Atmospheric
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Long-term characterization of organic and elemental carbon in the PM$_{2.5}$ fraction: the case of Athens, Greece

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Abstract. Organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC) and main ions were measured in a total of 1510 PM$_{2.5}$ daily aerosol samples collected from May 2008 to April 2013 in Athens, Greece. OC and EC concentrations were $2.1 \pm 1.3\,\mu g\,m^{-3}$ and $0.54 \pm 0.39\,\mu g\,m^{-3}$, accounting for $11 \pm 3\,\%$ and $3 \pm 1\,\%$ of PM$_{2.5}$ mass, respectively, with an average OC / EC ratio of 4.7 ± 3.1. Significant correlation was found between OC and EC during the whole period, indicating emissions by common primary sources on a regional scale. WSOC concentration ranged from 0.03 to $10.6\,\mu g\,m^{-3}$, with an average of $1.5 \pm 0.9\,\mu g\,m^{-3}$. By considering the Finokalia (Crete) station as a reference, it was estimated that, during the warm season in Athens, $67 \pm 7\,\%$ of emitted OC and $53 \pm 12\,\%$ of emitted EC is regional, while, during cold months, the regional contribution of OC is only $33 \pm 7\,\%$ and of EC $29 \pm 8\,\%$. Furthermore, secondary organic carbon (SOC) was calculated for the warm period of the year (April to October). The estimated SOC constituted about $75 \pm 6\,\%$ of PM$_{2.5}$ organic carbon in Athens, highlighting significant aging processes on a regional scale. In the period 2011–2013 and during wintertime, an increase in OC and EC levels was observed, attributed to an increase in wood burning for domestic heating due to the economic crisis.

1 Introduction

Atmospheric aerosol constitutes a crucial factor of air pollution since it presents adverse effects on health, environment and Earth radiative balance (EPA, 1996; WHO, 2003). Carbonaceous aerosol contributes to global warming, and black carbon is considered as the second most important agent of global warming after CO$_2$ (Probert and Tarrant, 1989; Robock and Graf, 1994; Galdos et al., 2013). Recent epidemiologic studies, have displayed the risks of exposure to increased levels of carbonaceous aerosols, revealing notable associations with cardiovascular mortality and morbidity (Ostro et al., 2010; Lipsett et al., 2011; Krall et al., 2013).

Establishing the carbonaceous content of atmospheric particles has been the objective of several studies as it represents an essential fraction of particulate matter (Alastuey et al., 2004; Na et al., 2004; Putaud et al., 2004; Querol et al., 2004; Yu et al., 2004; Yttri et al., 2007; Pey et al., 2010; Pio et al., 2011). These studies provide evidence for the relative importance of road traffic and high wintertime energy consumption, combined with unfavorable meteorological conditions and summertime traffic, but also indicate that secondary organic aerosol is a major source of carbonaceous aerosol in Europe. The formation mechanisms of organic carbon (OC) and elemental carbon (EC) have been under scrutiny during the last decade (Saylor et al., 2006; Pio et al., 2007; Schwarz et al., 2008; Pio et al., 2011; Grivas et al., 2012; Bougiatioti et al., 2013), with an emphasis on their biogenic and/or anthropogenic origin and subsequent effects.

Athens is located in the eastern Mediterranean, a well-known crossroad of long-range-transported aerosol from dis-

crete regional sources that are superimposed on other significant local sources of pollution (Lelieveld et al., 2002; Vrekoussis et al., 2005). A description of the Athens Basin and prevailing meteorological conditions has been provided in the literature (Chaloulakou et al., 2005; Grivas et al., 2008, 2012; Kanakidou et al., 2011; Theodosi et al., 2011). Studies performed in the Athens Basin demonstrated the prevailing emissions of carbonaceous aerosol all year round, namely from vehicles, fuel combustion and long-range transport (Chaloulakou et al., 2005; Sillanpaa et al., 2006; Grivas et al., 2012; Pateraki et al., 2012; Remoundaki et al., 2013). Nevertheless, it is essential to note that there are limited studies concerning the PM$_{2.5}$ fraction of aerosol in Athens, and the studies performed so far have been conducted for short time periods (4–11 months), mainly at urban locations.

To our knowledge, this is the first long-term (2008–2013) uninterrupted data record of carbonaceous aerosol in an extended area already burdened by long-range transport (eastern Mediterranean) and, in particular, in an urban agglomeration with degraded air quality – AQ – (Athens) and, thus, an enhanced health risk. The long measurement duration and the completeness of the data series allowed the performance of a thorough and concise investigation of carbonaceous aerosol properties, sources and variability in the area as a major part of this work. Additionally, the study covers a 5-year period that includes years before and during the economic recession occurring in Greece, enabling additional investigation of the significant impacts of the crisis on AQ. In particular, industrial activity was decelerated, vehicle use was limited and wood burning replaced conventional fuels for domestic heating due to the high heating oil prices. In many cases, the latter is reported to have a significant contribution to air pollution levels (Molnar et al., 2005; Sandradewi et al., 2008; Schmidl et al., 2008; Grange et al., 2013). Finally, a direct comparison between the urban background site of this study and a remote background site considered as reference for the extended eastern Mediterranean area (Finokalia, ACTRIS supersite; ACTRIS is the Aerosols, Clouds, and Trace gases Research InfraStructure Network, http://www.actris.net/) helped us shed light on regional patterns and processes, discriminating between regional and local emission sources.

2 Experimental setup

2.1 Sampling site

The measurements were conducted at the National Observatory of Athens premises in Penteli (38°2.94′ N, 23°51.78′ E, 495 m a.s.l). The site is located on top of a hill facing the city of Athens, which lies to the SSW (17 km from the city center), while, to the NNE, it is bordered by the Penteli Mountain. The major sources of air pollution in the close vicinity are expected to be vehicular emissions and residential heat-

ing. More details about the Greater Athens Area morphology and meteorological conditions are provided by Kanakidou et al. (2011) and references therein, while internal transport patterns in the urban complex are described by Melas et al. (1998). The station is considered as an urban background site, established and operated by the Institute of Environmental Research and Sustainable Development.

2.2 Sample collection

This study covers 5 years from May 2008 to April 2013, resulting in the daily collection of samples, totalling 1510 samples over the entire period. PM$_{2.5}$ aerosol samples were collected using a dichotomous partisol sampler (R&P Co) during most of the period (90 % of the sampling time) and a Partisol FRM Model 2000 air sampler (R&P Co) (10 % of the sampling time), operating at 15.0 and 16.7 L min^{-1}, respectively. Sampling duration was 24 h, starting at 14:00 LT.

Samples were collected on quartz fiber filters (4.7 cm, Whatman QMA). Filters were prebaked at 550 °C for 4 h to remove any absorbed organic material and were stored and transported to and from the field in petri dishes. After sampling they were stored until analysis. Filter blanks and blank field samples were also prepared and analyzed.

For the estimation and correction of the amount of adsorbed organic vapor on the sampling filter, a tandem filter collection method was applied (e.g., Turpin et al., 2000; Kirchstetter et al., 2001; Yttri et al., 2007). Two quartz fiber filters from the same lot were used in series, the front filter collects essentially 100 % of the particulate matter (and some gas-phase material), and the backup filter is exposed only to gas-phase compounds. The measured carbon content of the backup filter can be subtracted from that of the front filter to give an estimate of the particulate phase OC (Turpin et al., 2000; Novakov et al., 2005; Sillanpaa et al., 2005). Nevertheless, it has been reported that the back-to-back filter configuration does not allow enough time for equilibration of gases on the second filter, and therefore this approach could underestimate the positive OC artifact. Tandem filters were collected for a selected number of samples, using the aforementioned Partisol samplers. In our analyses, the backup filters indicated a positive OC artifact which was always smaller than 5 %; thus, no correction was applied.

2.3 Mass and chemical analyses

2.3.1 Aerosol mass

PM mass was determined by weighing the filters before and after sampling according to the United States, Environmental protection agency, manual reference method: RFPS-1298-126, using a Mettler Toledo MX5 microbalance (1 μg sensitivity). The filters (samples and blanks) remained for 48 h under controlled conditions (RH 40 ± 5 %, T 20 ± 3 °C) prior to each weighing.

2.3.2 OC–EC analysis

All quartz filters (samples and blanks) were analyzed by a thermal optical transmission technique, using a Sunset Laboratory Inc. (Oregon) carbon analyzer. A punch of $1\,cm^2$ was removed from the filter and loaded into the analyzer, as described by Bougiatioti et al. (2013) and Novakov et al. (2005). OC and EC were determined using the EUSAAR-2 (European Supersites for Atmospheric Aerosol Research) protocol (Cavalli et al., 2010). Briefly, the first phase subsumes four stages of heating to 200, 300, 450 and 650 °C in He atmosphere, while, during the second four-step temperature program, the sample is heated to 500, 550, 700 and 850 °C in He/O_2 atmosphere. The detection limit of the analysis was 0.26 and 0.05 $\mu g\,C\,cm^{-2}$ for OC and EC, respectively. The reported results were blank-corrected.

2.3.3 WSOC analysis

For the determination of the water-soluble organic carbon (WSOC) concentrations, punches of $2\,cm^2$ were removed from the filter and placed in an ultrasonic bath for 45 min using 15 mL of nanopure water. The sample extract was filtered using syringe filters (PALL IC (ion chromatography) Acrodisc (PES (polyethersulfone)), 0.45 μm, 13 mm). The solutions obtained after the filtration were analyzed for total organic carbon (TOC) using a Shimadzu TOC-V CSH total organic carbon analyzer. In short, the sample is injected into a combustion cell equipped with an oxidation catalyst (Pt) and is heated to 680 °C. TC (total carbon) is converted to carbon dioxide, and it is cooled, dehumidified and transferred through the carrier gas (synthetic air) to the NDIR (nondispersive infrared) gas analyzer. For the IC (inorganic carbon) analysis, the sample is injected to the IC reaction vessel, where it is acidified, to convert IC to carbon dioxide, and it is volatilized by a sparging process. Then the sample is transferred by the carrier gas to NDIR in order to be detected. Total water-soluble organic carbon is calculated by extracting inorganic water-soluble carbon from total water-soluble carbon (TOC = TC–IC) and is labeled as WSOC. The analytical detection limit for WSOC was 80 ppb. All data were corrected for the obtained blank levels.

2.3.4 Ion chromatography

Punches of $2\,cm^2$ from the quartz filters were extracted in an ultrasonic bath with 10 mL of nanopure water for 45 min and were then filtered using syringe filters (PALL IC Acrodisc (PES), 0.45 μm, 13 mm) to remove any insoluble species. The acquired filtered solutions were analyzed by ion chromatography for the determination of the main ionic species concentrations (anions: Cl^-, Br^-, NO^{-3}, SO_4^{-2}, PO_4^{-3}, $C_2O_4^{-2}$; cations: NH_4^+, K^+, Na^+, Mg^{+2}, Ca^{+2}). Anions were determined using a Dionex-500 ion chromatograph equipped with an Ion Pac AS4A-SC column and an

AG4A-SC precolumn, with an ASRS-300 suppressor. Anion separation was conducted with isocratic elution of $NaHCO_3$ (3.4 mM)/Na_2CO_3 (3.6 mM) as an eluent and a flow of 1.5 mL min^{-1}. For the determination of cations, an Ion Pac CS12A column and a CG12A guard column were used, with a CSRS-300 suppressor, under isocratic elution of 20 mM MSA (methanesulfonic acid) at a flow rate of 1.0 mL min^{-1}. The detection limit of the analysis was 20, 12, 40, 12 and 40 ppb for NH_4^+, K^+, Na^+, Mg^{+2} and Ca^{+2}, respectively, while the corresponding detection limit for all anions (Cl^-, Br^-, NO^{-3}, SO_4^{-2}, PO_4^{-3}, $C_2O_4^{-2}$) was 20 ppb. The reported concentrations were corrected for blanks.

3 Results and discussion

3.1 Mass concentrations of OC–EC and observed seasonal trends

The daily concentration levels of OC range from 0.1 to 8.5 $\mu g\,m^{-3}$ (average: $2.1 \pm 1.3\,\mu g\,m^{-3}$), contributing on average about $11 \pm 3\,\%$ to the total $PM_{2.5}$ mass. Accordingly, the mass concentration of EC ranges from 0.01 to 3.33 $\mu g\,m^{-3}$ (average: $0.54 \pm 0.39\,\mu g\,m^{-3}$), contributing $3 \pm 1\,\%$ to the total $PM_{2.5}$. OC and EC values from previous studies in Athens and other European sites are presented in Table 1. It should be noted that most of these studies refer to shorter time periods (4–11 months) and are for different site types. Compared to OC and EC concentrations in Athens back in 2003, this study reveals levels 3–4 times lower, while later studies revealed similar levels (or slightly higher, depending on the site type) in the range of 1.5–4 $\mu g\,m^{-3}$ for OC and 0.4–1.8 $\mu g\,m^{-3}$ for EC. OC concentrations from several studies in southern European cities (mainly western Mediterranean) during the period 2002–2006 are in the range of 3–9 $\mu g\,m^{-3}$, while EC values are in the range of 0.7–1.7 $\mu g\,m^{-3}$. Concentrations in an urban site in Istanbul during the period 2008–2009 appear much higher compared to the values of this study. Regional background concentration levels at the Finokalia site (Crete Island, 2004–2006) are on average 1.8 and 0.27 $\mu g\,m^{-3}$ for OC and EC, respectively.

Total carbon is calculated as the sum of OC and EC (TC = OC + EC), with OC accounting for $79 \pm 4\,\%$ of the total carbon and constituting the predominant carbon contributor, which is in accordance with findings in other European sites (e.g., Lonati et al., 2007; Sanchez de la Campa et al., 2009). However, the contribution of TC to PM in this study ($14 \pm 3\,\%$) is lower than what is reported in the literature for other urban/urban background locations (e.g., 25–46 % in Viana et al. (2006); 27–28 % in Lonati et al. (2007); about 19 % in Sanchez de la Campa et al. (2009); 29 % in Perrone et al. (2011); Querol et al. (2013)).

Conversion of OC to OM (organic matter) is recognized as one of the most critical factors of uncertainty in mass closure calculations (Yttri et al., 2007). Turpin and Lim (2001)

Table 1. PM$_{2.5}$ mass, OC, EC, WSOC concentrations and OC / EC ratios reported in the literature and compared to this study.

Location site*	Sampling period	PM$_{2.5}$ mass (μg m^{-3})	OC (μg m^{-3})	EC (μg m^{-3})	WSOC (μg m^{-3})	OC / EC
Athens, Urb-BG, current study	May 2008–Apr 2013	20 ± 11	2.±1.3	0.54 ± 0.39	–	4.7 ± 1.3
El Arenosillo, Urb-BG [1]	2 Jun 2005–30 Jun 2006	21	2.9	1.1	–	2.9
Barcelona, Urb-BG [2]	27 Jul–01 Sep 2004	16.4	3.7	0.8	1.6	4.6
Barcelona, Urb-BG [2]	16 Nov–16 Dec 2004	25.8	6.7	1.2	2.1	5.6
Duisburg, Urb-BG [3]	Oct–Nov 2002	14.7	–	1.32	–	–
Prague, Urb-BG [3]	Nov 2002–Jan 2003	29.6	–	1.69	–	–
Amsterdam, Urb-BG [3]	Jan–Mar 2003	25.4	–	1.37	–	–
Helsinki, Urb-BG [3]	Mar–May 2003	8.3	–	0.7	–	–
Barcelona, Urb-BG [3]	Mar–May 2003	20	–	1.52	–	–
Athens, Urb-BG[3]	Jun–Jul 2003	25.3	–	1.67	–	–
Salento Peninsula (Lecce), Urb-BG [4]	Mar–Dec 2007	19 ± 9	5.6 ± 2.8	1.5 ± 12	–	–
Milan, Urb-BG [56]	Aug 2002–Dec 2003, spor	24.5	9.2 ± 7.2	1.4 ± 0.4	–	–
Madrid, Urb-BG [7]	Jun 2009	–	2.71	0.94	–	–
Madrid, Urb-BG [7]	Jan–Feb 2010	–	1.2	1.53	–	–
Athens, urban**,[8]	Jan–Aug 2003	–	6.8	2.2	–	–
Istanbul, urban [9]	Jul 2008–Jun 2009	–	6.65	2.92	–	–
Athens, urban [10]	Feb–Dec 2010, spor	20	2.43	0.99	–	2.92 ± 0.6
Athens, suburb [11]	29 Feb–2 May and 4 Jun–5 Aug 2008	23.8	4.1	0.48	–	–
Athens, Traf-Ind [11]	29 Feb–2 May and 4 Jun–5 Aug 2008	24.7	1.46	1.8	–	–
Athens, Coa-BG [11]	29 Feb–2 May and 4 Jun–5 Aug 2008	19.2	2.39	0.44	–	–
Thessaloniki, Urb-Ind**,[12]	Jun–Sep 2007	–	6.4	2.91	–	2.2
Thessaloniki, Urb-Ind**,[12]	Dec 2006–Mar 2007	–	8.73	2.93	–	2.98
Thessaloniki, Urb-Traf**,[12]	Jun–Sep 2007	–	7.66	2.64	–	2.9
Thessaloniki, Urb-Traf**,[12]	Dec 2006–Mar 2007	–	8.07	1.82	–	4.43
Finokalia (Crete), remote [13]	Jul 2004–Feb 2007, spor	–	–	–	–	5.1
Finokalia (Crete), remote[14]	Jul 2004–Jul 2006, spor	–	1.8 ± 1.4	0.27 ± 0.18	–	–
Finokalia (Crete), remote [15]	10 Jul–23 Jul 2007	–	2.58 ± 1.12	0.36 ± 0.25	1.74 ± 0.86	–
Finokalia (Crete), remote [15]	24 Jul–6 Aug 2007	–	3.04 ± 1.55	0.32 ± 0.17	1.93 ± 0.84	–
Akrotiri (Chania, Crete), suburban [16]	Oct 2009	–	2.3 ± 1.2	0.8 ± 0.2	–	2.8 ± 1.0
El Campus (Spain), rural[1]	2 Jun 2005–30 Jun 2006	21	3	0.6	–	4.7
French Riviera, coastal [17]	5–29 May 2007	–	2.07–5.37	0.13–0.33	0.02–0.08	–
Montseny, Reg-BG [18]	2002–2007	–	2	0.2	–	–
Castillo de Bellver, Mallorca, Sub-BG [19]	8 Jan 2004–29 Feb 2005, spor	20	2.9	0.5	–	–

* Spor: sporadically
Urb-BG: urban background; Urb-Ind: urban industrial; Urb-Traf: urban traffic; Traf-Ind: traffic industrial; Sub-BG: suburban background; Coa-BG: coastal background
** PM$_{10}$ sampling
[1] Sanchez de la Campa et al. (2009) [2] Viana et al. (2007) [3] Sillanpää et al. (2006) [4] Perrone et al. (2011) [5] Lonati et al. (2008) [6] Lonati et al. (2007)
[7] Mirante et al. (2014) [8] Grivas et al. (2012) [9] Theodosi et al. (2010) [10] Remoundaki et al. (2013) [11] Pateraki et al. (2012) [12] Terzi et al. (2010)
[13] Bougiatioti et al. (2013) [14] Koulouri et al. (2008) [15] Bougiatioti et al. (2011) [16] Kopanakis et al. (2012) [17] Piazzola et al. (2012) [18] Pey et al. (2009a) [19] Pey et al. (2009b)

suggest the use of different conversion factors according to site type: 1.6 ± 0.2 for urban areas, 1.9–2.3 for aged aerosols and 2.2–2.6 for biomass burning. Taking into account that our site is an urban background station which is also affected by long-range transport (e.g., Sciare et al., 2005; Kanakidou et al., 2011; Pateraki et al., 2012; Remoundaki et al., 2013), we used the value of 2.1 (OM = 2.1 · OC). On average, OM accounts for 24 ± 6 % of PM$_{2.5}$, which is consistent with the value (22 %) provided by Remoundaki et al. (2013) for Athens, while it is lower than those reported at other European sites (e.g., Sillanpaa et al., 2005; Sanchez de la Campa et al., 2009).

In Fig. 1 the daily concentrations of OC and EC are presented for the whole sampling period (May 2008–April 2013). It is observed that OC and EC present significant co-variance for most of the period, with maxima mainly during the colder months. The seasonal variability in OC and EC is clearly demonstrated in Fig. 2, which reveals higher concentrations from November to March. This is mainly attributed to emissions from residential heating and low-altitude temperature inversions that trap local emissions of particulate OC and EC near the surface (e.g., Yttri et al., 2007). The minimum OC concentrations appear in late spring and early autumn, when there is no domestic heating and photochemistry is slowed down compared to summer. In the case of EC, minimum concentrations are found during the warmest months of the year, when there is less fuel combustion in Athens (the period of the summer vacations) and thus lower production of primary EC.

The summer-versus-winter contrast is further shown in Fig. 3 but on an annual basis. Winter refers to the December–February period of the December year, while summer means
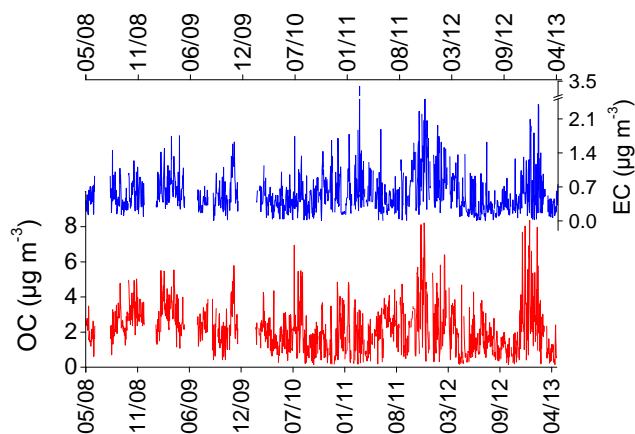
Figure 1. Daily OC and EC concentrations at Penteli station, Athens, for the period May 2008–April 2013.
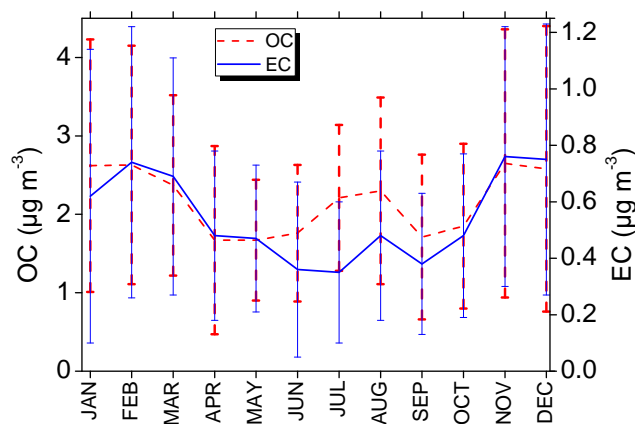

Figure 2. Average seasonal cycle of OC and EC concentrations calculated from daily values for the period May 2008–April 2013.

Figure 3. Average winter and summer OC and EC concentrations calculated from daily values and EC_{summer}-to-EC_{winter} median ratios for the period May 2008–April 2013.

June–August The EC summer levels after 2009 appear slightly reduced compared to 2008, coinciding with the economic recession period in Greece, which led to the reduction of traffic emissions and industrial activities (Vrekoussis et al., 2013). In winter, there is an increase during the last 2 years (2011–2012), attributed to Athens residents turning to wood burning on a large scale as their main domestic heating. Although OC presents a significant number of spikes during the winters of 2011 and 2012 (Fig. 1), mainly attributed to wood burning, the average values of OC do not present a clear interannual trend. Most probably this is because, contrary to EC, OC has, additionally, a significant secondary origin (see Sect. 3.5), and the influence from primary sources (wood burning) is balanced out in the average values but shows up as increased standard deviations (episodic nature) observed during winter 2011 and 2012 (a factor of 2 higher compared to previous years). The summer-to-winter ratio of EC mass concentration presents a significant declining trend from 0.99 in 2008 to 0.43 in 2012, illustrating the combined effect of
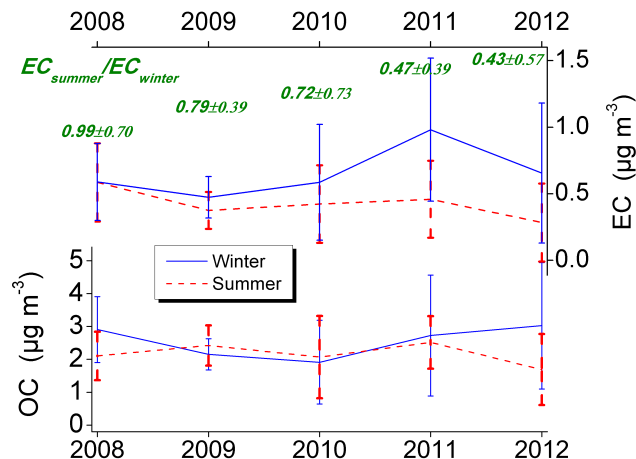
summer and winter changes in EC emissions, as related to the economic crisis (see Sect. 3.4).

3.2 OC / EC concentration ratios

The daily OC / EC ratios range from 0.5 to 29.3, with an average of 4.7 ± 1.3 for the 5-year period. These ratios are generally comparable with results from other Mediterranean sites (see Table 1); however, on a seasonal basis the OC / EC ratios ([OC / EC]$_{winter}$ = 4.6, [OC / EC]$_{summer}$ = 6.3) are higher than those reported for other urban background sites around the world [OC / EC]$_{winter}$ = 2.4–3.5, [OC / EC]$_{summer}$ = 1.3–3.9) as reviewed by Lonati et al. (2008). Higher ratios can be attributed either to secondary production from gas-to-particle conversion of VOCs (volatile organic compounds) (mainly during long-range transport of polluted air masses; Pio et al., 2007) or to primary sources such as biomass burning, during which high OC / EC ratios are exhibited (Amiridis et al., 2012).

In more detail, the seasonal cycle of the OC / EC ratio (Fig. 4) presents maximum values during summer (6.3), when photooxidation reactions lead to the production of secondary aerosol (increase in OC concentrations) (e.g., Viana et al., 2007) and the reduction of heating (decrease of EC concentration). In January (the coldest month of the year), the high OC / EC ratio could be attributed to the elevated OC concentrations, mainly due to fuel and/or biomass burning combustion for heating, that coincide with a comparatively smaller increase in the production of EC.

Overall, the high values of the OC / EC ratio (> 2) year-round, indicate the clear impact of additional processes like the production of secondary organic carbon. To estimate the primary and secondary origins of carbonaceous aerosol, the correlation between the OC and EC mass concentrations is investigated (e.g., Turpin and Huntzicker, 1995). In the
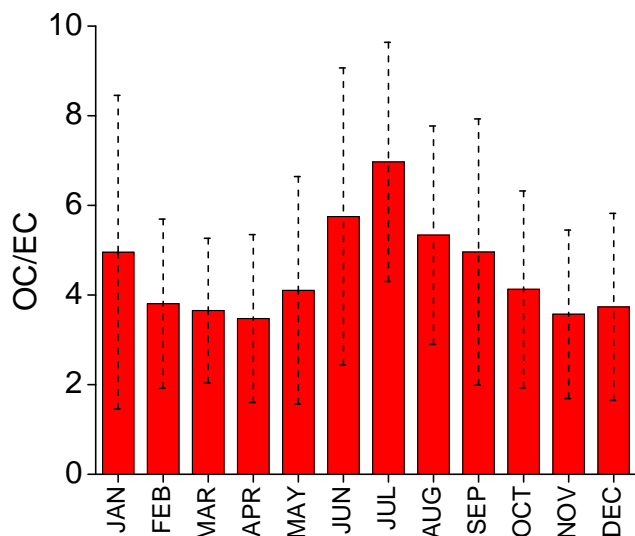
Figure 4. Average seasonal cycle of the OC / EC ratio calculated from daily values for the period May 2008–April 2013.

Figure 5. Scatterplot of the daily OC and WSOC concentrations for the period May 2008–April 2013.

present study, a statistically significant correlation is found between OC and EC for the whole period (not shown; $R^2 = 0.49$, slope $= 2.33$, $n = 1365$, $p < 0.001$), revealing that OC and EC emission rates are mostly proportional to each other (e.g., Na et al., 2004). A comparable correlation coefficient was reported by Koulouri et al. (2008) for another eastern Mediterranean, though remote coastal, location (Finokalia, Crete). The above findings suggest that a large fraction of OC and EC is emitted by common primary sources.

3.3 Water-soluble organic carbon

Water-soluble organic carbon (WSOC) is considered a major component of carbonaceous aerosol as it serves as a proxy for secondary organic aerosols due to its highly oxidized and soluble nature (Park et al., 2013).

The WSOC concentration in $PM_{2.5}$ ranged from 0.03 to 10.6 µg m^{-3}, with an average of 1.5 ± 0.9 µg m^{-3} and no significant differences between summer (1.7 ± 0.8 µg m^{-3}) and winter (1.6 ± 1.2 µg m^{-3}). These levels are similar to those reported for the remote coastal site of Finokalia, Crete, by Bougiatioti et al. (2011) but lower than those reported for Istanbul by Theodosi et al. (2010) (PM_{10} in urban site, see Table 1). The concentration of WSOC presents a statistically significant correlation with OC (Fig. 5) ($R^2 = 0.87$, $n = 1000$, $p < 0.001$), indicative of their common sources. Moreover, WSOC follows the seasonal trend of OC (Fig. 6) throughout the year, showing maximum values during winter and midsummer, when WSOC is either emitted from primary combustion sources, such as traffic and biomass burning, or is produced through atmospheric processing of volatile organic species (Park et al., 2013).

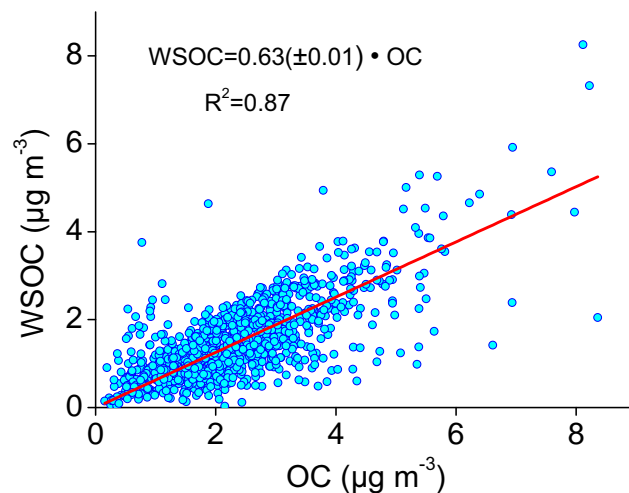WSOC usually consists of organic compounds that derive from the atmospheric oxidation of VOCs and gas particle
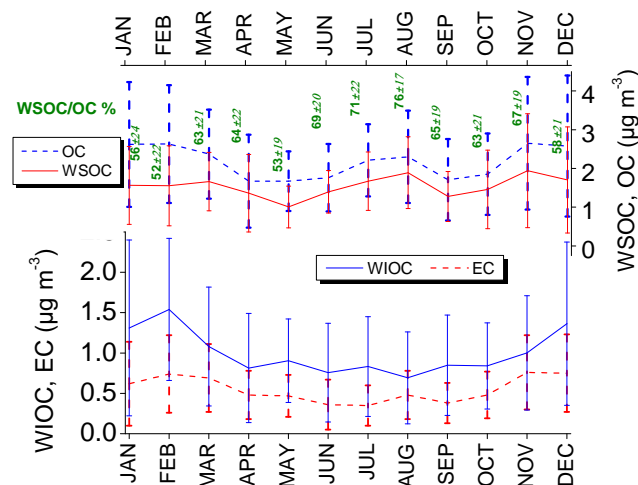

Figure 6. Average seasonal cycle of OC, EC, WSOC, WIOC concentrations and the WSOC / OC ratio calculated from daily values for the period May 2008–April 2013.

conversion (secondary OC), while the oxygenation of particulate OC may also occur in the particulate phase or via multiphase chemistry by the reaction of strong oxidants such as ozone or hydroxy radicals. As a result, the WSOC / OC ratio decreases in urban locations and near fossil fuel sources (~ 20 %) and increases at more remote sites due to aerosol aging (Pio et al., 2007).

In this study, the WSOC accounts, on average, for about 63 ± 7 % of the OC, which is in agreement with the value (67 %) reported by Bougiatioti et al. (2011) for Finokalia, Crete, but higher than the value (42 %) reported by Lonati et al. (2007) for Milan. The above findings indicate the dominant role of aerosol aging processes on the regional scale. Finally, the WSOC / OC ratio shows maximum values dur-

ing summer (Fig. 6), when there is intense photooxidation that leads to the production of secondary organic species.

The water insoluble organic carbon (WIOC) has been calculated through the subtraction of WSOC from the total OC concentration. On an annual basis, WIOC contributes about $39 \pm 7\%$ to OC. Although WIOC shows no significant correlation with EC on a daily basis, their seasonal cycles show covariance (Fig. 6), indicating that part of the production of WIOC can be attributed to primary sources such as fossil fuel combustion.

The concentration of non-sea-salt sulfate (nss-SO_4^{-2}) has been estimated using the equation described in Sciare et al. (2005) and Pio et al. (2007):

$$[\text{sea salt}] = [\text{Na}^+] + [\text{Cl}^-] + [\text{Mg}^{2+}] + [\text{ss}-\text{K}^+]$$

$$+[\text{ssCa}^{2+}] + [\text{ss}-\text{SO}_4^{2-}].$$

Sea salt sulfate (ss-SO_4^{2-}) was calculated in accordance with the composition of seawater and was then subtracted from the total sulfate concentration in order to calculate the quantity of non-sea-salt sulfate (nss-SO_4^{2-}).

The average value for the whole period is $3.0 \pm 2.0\,\mu\text{g m}^{-3}$, which is in agreement with the findings from other studies in Athens (Theodosi et al., 2011; Remoundaki et al., 2013). WSOC is weakly correlated to nss-SO_4^{-2} ($R^2 = 0.15$, $n = 1017$, $p < 0.001$ during summer; $R^2 = 0.26$ vs. $R^2 = 0.03$ during winter), suggesting that long-range transport and aerosol ageing could be considered as additional contributors to WSOC. Additionally, the low correlation between WSOC with nss-K^+ ($R^2 = 0.05$, $n = 1023$, $p < 0.001$) suggests the limited production of WSOC from biomass burning. Finally, the higher correlation coefficient of WSOC with EC ($R^2 = 0.35$, $n = 993$, $p < 0.001$) indicates that there is some contribution to WSOC from primary anthropogenic rather than biogenic sources. The dependence of WSOC on EC improves in winter (summer: $R^2 = 0.29$; winter: $R^2 = 0.44$), indicating the production of WSOC from primary sources (e.g., biomass burning).

Based on the above findings, the primary fossil fuel and wood combustion sources appear to contribute more to the winter WSOC concentrations, whereas during summer sources like oxidation processes of secondary products are more efficient in generating WSOC.

3.4 Sources of carbonaceous aerosol

The independent contribution of biomass burning and fossil fuel combustion emissions to organic-matter concentrations can be quantitatively estimated through the potassium–OC and potassium–EC correlations (e.g., Satsangi et al., 2012). In general, biomass burning contributes significantly to the atmospheric concentrations of water-soluble potassium (K^+), and the latter is applied as an inorganic tracer for aerosol derived from this source (e.g., Currie et al., 1994;

Pio et al., 2008; Schmidl et al., 2008), while fossil fuel combustion leads to minor production of potassium (e.g., Yang et al., 2005a, 2005b).

To utilize K^+ as a representative tracer of pure biomass burning emissions, we applied a correction for the contribution from sea salt. Sea salt potassium (ss-K^+) was obtained in accordance with the composition of seawater (Sciare et al., 2005; Pio et al., 2007; Bougiatioti et al., 2013) and was then subtracted from the total K^+ concentration to calculate the remaining non-sea-salt potassium (nss-K^+). The nss-K^+ concentrations were as high as $1.8\,\mu\text{g m}^{-3}$, with a 5-year average of $0.17 \pm 0.04\,\mu\text{g m}^{-3}$, comparable to the values reported by Koulouri et al. (2008). It is worth noting that part of the calculated nss-K^+ can be due to dust, either from Sahara desert or road-dust resuspension. In this line, the contribution from these sources in our $PM_{2.5}$ filters cannot be totally ruled out.

In this study, no significant correlations are calculated between nss-K^+ with OC and EC (neither do they correlate significantly on a seasonal basis; nss-K^+ vs. EC: summer $R^2 = 0.02$, winter $R^2 = 0.11$; nss-K^+ vs. OC: summer $R^2 = 0.02$, winter $R^2 = 0.04$), indicating that during the whole period, biomass burning does not constitute the main source of organic carbon and that the dominant primary source of EC is mainly fossil fuel combustion (such as traffic). On the other hand, based on high-resolution measurements (30 min) performed in winter 2013 (Mihalopoulos et al., unpublished data), a clear correlation was observed between nss-K^+, OC and EC in PM_1 during intense episodes of biomass burning. The absence of significant correlation between OC and nss-K^+ using the entire data set indicates that the influence of biomass burning during intense wood burning episodes (clearly shown in Fig. 1) is masked when calculating the 5-year summer and winter square correlation coefficients.

The annual means of nss-K^+ / OC and nss-K^+ / EC ratios (not shown) exhibit an increasing trend throughout the studied period which, in the case of nss-K^+ / EC, can be mostly attributed to the notable increase in nss-K^+ concentration compared to that of EC, supporting the influence of wood burning during the last years. In Fig. 7, EC and nss-K^+ concentrations are presented on a seasonal basis from 2008 to 2013, showing an anticorrelation in summer that indicates a limited role of biomass burning during that season. This behavior of EC during summer is indicative of accumulative EC from regional sources (such as fossil fuel combustion from traffic), combined with limited atmospheric washout due to precipitation. During winter, frequent rainfalls remove the regional EC, and thus, the covariance between EC and nss-K^+ mainly reflects local sources such as domestic heating.

3.5 Estimation of secondary organic carbon

Greece is significantly affected by the long-range transport of African dust and other aerosol types from distant anthropogenic pollution sources (e.g., Gerasopoulos et al., 2011;
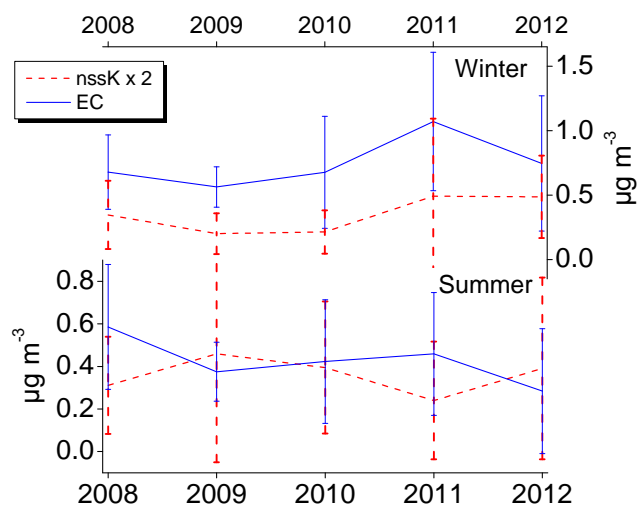
Figure 7. Average summer and winter nss-K$^+$ and EC concentrations calculated from daily values for the period May 2008–April 2013. Nss-K$^+$ concentrations were multiplied by 2 for visualization purposes.
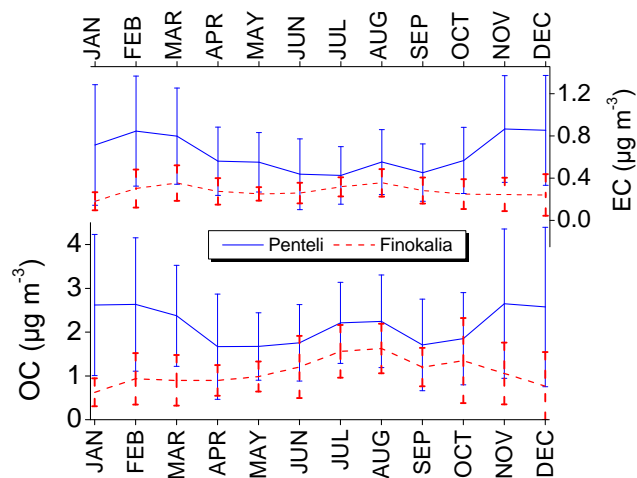

Figure 8. Average seasonal cycles of OC and EC concentrations at Penteli, Athens, and Finokalia, Crete, calculated from daily values, for the period May 2008–April 2013.

Kanakidou et al., 2011). Thus, the comparison between an urban background site and a remote site within the same geographical region would be a useful tool for exploring long-range transport vs. local sources in conjunction with aerosol ageing processes. In this line, OC and EC data from Finokalia (35°32′ N, 25°67′ N; http://finokalia.chemistry.uoc.gr) were used to represent remote conditions where the aged nature of aerosol has been previously established (Bougiatioti et al., 2009, 2011, 2013). Simultaneous measurements of OC and EC at the two sites were conducted for the period from May 2008 to March 2013, and the comparison of the measured levels and their covariance over the different seasons was used to infer the origins and processes responsible for the carbonaceous aerosol loading.

In order to estimate the secondary organic carbon (SOC), we applied the EC tracer method (Turpin and Huntzicker, 1995; Cabada et al., 2002), using the following equations:

$$(OC)_{tot} = (OC)_{pri} + (OC)_{sec} \qquad (1)$$

or

$$(OC)_{tot} = \left(\frac{OC}{EC}\right)_{pri} \cdot (EC)_{pri} + (OC)_{sec}, \qquad (2)$$

where $(OC/EC)_{pri}$ is the ratio for the local primary sources affecting the measured concentrations. A qualitative estimation of SOC using OC / EC ratios is valid only after careful inspection of local sources of OC and EC on a seasonal basis (e.g., Na et al., 2004).

In Fig. 8 the seasonal cycles of OC and EC at Penteli, Athens, and Finokalia, Crete, are shown. The levels of OC and EC in Athens are consistently higher than those at Finokalia, by 55 % in the warm season and up to 200 % in the cold season. By considering Finokalia station as a reference, it is estimated that during the warm season in Athens 67 ± 7 % of measured OC and 53 ± 12 % of EC is regional, while, during cold months, the regional contribution for OC is only 33 ± 7 % and for EC 29 ± 8 %. It is observed that from April to October there is an almost a constant difference between the two sites that increases notably during the coldest period of the year, from November to March.

During the warm period, due to the limited rain in the area, which favors the aging of polluted air masses (e.g., Perrone et al., 2011), a standard background is formed in the regional context. The increased values in Athens compared to Finokalia, can be attributed to an additional EC fraction due to traffic and to a constant fractional input of OC in addition to the fossil fuel road-transport-emitted aerosol, in agreement with Theodosi et al. (2011). According to Pio et al. (2007) and Theodosi et al. (2011), the simple use of the same primary OC / EC factor to estimate secondary carbon aerosol in rural and remote European areas in the warm season is adequate. Thus, from April to October in Athens, we estimated the contribution of primary and secondary organic aerosols in the organic carbon concentrations using Eq. (1) and applying an OC / EC$_{pri}$ ratio equal to 1, since traffic is the main active source during this time period (e.g., Lonati et al., 2008).

During this period, SOC ranges from 0.06 to 5.2 µg m^{-3}, with an average of 1.5 ± 0.9 µg m^{-3}, constituting about 75 ± 6 % of organic carbon in Athens. It is shown that SOC is a major contributor to OC during the warm season in the area, as also indicated by Bougiatioti et al. (2013) and Lonati et al. (2007), underlying the secondary nature of fine particles (Paterakis et al., 2012). In absolute values, the average in Athens is lower than the one (2.7 µg m^{-3}) reported by Sanchez de la Campa et al. (2009) in an urban background station in Spain. The monthly means of SOC
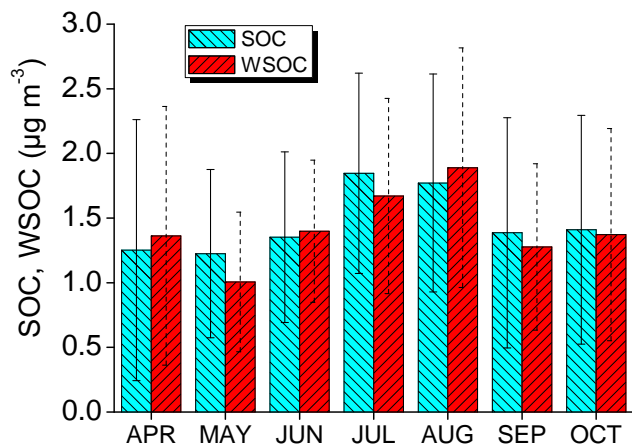
Figure 9. Average monthly variability (from April to October) of WSOC and estimated SOC concentrations, calculated from daily values, for the period May 2008–April 2013.

(Fig. 9) in the warm period present a maximum in summer (July–August), when there is intense photochemical activity that leads to the production of secondary organic carbon. WSOC, which is considered to be predominantly a secondary atmospheric product, also follows the seasonal variability of SOC (Fig. 9), a conclusion strengthened by the significant correlation between daily SOC and WSOC values ($R^2 = 0.53$, slope $= 0.69$, $n = 591$, $p < 0.001$). By contrast, the correlation between SOC and nss-SO_4^{-2} was much weaker ($R^2 = 0.22$, slope $= 1.00$, $n = 785$, $p < 0.001$), indicating fewer common sources between SOC and nss-SO_4^{-2}. Finally, it is worth noting the decreasing trend of SOC during the 5-year period of this study (not shown), accompanied by a decrease in WSOC (22 % reduction from 2008 to 2013) and nss-SO_4^{-2} (58 % reduction from 2008 to 2013). This downward tendency of the aforementioned concentrations can be attributed to the decrease in fuel consumption as a result of the economic crisis in Greece.

In the cold season, for the estimation of SOC and the relevant primary OC / EC ratio, fossil fuel and wood burning combustion from domestic heating should be also taken into account (Gelencsér et al., 2007; Lonati et al., 2007; Lonati et al., 2008). Since this ratio can vary greatly depending on the site and the different sources, it was not feasible to estimate SOC during the cold period. In Fig. 8, the difference between OC and EC levels at Finokalia (Crete) and Penteli (Athens), increases during the cold season compared to the warm season, reflecting the contribution of additional local sources in Athens. Assuming that vehicular traffic is stable throughout the year (Grivas et al., 2012) and long-range transport and meteorology are similar over both sites, the increase in OC and EC during the cold season can be attributed to an additional primary source, most probably heating. In addition by examining the difference of OC and EC levels between Athens and Finokalia during the winter months for the whole

period studied a notable increase during the 2011–2013 period compared to 2008–2010 is also observed (30 % in ΔOC and 80 % in ΔEC), mainly driven by wood burning activities that maximized during the last two winters (2011–2013) in most Greek cities (Saffari et al., 2013).

Unfortunately, statistical information or inventories for the use of wood in domestic heating in Athens are lacking entirely. Moreover, the only study addressing the increasing role of biomass burning on air quality in Greek cities is from Safari et al., (2013), who reported an increase in wood burning tracers at the same time as a decrease in fossil fuel tracers at Thessaloniki (the second most important Greek city) during the first winter with a significant increase in fuel price.

4 Conclusions

Continuous sampling of the PM$_{2.5}$ aerosol fraction on a daily basis was conducted in Athens (Penteli station, urban background) during a 5-year period (2008–2013). Subsequent chemical analyses allowed the determination of organic carbon (OC), elemental carbon (EC) and water-soluble organic carbon (WSOC) concentrations and the estimation of secondary organic carbon (SOC). A comparison with parallel measurements from a remote site on Crete (reference ACTRIS site for the eastern Mediterranean) enabled the identification and quantification of urban source contributions to regional background. The results of this study, coinciding with the beginning of the economic crisis in Greece, reflect the combined effect of limited vehicular circulation and increased wood combustion for domestic heating. This first long-term measurement of OC, EC and WSOC and the estimation of SOC provide a unique opportunity to qualify and quantify the rapidly changing air pollution characteristics in the area studied, which is a mandate for future air quality policies.

The main conclusions arising from this study are summarized below:

– OC and EC concentrations in Athens back in 2003, were 3–4 times higher compared to this study, while later studies revealed similar or slightly higher values depending on the site type. Average OC and EC concentrations are $2.1 \pm 1.3 \,\mu g \, m^{-3}$ and $0.54 \pm 0.39 \,\mu g \, m^{-3}$, respectively. OC and EC present covariance for most of the sampling period, while maximum values are observed during the coldest months of the year, when there is increased fuel combustion. The aforementioned outputs reveal that OC and EC emission rates are mostly proportional to each other, hence suggesting that OC and EC fractions are mainly emitted by common primary sources on a regional scale.

– On a seasonal basis, summer EC is formed by predominant regional sources (53 ± 12 % of EC), such as fossil fuel combustion (traffic), whereas, during winter, the

prevailing result of local sources such as fuel combustion is highlighted ($71 \pm 8\,\%$ of EC). EC during summertime decreases through the years, since there is a simultaneous reduction in traffic and industrial activity due to the economic crisis in Greece. By contrast, EC concentration during winter presents a significant increase since 2011, which can be attributed to the selection of wood as the major fuel source for domestic heating. OC concentration does not present a clear interannual pattern, probably because of the episodic nature of biomass burning, as seen from the increased calculated standard deviations that may have balanced out the aforementioned trend.

– Total carbon for the whole sampling period (sum of OC and EC) constitutes a significant part of $PM_{2.5}$ aerosol fraction ($TC / PM = \sim 14\,\%$), while OC accounts for $79 \pm 4\,\%$ of total carbon, constituting the predominant carbon contributor. Additionally, the estimated POM (particulate organic matter) accounts for $24 \pm 6\,\%$ of the collected fine aerosol.

– The total of 5-year samples provides an average OC / EC ratio of 4.7 ± 1.3, while on a seasonal basis the OC / EC ratios are higher than those reported for other urban background sites around the world. The elevated measured values of OC / EC ratio highlight the secondary nature of secondary organic carbon in the area especially during summertime. Additionally, the calculated correlation between OC and EC suggests that OC and EC fractions are emitted by common primary sources, while, simultaneously, there is impact of additional sources such as the production of secondary organic carbon. More specifically, with regard to primary emissions, it appears that the dominant primary source of EC is mainly fossil fuel combustion (such as traffic), while biomass emission sources contribute mainly during the cold period.

– The calculated WSOC average concentration is $1.5 \pm 0.9\,\mu g\,m^{-3}$, and it presents significant dependence on OC concentration, revealing their common sources and subsequently the predominant secondary nature of OC in the area studied. Furthermore, the estimated WSOC / OC ratio is $63 \pm 7\,\%$, illustrating the presence of aged aerosol at the site. In addition, this work indicates that emissions, from primary non-biomass-burning sources of water-soluble organic carbon and from secondary organic products, can contribute to some extent to the variability of organic carbon observed in the location studied.

– SOC presents maximum values during summer, when there is intense photochemical activity, while the intraannual variability of SOC is similar to that of WSOC,

highlighting significant aging processes as characteristic on the regional scale. SOC estimation was not feasible in the cold period (November to March).

– The comparison of OC and EC levels between the urban background and the remote coastal sites indicated an $80\,\%$ increase in EC, due to local sources in Athens during the cold season of the last 2 years (winter 2011–2012 and 2012–2013), when economic hardship led residents to wood burning on a large scale for heating purposes.

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