Science of the Total Environment 592 (2017) 115–123

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

The combined effect of reduced fossil fuel consumption and increasing biomass combustion on Athens' air quality, as inferred from long term CO measurements

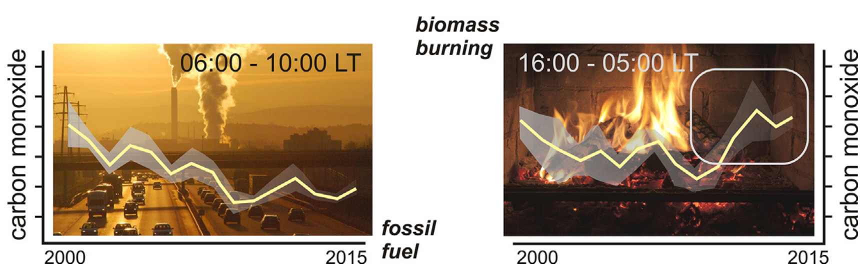
Myrto Gratsea [a,b], Eleni Liakakou [a], Nikos Mihalopoulos [a,b], Anastasios Adamopoulos [c], Eirini Tsilibari [c], Evangelos Gerasopoulos [a,*]

[a] Institute for Environmental Research and Sustainable Development, National Observatory of Athens, Greece
[b] Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, Greece
[c] Ministry of the Environment & Energy, Dept. of Air Quality, Athens, Greece

HIGHLIGHTS

- BC and long term CO measurements to evaluate the increasing role of biomass combustion
- Morning CO peaks decreased by 50% reflect reduction of fossil fuels use.
- Winter evening CO peaks increased by 37%–78% since 2012 reflect intense wood burning.
- CO_{wb} contributes 50% to the total CO emissions during night time.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 November 2016
Received in revised form 14 February 2017
Accepted 5 March 2017
Available online xxxx

Editor: D. Barcelo

Keywords:
Urban atmosphere
Biomass combustion
Carbon monoxide
Black carbon
Athens
Economic recession

ABSTRACT

To evaluate the role of biomass burning emissions, and in particular of residential wood heating, as a result of the economic recession in Greece, carbon monoxide (CO) atmospheric concentrations from five (5) stations of the National Air Pollution Monitoring Network in Athens, spanning the period 2000–2015, in conjunction with black carbon (BC) concentrations from the NOA (National Observatory of Athens) station at Thissio were analysed. The contribution of the different sources to the diurnal cycle of these two pollutants is clear, resulting to a morning peak, mainly due to traffic, and a late evening peak attributed both to fossil fuel (traffic plus central heating) and biomass combustion. Calculated morning and evening integrals of CO peaks, for the investigated period, show consistent seasonal modulations, characterised by low summer and high winter values. The summer and winter morning CO peak integrals demonstrate an almost constant decreasing trend of CO concentrations over time (by almost 50% since 2000), attributed to the renewal of passenger car fleet and to reduced anthropogenic activities during the last years. On the other hand, an increase of 23%–78% (depending on the monitoring site) in the winter evening integrals since 2012, provides evidence of the significant contribution of biomass combustion, which has prevailed over fossil fuel for domestic heating. CO emitted by wood burning was found to contribute almost 50% to the total CO emissions during night time (16:00–5:00), suggesting that emissions from biomass combustion have gained an increasing role in atmospheric pollution levels in Athens.

* Corresponding author.
E-mail address: egera@noa.gr (E. Gerasopoulos).

http://dx.doi.org/10.1016/j.scitotenv.2017.03.045
0048-9697/

1. Introduction

The economic recession that has engulfed Europe since 2008 had great impact on air quality in several European countries. The impact on air quality has been evaluated in several studies using in-situ (e.g. Cusack et al., 2013 and Lyamani et al., 2011) and satellite measurements (Castellanos and Boersma, 2012), revealing significant reduction of air pollutants attributed to reduced fuel consumption. The subsequent reduction of industrial activities and traffic emissions resulted in pollution reduction, while on the other hand, the extended use of biomass instead of oil for domestic heating, have resulted in severe smog episodes during winter (e.g Puxbaum et al., 2007; Favez et al., 2010 and references therein).

In Greece, the economic recession has vastly affected the general productivity, inducing changes in the field of air pollution, mainly in large cities. It has also led to changes in consumers' behaviour regarding the level and type of fuel consumption. For Athens in particular, Vrekoussis et al. (2013),using satellite observations, showed a 30–40% reduction in NO_2 tropospheric columns since 2008. Since 2011, when the economic crisis in Greece affected the price of oil, a great part of the population of Athens have been gradually relying on the use of wood stoves and fireplaces during winter months, as primary domestic heating devices. In addition, the use of biomass as fuel for central heating in Athens became legal in 2011, according to ministerial decision. The most recent survey from the Hellenic Statistical Authority conducted in 2011–12, reported that the main sources of heating in Greece are: fossil fuel (oil, 64%), biomass (12%), electricity (12%) and natural gas (9%). Additionally, 32% of those who use fossil fuel, they also burn wood in fireplaces. Fireplaces exist mainly in new buildings (constructed after 2000), the geographical distribution of which is mainly in Athens' northern and southern suburbs. However, wood stoves are used extensively in all areas (especially in poorer parts of the city), where the wood quality has been widely questioned (e.g. furniture). The smoke from wood burning during night time in combination with Athens' special topography (surrounded by three mountains to the North, West and Northeast favoring the accumulation of atmospheric pollutants) and shallow nocturnal atmospheric boundary layer (Kallos et al., 1993, Kassomenos et al., 1995, Fourtziou et al., 2017) gave rise to severe smog episodes. Similar episodes due to biomass burning have also been reported in the second most populated city of Greece, Thessaloniki (Saffari et al., 2013). Such smog episodes may have severe health impacts on population as it has been revealed by the relationship between human lung cancer and the long-term high concentrations of certain pollutants abundant in smog (Beeson et al., 1998). Air pollution in general is a major environmental risk, affecting human health (e.g. Voutsa et al., 2015; Dimitriou et al., 2013; Kampa and Castanas, 2008).

To track biomass burning activities, several tracers have been introduced. Fourtziou et al. (2017) evaluated a number of them for the case of Athens, including black carbon (BC) and carbon monoxide (CO). BC consists of pure carbon in several linked forms and it is formed through the incomplete combustion of fossil fuels, biofuel and biomass. It is a strong absorber of visible solar radiation in the atmosphere and therefore its concentration and distribution in the atmosphere has a positive impact on the radiation budget. Its lifetime in the atmosphere is several days to weeks. CO is produced by partial oxidation of hydrocarbons and its significant role in troposheric chemistry makes it an important trace gas of the atmosphere (Crutzen and Zimmermann, 1991). CO and especially BC are good indicators for combustion processes (e.g. Saurer et al., 2009). In the urban environment of Athens the main sources of CO and BC are traffic (Chaloulakou et al., 2003) and more recently biomass burning (Paraskevopoulou et al., 2014). An emission inventory constructed for Greece and the Greater Athens Area by Fameli and Assimakopoulos (2016) showed that regarding residential emissions, 67% of the emitted CO in Greece originates from fireplaces.

Overall, Athens is a megacity characterised by great abundance of atmospheric pollutants and frequent pollution episodes. The atmospheric environment of Athens has been the subject of several studies (e.g. Ziomas et al., 1998; Kalabokas et al., 1999) throughout time. Vehicle exhausts, industry and central heating during winter months are the main sources of air pollution in the city (Lalas et al., 1982). Reduction of pollution has been reported during 1984–1993 due to measures adopted for improving city's air quality (Fenger et al., 2013) and a following stabilisation until 2008, when the global economic crisis arose. The latter induced on one hand cut down of industrial activities and vehicle's use and on the other hand an increase of residential wood burning.

To our knowledge, the relative contribution ratio of wood burning and fossil fuel combustion to Athens' air quality is not known. In this work we used long-term CO measurements from three urban, two urban background and one suburban station in Athens, to access the impact of biomass burning and to relate it with the evolution of air quality and the economic recession in Greece. In addition simultaneous CO and BC measurements were performed at an urban background station during two winters period (2012–2013 and 2014–2015) to validate our use of CO as an efficient wood burning tracer. Section 2 provides a short description of the measurement sites and the instruments used. Section 3 presents the results of the statistical analysis including wood burning episodes identification, measurement sites intercomparison and assessment of the interannual variability. The development of a simple algorithm for distinguishing CO emitted from wood burning and fossil fuel combustion is also described. Finally, in Section 4 the main conclusions are presented.

2. Methodology

2.1. Sampling

Data used in this study were obtained from in-situ measurements of the National Observatory of Athens (NOA) at Thissio station (37° 58′ N, 23° 43′ E) and five more stations - Marousi (38° 01′ N, 23° 47′ E), N. Smyrni (37° 55′ N, 23° 42′ E), Athinas (37° 58′ N, 23° 43′ E), Geoponiki (37° 59′N, 23° 42′E) and Piraeus (37° 56′N, 23° 43′E) - of the National Air Pollution Monitoring Network (NAPMN), which is part of the Ministry of Environment and Energy network. Athinas, is located in the centre of the city near to a busy road and it is characterised as an urban traffic station. Marousi and N. Smyrni are urban background stations and are located in the northeast and south area of Athens, respectively (Fig. 1). Geoponiki is an industrial-suburban station and Piraeus (port) is in the south and is an urban traffic station.

Thissio sampling site is located on top of a hill in the historic centre of Athens, surrounded mostly by a pedestrian zone and some densely populated neighbourhoods, and it is considered as urban background station reflecting the average pollution of the city (Paraskevopoulou et al., 2015). The major sources of air pollution affecting the site are expected to be vehicular emissions and residential heating. In general, several particulate and gaseous components are being continuously monitored since December 2013 at Thissio station during intensive campaigns in winter, either by online in-situ monitoring or by sampling and subsequent chemical analysis at the laboratory (e.g. Fourtziou et al., 2017). Each of the intensive campaigns (winter 2013–2014 and 2014–2015) lasted for a period of approximately two months, from mid-December until mid-February.

BC measurements at Thissio station were obtained using a portable Aethalometer (AE-42, Magee Scientific) operating at 7 wavelengths (370, 470, 520, 590, 660, 880 and 950 nm) and a Multi Angle Absorption Photometer (MAAP 5012 Thermo company). CO was monitored by a Horiba APMA-360 series automatic gas analyser (scale: 0–10 ppmv, lower detectable limit: 0.2 ppmv, precision: $\pm$0.2 ppmv). The NAPMN network consists of 15 stations in Athens area providing data of atmospheric pollutant concentrations since 1983. CO is measured at five NAPMN stations and is determined using a Horiba APMA-360 series automatic gas analysers (NDIR technique, scale: 0–20 ppmv, lower detectable limit: 0.05 ppmv). The CO analysers provide 1-min concentrations.

Fig. 1. Map of the Athens area. Locations of the NAPMN monitoring sites and Thissio station. The Greater Area of Athens is marked.

In situ calibration of automatic analyzers is carried out on a monthly basis using a dynamic dilution system, while intermediate checks are performed according to EN 14626 and EN 14211. The mass flow controllers of the dynamic dilution system are calibrated every year at the premises of the Ministry of the Environment & Energy in agreement with the quality assurance programmes of the National Reference Laboratory for Air Quality. The linearity, zero drift and repeatability are main parameters, among others, that are checked for all analysers according to the relevant EN standards. CO cylinders are used for the in situ calibration of the gas analysers. These cylinders have been initially checked by a static dilution system in agreement with the National Reference Laboratory for Air Quality. The Laboratory of Air Quality is accredited according to EN ISO 17025, inter alia, for the performance of calibration of gas flow and determination of the composition of gas mixtures of CO using the static volumetric method. Meteorological data from NOA's station at Thissio was additionally retrieved.

2.2. Data analysis

Data sets of 1-hour averaged CO concentrations for the time period 2000–2015 were used for the analysis. Continuous BC measurements were performed at Thissio station from December 2013 to February 2014 and from November 2014 to February 2015. To discriminate between BC associated with fossil fuel (BC_{ff}) and wood burning (BC_{wb}) processes, a technique and corrections for multiple scattering and shadowing effects - as described in previous works (Sciare et al., 2011; Favez et al., 2010; Collaud, 2010; Weingartner et al., 2003) has been applied.

3. Results and discussion

3.1. Biomass burning episodes identification

Winter time (November 2014–February 2015) concentrations of CO, BC and BC_{wb} measured at the Thissio station are presented in Fig. 2, where severe spikes can be clearly seen. High values of BC, coinciding with BC_{wb} peaks, have been recorded during night time reaching in some cases 18 μg/m^3 mass concentrations. Minimum values are recorded before sunrise. In similar studies conducted for urban areas in Canada and Beijing, hourly BC concentrations varied from 0.1 μg/m^3 to 7 μg/m^3 and from 2.7 μg/m^3 to 6.1 μg/m^3, respectively (Sharma et al., 2002 and Wang et al., 2009). In Paris, biomass combustion has been estimated to contribute almost 20% of the total BC mass, at a representative for particulate pollution station at the centre of Paris (Crippa et al., 2013). A study conducted at an urban background station in Athens from 2008 to 2013 reveals an elevation of elemental carbon (EC) in the $PM_{2.5}$ fraction since 2011, reaching maximum daily concentrations higher than 3 μg/m^3 (Paraskevopoulou et al., 2014). Florou et al. (2016), report that domestic wood burning in Athens is in general a more significant organic aerosol (OA) source compared to traffic accounting for almost 40% of the OA versus 10% of the traffic. Finally, Fourtziou et al. (2017) show that during biomass burning episodes PM1 is consisted mainly of OA (>80%).

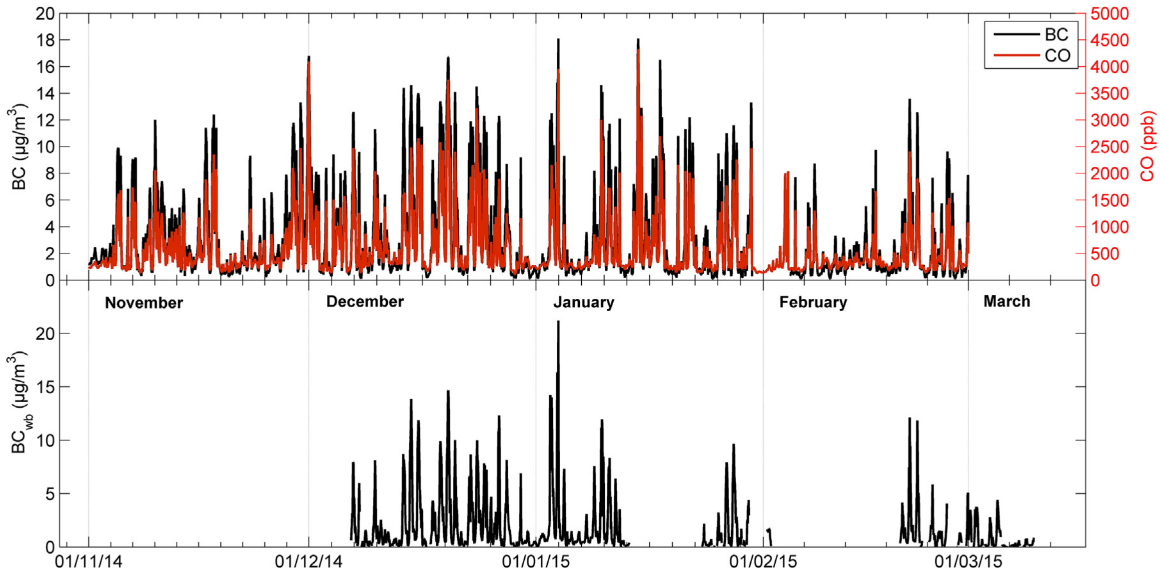


Fig. 2. Time series of 1-h averaged concentrations of CO (red line) and BC (black line, MAAP 5012) (upper panel) and BC_{wb} (lower panel, AE-42) at Thissio monitoring station.

An obvious coincidence of BC and CO peaks can be seen in Fig. 2. CO concentrations range from 200 to 3500 ppb. The 8-hour limit value for CO, 10 mg m^{-3} (~8000 ppb), has not been exceeded (Table 1). The peak values for both BC and CO appear in late evening and night when the use of fireplaces and wood stoves for heating purposes is more intense.

To follow the related to biomass burning, late evening buildup of CO and BC, during the transition from autumn to winter and the gradual restoration of normal concentrations towards spring, the mean diurnal cycles, calculated for each winter month separately at Thissio station, are used. (Fig. 3a & b). The diurnal variation of both species depicts two characteristic peaks: one in the morning (around 09:00 LT) which is due to traffic (morning rush hour) and the second one in the evening (around 22:00 LT) which is mainly attributed to wood burning. The morning peak is in consistency with other studies which have shown that the morning rush hours in Athens are from 8:00 LT until 11:00 LT (Katsoulis, 1996; Kourtidis et al., 1999). Both CO and BC start building up at 06:00 LT reaching a maximum at 09:00 LT and then they decrease towards noon. Thereafter, low values are maintained until 16:00 LT when they start building up again reaching a maximum at 22:00 LT. The slow decrease after midnight, when wood burning emissions are expected to be lower, could be attributed to the poor ventilation of the Athens basin during night time, in combination with a shallow nocturnal boundary layer (Kassomenos et al., 1995), leading to entrapment of pollution.

Studies focusing on wood burning in Athens have showed that smog episodes are related to low wind speed, absence of precipitation (Fourtziou et al., 2017) and low nocturnal mixing layer height (Gerasopoulos et al., 2016). In this study, the influence of the meteorological conditions and the subsequent local circulation patterns on the BC concentrations measured at Thissio is investigated for the particular period covered in Fig. 2. Wind speed and wind direction data, from the meteorological station at Thissio, are used and presented in Fig. 4. High BC concentrations are encountered during low wind speed conditions (u < 3 m/s), both during day time and night time, highlighting the important role of ventilation and internal city air mass transport patterns to air quality. During evening and night time (17:00–04:00LT) BC

Table 1
BC and CO basic statistics (hourly resolution) from November 2014 until February 2015. The corresponding values for winter 2013–14 are also reported in brackets.

	Average	Median	Minimum	Maximum
BC (μg/$μ^3$)	2.95 ± 3.25 (2.93 ± 3.28)	2.05 (1.60)	0.09 (0.18)	18.09 (26.84)
CO (ppb)	556 ± 525 (606 ± 609)	368 (340)	106 (97)	4326 (3544)

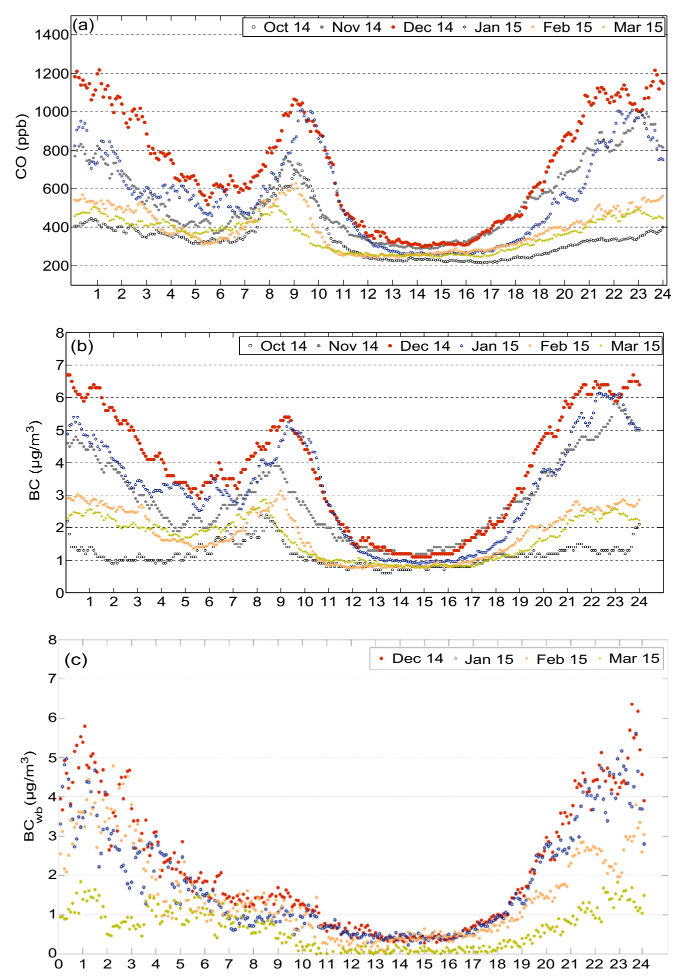


Fig. 3. Mean diurnal variation per month for CO (a), BC (b) and BC_{wb} (c) concentration measurements at Thissio station.

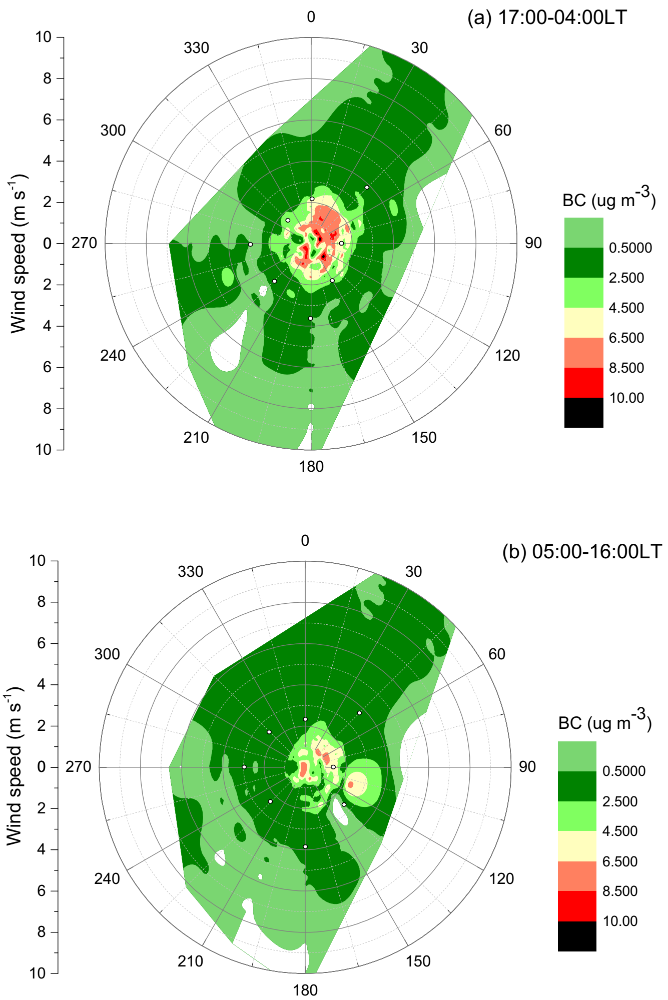


Fig. 4. Hourly BC concentration values as a function of wind direction and wind speed for 17:00–04:00LT (a) and 05:00–16:00LT (b). White spots represent the mean wind speed per direction.

concentrations exceed daytime concentrations and this finding does not depend on the direction of the air masses under low speed conditions.

The CO and BC morning peaks in December and January are almost 50% higher compared to November's and February's peak. The evening peaks in November, December and January are increased by a factor of 2 compared to February. Although November also exhibits significant BC concentrations, December and January are colder months (mean temperatures 12.7 °C and 9.9 °C, respectively) compared to November (14.9 °C) and subsequently more representative of wintertime conditions. The high peaks in January are probably linked to extensive periods of stationary anticyclonic conditions, usually occurring in Athens during January (Van Dop and Kallos, 2012), leading to poor dispersion conditions. Indeed, according to surface analysis charts from UKMO (United Kingdom Met Office, www.metoffice.gov.uk), until at least January 21st the peaks are linked to anticyclonic conditions.

The BC_{wb} concentration shows a characteristic diurnal variability (Fig. 3c). In contrast to CO and BC, the diurnal variation of BC_{wb} depicts only one peak at around 22:00 LT (which coincides with the evening peak of CO and BC), due to biomass combustion emissions during night time. The peaks in December and January are, just like in the CO and BC case, increased by a factor of 2 compared to February and March.

Considering the above findings, it can be deduced that smog episodes are more intense and frequent during December and January; therefore these two months are hereafter considered as the typical winter months for the analysis following in the next sections.

3.2. Contribution of biomass burning to evening CO concentrations

The contribution of wood burning to air pollution loads could be assessed by distinguishing the sources (fossil fuel versus wood burning) which contribute to the CO load in the atmosphere. Although the wood burning contribution to BC concentrations (particulate matter pollutant) has already been calculated, as discussed in Section 2.2, there is no direct way to distinguish CO sources from the existing measurements. An indirect method is proposed here, to enable an overview of the contribution of the different sources to CO as well.

Making the assumption that the influence of wood burning in the atmosphere during morning hours is insignificant, we considered that the recorded CO morning values are attributed entirely to fossil fuel burning. Linear regression analysis is applied on CO and BC_{ff} morning (07:00–10:00) data for the period December 2014–February 2015 (Fig. 5a), revealing a significant correlation ($R^2 = 0.89$, N = 336). The regression equation ($y = 241.6(\pm 3.6)x$, setting y-intercept = 0) is then applied to evening BC_{ff} data (21:00–00:00 LT) calculating in that way the evening CO_{ff} (Carbon Monoxide from fossil fuel combustion). Subtracting the calculated CO_{ff} from the measured CO, CO emitted by wood burning (CO_{wb}) is finally obtained. A qualitative validation of the obtained CO_{wb} is performed using the BC_{wb} measurements (Fig. 5b). The results indicate a significant correlation ($R^2 = 0.76$, $y = (72.0 \pm 2.9)x + 170(\pm 14)$).

This analysis reveals a contribution of CO_{wb} to the total CO up to approximately 50% on average during night (21:00–00:00 LT), showing once more the increasing role of the biomass combustion in the levels and diurnal variability of pollutants in Athens.

Given that CO and BC at Thissio station are very well correlated ($R^2 = 0.94$, N = 2756), we have focused on CO measurements in order to study the trends during the last 15 years. CO is also well correlated with BC_{wb} ($R^2 = 0.80$, N = 1169). CO is a good indicator for traffic emissions during morning hours and also a good indicator for both fossil fuel and biomass burning during night time. In this study, CO has been chosen over BC for the analysis, due to the long-term availability of its monitoring in Athens.

3.3. Comparison of CO measurements: site representativeness

Data from the Thissio station has been analysed and presented so far. Hence, it is important to examine whether the specific monitoring station can be considered as representative of the air quality in Athens.

For this, the CO measurements at Thissio station were compared to observations from NAPMN stations (Marousi, N. Smyrni, Athinas, Geoponiki, Piraeus), during one winter period (2013–2014). Indicatively, the scatter plot of CO concentrations at Thissio versus Athinas, for the period December 2013–January 2014, is shown in Fig. 6. Athinas and Thissio measurements are significantly correlated ($R^2 = 0.78$, N = 1077), which is expected given the vicinity of the two sites. However, CO concentrations observed at Athinas, compared to Thissio station, are higher by almost a factor of 2, which is explained by the type of the sites (Athinas-urban traffic, Thissio-central but away from immediate exposure to traffic sources). Similarly, Marousi and N. Smyrni CO measurements are also significantly correlated with Thissio ($R^2 = 0.63$, N = 1076 and $R^2 = 0.76$, N = 1077, respectively) and the recorded concentrations are correspondingly 55% and 75% higher than the measurements at Thissio. The correlation is also significant for Geoponiki and Piraeus ($R^2 = 0.58$, N = 1074 and $R^2 = 0.59$, N = 1075, respectively) with 65% and 120% higher CO concentrations, respectively, when compared to Thissio. The correlation coefficients (R) between CO measurements in all stations are shown in Table 2. The high correlation between the five NAPMN sites and Thissio, as well as the relative difference in absolute levels, support the characterisation of Thissio as an urban background site, non-intensively affected by local traffic.

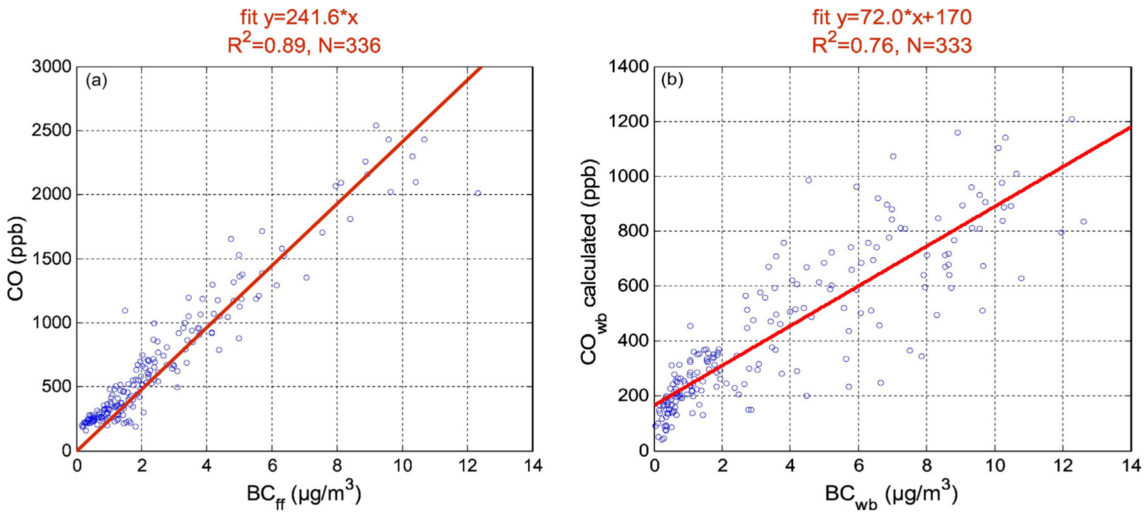


Fig. 5. Scatter plot between BC_{ff} and CO morning (07:00–10:00) measurements at Thissio station for the period December 2014–February 2015 (left panel). Scatter plot between calculated BC_{wb} evening (21:00–00:00) measurements and calculated CO_{wb} for the same time period (right panel).

3.4. Analysis of interannual variability

For achieving interpretable results for the CO trend during the last 15 years and for estimating the effect of the wood burning on this trend, the integrals of the morning and evening peaks for each day and for each season separately were calculated. The integrals are calculated between 06:00 LT and 10:00 LT in the morning and 16:00 LT and 05:00 LT in the evening. The area below the peak, defined by these two points and the x-axis, is considered as background value and is subtracted (Fig. 7). The mean integrals for winter (December–January) and summer months (July–August) for the five NAPMN stations representing urban and urban background environment, are presented in Fig. 8.

During summer, CO is released into the atmosphere of Athens mainly via fossil fuel combustion processes (e.g. vehicle exhausts). The low summer values (Fig. 8a) are attributed to photochemistry (oxidation by OH radicals), reduced traffic (vacation period) and more efficient dispersion of the pollutants due to deep mixing heights and strong thermal circulations that lead to better ventilation conditions (Kassomenos et al., 1995). Winter morning values are enhanced by a factor of 3 (Fig. 8c) compared to summer and this can be attributed to i) the extensive use of central heating, ii) decreased photochemistry, iii) shallower boundary layer and iv) poor dispersion due to stationary conditions.

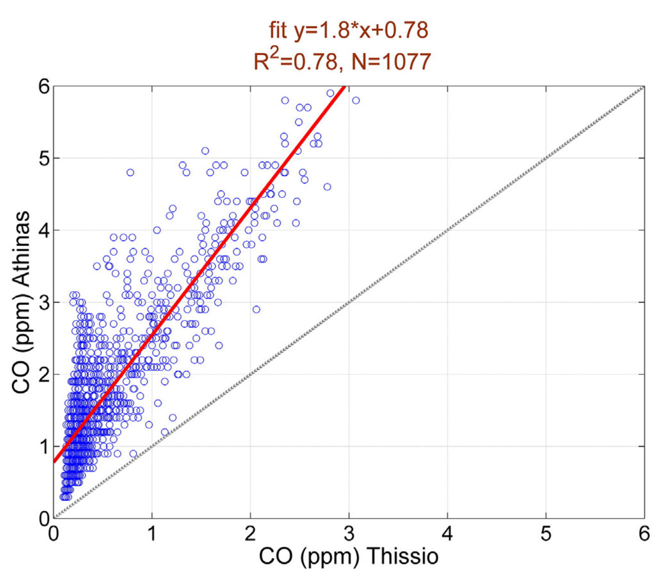


Fig. 6. Scatter plot between CO measurements at Thissio station and CO measurements at Athinas station, for winter (December–January) 2013–14.

The gradual decrease over the years, both in winter and summer morning peak integrals, is most likely resulting from the gradual replacement of old vehicles with new ones (catalytic converters), along with the economic recession starting in 2008. Fameli and Assimakopoulos (2016) estimated that CO traffic emissions were decreased by 40% during the period 2006–2012. In this study, the winter morning integrals are approximately 50% decreased during the period 2000–2010 and from 2010 on, no further decrease is observed. Low integral values are also observed in the summer evening peaks (Fig. 8b), along with a gradual decrease over the years, once more attributed to reduced traffic and depollution strategies. Since 2012, biomass burning has prevailed over fossil fuel for domestic heating purposes and this can be clearly seen in the winter evening integrals (Fig. 8d). The increasing over time values of the winter evening integrals of CO, during this period, indicates a dominant influence of wood burning during nighttime in all five stations. This is also supported by the fact that the more recent winter months were not characterised by lower temperature values compared to previous years. More specifically, the mean winter temperature, for the months considered in this analysis, is 10.5 °C for the period 2000–2011 and 10.7 °C for the rest of the time period. The mean value (7.3) of the winter evening integrals at Athinas station during the last 4 years is 78% higher than the mean value (4.1) of the previous years. The corresponding percentages for Marousi, N.·Smyrni, Geoponiki and Piraeus are 59% (8.9 versus 5.6 mean value), 37% (8.2 vs 6.0 mean value), 37% (7.0 vs 5.1 mean value) and 23% (5.4 vs 4.4 mean value) respectively.

In order to highlight the relative competition between the reduction of CO due to traffic and its late evening increase due to wood burning, we have calculated the ratio of CO_{ev}/CO_{mor} using the peak value at 09:00 LT for CO_{mor} and the peak value at 22:00 LT for CO_{ev}. In Fig. 9, the interannual trend of the mean ratio of CO_{ev}/CO_{mor} for wintertime

Table 2
Correlation matrix of CO for all monitoring stations.

Monitoring stations	Thissio	Athinas	Marousi	N. Smyrni	Geoponiki	Piraeus
Thissio		0.882	0.791	0.875	0.759	0.766
Athinas	0.882		0.758	0.805	0.743	0.808
Marousi	0.791	0.758		0.745	0.755	0.678
N. Smyrni	0.875	0.805	0.745		0.727	0.753
Geoponiki	0.759	0.743	0.755	0.727		0.754
Piraeus	0.766	0.808	0.678	0.753	0.754	

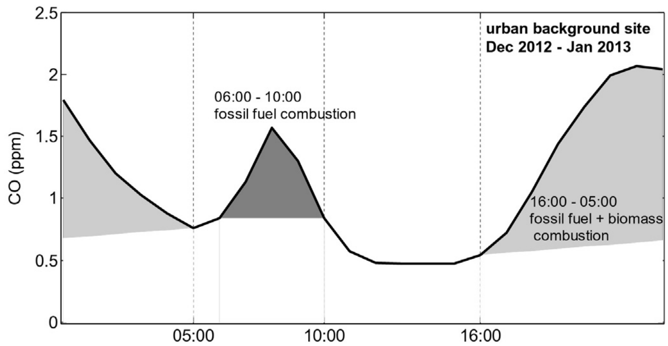


Fig. 7. CO winter (December 2012–January 2013) diurnal variability for N.·Smyrni station. The calculated morning integral (dark grey) and evening integral (light grey) are here shown as a typical example of the methodology followed.

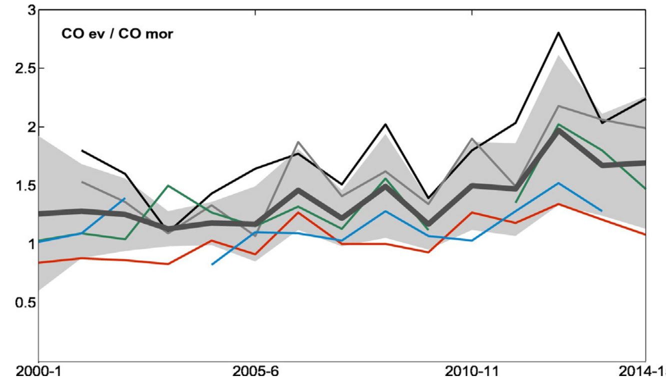


Fig. 9. Mean annual evolution of the CO_{ev}/CO_{mor} ratio in winter for Marousi (black line), N. Smyrni (grey line), Athinas (red line), Geoponiki (green line) and Piraeus (blue line) stations. The dark grey curve corresponds to the mean value of all five stations and the grey shaded area on either side of the mean curve represents the standard deviation (1 σ). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

is presented. The ratio subtracts the influence of fossil fuel and what it remains mainly highlights the impact of wood burning. The mean ratio was calculated from the daily ratios. Since the CO_{ev} peak is mostly controlled by changes in wood burning, while the morning peak is due to traffic emissions (traffic rush hour), the ratio of CO_{ev}/CO_{mor} actually subtracts the influence of fossil fuel and thus it could serve as an additional good indicator of the increasing importance of wood burning in Athens.

The increase of biomass burning during evening and night time since 2012 (along with the stabilisation of morning CO values during the same period) leads to a gradual enhancement of the CO_{ev}/CO_{mor} ratio. The increase is more obvious at the urban background stations: 41% (mean ratio = 1.61 until 2012 & 2.27 from 2012 on) and 33% (mean ratio = 1.45 until 2012 & 1.93 from 2012 on) for Marousi and N. Smyrni stations, respectively. However, at Athinas monitoring station, the increased biomass combustion is partly counterbalanced by the generally elevated traffic emissions, resulting in slighter increase (22%) of the CO_{ev}/CO_{mor} ratio (mean ratio = 0.98 until 2012 & 1.20 from 2012 on). These results demonstrate once more the increasing role of biomass combustion in the air quality of Athens' basin.

4. Summary and conclusions

15 years of surface CO observations from five monitoring stations in Athens, along with simultaneous BC and CO measurements during two intense winter campaigns (Dec 13–Feb 14 & Dec14–Feb15) at Thissio station (urban station), were analysed in this study, in an attempt to shed light on the relative contribution of biomass burning versus fossil fuel combustion in Athens' air quality and to reveal the enhancement of wood burning during the more recent years of the economic crisis in Greece.

Both CO and BC follow identical diurnal patterns characterised by two distinct peaks: a morning peak (around 09:00 LT) attributed to the traffic rush hour and an evening peak (around 22:00 LT) consistent with the increased contribution of biomass combustion during night time. The deconvolution of BC to its components, namely wood burning (BC_{wb}) and fossil fuel combustion (BC_{ff}), allows us to understand the current contributions of the two processes in BC levels. However, since BC measurements are available only during the last years, the

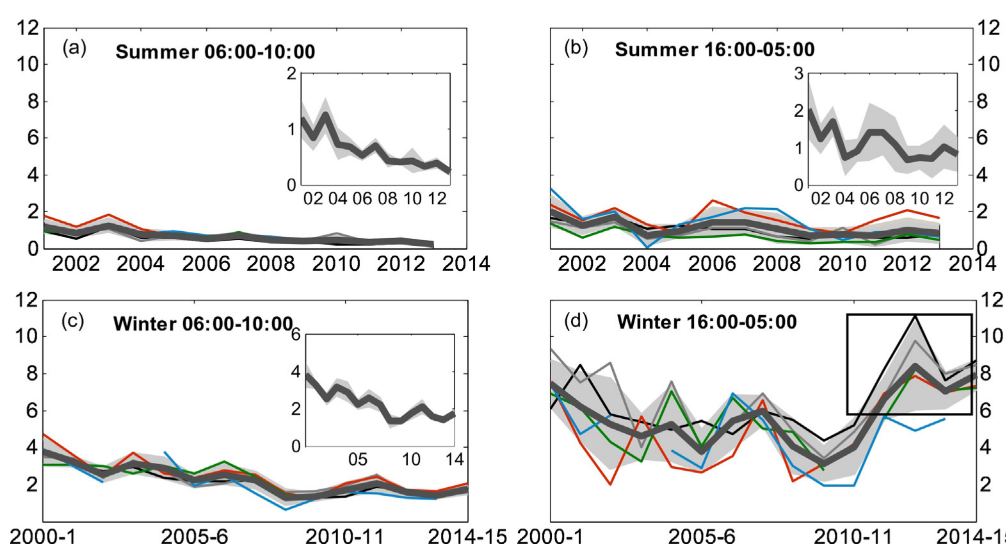


Fig. 8. Mean integrals of the morning and evening CO peaks for summer (top panels) and winter months (bottom panels) calculated for Marousi (black line), N.·Smyrni (light grey line), Athinas (red line), Geoponiki (green line) and Piraeus (blue line) stations (please consider the different scale used in each case). The dark grey curve corresponds to the mean value of all five stations and the grey shaded area represents the standard deviation (1 σ). In the internal panels in (a), (b) and (c) the mean value is reproduced in different scale to highlight the existing trend over time. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

aforementioned relation between BC and CO, was used to go back in time.

The interannual changes of the relevant contribution of wood burning and fossil fuel combustion were revealed via calculation of morning (06:00–10:00 LT) and evening (16:00–05:00 LT) integrals of the CO concentrations for the last 15 years. The results of this analysis demonstrate that:

(i) CO concentrations during the morning traffic peak decrease constantly over time (by almost 50% since 2000) and during both seasons (summer, winter). This reflects the decrease of fossil fuel combustion during the last 15 years, which can be attributed both to the gradual renewal of the vehicles fleet (or other countermeasures adopted to achieve EU cut of pollutant emissions), and to the economic crisis during the last years. The latter has been evidenced in Greece as a general cut down on industrial activity and vehicles use.

(ii) The impact of biomass burning becomes dominant during winter since 2011, when the price of oil was affected by the financial crisis. This is evident by the respective significant increase of winter evening CO integrals. The competition between activities cut down due to the crisis and the increase of wood burning use is shown via the ratio between evening CO peak values to morning values, which has been constantly increasing during the last four years (41% increase at urban background stations).

The decomposition of CO to CO_{wb} and CO_{ff}, showed that CO_{wb} contribution is about 50% during night time (21:00–00:00 LT), suggesting that emissions from biomass combustion have indeed gained an increasing role in night time atmospheric pollution levels in Athens.

Overall, it is deduced that the shift of Athens' habitants to wood burning, as major fuel for heating purposes, has significant impact on Athens' air quality (as revealed by the CO levels), which is to the opposite direction of the impact from reduced fossil fuel consumption. The importance of this study lies on the fact that it quantifies the diachronic changes in air pollution in Athens and links it with several socioeconomic factors (e.g. measures, economic crisis, behavioural changes), while it can serve as reference in the future for assessing and evaluating expected mitigation measures. The intensive campaigns that have taken place in Athens during the last few winters provide significant information and details about the physical and chemical characteristics of wood burning in Athens, and will support the increasing evidence of the impacts of residential wood burning not only in Greece but also in Europe as a whole.

Acknowledgements

This study was in part supported by the Excellence Research Program GSRT (2015–2017) ARISTOTELIS "Environment, Space and Geodynamics/Seismology 2015–2017" in the framework of Programmatic Agreements between Research Centres GSRT 2015–2017 and by the "Development Proposals of Research Entities - KRIPIS" project, funded by Greece and ERDF/EU in the frame of NSRF and the O.P. Competitiveness and Entrepreneurship and the Regional Operational Program of Attica, Action: "THESPIA-Development of synergistic and integrated methods and tools for monitoring, management and forecasting of Environmental parameters and pressures". The authors acknowledge the Hellenic Ministry of the Environment & Energy, Dept. of Air Quality, for the provision of datasets used in this study. We also thank K. Fameli for developing the map of Athens.

References

Beeson, W.L., David, E.A., Knutsen, F., 1998. Long-term concentrations of ambient air pollutants and incident lung cancer in California adults: results from the AHSMOG study. Environ. Health Perspect. 106 (12), 813–823.

Castellanos, P., Boersma, K.F., 2012. Reductions in nitrogen oxides over Europe driven by environmental policy and economic recession. Sci. Rep. 2 (265). http://dx.doi.org/10.1038/srep00265.

Chaloulakou, A., Kassomenos, P., Spyrellis, N., Demokritou, P., Koutrakis, P., 2003. Measurements of PM_{10} and $PM_{2.5}$ particle concentrations in Athens, Greece. Atmos. Environ. 37, 649–660.

Collaud, Coen M., 2010. Minimizing light absorption measurement artifacts of the aethalometer: evaluation of five correction algorithms. Atmos. Meas. Tech. 3: 457–474. http://dx.doi.org/10.5194/amt-3-457-2010.

Crippa, M., De Carlo, P.F., Slowik, J.G., Mohr, C., Heringa, M.F., Chirico, R., Poulain, L., Freutel, F., Sciare, J., Cozic, J., Di Marco, C.F., Elsasse, M., Nicolas, J.B., Marchand, N., Abidi, E., Wiedensohler, A., Drewnick, F., Schneider, J., Borrmann, S., Nemitz, E., Zimmermann, R., Jaffrezo, J.L., Prévot, A.S.H., Baltensperger, U., 2013. Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris. Atmos. Chem. Phys. 13:961–981. http://dx.doi.org/10.5194/acp-13-961-2013.

Crutzen, P.J., Zimmermann, P.H., 1991. The changing photochemistry of the troposphere. Tellus 43, 136–151.

Cusack, M., Pérez, N., Pey, J., Alastuey, A., Querol, X., 2013. Source apportionment of fine PM and sub-micron particle number concentrations at a regional background site in the western Mediterranean: a 2.5 year study. Atmos. Chem. Phys. 13, 5173–5187.

Dimitriou, K., Paschalidou, A.K., Kassomenos, P.A., 2013. Assessing air quality with regards to its effect on human health in the European Union through air quality indices. Ecol. Indic. 27:108–115. http://dx.doi.org/10.1016/j.ecolind.2012.11.023.

Fameli, K., Assimakopoulos, V., 2016. The new open flexible emission inventory for Greece and the Greater Athens Area (FEI-GREGAA): account of pollutant sources and their importance from 2006–2012. Atmos. Environ. 137:17–37. http://dx.doi.org/10.1016/j.atmsenv.2016.04.004.

Favez, O., El Haddad, I., Piot, C., Borave, A., Abidi, E., Marchand, N., Jaffrezo, J.-L., Besombes, J.-L., Personnaz, M.-B., Sciare, J., Wortham, H., George, C., D'Anna, B., 2010. Inter-comparison of source apportionment models for the estimation of wood burning aerosols during wintertime in an Alpine city (Grenoble, France). Atmos. Chem. Phys. 10 (12), 5295–5314.

Fenger, J., Hertel, O., Palmgren, F., 2013. Urban Air Pollution – European Aspects, Environmental Pollution. Springer Science & Business Media http://dx.doi.org/10.1007/978-94-015-9080-8 (ISBN 978-90-481-5147-9).

Florou, K., Papanastasiou, D., Pikridas, M., Kaltsonoudis, C., Louvaris, E., Gkatzelis, E., Patoulias, D., Mihalopoulos, M., Pandis, S., 2016. The contribution of wood burning and other pollution sources to wintertime organic aerosol levels in two Greek cities. Atmos. Chem. Phys. Discuss. http://dx.doi.org/10.5194/acp-2016-721.

Fourtziou, L., Liakakou, E., Stavroulas, I., Theodosi, C., Zarbas, P., Psiloglou, B., Sciare, J., Maggos, T., Bairachtari, K., Bougiatioti, A., Gerasopoulos, E., Sarda, R., Bonnaire, N., Mihalopoulos, N., 2017. Multi-tracer approach to characterize domestic wood burning in Athens (Greece) during wintertime. Atmos. Environ. 148:89–101. http://dx.doi.org/10.1016/j.atmsenv.2016.10.011.

Gerasopoulos, E., Gratsea, M., Liakakou, E., Lianou, M., Psiloglou, B., Kappos, N., Kambezidis, H., Mihalopoulos, N., 2016. An overview of biomass burning impacts on Athens air quality and analysis of its increasing significance, 13th International Conference on Meteorology. Climatol. Atmos. Phys. COMECAP.

Kalabokas, P., Viras, L., Repapis, C., 1999. Analysis of the 11-year record (1987-1997) of air pollution measurements in Athens, Greece. Part I: Primary air pollutants. Glob. Nest: Int. J. 1 (3), 157–167.

Kallos, G., Kassomenos, P., Pielke, R., 1993. Synoptic and mesoscale weather conditions during air pollution episodes in Athens, Greece. Bound.-Layer Meteorol. 62, 163–184.

Kampa, M., Castanas, E., 2008. Human health efects of air pollution. Environ. Pollut. 151 (2):362–367. http://dx.doi.org/10.1016/j.envpol.2007.06.012.

Kassomenos, P., Kotroni, V., Kallos, G., 1995. Analysis of climatological and air quality observations from greater Athens area. Atmos. Environ. 29 (24), 3671–3688.

Katsoulis, B., 1996. The relationship between synoptic, mesoscale and microscale meteorological parameters during poor air quality events in Athens, Greece. Sci. Total Environ. 181, 13–24.

Kourtidis, K.A., Ziomas, I.C., Rappenglueck, B., Proyou, A., Balis, D., 1999. Evaporative traffic hydrocarbon emissions, traffic CO and speciated HC traffic emissions from the city of Athens. Atmos. Environ. 33, 3831–3842.

Lalas, D.P., Veirs, V.R., Karras, G., Kallos, G., 1982. An analysis of the SO2 concentration levels in Athens, Greece. Atmos. Environ. 16, 531–544.

Lyamani, H., Olmo, F.J., Foyo, I., Alados-Arboleds, L., 2011. Black carbon aerosols over an urban ares in south-eastern Spain: changes detected after the 2008 economic crisis. Atmos. Environ. 45, 6423–6432.

Paraskevopoulou, D., Liakakou, E., Gerasopoulos, E., Theodosi, C., Mihalopoulos, N., 2014. Long-term characterization of organic and elemental carbon in the $PM_{2.5}$ fraction: the case of Athens, Greece. Atmos. Chem. Phys. 14:13313–13325. http://dx.doi.org/10.5194/acp-14-13313-2014.

Paraskevopoulou, D., Liakakou, E., Gerasopoulos, E., Mihalopoulos, N., 2015. Sources of atmospheric aerosol from long-term measurements (5 years) of chemical composition in Athens, Greece. Sci. Total Environ. 527–528:165–178. http://dx.doi.org/10.1016/j.scitotenv.2015.04.022.

Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, A., Legrand, M., Preunkert, S., Pio, C.A., 2007. Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background. J. Geophys. Res. Atmos. 112 (23).

Saffari, A., Daher, N., Samara, C., Voutsa, D., Kouras, A., Manoli, E., Karagkiozidou, O., Vlachokostas, C., Moussiopoulos, N., Shafer, M., Schauer, J., Sioutas, C., 2013. Increased biomass burning due to economic crisis in Greece and its adverse impact on wintertime air quality in Thessaliniki. Environ. Sci. Technol. 47 (23):13313–13320. http://dx.doi.org/10.1021/es403847h.

Saurer, M., Prevot, A.S.H., Domnen, J., Sandradewi, J., Baltensperger, U., Siegwolf, T.H., 2009. The influence of traffic and wood combustion on the stable isotopic composition of carbon monoxide. Atmos. Chem. Phys. 9, 3147–3161.

Sciare, J., D'Argouges, O., Sarda-Estve, R., Gaimoz, C., Dolgorouky, C., Bonnaire, N., Favez, O., Bonsang, B., Gros, V., 2011. Large contribution of water-insoluble secondary organic aerosols in the region of Paris (France) during wintertime. J. Geophys. Res.-Atmos. 116 (22).

Sharma, S., Brook, J.R., Cachier, H., Chow, J., Gaudenzi, A., Lu, G., 2002. Light absorption and thermal measurements of black carbon in different regions of Canada. J. Geophys. Res. 107 (D24) (AAC 11-1-AAC 11-11). 10.1029/2002JD002496.

Van Dop, H., Kallos, G., 2012. Air Pollution Modeling and Its Application IX. Nato Challenges of Modern Society 17. Springer Science & Business Media (ISBN: 1461530520, 9781461530527).

Voutsa, D., Anthemidis, A., Giakisikli, G., Mitani, K., Besis, A., Tsolakidou, A., Samara, C., 2015. Size distribution of total and water-soluble fractions of particle-bound elements – assessment of possible risks via inhalation. Environ. Sci. Pollut. Res. 22 (17):13412–13426. http://dx.doi.org/10.1007/s11356-015-4559-7.

Vrekoussis, M., Richter, A., Hilboll, A., Burrows, J.P., Gerasopoulos, E., Lelieveld, J., Barrie, L., Zerefos, C., Mihalopoulos, N., 2013. Economic crisis detected from space: air quality observations over Athens/Greece. Geophys. Res. Lett. 40:458–463. http://dx.doi.org/10.1002/grl.50118.

Wang, X., Westerdahl, D., Chen, L.C., Wu, Y., Hao, J., Pan, X., Guo, X., Zhang, K.M., 2009. Evaluating the air quality impacts of the 2008 Beijing Olympic games: on-road emission factor and black carbon profiles. Atmos. Environ. 43:4535–4543. http://dx.doi.org/10.1016/j.atmosenv.2009.06.054.

Weingartner, E., Saathoff, H., Schnaiter, M., Streit, N., Bitnar, B., Baltensperger, U., 2003. Absorption of light by soot particles: determination of the absorption coefficient by means of aethalometers. J. Aerosol Sci. 34:1445–1463. http://dx.doi.org/10.1016/S0021-8502(03)00359-8.

Ziomas, I., Tzoumaka, P., Balis, D., Melas, D., Zerefos, C., Klemm, O., 1998. Ozone episodes in Athens, Greece.A modelling approach using data from the medcaphot-trace. Atmos. Environ. 32 (12), 2313–2321.