably higher than those reported for rural Greek sites (0.09–0.68 μg m^{-3} for EC, 0.28–2.23 μg m^{-3} for OC; Bardouki et al. 2003).

The average contributions of OC and EC to total measured PM_{10} mass at the UT site were 22 and 14 %, respectively, rationally higher than those previously measured at urban sites experiencing lower traffic density [12–16 % for OC and 3.6–6.3 % for EC in Thessaloniki (Terzi et al. 2010); 13.6 and 4.3 % for OC and EC in Athens (Grivas et al. 2012)]. Average contributions of OC and EC to total measured PM_{10} mass at the UB site were 19 and 2.7 %, respectively. The corresponding contributions of OC and EC to total measured $PM_{2.5}$ mass were 26 and 19 % at the UT site vs. 23 and 3 % at the UB site, respectively. Relative contributions of OC and EC in the range of 15–38 % and 5.4–9.0 % have been reported for urban background sites of other European cities (Sillanpää et al. 2005; Lonati et al. 2007). The total carbonaceous material, OM (value obtained after applying a 1.6 factor to the OC concentrations, Terzi et al. 2010) plus EC, accounted for 57 and 73 % in PM_{10} and $PM_{2.5}$ at the UT site vs. 34 and 42 % at the UB site, respectively, in accordance to reported values (41 and 62 % vs. 32 and 42 %) for Madrid (Salvador et al. 2012).

Size distribution of OC and EC

Insights on the fractionation of carbonaceous material between fine and coarse mode can be gained by calculating the $OC_{2.5}/OC_{10}$ and $EC_{2.5}/EC_{10}$ ratio values (Table 2).

The average $PM_{2.5}/PM_{10}$ ratio values at the UT and the UB site were found to be 0.61 and 0.67, respectively, suggesting that a considerable portion of particle mass is distributed in the coarse fraction. The coarse fraction is relatively larger at the UT site reflecting the stronger impact from traffic-induced resuspension of road dust.

At both sites, the $OC_{2.5}/OC_{10}$ and $EC_{2.5}/EC_{10}$ ratios were significantly higher than those of the PM mass indicating that 84 and 81 % on average of EC associated to PM_{10} is distributed in the fine particle fraction at the UT and the UB sites, respectively. The corresponding proportions for OC were and 78 and 86 % on average, respectively. In consistency with reported results from other areas, the distribution in the fine fraction is relatively lower in the warm season suggesting emissions of carbonaceous matter in the coarse size range (Sillanpaa et al. 2006; Hueglin et al. 2005; Harrison and Yin 2008; Duarte et al. 2008; Cheung et al. 2011).

Differences in the size distribution of EC and OC can be explained by the fact that EC is only associated with incomplete combustion processes, which release into the atmosphere carbonaceous matter mainly in the form of submicrometer particles; on the other hand, OC emissions are distributed over a wider range of particle sizes, since OC is also generated by condensation processes in the car exhaust system, whereas the mechanical wear of tires in urban areas is also known to be a source of supermicrometer OC particles to the atmosphere (Thorpe and Harrison 2008). In addition to this, particles of biological origin, like plant debris, pollen, fungal spores, etc., also accumulate in the aerosol coarse size range (Bauer et al. 2002; Matthias-Maser and Jaenicke 2000).

Seasonal variations

Mean seasonal concentrations of PM_{10}, $PM_{2.5}$ and associated OC and EC fractions are shown in Fig. 2. The nonparametric median test indicated that concentrations of PM_{10} were higher in the cold months at both sites, although the difference was statistically significant ($P<0.05$) only at the UB site. Concentrations of $PM_{2.5}$ were significantly higher in the cold months at both sites ($P<0.05$). Higher wintertime concentrations of PM is a result of potential increase in anthropogenic emissions in combination with the subsidence of the atmospheric mixing layer and the prevailing stable atmospheric conditions during the cold period of the year. The cold season

Table 2 Relative distribution of PM mass, OC and EC in the $PM_{2.5}$ and the PM_{10} size fractions (mean±SD)

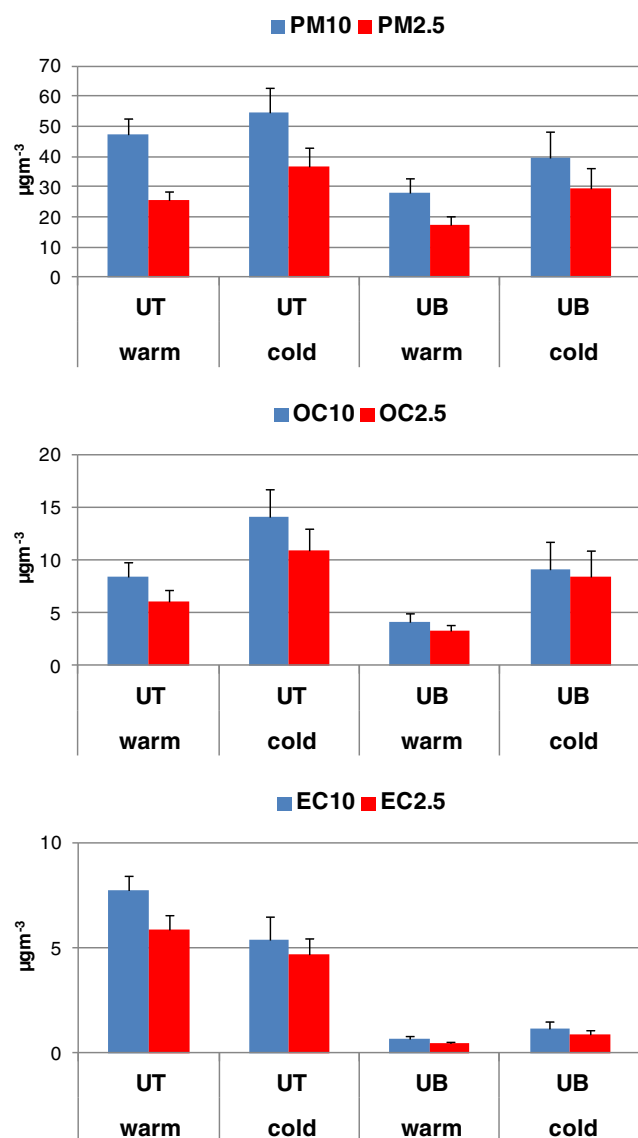|	Warm season			Cold season		
	$PM_{2.5}/PM_{10}$	$OC_{2.5}/OC_{10}$	$EC_{2.5}/EC_{10}$	$PM_{2.5}/PM_{10}$	$OC_{2.5}/OC_{10}$	$EC_{2.5}/EC_{10}$
UT	0.54 ± 0.06	0.72 ± 0.16	0.76 ± 0.11	0.68 ± 0.14	0.84 ± 0.29	0.93 ± 0.34
UB	0.59 ± 0.22	0.81 ± 0.20	0.73 ± 0.21	0.76 ± 0.15	0.91 ± 0.29	0.88 ± 0.36

Fig. 2 Mean seasonal concentrations of PM_{10}, $PM_{2.5}$, and associated OC and EC fractions at the urban-traffic (*UT*) and the urban background (*UB*) sites

concentrations were higher than those of the warm season by a factor of 1.4 for PM_{10} and 1.7 for $PM_{2.5}$ exhibiting a stronger seasonal impact on the finer fraction similarly to Querol et al. (2001).

Interestingly, OC and EC concentrations exhibited different seasonal patterns at the two sites. At the UB site, both OC and EC fractions exhibited significantly higher concentrations in the cold months, although the difference for EC_{10} was not statistically significant at the $P < 0.05$ level. At the UT site, both OC and EC fractions exhibited statistically significant seasonal differences ($P < 0.05$) with, however, reverse pattern; while OC_{10} and $OC_{2.5}$ were higher in the cold period, EC_{10} and $EC_{2.5}$ were more prominent in the warm period. As EC is a primary pollutant derived from ground-level combustion

sources, primarily vehicular traffic, higher concentrations are expected in the colder months of the year due to less effective dispersion processes (Harrison and Yin 2008). Under this approach, the higher levels of EC_{10} and $EC_{2.5}$ found at the UT site in the warm months appear as a peculiarity. Nevertheless, this seasonal pattern is confirmed by previous EC_{10} data from another central site in Thessaloniki (Terzi et al. 2010). Therefore, the higher EC levels in summer are not a consequence of the monitor location and could be possibly related to the enhanced maritime emissions in summer in combination to the prevailing SSW winds that are more frequent during this season than during winter.

The seasonal pattern of OC found in this study, with higher levels in the cold season, is in contrast to those found in Athens, southern Greece, where OC concentrations were significantly higher in the warm season suggesting photochemical formation of secondary organic aerosol (Grivas et al. 2012), but is in agreement to other studies carried out in Milan (Lonati et al. 2007), Barcelona (Viana et al. 2006), and various sites within the UK West Midlands (Harrison and Yin 2008). It can therefore be concluded that the higher OC concentrations in winter are likely due to secondary formation by condensation processes fostered by the low winter temperature and by the low boundary layer height typical of the winter period. In fact, condensation of semivolatile gaseous precursors is enhanced by low temperature, whereas temperature inversions limit their dilution and allow for supersaturation conditions with the exceedance of the equilibrium vapor pressure (Pandis et al. 1992; Odum et al. 1996). Other processes that can contribute to cold-season OC levels are the adsorption of semivolatile OCs onto existing solid particles and the dissolution of soluble gases that can undergo reactions in particles (Pandis et al. 1992; Odum et al. 1996).

Intersite comparison

Considering only the sampling dates that were common between the two sites, the urban-traffic increment above the urban background was calculated for PM, OC, and EC (Fig. 3). As seen, EC_{10} and $EC_{2.5}$ concentrations at UT constantly exceeded the corresponding EC fractions at UB revealing that locally generated road traffic emissions are superimposed upon the urban EC background. UT also exceeded UB concerning OC_{10} and PM_{10}, with only one exception during winter when OC_{10} and PM_{10} levels were higher at the UB site. Nevertheless, a negative traffic-background increment was frequently evidenced for $PM_{2.5}$ and $OC_{2.5}$ during February possibly indicating influence from local emissions from residential wood and other biomass burning.

The mean PM mass increment was 18.4±10.2 and 8.8± 8.8 $\mu g\ m^{-3}$ for PM_{10} and $PM_{2.5}$, respectively, in agreement to the average mass increments of 11.5 $\mu g\ m^{-3}$ of PM_{10} and 8.0 $\mu g\ m^{-3}$ of $PM_{2.5}$ reported for four site pairs in UK (Harrison et al. 2004). The mean mass increments of OC_{10}
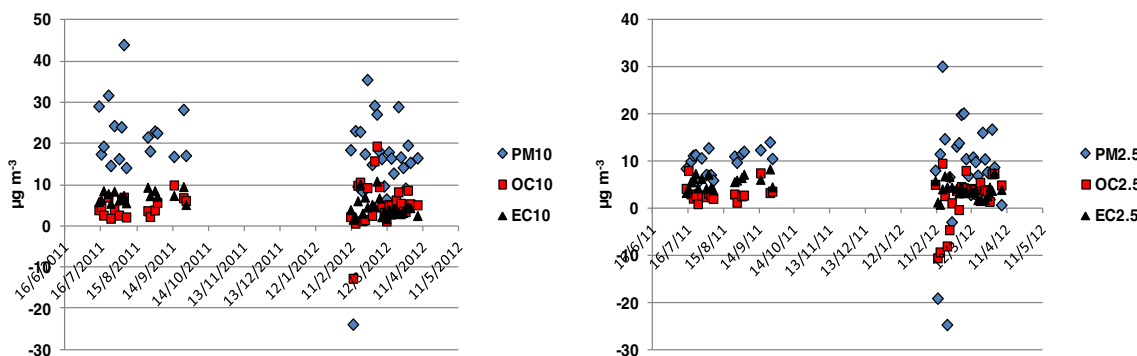
Fig. 3 Urban-traffic over urban background increments for PM, OC, and EC fractions

and EC_{10} were 5.1 ± 4.7 and 5.5 ± 2.4 μg m^{-3}, respectively, while those of $OC_{2.5}$ and $EC_{2.5}$ were 2.7 ± 4.2 and 4.6 ± 1.8 μg m^{-3}, respectively, indicating that the roadside particle increment is comprised mainly of organic carbon and secondarily by elemental carbon.

Significant intersite correlations were found for PM_{10} ($r= 0.82$) and $PM_{2.5}$ ($r=0.75$) indicating that both sites are influenced by similar sources and atmospheric processes. OC fractions exhibited relatively lower intersite correlations than PM ($r=0.56$ for OC_{10} and $r=0.52$ for $OC_{2.5}$), whereas EC, in both particle fractions, did not exhibit any correlation between the two sites suggesting that it originates from different combustion sources, summertime sources at UT vs. wintertime sources at UB.

The OC/EC ratio

The mean OC/EC ratio at the UT site was calculated as 1.96 ± 1.16 in PM_{10} and 1.86 ± 1.38 in $PM_{2.5}$, respectively, contrasting the clear prevalence of OC over EC at the UB site, where mean OC/EC ratios were 7.52 ± 2.81 in PM_{10} and 8.08 ± 2.64 in $PM_{2.5}$, respectively.

In general, the OC/EC ratio values found at the two sites are within the range of values reported for other European sites showing that OC/EC ratios are <2 at kerbside sites (with the exception of tunnels), 2–9 at urban background sites, and increase with decreasing anthropogenic emissions reaching values >10 at rural sites due to the decrease in EC levels typically linked to traffic (Viana et al. 2006). Increased OC/ EC ratio in the rural atmosphere may result from a different contribution of primary carbon sources, but more probably is a consequence of the consistent presence of long-range transported aerosol always containing some secondary organic carbon in nonurban areas (Castro et al. 1999). In addition, the atmosphere is continuously oxidizing volatile organic compounds (VOCs) from other sources, which will also condense onto airborne particles thereby increasing the OC/EC ratio. It consequently appears likely that the aging of polluted air on an urban and regional scale is leading to an increase in the OC/EC ratio in a way which is broadly consistent between

many European cities (Pio et al. 2011). The OC/EC ratio has been found to increase in the coarse particle fraction; for instance, Sillanpaa et al. (2006) found OC/EC ratios of approximately 5–6 in the coarse particle fraction of Prague, Amsterdam and Barcelona, probably due to high OC content of crustal materials or to OC adsorption onto soil dust particles that are collected simultaneously during sampling (Cheung et al. 2011).

In the present study, the mean OC/EC ratio at the UT site is apparently close to the corresponding values reported for vehicular emissions (0.5–0.8 for heavy-duty diesel vehicles and 1.7–2.3 for light-duty gasoline vehicles; Na et al. 2004; Pio et al. 2011) revealing the strong traffic influence at this site. It has been found that the emission rates of EC and OC from diesel engines depends on various factors, such as the engine load, the temperature, and the dilution of exhaust. OC is higher at idling and drops down with the increase in engine load, whereas EC has an opposite trend being higher at high load as a result of the use of more fuel that produces higher temperatures and a lack of oxygen (Sharma et al. 2005).

Residential heating (wood combustion of 4.2 and natural gas home appliance of 12.7), forest fire (14.5), and dust from paved roads (13.1) have shown remarkably higher OC/EC ratios (Na et al. 2004). OC/EC ratios in emissions from fireplaces/woodstoves are largely variable ranging from relatively low values (2.8–7.5) up to high values (26–119) (Zhang
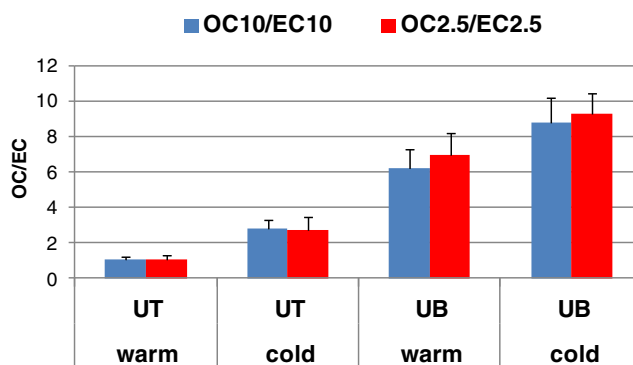

Fig. 4 Mean seasonal values of OC/EC ratios in PM_{10} and $PM_{2.5}$ fractions (*UT* urban-traffic site, *UB* urban background site)

et al. 2013 and references herein). The mean OC/EC ratio found at the UB site in PM$_{2.5}$ (8.08) is very close to the corresponding value found in Prague (8.7) that was attributed to wood combustion (Na et al. 2004).

Mean seasonal values of OC/EC ratios in PM$_{10}$ and PM$_{2.5}$ fractions are provided in Fig. 4. As seen, in both particle fractions, the OC/EC ratio values were higher in the cold season—as a result of elevated OC levels rather than of lower EC concentrations—particularly at the urban site, where the cold-season value was 2.5 times higher than the corresponding warm-season value. Elevated OC/EC ratios are often anticipated during summer considering the higher ambient temperatures, the expected enhanced volatilization of organic species from vegetation, and the expected increased secondary organic aerosol formation from both biogenic and anthropogenic VOCs (Plaza et al. 2011). Nevertheless, higher wintertime OC/EC ratios have been reported in several studies attributable to coal or biomass consumption for residential heating, which contributes more to OC than EC and also increases emissions of volatile organic precursors, as well as to lower temperatures leading to adsorption and condensation of semivolatile organic compounds onto existing solid particles (Li et al. 2012; Lonati et al. 2007); finally, the low mixing layer height in winter would enhance the SOC formation (Strader et al. 1999).

Estimation of secondary organic carbon

For particulate matter control strategies, it is necessary to quantify the contributions of primary and secondary organic carbon (POC and SOC, respectively) to carbonaceous aerosol. Nevertheless, since the direct measurement of SOC is not possible as it derives from various physical and chemical transformation processes, the estimation of SOC concentrations is largely dependent on the applied methodology.

A commonly used approach for the indirect evaluation of SOC in atmospheric particles is the EC tracer method, which is based on the minimum values of OC/EC ratios, (OC/EC)$_{min}$, considering that they represent samples containing exclusively primary carbonaceous aerosol from fossil fuel combustion (Turpin and Huntzicker 1995; Castro et al.

1999; Viidanoja et al. 2002). In this approach, the concentration of SOC is estimated from the following equation:

$$SOC = OC - EC \times \left(OC/EC \right)_{min} \tag{1}$$

where OC is the sum of SOC and POC.

Since the primary emission ratio can vary as an effect of seasonal and diurnal variations in the primary emissions mixture, and also due to the effects of meteorology and the impact of stationary sources (Strader et al. 1999; Plaza et al. 2011), the corresponding wintertime and summertime (OC/EC)$_{min}$ ratios were used to obtain the daily SOC estimates (Na et al. 2004; Pio et al. 2011). The seasonal (OC/EC)$_{min}$ values and the resulting secondary contribution to organic aerosol and particle mass at the two sites during the cold and the warm period are presented in Table 3.

As seen, the (OC/EC)$_{min}$ values at the UT site were significantly lower than those at the UB site in accordance to the values reported by Pio et al. (2011) for urban/rural and kerbside locations in Europe. Relative decrease in the (OC/EC)$_{min}$ ratio from PM$_{10}$ to PM$_{2.5}$ was observed at UT possibly indicative of OC-rich road dust resuspension in the coarse particle fraction. The opposite appeared at the UB site possibly indicative of OC-rich primary emissions in the fine particle fraction. The (OC/EC)$_{min}$ values at the UT site (0.65 in PM$_{10}$ vs. 0.56 in PM$_{2.5}$) were in agreement to those reported for double kerbside sites in Madrid and Lisbon (0.55 in PM$_{10}$ vs. 0.30 in PM$_{2.5}$; Pio et al. 2011), or for central sites of Birmingham, UK and Oporto, Portugal (1.1; Castro et al. 1999). These values are also in agreement to the OC/EC ratios in particle emissions during fossil fuel combustion that are often lower than 1 (e.g., Handler et al. 2008; Huang et al. 2006; Shah et al. 2004).

The (OC/EC)$_{min}$ values at the UB site (3.25 in PM$_{10}$ vs. 3.40 in PM$_{2.5}$) were significantly higher than those at the UT site. These values are higher than those reported for urban background sites in Portugal, Spain and UK (~1.0 for PM$_{10}$ and 0.7 for PM$_{2.5}$; Pio et al. 2011), but closer to the value found in the coastal/rural Areao, Portugal under conditions of contamination from wood burning emissions (2.6; Castro et al. 1999). Wang et al. (2005) also found higher (OC/EC)$_{min}$ ratio in wintertime atmospheric aerosols at a wood/

Table 3 Secondary organic carbon (SOC) contribution to total OC and PM mass at the urban-traffic (UT) and urban background (UB) sites

		Warm season				Cold season			
		(OC/EC)$_{min}$	SOC (μg m^{-3})	SOC/OC (%)	SOC/PM (%)	(OC/EC)$_{min}$	SOC (μg m^{-3})	SOC/OC (%)	SOC/PM (%)
UT	PM$_{10}$	0.65	3.35±2.64	35±19	6±4	1.13	7.26±4.52	50±23	12±6
	PM$_{2.5}$	0.56	2.73±2.37	39±22	10±8	0.96	7.06±5.14	54±25	17±10
UB	PM$_{10}$	3.25	1.86±1.10	43±19	6±4	3.57	5.04±3.65	55±17	13±5
	PM$_{2.5}$	3.40	1.61±1.20	46±17	9±5	5.21	3.53±3.21	40±16	11±6

coal burning site than at a traffic site (1.8 vs. 1.2). Interestingly, our (OC/EC)$_{min}$ values at the UB site are close to the OC/EC ratios reported for the residential burning of Austrian woods (2.6–5.7; Schmidl et al. 2008), for PM$_{10}$ emissions from the woodstove combustion of common Portuguese biofuels (3.1–31; Gonçalves et al. 2010), for fresh smoke plumes from boreal wild land fires (6.7; Saarnio et al. 2010, as well as to the "best-estimate" of 6 found by Gelencsér et al. (2007) for the biomass burning OC/EC ratio in aerosol samples collected at European rural background sites. Therefore, measured EC at the UB site was assumed to be the sum of EC from fossil fuel and biomass burning.

The elevation of the OC/EC minimum ratio with additional OC, presumably SOC, in urban background air, even during winter, has also been reported by Pio et al. (2011). According to the authors, the origin of this additional OC is still unclear but might include the contribution of other OC primary sources than fossil fuel combustion and biomass burning, as well as evaporation, oxidation, and condensation processes affecting organic aerosol loadings and composition in the atmosphere.

(OC/EC)$_{min}$ values were higher in winter than in summer, by a factor of 1.7 in both particle fractions of the UT site, and by a factor of 1.5 in the PM2.5 fraction of the UT site. Similar seasonal pattern with higher wintertime (OC/EC)$_{min}$ has also been reported for the coastal/rural Areao, Portugal affected by emissions from wood burning (Castro et al. 1999), as well as for Hong Kong (Yuan et al. 2006), in contrast to other studies reporting lower (OC/EC)$_{min}$ values in winter than in summer due to the seasonal variation of photochemical activity (Pio et al. 2011). The higher wintertime (OC/EC)$_{min}$ value found in this study at the UB site might be attributed to residential wood burning. On the other hand, the higher wintertime (OC/EC)$_{min}$ value at the UT site probably suggest large emissions of semivolatile organic compounds from traffic. It might be assumed that, if the fraction of semivolatile organic compounds in the aerosol is large, the concentration of particulate organic carbon would depend significantly upon air temperature; therefore, changes in ambient temperature from winter to summer would result in a decrease in the minimum OC/EC ratio as a consequence of semivolatile primary organic compound evaporation at higher temperatures in summer.

Due to emissions and meteorological conditions, at both sites and in both particle fractions, wintertime SOC were 2.5–3 times higher the summertime SOC (Table 3). Higher average concentrations of SOC in winter than in summer has also been reported for roadside, urban background, and rural sites in UK West Midlands, suggestive of long-range transport and temperature (through semivolatility) having a major influence on secondary OC concentrations (Harrison and Yin 2008), as well as for Milan, where miscellaneous OC in winter, including the secondary aerosols from traffic, plus primary and secondary aerosols from stationary combustion, was found to contribute more than in summer (92 vs. 84 %, respectively;

Lonati et al. 2007). Nevertheless, in other studies, highest SOC production was found during summer related to the increasing in photochemical activity (Castro et al. 1999; Plaza et al. 2011; Grivas et al. 2012).

As seen in Table 3, the secondary contribution to organic aerosol at the UT site can be as high as 50 and 35 % in the PM$_{10}$ fraction in the cold and the warm periods, respectively, with relatively higher contributions in the PM$_{2.5}$ fraction (54 and 39 %, respectively). Expectedly, the corresponding contributions at the UB site were comparatively higher, 59 and 43 % in PM$_{10}$, 61 and 46 % in PM$_{2.5}$ in the cold and the warm periods, respectively. The contributions of SOC to OC found in this study are within the range of reported values calculated using the minimum OC/EC ratio as variant in the EC tracer method for other cities [33 % in Athens (Grivas et al. 2012); 42 % in Oporto (Castro et al. 1999); 47 % in Toulouse (Calvo et al. 2008); 55–63 % in Birmingham (Harrison and Yin 2008); 70–84 % in winter vs. 80–92 % in summer in Madrid (Plaza et al. 2011); 41–46 % in PM$_{2.5}$ and 56–66 % in PM$_{10}$ in Tianjin, China (Li et al. 2012); 26 % in Auckland (Wang et al. 2005); and 48 % in PM$_{10}$ and 56 % in PM$_{2.5}$ in Costa Rica (Murillo et al. 2013)].

The contribution of SOC to particle mass was also higher in the cold season in both particle fractions ranging between a minimum of 6 % in summertime PM$_{10}$ at both sampling sites and a maximum of 17 % in wintertime PM$_{2.5}$ at the UT site. These values are in agreement with those found in Tianjin, China (7.4–9.0 % for PM$_{10}$ vs. 4.9–5.6 % for PM$_{2.5}$; Li et al. 2012).

OC–EC intercorrelation

A totally distinct OC–EC intercorrelation pattern was evidenced at the two sampling sites (Fig. 5). At the UB site, OC appeared to be strongly correlated with EC in both particle fractions, with correlation coefficients r=0.78 (OC$_{10}$–EC$_{10}$) and r=0.88 (OC$_{2.5}$–EC$_{2.5}$), suggesting that the major fraction of OC at this site is generated as primary particles along with EC. Strong OC–EC intercorrelations have also been found in several studies (Grivas et al. 2012; Li et al. 2012), also in Thessaloniki at urban sites with lower traffic density (Terzi et al. 2010). Silanpaa et al. (2005) found OC$_{2.5}$–EC$_{2.5}$ correlations ranging from relatively low values (0.44 in Prague) up to high values (0.95 in Barcelona).

In contrast to UB, at the UT site, OC and EC appeared mostly uncorrelated in both particle fractions indicating that the sources of OC is likely different from or in addition to those of EC. Lack of OC–EC correlation in PM$_{2.5}$ has also been found in Milan probably as a result of different emission patterns (Lonati et al. 2007). It has been reported that the association between OC and EC may vary in different particle fractions. Cheung et al. (2011) found strong OC–EC correlation in fine and ultrafine particles of Los Angeles; however, the correlation was low in the coarse particle fraction (PM$_{10–2.5}$)
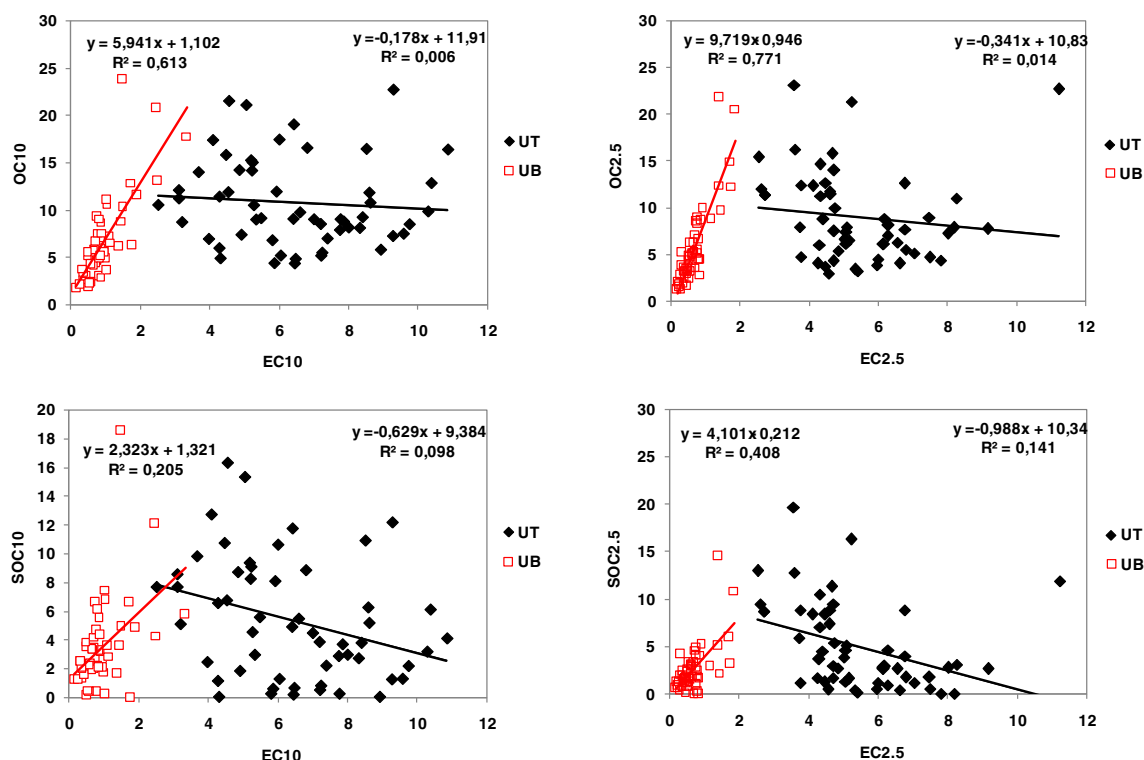
Fig. 5 Least square regression of OC and SOC on EC at the urban-traffic (*UT*) and the urban background (*UB*) sites

attributable either to common sources of OC and crustal materials or to OC adsorption onto soil dust particles that are collected simultaneously during sampling.

The lack of OC–EC correlation at UT also indicates limited impact of primary combustion sources on the formation of SOC, something that is supported by the poor inverse correlation between SOC and EC found at this site ($r = -0.31$ in the PM_{10} and -0.38 in the $PM_{2.5}$ fraction). SOC and EC were more strongly correlated at the UB site ($r = 0.45$ and 0.64 in the PM_{10} and the $PM_{2.5}$ fraction, respectively). In general, SOC is less correlated with EC in urban areas than in the rural atmosphere. In urban sites, the key factor determining secondary particulate organic formation is the existence of favorable meteorological conditions because VOC precursors are always present in excess as result of fresh road transport emissions. In the rural atmosphere, as a result of the larger distance from sources, the probability of occurrence of favorable conditions for gas-to-particle conversion during transport is higher. The main influence on both EC and secondary OC concentrations is the origin and degree of pollution of the air mass. Thus, within a given season, the correlation between the two variables is high (Castro et al. 1999).

Correlations of OC/EC with gaseous pollutants
and meteorological parameters

Table 4 provides summary concentrations of gaseous pollutants and meteorological parameters measured in situ during PM sampling at the urban-traffic and the urban background sites. Correlations of EC and OC with these parameters, as well as with PM mass are presented in Table 5.

Table 4 Concentrations of gaseous pollutants and meteorological parameters during sampling at the urban-traffic and the urban-background sites

Parameter	Units	Mean	SD	Median	Min	Max
Urban-traffic site, UT (*N*=57)						
SO_2	µg m^{-3}	4.6	4.4	3.0	1.0	21
NO	µg m^{-3}	116	61	102	29	300
NO_2	µg m^{-3}	91	18	89	51	125
O_3	µg m^{-3}	44	8.8	44	25	63
CO	mg m^{-3}	1.7	0.6	1.6	0.8	4.1
T	°C	21	9.5	26	3.5	33
RH	%	52	12	49	32	84
Wind speed	m s^{-1}	0.3	0.1	0.3	0.1	0.6
Urban-background site, UB (*N*=54)						
SO_2	µg m^{-3}	–	–	–	–	–
NO	µg m^{-3}	14	9.0	15	2.0	45
NO_2	µg m^{-3}	26	15	21	2.3	67
O_3	µg m^{-3}	75	13	77	43	101
CO	mg m^{-3}	0.4	0.2	0.4	0.1	1.0
T	°C	17	9.4	20	−0.2	30
RH	%	57	14	53	32	96
Wind speed	m s^{-1}	2.3	1.5	1.8	0.7	7.2

Table 5 Correlations of OC and EC with PM mass, gaseous pollutants, and meteorological parameters

	PM$_{10}$	PM$_{2.5}$	NO	NO$_2$	O$_3$	CO	T	RH	Wind speed
Urban-traffic site, UT ($N=53$)									
OC$_{10}$	**0.75**	**0.74**	**0.68**	**0.41**	**−0.45**	0.25	**−0.45**	0.21	−0.15
EC$_{10}$	0.01	−0.22	*−0.28*	−0.10	0.07	−0.25	**0.61**	**−0.46**	0.14
OC$_{2.5}$	**0.65**	**0.81**	**0.55**	*0.29*	*−0.37*	0.26	**−0.56**	0.17	*−0.32*
EC$_{2.5}$	−0.16	*−0.38*	−0.11	−0.09	−0.12	−0.11	*0.34*	**−0.45**	0.05
SOC$_{10}$	**0.78**	**0.77**	**0.59**	*0.34*	**−0.40**	*0.28*	**−0.43**	*0.34*	*−0.31*
SOC$_{2.5}$	**0.65**	**0.79**	**0.45**	*0.30*	*−0.28*	−0.04	−0.26	−0.21	0.21
POC$_{10}$	0.19	0.17	**0.45**	*0.30*	*−0.28*	−0.04	−0.26	−0.21	0.21
POC$_{2.5}$	0.04	−0.05	*0.35*	0.17	−0.22	0.19	*−0.32*	−0.27	0.25
Urban-background site, UB ($N=54$)									
OC$_{10}$	**0.84**	**0.92**	**0.56**	**0.81**	**−0.48**	**0.56**	**−0.54**	**0.41**	*−0.33*
EC$_{10}$	**0.70**	**0.66**	**0.53**	**0.82**	**−0.38**	**0.44**	*−0.27*	0.21	**−0.46**
OC$_{2.5}$	**0.78**	**0.91**	**0.54**	**0.74**	**−0.49**	**0.57**	**−0.61**	**0.44**	−0.21
EC$_{2.5}$	**0.73**	**0.78**	**0.51**	**0.81**	**−0.39**	**0.53**	**−0.47**	0.25	*−0.31*
SOC$_{10}$	**0.74**	**0.88**	**0.44**	**0.61**	**−0.43**	**0.50**	**−0.56**	**0.45**	−0.18
SOC$_{2.5}$	**0.67**	**0.80**	**0.40**	**0.50**	**−0.44**	**0.40**	**−0.50**	**0.49**	−0.15
POC$_{10}$	**0.71**	**0.67**	**0.56**	**0.82**	**−0.39**	**0.46**	*−0.34*	0.22	**−0.42**
POC$_{2.5}$	**0.64**	**0.71**	**0.54**	**0.69**	**−0.46**	**0.45**	**−0.60**	*0.30*	−0.18

Correlation coefficients significant at least at the 99 % confidence level are bold-faced while those significant at least at the 95 % confidence level are italicized.

As seen, at the UT site, OC was significantly correlated with PM mass in contrast to EC that was mostly uncorrelated. At the UB site, both carbonaceous species were significantly correlated with PM mass with OC exhibiting relatively stronger correlations than EC. The higher correlation of OC with PM is relevant to the fact that OC is determined by sources additional to fuel combustion (such as secondary aerosol formation and biogenic emissions), which are important for the determination of PM levels, as well. Other investigators have also reported higher correlations for PM with OC than with EC (Sillanpaa et al. 2006; Grivas et al. 2012).

Surprisingly, at the UT site, the correlations of carbonaceous species with gaseous pollutants such as NO, NO$_2$, and CO were mostly insignificant, excepting those of OC with NO. Given that this site is strongly affected by traffic emissions, the lack of reasonable correlation of EC with NO, a primary pollutant emitted from combustion processes, or CO produced via incomplete combustion processes, mainly via motor vehicles exhaust, cannot be explained. Possible differences in sources of EC and CO, including factors such as the type of fuel consumed by vehicles used at the sampling location, engine efficiency, or load, have been suggested as possible reason for the lack of EC–CO correlation in other studies (Yu et al. 2009). The same reasons could be hypothesized in this study, too, in addition to the potential nontraffic origin of EC from the harbor area during summer mentioned above. In contrast to UT, at the UB site, significant positive correlations were found for OC and EC with gaseous pollutants NO/NO$_2$ and CO in both particle fractions confirming their significant primary nature.

Statistical associations of SOC displayed in Table 5 show that, at both sites, it drives an important part of PM variability, while its production is favored under low ambient temperatures. Surprisingly, at both sites, SOC appeared to correlate with NO, also with CO at the UB site, similarly with primary organic carbon (POC), thus suggesting that it is associated with primary combustion-generated carbon emissions. Correlations of SOC with O$_3$ were negative at both sites, although more significant at the UB site, also suggesting an important primary nature for OC. This is in contrast to other studies, where a photochemical nature was concluded for OC (Grivas et al. 2012; Plaza et al. 2006; Yu et al. 2009).

Negative correlations of both OC and EC with wind speed, indicative of a wind dilution effect, were evidenced at the UB site (Table 5), in agreement to studies at other urban sites (Grivas et al. 2012). A reverse correlation with wind speed was also found at the UT site for OC, though weaker due to the very weak winds prevailing in the city center (Table 4). Although not shown in Table 5, it is worth to note that EC$_{10}$ and EC$_{2.5}$ at this site appeared to correlate positively with wind speed in winter ($r=0.32$ and $r=0.22$, respectively) suggesting possible transport from combustion sources other than local traffic.

Source origin of carbonaceous aerosols

The possibility for long- or regional-scale origin of carbonaceous aerosols was evaluated by means of air parcel backward trajectories and satellite fire maps.

The 72-h air parcel backward trajectory analysis clearly showed that air masses arriving at Thessaloniki during the study period originated mostly (>80 %) from the northern sector covering Western, Central, and Eastern Europe (Fig. 6). Interestingly, the highest mean concentrations of PM, OC, and EC appeared to associate with western air masses originating from relatively short distances, 500–

1,000 km upwind of Thessaloniki. Elevated OC/EC ratios and non-sea salt water-soluble potassium concentrations ($nssK^+$, not presented here) appeared with air masses of the northeastern sector, most frequent in August and September, possibly suggesting some transport of biomass burning aerosol from the countries surrounding the Black Sea (Ukraine, Russia, Romania, Bulgaria, and Moldavia). Transport of
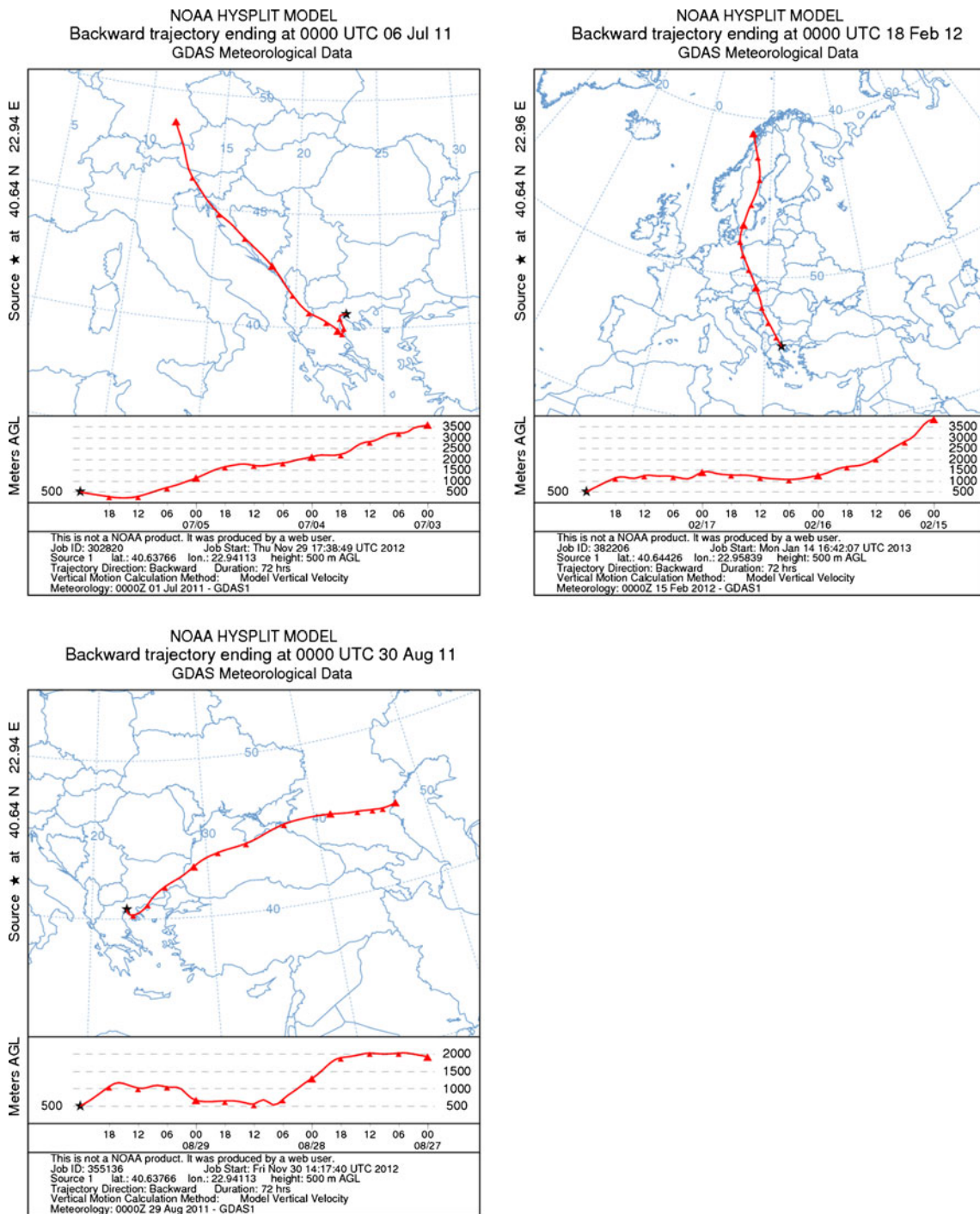

Fig. 6 Prevalent 72-h back air mass trajectories arriving at the study area

Fig. 7 Fires over Europe during the study (The maps accumulate locations of fires detected by MODIS on board the Terra and Aqua satellites over a 10-day period. Each *colored dot* indicates a location where MODIS detected at least one fire during the compositing period. Color ranges from *red* where the fire count is low to *yellow* where number of fires is large)
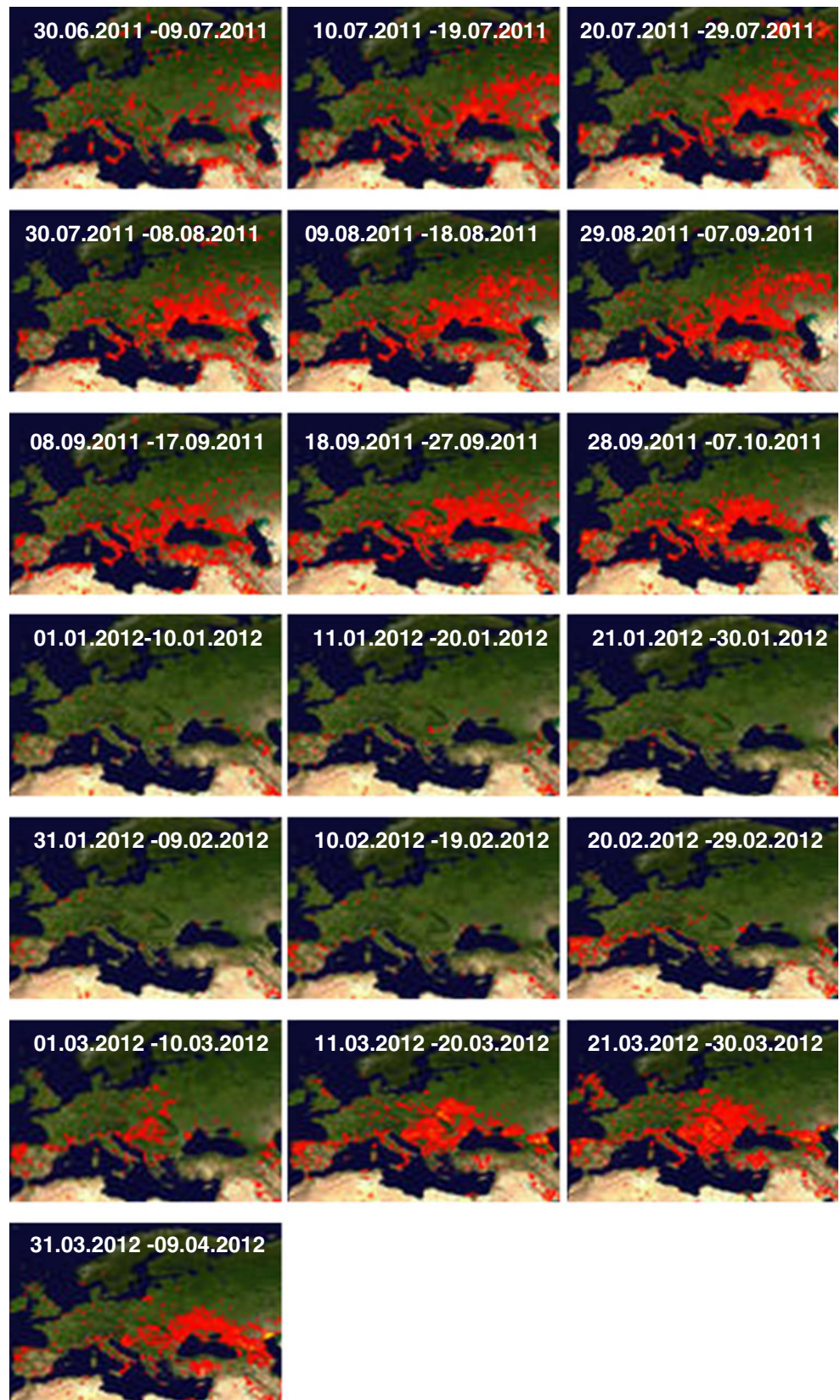
biomass burning aerosols in northern Greece, when air masses originate from the regions surrounding the Black Sea, has

been previously concluded from aerosol optical depth measurements (Kazadzis et al. 2007). Nevertheless, it is not

possible with our data to assert the external origin of OC due to the fact that these trajectories frequently coincide with anticyclonic conditions on the surface levels leading to air mass stagnation.

The fires detected over Europe during the study period by MODIS on board the Terra and Aqua satellites were further examined (http://rapidfire.sci.gsfc.nasa.gov/firemaps). The fire maps shown in Fig. 7 accumulate the locations of fires over a 10-day period. As seen, the entire summertime sampling period (July–September) was characterized by a great number of fires located not only in the countries surrounding the Black Sea but also to the north and west of Greece. During the wintertime sampling period, fires were uncommon in

January and February starting being more frequent in March. Interestingly, the highest PM and OC concentrations were associated with the fire-free time period of February 2012 suggesting origin from local sources rather than transport of biomass burning aerosol.

The concentration roses of carbonaceous aerosol shown in Fig. 8 can provide significant insights into the distribution of local emission sources around the two sampling sites. At the UB site, highest PM concentrations were mainly associated with winds from the SW and the NW sectors. This finding can be attributed to a synergy among local emission sources in the heavily urbanized and densely populated western part of the city and the local circulating system of sea/land breeze; sea

Fig. 8 Wind roses of PM_{10} and $PM_{2.5}$ masses and associated OC and EC concentrations
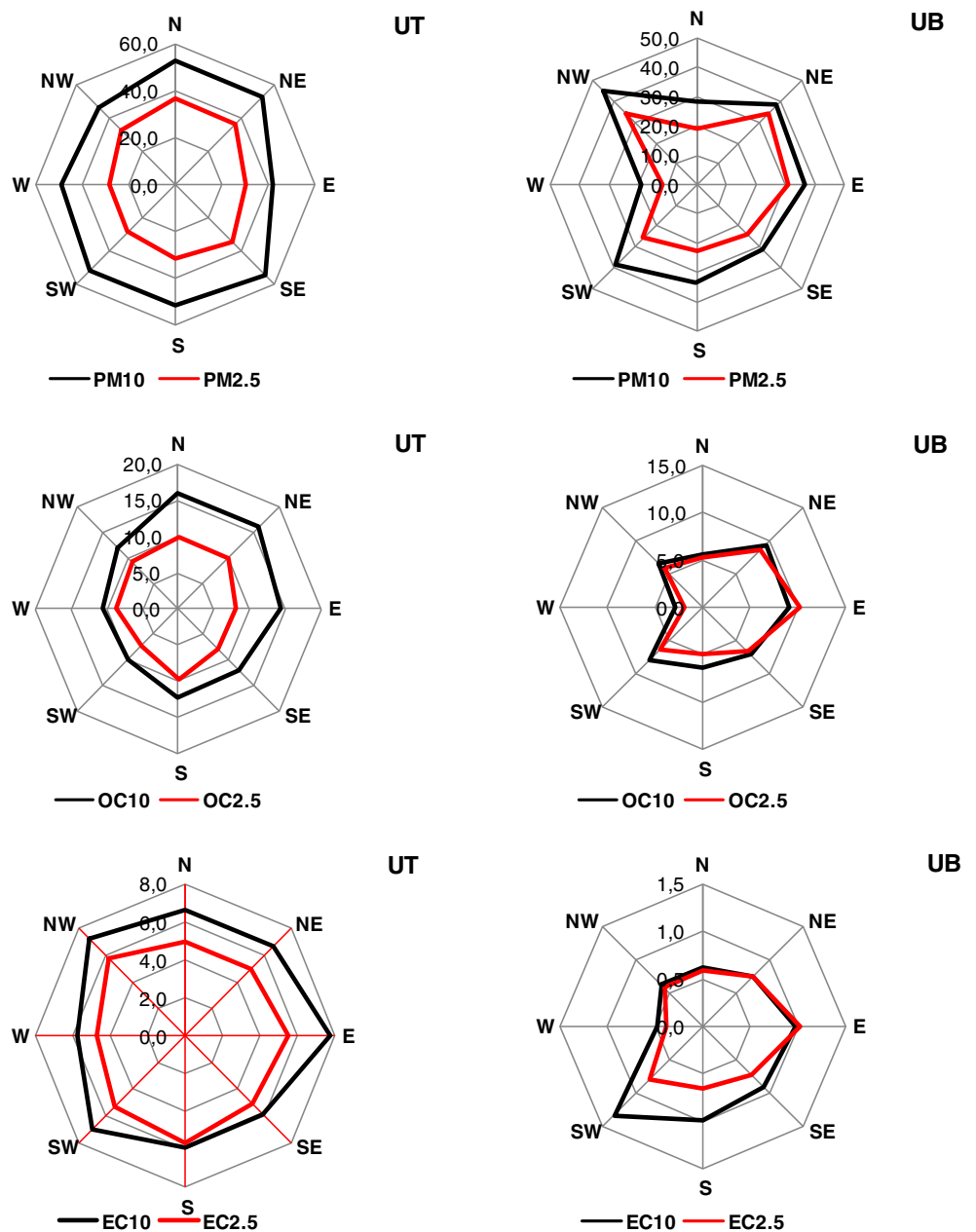
breeze blows from SW–SE directions during daytime changing to NW–NE land breeze during night-time. Thus, primary particles are trapped in the sea/land breeze cell and are recirculated over the city. During nighttime, land breeze transports particles from the urban and the industrial area towards the Gulf of Thermaikos, while during daytime, the particulate pollution is transported over the urban area of the city. The prevailing role of sea/land breeze in particulate pollution circulation over Thessaloniki has been previously reported (Kassomenos et al. 2011). In the absence of any large-scale circulation system, this local mechanism can become very effective in particle accumulation, especially when combined with strong temperature inversions and atmospheric stability due to strong anticyclonic conditions. It is worth mentioning that the above mechanism is more evident at the UB than the UT site probably due to the higher altitude above sea level (175 m), which ensures a weaker influence of the urban surface roughness and results in stronger winds throughout the year, as well as to the proximity of UB to the western conurbation and the industrial part of the city.

The OC concentration rose at the UB site was similar to those of PM with a stronger association with the NE–E sector suggesting some influence from the peripheral road and the residential communities located to this direction. On the contrary, the EC concentration rose, particularly those of EC_{10}, exhibited a remarkable association with SW winds suggesting influence from combustion emissions occurring in the city.

PM, OC, and EC at the UT site exhibited weaker associations with wind direction due to the very weak air circulation at this site.

Conclusions

OC and EC concentrations, associated to PM_{10} and $PM_{2.5}$ particle fractions, were concurrently determined over the warm and the cold period of the year at an UT and an UB site in Thessaloniki, northern Greece. Mean OC and EC concentrations at the UT site, in both fractions, were higher than those at the UB site, in accordance with the intense presence of emission sources (heavy vehicular traffic and/or harbor activity) and the poor dispersion conditions prevailing in the city center. Nevertheless, a negative UT-UB increment was frequently evidenced for $OC_{2.5}$ and $PM_{2.5}$ during the cold period possibly indicative of local residential wood burning. At both sites, more than 80 % of OC and EC appeared to be distributed in the $PM_{2.5}$ particle fraction, particularly in the cold season. At both sites, OC was significantly higher in the cold months as a combination of stronger air pollution sources in conjunction with poor mixing of the boundary layer; yet, an inverse seasonal pattern was evidenced for EC at the UT site suggesting summertime emissions probably originating from the harbor area. Correlations with gaseous pollutants

confirmed the significant primary nature of carbons observed at both sites. The average contribution of SOC to total OC was found to be 43 and 47 % in the PM_{10} and the $PM_{2.5}$ fraction at the UT site, respectively, exhibiting relative increase at the UB site (51 and 54 % in the PM_{10} and the $PM_{2.5}$ fraction, respectively). At both sites, SOC contributions were higher in the cold than in the warm season, implying that other factors rather than photochemical activity have a major influence on secondary OC concentrations, i.e., condensation of semivolatile organic species or adsorption onto existing solid particles and stationary combustion. No clear evidence for long-range transport of carbonaceous aerosol was obtained. Conclusively, OC and EC concentrations at the two sites showed a strong dependence on local settings, i.e., the vicinity of local emission sources in conjunction with the local meteorology.

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