

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 $2.1 \pm 1.3 \mu\text{g m}^{-3}$ and $0.54 \pm 0.39 \mu\text{g m}^{-3}$, 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 at a regional scale. WSOC concentration ranged from 0.03 to $10.6 \mu\text{g m}^{-3}$, with an average of $1.5 \pm 0.9 \mu\text{g m}^{-3}$. By considering 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 for OC is only $33 \pm 7\%$ and for 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, at a regional scale. In the period 2011-2013 and during wintertime, an increase in OC and EC levels was observed, attributed to increase of wood burning for domestic heating due to the economic crisis.

1 **1 Introduction**

2 Atmospheric aerosol constitutes a crucial factor of air pollution since it presents
3 adverse effects on health, environment and Earth radiative balance (EPA, 1996;
4 WHO, 2003). Carbonaceous aerosol contributes to global warming, and black carbon
5 is considered as the second most important agent of global warming after CO₂
6 (Probert and Tarrant, 1989; Robock and Graf, 1994; Galdos et al., 2013). Recent
7 epidemiologic studies, have displayed the risks of exposure to increased levels of
8 carbonaceous aerosols, revealing notable associations with cardiovascular mortality
9 and morbidity (Ostro et al., 2010; Lipsett et al., 2011; Krall et al., 2013).

10 The carbonaceous content of atmospheric particles has been the objective of several
11 studies as it represents an essential fraction of particulate matter (Alastuey et al.,
12 2004; Na et al., 2004; Putaud et al., 2004; Querol et al., 2004; Yu et al., 2004; Yttri et
13 al., 2007; Pey et al., 2010; Pio et al., 2011). These studies provide evidence for the
14 relative importance of road traffic and wintertime high energy consumption,
15 combined with unfavorable meteorological conditions, and summertime traffic but
16 also secondary organic aerosol as major sources of carbonaceous aerosol in Europe.
17 The formation mechanisms of organic carbon (OC) and elemental carbon (EC) have
18 been under scrutiny during the last decade (Saylor et al., 2006; Pio et al., 2007;
19 Schwarz et al., 2008; Pio et al., 2011; Grivas et al., 2012; Bougiatioti et al., 2013),
20 placing emphasis on their biogenic and/or anthropogenic origin and subsequent
21 effects.

22 Athens is located in Eastern Mediterranean, a well-known crossroad of long range
23 transported aerosol from discrete regional sources that are superimposed on other
24 significant local sources of pollution (Lelieveld et al., 2002; Vrekoussis et al., 2005).
25 A description of the Athens basin and prevailing meteorological conditions has been
26 provided in the literature (Chaloulakou et al., 2005; Grivas et al., 2008; Kanakidou et
27 al., 2011; Theodosi et al., 2011; Grivas et al., 2012). Studies performed in Athens
28 basin demonstrated the prevailing emissions of carbonaceous aerosol all year round,
29 namely vehicles, fuel combustion and long-range transport (Chaloulakou et al., 2005;
30 Sillanpaa et al., 2006; Grivas et al., 2012; Pateraki et al., 2012; Remoundaki et al.,
31 2013). Nevertheless, it is essential to mark that there are limited studies concerning
32 PM_{2.5} fraction of aerosol in Athens and the works performed so far have been
33 conducted for short time periods (4 – 11 months), mainly at urban locations.

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

20

21 **2 Experimental**

22 **2.1 Sampling site**

23 The measurements were conducted at the National Observatory of Athens premises in
24 Penteli (38° 2.94'N, 23° 51.78'E, 495ma.s.l.). The site is located on top of a hill facing
25 the city of Athens to S-SW (17 km from the city center), while to the N-NE sector it is
26 surrounded by the Penteli Mountain. The major sources of air pollution in the close
27 vicinity are expected to be vehicular emissions and residential heating. More details
28 about the Greater Athens Area morphology and meteorological conditions are
29 provided by Kanakidou et al., (2011; and references therein), while internal transport
30 patterns in the urban complex are described by Melas et al. (1998). The station is
31 considered as an urban background site, established and operated by the Institute of
32 Environmental Research and Sustainable Development.

1

2 **2.2 Samples collection**

3 This study covers five years from May 2008 to April 2013, resulting in the collection
4 of 1510 samples on a daily basis. PM_{2.5} aerosol samples were collected using a
5 Dichotomous Partisol sampler (R&P Co) during most of the period (90% of the
6 sampling time) and a Partisol FRM Model 2000 air sampler (R&P Co) (10% of the
7 sampling time), operating at 15.0 and 16.7 L/min, respectively. Sampling duration
8 was 24h starting at 14:00 LT.

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

13 For the estimation and correction of the amount of adsorbed organic vapor on the
14 sampling filter, a tandem filter collection method was applied (e.g. Turpin et al., 2000;
15 Kirchstetter et al., 2001; Yttri et al., 2007). Two quartz fiber filters from the same lot
16 were used in series, the front filter collects essentially 100% of the particulate matter
17 (and some gas-phase material) and the backup filter is exposed only to gas-phase
18 compounds. The measured carbon content of the backup filter can be subtracted from
19 that of the front filter to give an estimate of the particulate phase OC (Turpin et al.,
20 2000; Novakov et al., 2005; Sillanpaa et al., 2005). Nevertheless, it has been reported
21 that the back-to-back filter configuration does not allow enough time for equilibration
22 of gases on the second filter, and therefore this approach could underestimate the
23 positive OC artefact. Tandem filters were collected for a selected number of samples,
24 using the aforementioned Partisol samplers. In our analyses, the backup filters
25 indicated a positive OC artifact which was always smaller than 5%, thus no correction
26 was applied.

27

28 **2.3 Mass and chemical analyses**

29

30 **2.3.1 Aerosol Mass**

31 PM mass was determined by weighing the filters before and after sampling according
32 to the U.S. EPA RFPS-1298-126 method, using a Mettler Toledo MX5 microbalance

1 (1 μg sensitivity). The filters (samples and blanks) remained for 48 h under controlled
2 conditions (RH 40 \pm 5%, T 20 \pm 3°C), prior to each weighing.

3

4 **2.3.2 OC – EC analysis**

5 All quartz filters (samples and blanks) were analyzed by a thermal optical
6 transmission technique, using a Sunset Laboratory Inc. (Oregon) carbon analyzer. A
7 punch of 1 cm^2 was removed from the filter and loaded into the analyzer as described
8 by Bougiatioti et al. (2013) and Novakov et al. (2005). OC and EC were determined
9 using the EUSAAR-2 protocol (Cavalli et al., 2010). Briefly, the first phase subsumes
10 4 stages of heating at 200, 300, 450 and 650°C at He atmosphere, while, during the
11 second 4-step temperature program, the sample is heated at 500, 550, 700 and 850°C
12 at He/O₂ atmosphere. The detection limit of the analysis was 0.26 and 0.05 $\mu\text{g C cm}^{-2}$
13 for OC and EC, respectively. The reported results were blank-corrected.

14

15 **2.3.3 WSOC analysis**

16 For the determination of the Water Soluble Organic Carbon (WSOC) concentrations,
17 punches of 2 cm^2 were removed from the filter and placed in an ultrasonic bath for 45
18 minutes using 15mL of nanopure water. The sample extract was filtered using syringe
19 filters (PALL IC Acrodisc (PES), 0.45 μm , 13 mm). The solutions obtained after the
20 filtration were analyzed for total organic carbon (TOC) using a Shimadzu TOC-V
21 CSH Total Organic Carbon Analyzer. In short, the sample is injected into a
22 combustion cell equipped with oxidation catalyst (Pt) and is heated at 680°C. TC
23 (Total Carbon) is converted to carbon dioxide and it is cooled, dehumidified and
24 transferred through the carrier gas (synthetic air) to the NDIR (Non-Dispersive Infra-
25 Red) gas analyzer. For the IC (Inorganic Carbon) analysis, the sample is injected to
26 the IC reaction vessel where it is acidified, to convert IC to carbon dioxide, and it is
27 volatilized by a sparging process. Then the sample is transferred by the carrier gas to
28 NDIR in order to be detected. Total water soluble organic carbon is calculated by
29 extracting inorganic water soluble carbon from total water soluble carbon (TOC=TC–
30 IC) and is labeled as WSOC. The analytical detection limit for WSOC was 80ppb. All
31 data were corrected for the obtained blank levels.

32

2.3.4 Ion chromatography

Punches of 2 cm² from the quartz filters were extracted in ultrasonic bath with 10ml of nanopure water, for 45 minutes, 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 (IC) for the determination of the main ionic species concentrations (anions: Cl⁻, Br⁻, NO⁻³, SO⁻², PO⁻³, C₂O⁻² and 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 pre-column, with an ASRS-300 suppressor. Anions' separation was conducted with isocratic elution of NaHCO₃ (3.4 mM) / Na₂CO₃ (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 was used, with a CSRS-300 suppressor, under isocratic elution of 20 mM MSA (Methanesulphonic 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⁻², PO⁻³, C₂O⁻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 μg m⁻³ (average: 2.1 ±1.3 μg m⁻³), contributing on average about 11±3% to the total PM_{2.5} mass. Accordingly, the mass concentration of EC ranges from 0.01 to 3.33 μg m⁻³ (average: 0.54±0.39 μg m⁻³), contributing 3±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 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 μg m⁻³ for OC and 0.4-1.8 μg m⁻³ for EC. OC concentrations from several studies in southern Europe cities (mainly western Mediterranean) during the period 2002-2006 are in the range 3-9 μg m⁻³ while EC values are in the range 0.7-1.7 μg m⁻³. Concentrations in an urban site in Istanbul

1 during the period 2008-2009 appear much higher compared to the values of this study.
2 Regional background concentration levels at the Finokalia site (Crete Island, 2004-
3 2006) are on average 1.8 and 0.27 $\mu\text{g m}^{-3}$, for OC and EC, respectively.

4 Total carbon is calculated as the sum of OC and EC ($\text{TC}=\text{OC}+\text{EC}$), with OC
5 accounting for 79 \pm 4% of the total carbon, constituting the predominant carbon
6 contributor, in accordance with findings in other European sites (e.g. (Lonati et al.,
7 2007; Sanchez de la Campa et al., 2009). However, the contribution of TC to PM in
8 this study (14 \pm 3%) is lower than what is reported in the literature for other
9 urban/urban background locations (e.g. 25-46% in Viana et al. (2006); 27-28% in
10 Lonati et al. (2007); about 19% in Sanchez de la Campa et al. (2009); 29% in Perrone
11 et al. (2011); Querol et al. (2013)).

12 Conversion of OC to OM (Organic Matter) is recognized as one of the most critical
13 factors of uncertainty in mass closure calculations (Yttri et al., 2007). Turpin and Lim
14 (2001) suggest the use of different conversion factors per site type: 1.6 \pm 0.2 for urban
15 areas, 1.9–2.3 for aged aerosols, and 2.2–2.6 for biomass burning. Taking into
16 account that our site is an urban background station also affected by long range
17 transport (e.g. Sciare et al., 2005; Kanakidou et al., 2011; Pateraki et al., 2012;
18 Remoundaki et al., 2013), we used the value of 2.1 ($\text{OM}=2.1\cdot\text{OC}$). On average, OM
19 accounts for 24 \pm 6% of $\text{PM}_{2.5}$ which is consistent with the value (22%) provided by
20 Remoundaki et al. (2013) for Athens, while lower to those reported in other European
21 sites (e.g. Sillanpaa et al., 2005; Sanchez de la Campa et al., 2009).

22 In Fig. 1 the daily concentrations of OC and EC are presented for the whole sampling
23 period (May 2008-April 2013). It is observed that OC and EC present significant
24 covariance for most of the period, with maxima mainly during the colder months. The
25 seasonal variability in OC and EC is clearly demonstrated in Fig. 2, which reveals
26 higher concentrations from November to March. This is mainly attributed to
27 emissions from residential heating and low altitude temperature inversions that trap
28 local emissions of particulate OC and EC near the surface (e.g. Yttri et al., 2007). The
29 minimum OC concentrations appears in late spring and early autumn, when there is
30 no domestic heating and photochemistry is slowed down compared to summer. In the
31 case of EC, minimum concentrations are found during the warmest months of the

1 year, when there is less fuel combustion in Athens (period of summer vacations) and
2 thus lower production of primary EC.

3 The summer versus winter contrast is further shown in Fig. 3, on an annual basis.
4 Winter refers to Dec.-Feb. period of the December year, while summer to Jun.-Aug.
5 The EC summer levels after 2009 appear slightly reduced compared to 2008,
6 coinciding the economic recession period in Greece, which led to reduction of traffic
7 emissions and industrial activities (Vrekoussis et al., 2013). In winter, there is an
8 increase during the last two years (2011-2012), attributed to the massive turn of
9 Athens residents in wood burning for main domestic heating. Although OC presents a
10 significant number of spikes during the winters of 2011 and 2012 (Fig. 1), mainly
11 attributed to wood burning, the average values of OC do not present a clear inter-
12 annual trend. Most probably this is because, contrary to EC, OC has additionally a
13 significant secondary origin (see section 3.5) and the influence from primary sources
14 (wood burning) is balanced out in the average values but are shown up as increased
15 standard deviations (episodic nature) observed during winter 2011 and 2012 (a factor
16 2 higher compared to previous years). The summer to winter ratio of EC mass
17 concentration presents a significant declining trend from 0.99 in 2008 to 0.43 in 2012,
18 illustrating the combined effect of summer and winter changes in EC emissions, as
19 related to the economic crisis (see section 3.4).

20

21 **3.2 OC/EC concentration ratios**

22 The daily OC/EC ratios range from 0.5 to 29.3, with an average of 4.7 ± 1.3 for the 5-
23 year period. These ratios are generally comparable with results from other
24 Mediterranean sites (see Table 1), however, on a seasonal basis the OC/EC ratios
25 ($[\text{OC/EC}]_{\text{winter}}=4.6$, $[\text{OC/EC}]_{\text{summer}}=6.3$) are higher than those reported for other urban
26 background sites around the world ($[\text{OC/EC}]_{\text{winter}}=2.4-3.5$, $[\text{OC/EC}]_{\text{summer}}=1.3-3.9$) as
27 reviewed by Lonati et al. (2008). Higher ratios can be attributed either to secondary
28 production from gas to particle conversion of VOCs (mainly during long-range
29 transport of polluted air masses; Pio et al., 2007) or to primary sources such as
30 biomass burning, during which high OC/EC ratios are exhibited (Amiridis et al.,
31 2012).

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

8 Overall, the high values of OC/EC ratio (>2) year round, indicate the clear impact of
9 additional processes like the production of secondary organic carbon. To estimate the
10 primary and secondary origins of carbonaceous aerosol, the correlation between the
11 OC and EC mass concentrations is investigated (e.g. Turpin and Huntzicker, 1995). In
12 the present study a statistically significant correlation is found between OC and EC
13 for the whole period (not shown, $R^2=0.49$, slope=2.33, $n=1365$, $p<0.001$), revealing
14 that OC and EC emission rates are mostly proportional to each other (e.g. Na et al.,
15 2004). A comparable correlation coefficient was reported by Koulouri et al. (2008) for
16 another Eastern Mediterranean, though remote coastal, location (Finokalia, Crete).
17 The above suggest that a large fraction of OC and EC fractions is emitted by common
18 primary sources.

19

20 **3.3 Water Soluble Organic Carbon**

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

24 The WSOC concentration in $PM_{2.5}$ ranged from 0.03 to $10.6 \mu\text{g m}^{-3}$, with an average
25 of $1.5\pm 0.9 \mu\text{g m}^{-3}$, and no significant differences between summer ($1.7\pm 0.8 \mu\text{g m}^{-3}$)
26 and winter ($1.6\pm 1.2 \mu\text{g m}^{-3}$). These levels are similar to those reported for the remote-
27 coastal site of Finokalia, Crete, by Bougiatioti et al. (2011), but lower than those
28 reported for Istanbul by Theodosi et al. (2010) (PM_{10} in urban site, see Table 1). The
29 concentration of WSOC presents a statistically significant correlation with OC (Figure
30 5) ($R^2=0.87$, $n=1000$, $p<0.001$), indicative of their common sources. Moreover,
31 WSOC follows the seasonal trend of OC (Figure 6) throughout the year, showing
32 maximum values during winter and mid-summer, when WSOC is either emitted from

1 primary combustion sources, such as traffic, and biomass burning or is produced
2 through atmospheric processing of volatile organic species (Park et al., 2013).

3 WSOC usually consists of organic compounds that derive from the atmospheric
4 oxidation of VOCs and gas particle conversion (secondary OC), while the
5 oxygenation of particulate OC may also occur in the particulate phase or via
6 multiphase chemistry by reaction of strong oxidants such as ozone or hydroxy
7 radicals. As a result, the WSOC/OC ratio decreases in urban locations and near fossil
8 fuel sources (~20%) and increases at more remote sites due to aerosol aging (Pio et
9 al., 2007).

10 In this study, the WSOC accounts, on average, for about $63\pm 7\%$ of the OC, which is
11 in agreement with the value (67%) reported by Bougiatioti et al. (2011) for Finokalia,
12 Crete, but higher than the value (42%) reported by Lonati et al. (2007) for Milan. The
13 above indicate the dominant role of aerosol aging processes at the regional scale.
14 Finally, the WSOC/OC ratio shows maximum values during summer (Figure 6), when
15 there is intense photo oxidation that leads to the production of secondary organic
16 species.

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

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

$$25 \quad [\text{sea salt}] = [\text{Na}^+] + [\text{Cl}^-] + [\text{Mg}^{2+}] + [\text{ss-K}^+] + [\text{ssCa}^{2+}] + [\text{ss-SO}_4^{2-}]$$

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

29 The average value for the whole period is $3.0\pm 2.0 \mu\text{g m}^{-3}$, which is in agreement with
30 the findings from other studies in Athens (Theodosi et al., 2011; Remoundaki et al.,
31 2013). WSOC is weakly correlated to nss-SO_4^{2-} ($R^2=0.15$, $n=1017$, $p<0.001$, during

1 summer $R^2=0.26$ vs $R^2=0.03$ during winter), suggesting that long-range transport and
2 aerosol ageing could be considered as additional contributors to WSOC. Additionally,
3 the low correlation between WSOC with nss-K^+ ($R^2=0.05$, $n=1023$, $p<0.001$)
4 propounds limited production of WSOC from biomass burning. Finally, the higher
5 correlation coefficient of WSOC with EC ($R^2=0.35$, $n=993$, $p<0.001$) indicates that
6 there is some contribution to WSOC from primary anthropogenic sources rather than
7 biogenic. The dependence of WSOC to EC is improving in winter (summer: $R^2=0.29$;
8 winter: $R^2=0.44$), indicating production of WSOC from primary sources (e.g. biomass
9 burning).

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

14

15 **3.4 Sources of carbonaceous aerosol**

16 The independent contribution of biomass burning and fossil fuel combustion
17 emissions to organic matter concentrations could be quantitatively estimated through
18 the potassium-OC and potassium-EC correlations (e.g. Satsangi et al., 2012). In
19 general, biomass burning contributes significantly to the atmospheric concentrations
20 of water soluble potassium (K^+) and the latter is applied as an inorganic tracer for
21 aerosol derived from this source (e.g. Currie et al., 1994; Pio et al., 2008; Schmidl et
22 al., 2008), while fossil fuel combustion leads to minor production of potassium (e.g.
23 Yang et al., 2005a; Yang et al., 2005b).

24 To utilize K^+ as a representative tracer of pure biomass burning emissions, we have
25 applied a correction for the contribution from sea salt. Sea salt potassium (ss-K^+) was
26 obtained in accordance with the composition of sea water (Sciare et al., 2005; Pio et
27 al., 2007; Bougiatioti et al., 2013) and was then subtracted from the total K^+
28 concentration, to calculate the remaining non-sea salt potassium (nss-K^+). The nss-K^+
29 concentrations were up to $1.8 \mu\text{g m}^{-3}$, with a 5-year average of $0.17\pm 0.04 \mu\text{g m}^{-3}$,
30 comparable to the values reported by Koulouri et al. (2008). It is worth noting that
31 part of the calculated nss-K^+ can be due to dust either from Sahara desert or road-dust

1 re-suspension. In this line, the contribution from these sources in our PM_{2.5} filters
2 cannot be totally ruled out.

3 In this study, no significant correlations are calculated between nss-K⁺ with OC and
4 EC (neither do they correlate significantly on a seasonal basis; nss-K⁺ vs EC: summer
5 R²=0.02, winter R²=0.11; nss-K⁺ vs OC: summer R²=0.02, winter R²=0.04),
6 indicating that during the whole period, biomass burning does not consist the main
7 source of organic carbon and that the dominant primary source of EC is mainly fossil
8 fuel combustion (such as traffic). On the other hand based on high resolution
9 measurements (30 min) performed in winter 2013 (Mihalopoulos et al, unpublished
10 data) a clear correlation was observed between nss-K⁺, OC and EC in PM₁ during
11 intense episodes of biomass burning. The absence of significant correlation between
12 OC and nss-K⁺ using the entire data set indicates that the influence of biomass
13 burning during intense wood burning episodes (clearly shown in Fig. 1) is masked
14 when calculating the five year summer and winter square correlation coefficients.

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

26

27 **3.5 Estimation of Secondary Organic Carbon**

28 Greece is significantly affected by long-range transport of African dust and other
29 aerosol types from distant anthropogenic pollution sources (e.g. Gerasopoulos et al.,
30 2011; Kanakidou et al., 2011). Thus, the comparison between an urban background
31 site and a remote site within the same geographical region would be a useful tool for
32 exploring long range transport vs local sources in conjunction with aerosol ageing

1 processes. In this line, OC and EC data from Finokalia (35°32'N, 25°67'N;
2 <http://finokalia.chemistry.uoc.gr>) were used to represent remote conditions where the
3 aged nature of aerosol has been previously established (Bougiatioti et al., 2009;
4 Bougiatioti et al., 2011; Bougiatioti et al., 2013). Simultaneous measurements of OC
5 and EC at the two sites were conducted for the period from May 2008 to March 2013,
6 and the comparison of the measured levels and their covariance over the different
7 seasons was used to infer the origins and processes responsible for the carbonaceous
8 aerosol loading.

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

$$11 \quad (OC)_{tot} = (OC)_{pri} + (OC)_{sec} \quad (1) \text{ or}$$

$$12 \quad (OC)_{tot} = \left(\frac{OC}{EC}\right)_{pri} \cdot (EC)_{pri} + (OC)_{sec} \quad (2)$$

13 where $(OC/EC)_{pri}$ is the ratio for the local primary sources affecting the measured
14 concentrations. A qualitative estimation of SOC using OC/EC ratios is valid only after
15 careful inspection of local sources of OC and EC on a seasonal basis (e.g. Na et al.,
16 2004).

17 In Fig. 8 the seasonal cycles of OC and EC at Penteli-Athens and Finokalia-Crete are
18 shown. The levels of OC and EC in Athens are constantly higher than those at
19 Finokalia, by 55% in the warm season up to 200% in the cold season. By considering
20 Finokalia station as a reference, it is estimated that in Athens during the warm season
21 $67 \pm 7\%$ of measured OC and $53 \pm 12\%$ of EC is regional, while during cold months, the
22 regional contribution for OC is only $33 \pm 7\%$ and for EC $29 \pm 8\%$. It is observed that
23 from April to October there is an almost a constant difference between the two sites
24 that increases notably during the coldest period of the year, from November to March.

25 During the warm period, due to the limited rain in the area which favors the aging of
26 polluted air masses (e.g. Perrone et al., 2011), a standard background is formed at the
27 regional context. The increased values in Athens compared to Finokalia, can be
28 attributed to an additional EC fraction due to traffic and a constant fractional input of
29 OC added to the fossil fuel road transport emitted aerosol, in agreement with
30 Theodosi et al. (2011). According to Pio et al. (2007) and Theodosi et al. (2011) the

1 simple use of the same primary OC/EC factor to estimate secondary carbon aerosol in
2 rural and remote European areas in the warm season, is adequate. Thus, from April to
3 October in Athens, we estimated the contribution of primary and secondary organic
4 aerosols in the organic carbon concentrations using Eq. (2) and applying an OC/EC_{pri}
5 ratio equal to 1, since traffic is the main active source during this time period (e.g.
6 Lonati et al.; 2008).

7 During this period, SOC ranges from 0.06 to 5.2 $\mu\text{g m}^{-3}$, with an average of 1.5 ± 0.9
8 $\mu\text{g m}^{-3}$, constituting about $75\pm 6\%$ of organic carbon in Athens. It is shown that SOC
9 is a major contributor to OC during the warm season in the area, as also indicated by
10 Bougiatioti et al. (2013) and Lonati et al. (2007), underlying the secondary nature of
11 fine particles (Pateraki et al., 2012). In absolute values, the average in Athens is lower
12 than the one ($2.7 \mu\text{g m}^{-3}$) reported by Sanchez de la Campa et al. (2009) in an urban
13 background station in Spain. The monthly means of SOC (Figure 9) in the warm
14 period present maximum in summer (Jul-Aug), when there is intense photochemical
15 activity that leads to the production of secondary organic carbon. WSOC, which is
16 considered to be predominantly a secondary atmospheric product, also follows the
17 seasonal variability of SOC (Figure 9), a conclusion strengthened by the significant
18 correlation between daily SOC and WSOC values ($R^2=0.53$, slope=0.69, $n=591$,
19 $p<0.001$). Contrary, the correlation between SOC and nss-SO_4^{-2} was much weaker
20 ($R^2=0.22$, slope=1.00, $n=785$, $p<0.001$), indicating less common sources between
21 SOC and nss-SO_4^{-2} . Finally, it is worth noting the decreasing trend of SOC during the
22 five year period of this study (not shown), accompanied by a decrease in WSOC (22%
23 reduction from 2008 to 2013) and nss-SO_4^{-2} (58% reduction from 2008 to 2013). This
24 downward tendency of the aforementioned concentrations can be attributed to the
25 decrease in fuel consumption, as a result of the economic crisis in Greece.

26 In the cold season, for the estimation of SOC and the relevant primary OC/EC ratio,
27 fossil fuel and wood burning combustion from domestic heating should be also taken
28 into account (Gelencsér et al., 2007; Lonati et al., 2007; Lonati et al., 2008). Since this
29 ratio can vary largely depending on the site and the different sources, it was not
30 feasible to estimate SOC during the cold period. In Fig. 8, the difference between OC
31 and EC levels at Finokalia (Crete) and Penteli (Athens), increases during the cold
32 season compared to warm, reflecting the contribution of additional local sources in
33 Athens. Assuming that the vehicular traffic is stable throughout the year (Grivas et al.,

1 2012) and long range transport and meteorology is similar over both sites, the increase
2 in OC and EC during the cold season, can be attributed to an additional primary
3 source, most probably heating. In addition by examining the difference of OC and EC
4 levels between Athens and Finokalia during the winter months for the whole studied
5 period a notable increase during the 2011-2013 period compared to 2008-2010 is also
6 observed (30% in Δ OC and 80% in Δ EC), mainly driven by wood burning activities
7 maximized during the last two winters (2011-2013) in most Greek cities (Saffari et
8 al., 2013).

9 Unfortunately, statistical information or inventories for the use of wood in domestic
10 heating in Athens are totally missing. Moreover, the only study addressing the
11 increasing role of biomass burning on air quality in Greek cities is from Safari et al.,
12 (2013), who reported an increase in wood burning tracers at the same time with a
13 decrease in fossil fuel tracers, at Thessaloniki (the second most important Greek city)
14 and during the first winter with a significant increase in fuel price.

15 **4 Conclusions**

16 Continuous sampling of the PM_{2.5} aerosol fraction on a daily basis was conducted in
17 Athens (Penteli station, urban background) during a five year period (2008-2013).
18 Subsequent chemical analyses allowed the determination of organic carbon (OC),
19 elemental carbon (EC) and water soluble organic carbon (WSOC) concentrations and
20 the estimation of secondary organic carbon (SOC). A comparison with parallel
21 measurements from a remote site on Crete Island (reference ACTRIS site for Eastern
22 Mediterranean) enabled the identification and quantification of urban sources
23 contribution on regional background. The results of this study, coinciding with the
24 beginning of the economic crisis in Greece, reflect the combinational effect of limited
25 vehicular circulation and increased wood combustion for domestic heating. This first
26 long term measurement of OC, EC, WSOC and the estimation of SOC provide a
27 unique opportunity to qualify and quantify the rapidly changing air pollution
28 characteristics in the studied area, which is a mandate for future air quality policies.

29 The main conclusions arising from this study are summarized below:

- 30 • OC and EC concentrations in Athens back in 2003, were 3-4 times higher
31 compared to this study, while later studies revealed similar or slightly higher
32 values depending on the site type. Average OC and EC concentration is

1 2.1±1.3 $\mu\text{g m}^{-3}$ and 0.54±0.39 $\mu\text{g m}^{-3}$, respectively. OC and EC present
2 covariance for most of the sampling period while maximum values are
3 observed during the coldest months of the year, when there is increased fuel
4 combustion. The aforementioned outputs reveal that OC and EC emission
5 rates are mostly proportional to each other, suggesting hence that OC and EC
6 fractions are mainly emitted by common primary sources at a regional scale.

- 7 • On a seasonal basis, summer EC is formed by predominant regional sources
8 (53±12% of EC), such as fossil fuel combustion (traffic), whereas during
9 winter, the prevailing result of local sources such as fuel combustion is
10 highlighted (71±8% of EC). EC during summertime is decreasing through the
11 years, since there is a simultaneous reduction in traffic and industrial activity,
12 due to the economic crisis in Greece. On the contrary, EC concentration
13 during winter presents a significant increase since 2011, which can be
14 attributed to the selection of wood as the major fuel source for domestic
15 heating. OC concentration does not present a clear inter-annual pattern,
16 probably because of the episodic nature of biomass burning, as depicted from
17 the increased calculated standard deviations that may have balanced out the
18 aforementioned trend.
- 19 • Total carbon for the whole sampling period (sum of OC and EC) constitutes a
20 significant part of PM_{2.5} aerosol fraction (TC/PM= ~14%), while OC accounts
21 for 79±4% of total carbon, constituting the predominant carbon contributor.
22 Additionally, the estimated POM accounts for 24±6% of the collected fine
23 aerosol.
- 24 • The total of five-year samples provides an average OC/EC ratio of 4.7±1.3,
25 while on a seasonal basis the OC/EC ratios are higher than those reported for
26 other urban background sites around the world. The elevated measured values
27 of OC/EC ratio highlight the secondary nature of secondary organic carbon in
28 the area especially during summertime. Additionally, the calculated
29 correlation between OC and EC suggests that OC and EC fractions are emitted
30 by common primary sources while, simultaneously there is impact of
31 additional sources like production of secondary organic carbon. More
32 specifically, in regards to primary emissions, it appears that the dominant

1 primary source of EC is mainly fossil fuel combustion (such as traffic) while,
2 biomass emission sources contributes mainly during the cold period.

- 3 • The calculated WSOC average concentration is $1.5 \pm 0.9 \mu\text{g m}^{-3}$, and it presents
4 significant dependence on OC concentration, revealing their common sources
5 and subsequently the predominant secondary nature of OC in the studied area.
6 Furthermore, the estimated WSOC/OC ratio is $63 \pm 7\%$, illustrating the
7 presence of aged aerosol in the site. In addition, this work indicates that
8 emissions, from primary non-biomass burning sources of water-soluble
9 organic carbon and from secondary organic products, can contribute to some
10 extent to the variability of organic carbon observed in the studied location.
- 11 • SOC presents maximum values during summer, when there is intense
12 photochemical activity, while the intra-annual variability of SOC is similar to
13 that of WSOC, highlighting significant aging processes as characteristic at the
14 regional scale. SOC estimation was not feasible in the cold period (November
15 to March).
- 16 • The comparison of OC and EC levels between the urban background and the
17 remote-coastal sites indicated an 80% increase of EC, due to local sources in
18 Athens, during the cold season of the last two years (wintertime 2011-2012
19 and 2012-2013), when economic hardship massively led residents to wood
20 burning for heating purposes.

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29 30 31 **References**

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24

- 1 **Table 1:** PM_{2.5} mass, OC, EC, WSOC concentrations and OC/EC ratios reported in
- 2 bibliography compared to this study.

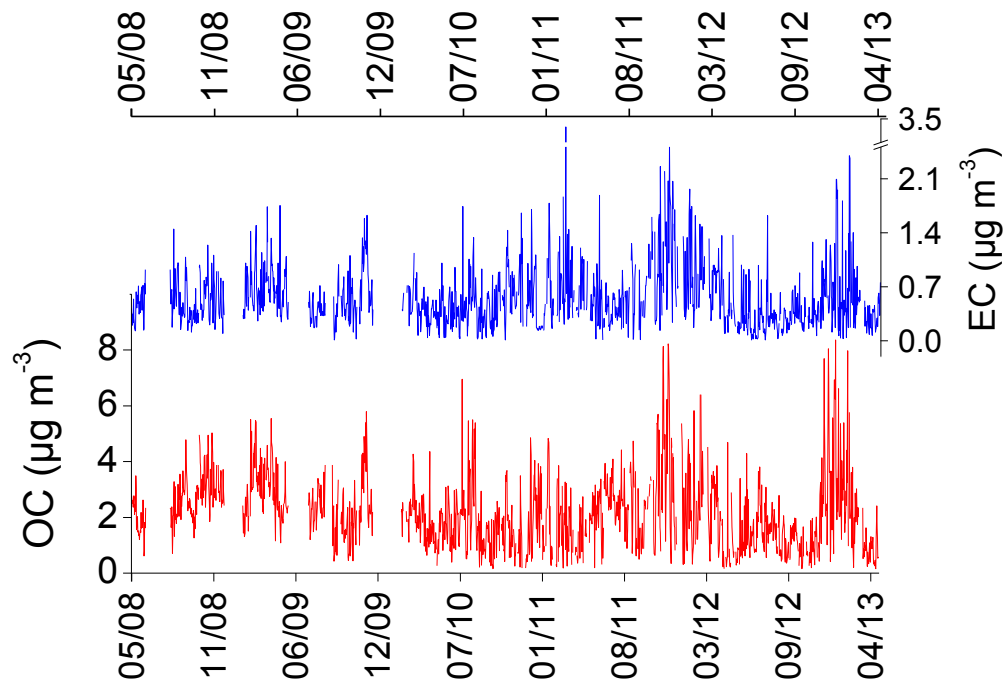
Location Site*	Sampling Period	PM _{2.5} mass (µg m ⁻³)	OC (µg m ⁻³)	EC (µg m ⁻³)	WSOC (µg m ⁻³)	OC/EC
Athens, Urb-BG, Current study	May 2008-April 2013	20±11	2.±1.3	0.54±0.39	-	4.7±1.3
El Arenosillo (Spain), Urb-BG ^[1]	02/06/2005-30/06/2006	21	2.9	1.1	-	2.9
Barcelona, Urb-BG ^[2]	27/07-01/09/2004	16.4	3.7	0.8	1.6	4.6
Barcelona, Urb-BG ^[2]	16/11-16/12/2004	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's pen. (Lecce), Urb-BG ^[4]	Mar-Dec/2007	19±9	5.6±2.8	1.5±1.2	-	-
Milan, Urb-BG ^{[5] [6]}	Aug/2002-Dec/2003, spor	24.5	9.2±7.2	1.4±0.4	-	-
Madrid, Urb-BG ^[7]	June/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]	29/02-02/05 & 04/06-05/08/2008	23.8	4.1	0.48	-	-
Athens, Traf-Ind ^[11]	29/02-02/05 & 04/06-05/08/2008	24.7	1.46	1.8	-	-
Athens, Coa-BG ^[11]	29/02-02/05 & 04/06-05/08/2008	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]	10/7-23/7/2007	-	2.58±1.12	0.36±0.25	1.74±0.86	-
Finokalia (Crete), Remote ^[15]	24/7-6/8/2007	-	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]	02/06/2005-30/06/2006	21	3	0.6	-	4.7
French Riviera, Coastal ^[17]	5-29/5/2007	-	2.07-5.37	0.13-0.33	0.02-0.08	-
Montseny, Reg-BG ^[18]	2002-2007	-	2	0.2	-	-
C. de Belver, Mallorca, Sub-BG ^[19]	8/1/2004-29/2/2005, spor	20	2.9	0.5	-	-

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- 4 * spor: Sporadically, Urb-BG: Urban Background, Urb-Ind: Urban Industrial, Urb-Traf: Urban Traffic,
- 5 Traf-Ind: Traffic Industrial, Sub-BG: Suburban Background, Coa-BG: Coastal Background.

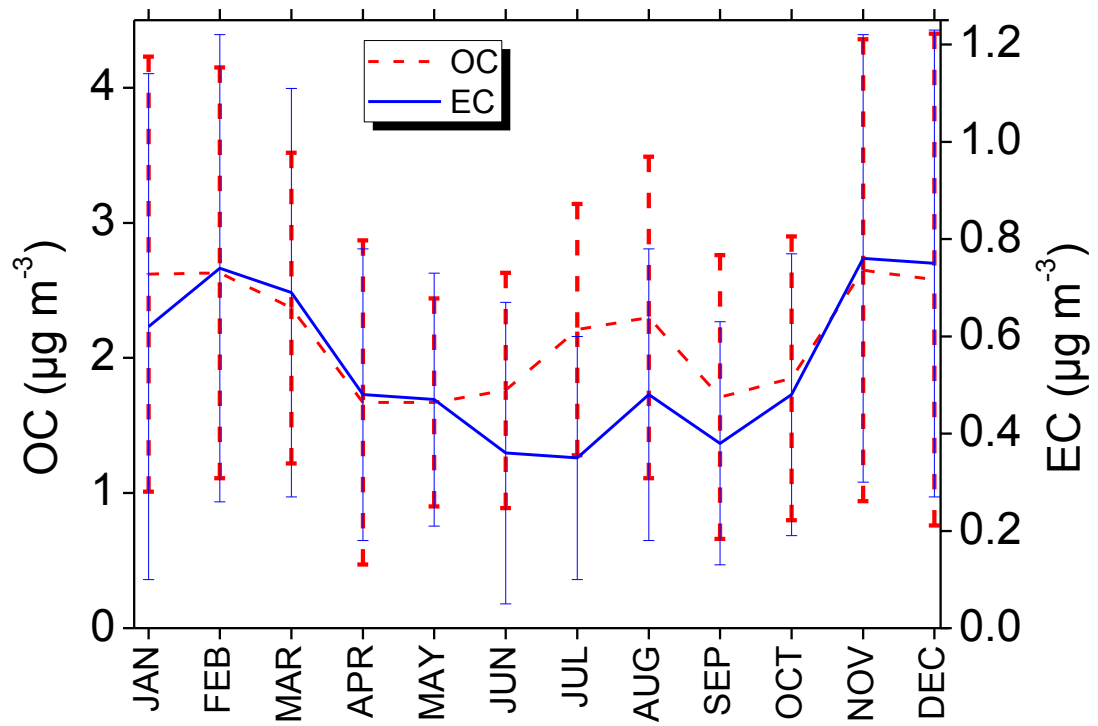
1 **PM₁₀ sampling

2 ¹(Sanchez de la Campa et al., 2009) ²(Viana et al., 2007) ³(Sillanpaa et al., 2006) ⁴(Perrone et al.,
3 2011) ⁵(Lonati et al., 2008) ⁶(Lonati et al., 2007) ⁷(Mirante et al., 2014) ⁸(Grivas et al., 2012)
4 ⁹(Theodosi et al., 2010) ¹⁰(Remoundaki et al., 2013) ¹¹(Pateraki et al., 2012) ¹²(Terzi et al., 2010)
5 ¹³(Bougiatioti et al., 2013) ¹⁴(Koulouri et al., 2008) ¹⁵(Bougiatioti et al., 2011) ¹⁶(Kopanakis et al.,
6 2012) ¹⁷(Piazzola et al., 2012) ¹⁸(Pey et al., 2009a) ¹⁹(Pey et al., 2009b)
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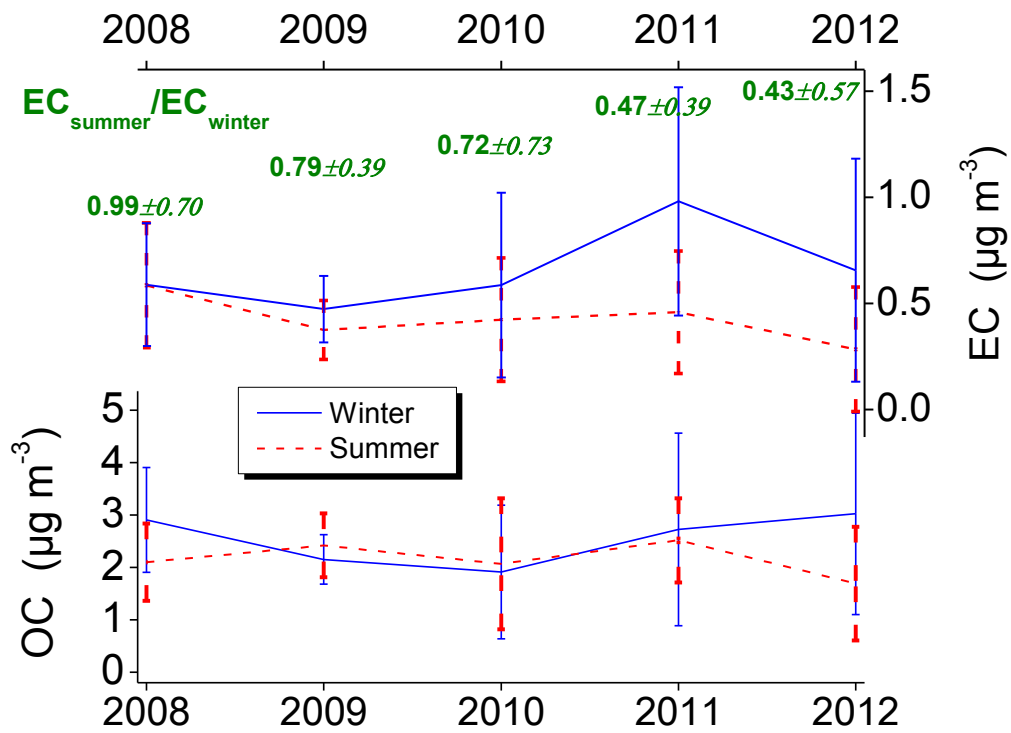
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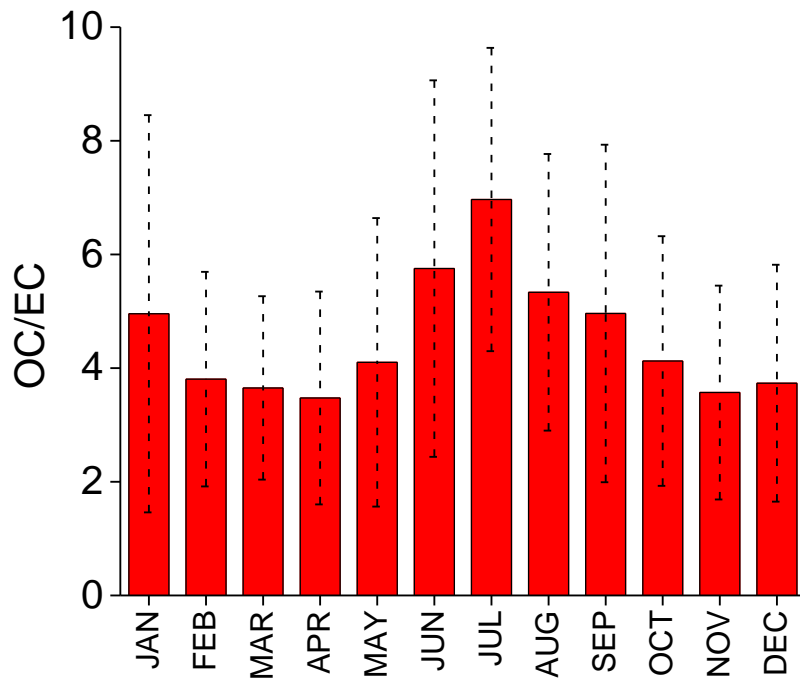
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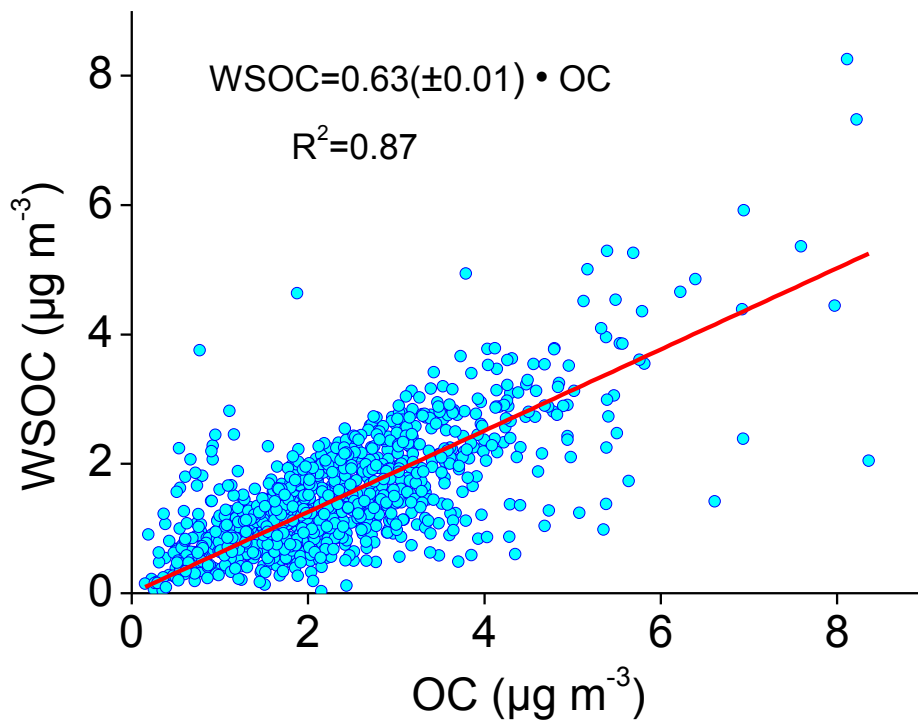
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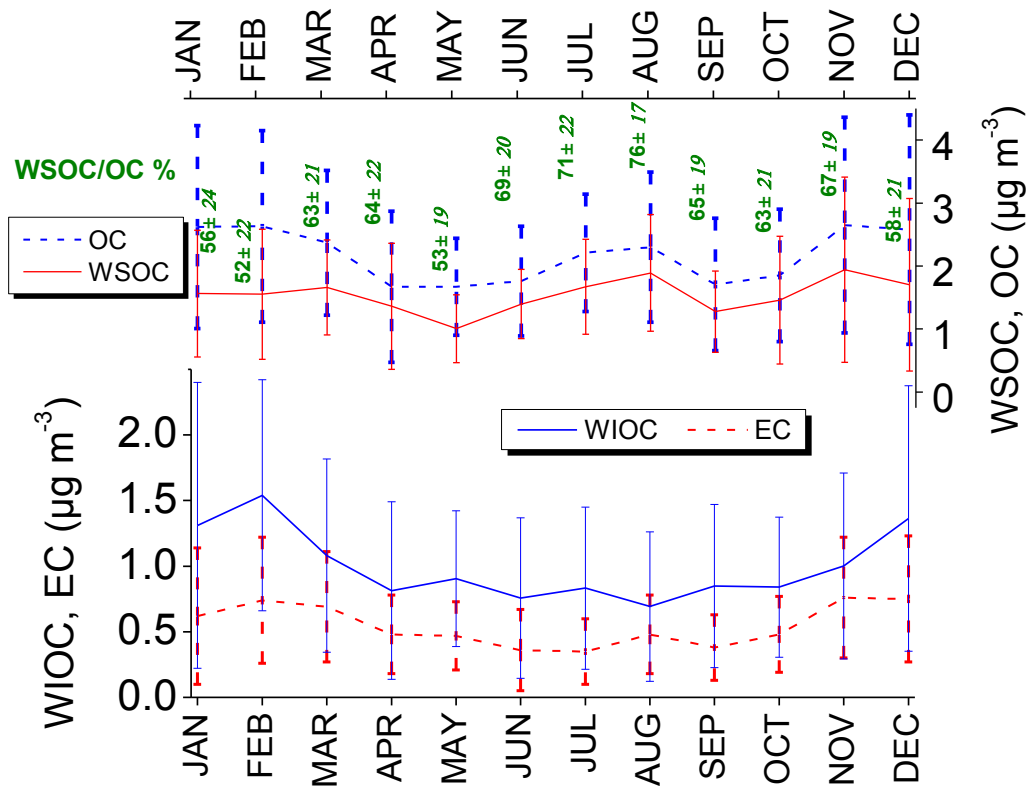
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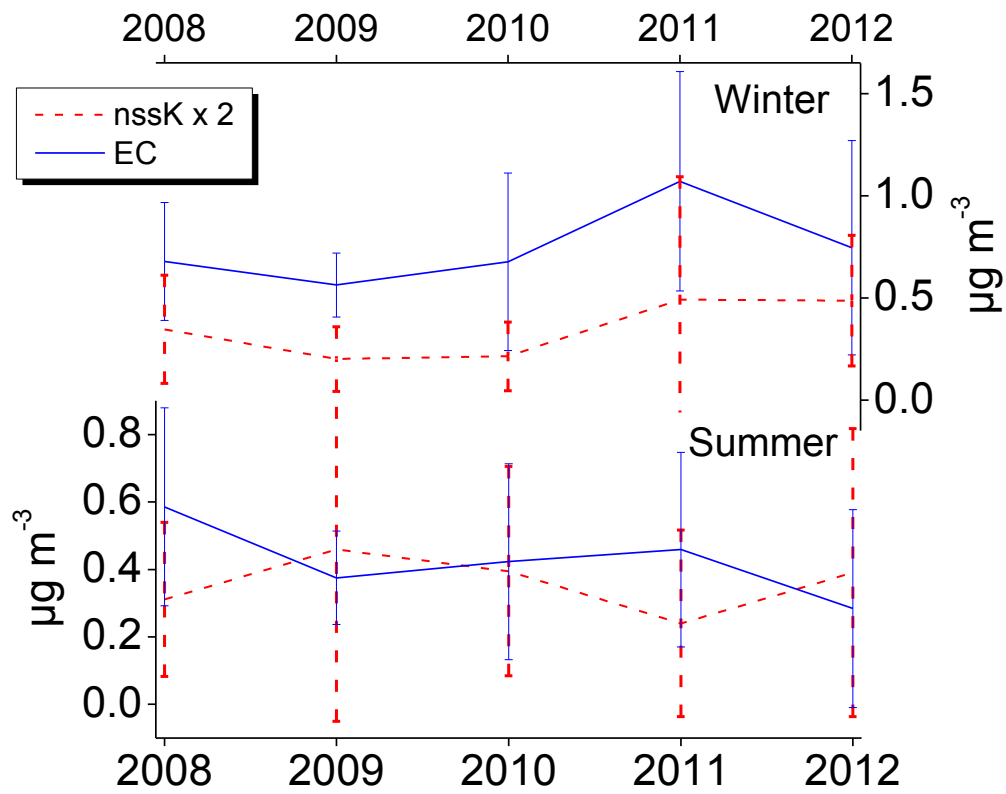
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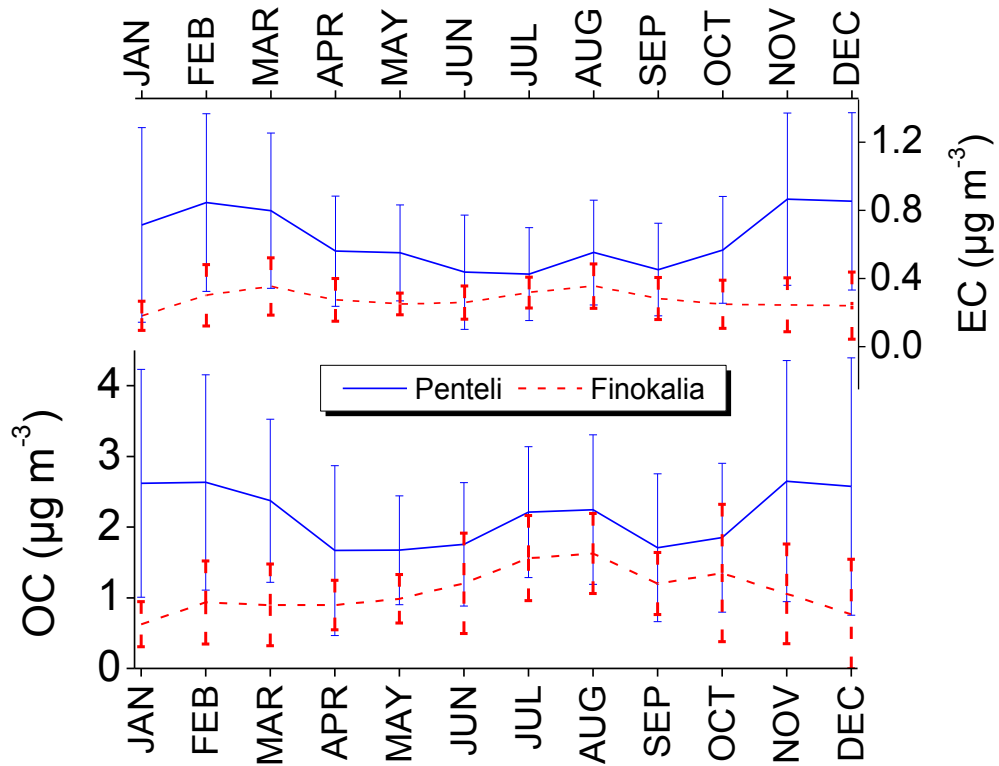
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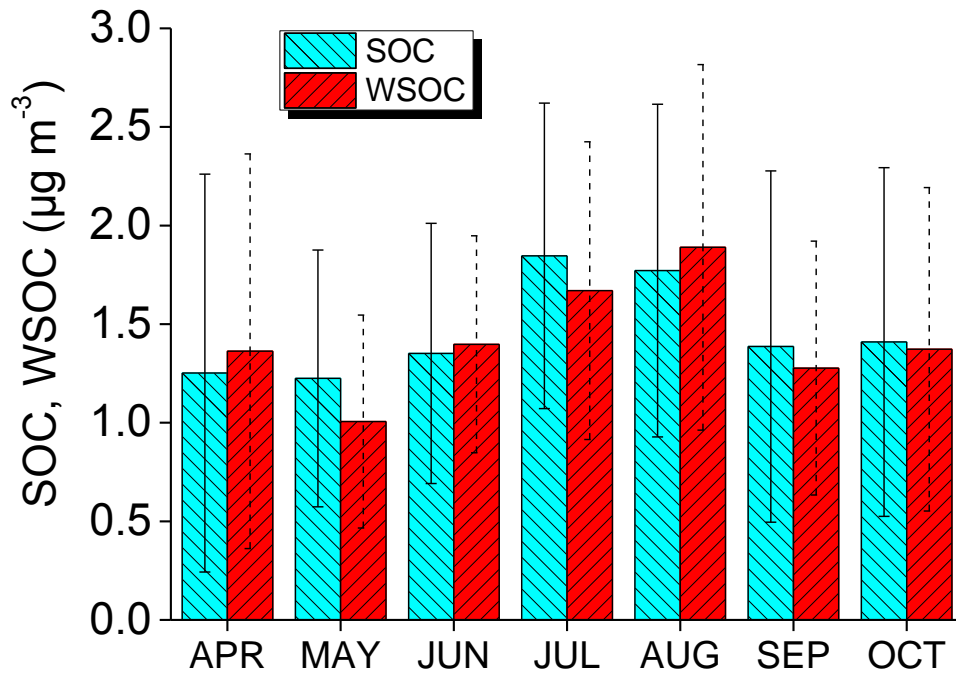
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