



A modeling study of the impact of the 2007 Greek forest fires on the gaseous pollutant levels in the Eastern Mediterranean



A. Poupkou^{a,*}, K. Markakis^a, N. Liora^a, T.M. Giannaros^{a,2}, P. Zanis^b, U. Im^{c,1}, N. Daskalakis^{c,d}, S. Myriokefalitakis^c, J.W. Kaiser^{e,f,g}, D. Melas^a, M. Kanakidou^c, T. Karacostas^b, C. Zerefos^{h,i}

^a Laboratory of Atmospheric Physics, Department of Physics, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece

^b Department of Meteorology and Climatology, School of Geology, Aristotle University of Thessaloniki, Thessaloniki, Greece

^c Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, Irakleio, Greece

^d Foundation for Research and Technology – Hellas, Institute of Chemical Engineering Sciences, Patras, Greece

^e King's College London, London, United Kingdom

^f European Centre for Medium-Range Weather Forecasts, Reading, United Kingdom

^g Max Planck Institute for Chemistry, Mainz, Germany

^h Research Centre for Atmospheric Physics and Climatology, Academy of Athens, Athens, Greece

ⁱ Navarino Environmental Observatory (N.E.O.), Messinia, Greece

ARTICLE INFO

Article history:

Received 21 January 2014

Received in revised form 15 May 2014

Accepted 15 May 2014

Available online 25 May 2014

Keywords:

Forest fires

Eastern Mediterranean

Air quality

Process analysis

ABSTRACT

The main objective of the present study is the assessment of the non-radiative impact on the lower troposphere air quality of the intense biomass burning events that took place in the Eastern Mediterranean, when wild forest fires were burning in Peloponnesus (Greece) at the end of August 2007. The MM5-CAMx modeling system was applied in the Eastern Mediterranean in high spatial and temporal resolution for the period 23 to 31 August 2007, forced by biomass burning emission fluxes from the Global Fire Emissions Database (version 3.0), in day-to-day temporal and 0.1° spatial variability from the Global Fire Assimilation System. Enhancements of the CO and NO_x concentrations over almost the entire modeling domain were estimated due to the biomass burning, which were more pronounced over the burnt areas and maximum over the Peloponnesus forest fires. The domain-wide near surface mean concentration was higher by +6% for CO and +11% for NO_x because of the biomass burning. The near surface O₃ values were reduced over the fire hot spots but increased over the greater part of the modeling domain. On the 26th August 2007, the maximum O₃ concentrations reduction of about 12 ppb (i.e. –34%) was calculated over the Peloponnesus fires while the highest O₃ increase of about 27 ppb (i.e. +52%) was estimated over the sea at 500 km downwind the Peloponnesus large forest fires. The process analysis revealed that on that day, the inclusion of the biomass burning emissions resulted in an enhancement of the daytime gas phase O₃ production in the boundary layer in the Eastern Mediterranean and during some daytime hours in a change of the chemical regime from O₃ destruction to O₃ production. From 6 to 16 UTC, the O₃ photochemistry in the boundary layer was VOC-sensitive close to the Peloponnesus fires, gradually changing to NO_x-sensitive in the downwind fire plume. In the same period, the maximum impact on the oxidizing capacity of the boundary layer was an increase by 0.25 ppt for OH and a reduction by 13 ppt for HO₂ mean concentrations over the Peloponnesus forest fires and an increase by 12 ppt for HO₂ in the downwind plume.

© 2014 Elsevier B.V. All rights reserved.

* Corresponding author. Tel.: +30 2310998009.

E-mail address: poupkou@auth.gr (A. Poupkou).

¹ Now at: Joint Research Centre (JRC), Air and Climate Unit, Ispra (VA), Italy.

² Now at: National Observatory of Athens, Institute of Environmental Research and Sustainable Development, Vas. Pavlou & I. Metaxa, 15236, Penteli, Athens, Greece.

1. Introduction

Open biomass burning has been recognized as an important source of pollutants emitted in the atmosphere, mainly carbon monoxide (CO), nitrogen oxides (NO_x), volatile organic compounds (VOCs) and particulate matter (PM). Biomass burning is critical for the air quality on local, regional and hemispheric scales and is an important component of the climate system (Carvalho et al., 2011; Sofiev et al., 2009; Schultz et al., 2008). Their impact on air quality depends also on whether the plume is confined in the boundary layer or emitted also above it and transported downwind over very long distances, e.g. emission and transport of ozone (O₃) precursors, such as CO, NO_x, and VOCs, the chemistry of which can produce large surface O₃ concentrations far away from the initial emission location (Amiridis et al., 2010; Coheur et al., 2009; Freitas et al., 2007; Langmann et al., 2009; Morris et al., 2006).

The Eastern Mediterranean during summertime is characterized by specific meteorological and climate conditions (i.e. sunny, hot and dry climate) that favor the enhanced photochemistry and the possible increased danger for fire events. North sector winds, i.e. the Etesian winds, are blowing in the Aegean Sea with great constancy during the summer and early autumn. The Etesians blow in sequences of several days and can reach gale force (Poupkou et al., 2011) allowing long range transport of pollution and possibly enhancing the fire propagation in case of a biomass burning event in Greece. In summer, in the Eastern Mediterranean, the biomass burning emissions are mixed with a diversity of anthropogenic emissions of pollutants emitted in urban scale, i.e. in the megacity of Istanbul and other large urban agglomerations like Athens, as well as in regional scale, like for example the pollutant emissions from the maritime transport in the study domain which connects Europe, Asia and Africa and is characterized by long coastline and numerous islands. They are also mixed with natural emissions (e.g. high VOCs emissions from vegetation in summertime) (Symeonidis et al., 2008).

Including fire effects on the air quality assessment and modeling has become more frequent during the past decade (Martins et al., 2012; Konovalov et al., 2011; Pfister et al., 2008; Junquera et al., 2005). Evaluating and accounting for biomass burning emissions in the analyses of regional air quality and climate model results are important especially for the southeastern Europe, since future scenarios on climate change indicate that the already hot and dry climate of this area is expected to become warmer and drier (Zanis et al., 2009) and such climate conditions may trigger increased fire occurrence (Amiridis et al., 2012). Under this view, this study makes a contribution to the limited modeling studies related with the impact of biomass burning on the air quality in the Eastern Mediterranean (Drori et al., 2012; Hodnebrog et al., 2012; Lazaridis et al., 2008) and to the climate change impact research.

The inclusion of gas and particulate emissions from open biomass burning in chemistry transport models is a challenging task because of the large uncertainties related to the estimation of fire pollutant emissions and the injection height of the smoke. The main uncertainties in the estimation of biomass burning emissions are related to the detection of fires, the emission factors associated with the type of vegetation, the

pollutants emitted, the temporal evolution of fires and the vegetation and fire characteristics. Emission factors for over 100 chemical components have been experimentally calculated for a range of biomes (Akagi et al., 2011; Andreae and Merlet, 2001). However, several important features of fires that influence the amount of material emitted by the fire may not be captured in many emission factors used in these estimates, including the fire phases (i.e. the flaming and smoldering phases). In addition, variation in timing of fires (or seasonality) is responsible for variation of emission factors within a biome (Keywood et al., 2013). According to Langmann et al. (2009) and Monks et al. (2009), the accumulation of uncertainties at virtually every step in the emission estimation process results in a factor of two variations in global estimates of carbon emissions from fires. The existence of large differences that can be of an order of magnitude, in the European scale forest fires CO emissions has been identified in NATAIR (2007). Large forest fires can generate smoke plumes with large vertical extent due to the release of heat in the combustion process. Determining the correct injection height of emissions is essential since transport and deposition processes are very sensitive to altitude (Pizzigalli et al., 2012). Methods have been proposed in literature to estimate the injection height of fire emissions either using some empirical relationship between the injection height and fire intensity (Lavoue et al., 2000) or estimations of the fire buoyant efficiency (Hodzic et al., 2007) or a more refined sub-grid scale plume rise mechanism (Freitas et al., 2007). However, in air quality modeling studies, fire emissions are commonly distributed within the boundary layer or in a few layers close to the surface (Martins et al., 2012; Wang et al., 2006).

There have been previously studies revealing the important impact of open biomass burning on the air quality in regional scale. Konovalov et al. (2011) used a modified version of the chemistry transport model CHIMERE in order to study the influence of the numerous biomass burning events during the 2010 summer over the European Russia on the air pollution levels in the Moscow region. The model results showed that the wildfires were the principal factor causing air pollution episodes associated with extremely high levels of daily mean CO and PM10 concentrations (up to 10 mg m⁻³ and 700 µg m⁻³ in the averages over available monitoring sites, respectively). Lazaridis et al. (2008) applied the air quality modeling system UAM-AERO to quantify the contribution of widespread forest fires in the Greek mainland to the air pollution levels in Greece during the period 12 to 16 July 2000. It was estimated that the forest fire emissions were the largest contributors to the gaseous and particulate air pollution problem in regions tens of kilometers away from the fire source. An average contribution of 50% to the PM10 concentration over the region around the burnt area and downwind of the fire source (approximately 500 km) was calculated with a maximum of 80%, whereas, for CO, the average contribution was 50% during the study period. The photochemical model CAMx was used to characterize the extent of dispersion of the vegetation fire emissions and the photochemistry associated with the fire emissions in southeast Texas in August and September of 2000 (Junquera et al., 2005). The study revealed that although the dispersion and photochemical impacts varied from fire to fire, for fires less than 10,000 acres, the greatest enhancements of CO and O₃ concentrations due to the fire emissions were generally

confined to regions within 10–100 km of the fire. Within 10 km of these fires, CO concentrations exceeded 2 ppm and O₃ concentrations were enhanced by 60 ppb. Simulations with and without biomass burning emissions with the Models-3 CMAQ model were conducted to quantify the impacts of biomass burning on tropospheric concentrations of CO and O₃ in Southeast Asia during the period 17 to 24 March 2001 when considerable biomass burning took place in southeast Asia and southern China (Zhang et al., 2003). Biomass burning was found to contribute more than 50% of the CO concentrations and up to 40% of the O₃ concentrations in the boundary layer over the major source regions.

The summer of 2007 was one of the worst fire seasons for the Eastern Mediterranean. Large forest fires took place in Greece (more specifically in Peloponnesus and Evia) from late August to early September 2007. The fires in Peloponnesus were more severe during the period from 23 to 31 August 2007. Apart from the direct tragic fire damage (human losses and land burnt), large quantities of pollutants were emitted in the atmosphere influencing its composition. The fires broke out after three consecutive heat waves, while their increasing size was a result of the extreme drought and hot conditions coupled with very strong winds, especially in the last week of August in Peloponnesus (EC, 2008). According to Founda and Giannakopoulos (2009), the 2007 summer was abnormally warm for many areas of southeastern Europe, the Balkan Peninsula and parts of Asia Minor with departures from the seasonal means exceeding 4 °C in some areas but also distinct periods of extremely hot weather. Seasonal (June to August) temperature anomalies at the National Observatory of Athens exceeded 3 °C corresponding to more than 3 standard deviations with respect to the 1961–1990 reference period. According to the results of the regional climate models, the frequency of heat waves, similar to those of the summer 2007, is expected to increase in the Eastern Mediterranean due to climate change (Hodnebrog et al., 2012; Turquety et al., 2009).

The intense 2007 Greek forest fires and their impact on the chemical composition of the atmosphere in the Eastern Mediterranean have been presented in a few previous studies which were based mainly on the use of remote sensing observations (Coheur et al., 2009; Kaskaoutis et al., 2011; Liu et al., 2009; Turquety et al., 2009). In Hodnebrog et al. (2012), two regional atmospheric chemistry models were used, in rather coarse resolution (25 km), in order to quantify the influences of various processes (including forest fire emissions) on the elevated O₃ levels in the Eastern Mediterranean during summer 2007. According to Hodnebrog et al. (2012), forest fire emissions from Greece and Albania contributed substantially to O₃ production, particularly in the latter half of July and in the end of August 2007. In the seasonal average, the models calculated forest fire impacts on daily maximum O₃ up to 18 ppbv near the center of the plume, but with large differences between the two different emission inventories used in the study (the Fire INventory from NCAR (version 1) (FINN v.1) (Wiedinmyer et al., 2011) and the Global Fire Emission Database (version 2) (GFED v.2) (Van der Werf et al., 2006)).

In this paper, we use a high resolution pollutant emission inventory and air quality modeling system, in order to investigate the non-radiative impact on the near surface and boundary layer air quality and the atmospheric processes

in the Eastern Mediterranean of an intense open biomass burning event as that of the extreme forest fires in Greece in the end of August 2007 (during the same period, widespread fires occurred in Albania too). Emphasis is given on the gas phase pollutants. In Section 2, the modeling system and the emission data used are presented. In Section 3, CAMx results are verified against ground-based observations and the changes due to open biomass burning in the CO, NO_x and O₃ concentrations near the surface and in the boundary layer are presented for the study area. Section 4 is devoted to the discussion of the results from the physical and chemical process analysis performed which are linked with the impact of biomass burning on the atmospheric processes that determine the concentrations of several pollutants like O₃, NO_x, CO and HNO₃, and on the oxidizing capacity of the atmosphere in the boundary layer in the Eastern Mediterranean. In the same section, the O₃ sensitivity with respect to its precursors (VOCs and NO_x) in the case of the extreme biomass burning event in the study area is examined. The conclusions of this study are presented in Section 5.

2. Data and methodology

In the present study, a three-dimensional modeling system was applied that consisted of the photochemical air quality model CAMx (version 5.30), off-line coupled with the meso-scale meteorological model MM5 (version 3.7). MM5 and CAMx are well documented numerical models which are widely used by the scientific community for the simulation of air quality in regional scale. CAMx has the advantage of being applied with the option of the process analysis tool which has been designed to provide in-depth analyses of the physical and chemical processes in an air quality model and which was necessary in order to better describe the impact on the air quality of the intense biomass burning events that took place in Greece in late August 2007 (see the Discussion section).

The study area was the Eastern Mediterranean. The MM5 and CAMx models have been used in previous published studies in order to simulate the air quality in the Eastern Mediterranean either independently (Poupkou et al., 2009; Astitha et al., 2008; Amiridis et al., 2007; Zanis et al., 2007) or jointly (Katrakou et al., 2007; Poupkou et al., 2006). The MM5–CAMx modeling system has been also used for air quality forecasting purposes over the Balkan Peninsula in the framework of the EU FP6 project “Global and regional Earth-system Monitoring using Satellite and in-situ data” (GEMS). The simulation period extended from 23 to 31 August 2007. During these days, Greece suffered the worst forest fires in the past 50 years (Liu et al., 2009). Five major fires in Peloponnesus burnt a total of 170,000 ha while two other fires at the same time in Evia burned 25,000 ha of land and more than 70% of the final total burnt areas in the 2007 season resulted from the above 7 forest fires (EC, 2008).

Following is a more detailed presentation of the modeling system applied along with the description of the input data used.

2.1. Modeling system description

2.1.1. The meteorological model

MM5 is a limited-area, nonhydrostatic, terrain following sigma-coordinate model designed to simulate or predict the

mesoscale atmospheric circulation (Grell et al., 1994). MM5 produced the gridded, hourly meteorological data that were necessary to drive the air quality model over the study domain. MM5 was implemented with the option of two-way nesting for two nested grids. The coarse grid, covering Europe, consisted of 199×175 grid cells having horizontal spatial resolution of 30 km. The fine grid, having a horizontal mesh width of 10 km, covered the Eastern Mediterranean area and consisted of 220×181 grid cells. Both grids had the same vertical structure of 29 σ levels. The model top was at 100 hPa. For the MM5 simulations, initial and boundary conditions were developed using the $1^\circ \times 1^\circ$ spatial resolution and 6-h temporal resolution final atmospheric analysis (FNL) surface and pressure level data of the National Centre for Environmental Predictions (NCEP). The elevation and the 25-category land-use data were derived from the U.S. Geological Survey Data Center and had 10-min and 5-min horizontal resolution for the coarse and fine domain, respectively.

2.1.2. The air quality model

The Comprehensive Air quality Model with extensions (CAMx) is an Eulerian photochemical dispersion model that allows for an integrated “one-atmosphere” assessment of atmospheric pollution over many scales ranging from sub-urban to continental (ENVIRON, 2010). CAMx simulated the emission, dispersion, chemical reaction, and removal of pollutants in the troposphere by solving the Eulerian continuity equation for each chemical species on a three-dimensional Lambert Conic Conformal (LCC) grid with 174×208 grid cells of high spatial resolution (10 km) covering the Eastern Mediterranean area (Fig. 1). The vertical domain consisted of 17 vertical layers extending

up to about 10 km above ground level (agl). The first model layer height was about 25 m agl. The gas-phase chemical mechanism employed was the 2005 version of Carbon Bond (CB05) (Yarwood et al., 2005).

The daily varying chemical boundary conditions for CAMx runs were taken from the global model TM4-ECPL (Myriokefalitakis et al., 2011). CAMx was applied with a one week spin-up period.

The zero-out modeling method was used and 2 emission scenarios were examined; CAMx was applied including (“with BB” scenario) and excluding (“without BB” scenario) open biomass burning emissions.

2.1.3. Pollutant emission data

The gaseous (NO_x, sulfur dioxide (SO₂), non-methane volatile organic compounds (NMVOCs), ammonia (NH₃) and CO) and particulate matter (PM₁₀ and PM_{2.5}) anthropogenic emission inventory used in CAMx runs for the area emission sources in the study area was compiled by the French National Institute for Industrial Environment and Risks (INERIS) (data provided in the framework of the EU project CITYZEN) (Im et al., 2011a). The emission inventory was based on the 0.5° resolution annual sectoral emission data for the reference year 2007 taken from the EMEP database. The EMEP emissions were regridded to a high resolution $0.1^\circ \times 0.1^\circ$ longitude/latitude grid using as a proxy the high resolution (300 m) global land cover database of GlobCover (<http://ionial.esrin.esa.int/>). Only for the energy sector, pollutant emissions were taken from The Netherlands Organisation (TNO) emission database (reference year 2005) since the database included annual emission data for both point and area energy sector sources (area emissions were in 30 km spatial resolution) (Kuenen et al., 2011).

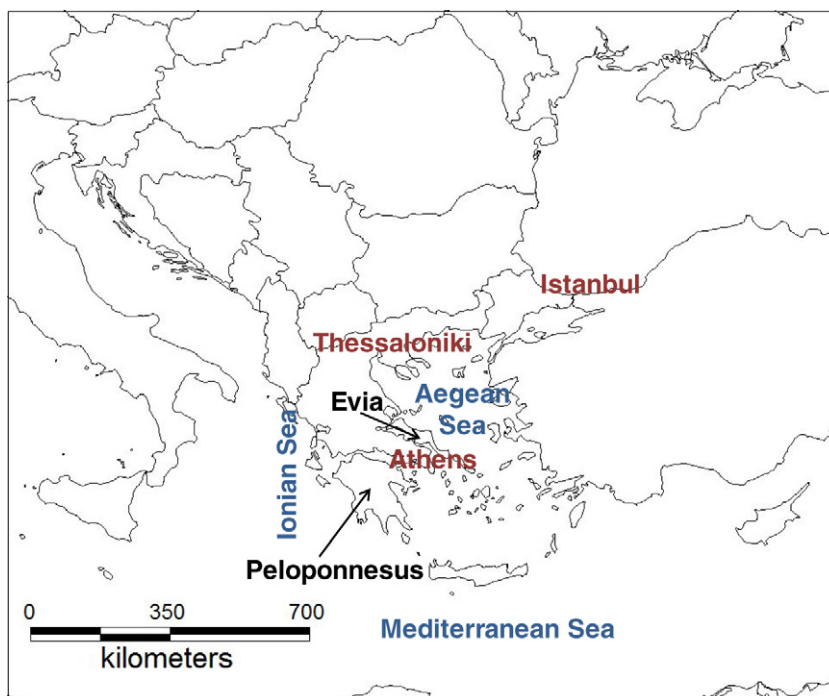


Fig. 1. The CAMx modeling domain.

For the large Greek urban agglomerations of Athens and Thessaloniki and the Istanbul megacity, detailed emissions were accounted for according to Markakis et al. (2010a, 2010b, 2012), calculated while employing bottom-up methodologies for the most important anthropogenic emission source sectors and using real activity information as well as high resolution digital maps (EEA, 2000) to distribute the emissions. As for the emission sectors for which detailed activity data were not available, top-down methodologies were applied. More specifically, the inventory for the city of Istanbul included gridded (in 2 km spatial resolution) and hourly resolved emission rates for gaseous and PM pollutants (Markakis et al., 2012). Emissions of several sources such as road transport, combustion in industries, domestic combustion and cargo shipping were calculated on the basis of detailed activity data provided by the local authorities. The gaseous and PM pollutant emission inventories for the cities of Athens and Thessaloniki were compiled in 2 km resolution using activity information and statistics for the traffic loads in the major roads of the cities, the heating fuel consumptions, the off-road vehicle fleets and the emissions for all major industrial units (Markakis et al., 2010a, 2010b). The aforementioned emission inventories have already been employed and evaluated in previous modeling studies (Im et al., 2010, 2011a, 2011b, 2012).

The annual and spatially resolved sectoral emission data for the Eastern Mediterranean and for the cities of Athens, Thessaloniki and Istanbul were spatially integrated, separately for each emission sector, in the 10 km spatial resolution CAMx grid with the use of the MOSES emission model (Markakis et al., 2013). Following, the emissions were temporally analyzed and chemically speciated using the MOSES emission model. Finally, the emission data were summed up so as to compile the temporal analysed and chemically speciated inventory of the total anthropogenic emissions over the 10 km spatial resolution CAMx grid.

Emissions from natural sources were also accounted for in the simulations. More specifically, the emissions of biogenic NMVOCs, sea salt and windblown dust were estimated in 10 km spatial resolution and on hourly basis while applying the Natural Emission Model (NEMO) which was driven by the meteorology of the MM5 model (Markakis et al., 2009; Poupkou et al., 2010).

The open biomass burning emission data that were used for the simulations were produced in the framework of the FP7 EU project MACC (Kaiser et al., 2011). The data were based on the Global Fire Emissions Database (GFED, version 3.0) (van der Werf et al., 2010). GFED3.0 includes fire emissions for the 1997–2008 period on a $0.5^\circ \times 0.5^\circ$ spatial resolution with a monthly time step, calculated with the use of a revised version of the CASA biogeochemical model and improved satellite-derived estimates of area burned and plant productivity. In the framework of MACC project, the Global Fire Assimilation System (GFAS) (Kaiser et al., 2012) was developed to represent the global distribution of fires on high spatial resolution grids ($0.5^\circ \times 0.5^\circ$ and $0.1^\circ \times 0.1^\circ$) based on MODIS observations of Fire Radiative Power (FRP). The daily representations of the MODIS observations in GFAS were used to redistribute the GFED3.0 emission data with higher spatial and temporal (daily values) resolutions. These fire emission data (up to the year 2008) have already

been used in the MACC eight-year reanalysis of the global atmospheric composition covering the period 2003–2010 (Inness et al., 2013).

Biomass burning emissions of the following pollutants were included in the CAMx runs: CO, NO_x, NH₃, SO₂, methane (CH₄), NMVOCs and PM_{2.5}. The 0.1° spatial resolution GFED3 emissions were reprojected in the 10 km spatial resolution LCC CAMx grid over the Eastern Mediterranean using a Geographical Information System (GIS). In order to allow the vertical distribution of the biomass burning emissions within CAMx, the fires had to be modeled as point sources (Junquera et al., 2005). Each fire was modeled as a series of point sources with identical location (i.e. the center of each grid cell) and different heights, so that the emissions would be distributed vertically within the CAMx layers. About 60% of the emissions were injected in the first 1000 m agl and 40% of the emissions from 1000 m to 2000 m agl according to Dentener et al. (2006). This is in consistency with Liu et al. (2009) according to which on the 26th August 2007, when the fires in Peloponnesus were burning severely, the satellite sensor Multiangle Imaging SpectroRadiometer (MISR) retrieved smoke plume top heights indicated that the smoke in the fire source area in the west coast of Peloponnesus might have been injected as high as about 2.5 km. The emissions from each point source were instantly dispersed into the entire grid cell volume, given by the grid cell area and the height of the vertical layer. No diurnal variation of the daily wildfire emission data was assumed in the model runs (Junquera et al., 2005). FRP observations of the SEVIRI sensor onboard the geostationary satellite Meteosat-9 show that this is a reasonable approximation as the fires burnt throughout the nights, with a minimal intensity of about 20–50% of the daytime maxima (Kaiser et al., 2009).

Fig. 2 presents CO biomass burning emission data for the period from 23 to 31 August 2007. During this period, in the modeling domain, the fires were spatially extended mostly over Greece (mainly in Peloponnesus and Evia) and over Albania. As shown in Fig. 2, the fires burnt in the north part of Albania were more intense compared to those in the south of the country. The domain-wide biomass burning emissions and those over Peloponnesus were higher on the 25th and 26th August 2007. On these days, fires were burning at multiple sites of the study area which were more intense over Peloponnesus, Evia, Albania (mainly north), south-western FYROM and south-eastern Bulgaria. The maximum CO emission rates were found over Peloponnesus due to the large fires in extended forested areas.

The importance of the open biomass burning with respect to the amounts of pollutants emitted in the atmosphere can be identified in Table 1 which shows the anthropogenic and biomass burning gaseous pollutant emissions in Greece for the simulation period from 23 to 31 August 2007, as well as for the 25th of August 2007 when biomass burning emissions maximized. For the time period from 23 to 31 August 2007, the biomass burning emissions for all pollutants except for SO₂ are much higher than the anthropogenic ones with biomass burning to anthropogenic emission ratios that range from about 1.5 for NO_x (expressed as N) to about 35.5 for NH₃. The biomass burning SO₂ emissions are equal to about 40% of the anthropogenic emissions. On the 25th of August 2007, the biomass burning to anthropogenic emission ratios are much more pronounced. Even SO₂ biomass burning

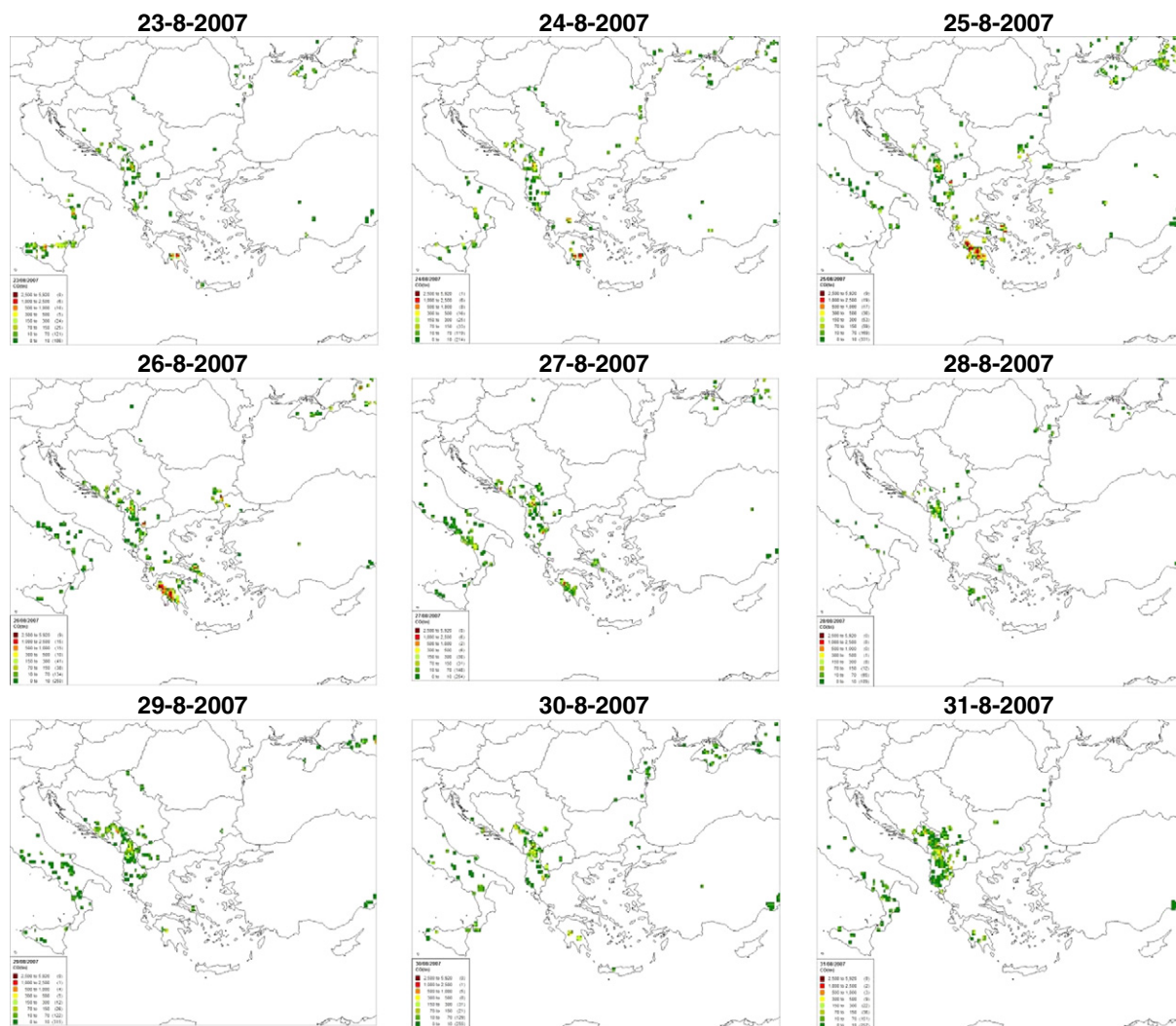


Fig. 2. Daily CO emissions (in t/gridcell/day) due to biomass burning in the Eastern Mediterranean for the period 23 to 31 August 2007.

emissions become higher than the anthropogenic ones by about 1.7 times.

In Table 2, the biomass burning emission data of this study for Greece are compared with estimated emission values published in previous studies for other fire events and time periods in different European countries and regions. Table 2 reveals that the biomass burning pollutant amounts emitted in Greece during the 9-day period from 23 to 31 August 2007 can be considered comparable with the forest fire emissions in Greece during the month of July 2000 and those in Portugal for the whole 2004 and 2005 fire seasons. The CO biomass burning emissions of this study for Greece are at least one order of magnitude lower than those from the wildfires in European Russia during the months of July and August 2010.

2.2. Metrics for of CAMx performance evaluation

The first model layer results of the photochemical model, applied when accounting for the biomass burning emissions in

model runs, were compared with observational data from suburban and rural stations in the Eastern Mediterranean so as to evaluate the model performance. Measured air quality data were taken from the EMEP Monitoring Network and the National Air Pollution Monitoring Network of the Hellenic Ministry of Environment, Energy and Climate Change (HMECC). Table S1 (provided in the Supplement) provides a description of the monitoring stations used to validate CAMx. The rural stations Aya Marina, Aliartos and Finokalia are located in Cyprus, Central Greece and Crete respectively. The suburban stations Liosia, Votanikos, Lykovrisi, Thrakomakedones, Agia Paraskevi, and Zografou are located in the greater Athens area, while the suburban stations Kalamaria and Neochorouda are sited in the greater Thessaloniki area. The stations of urban characterization were excluded from the evaluation analysis because they cannot be resolved by the model results. A map presenting the locations of the monitoring stations is provided in Fig. S1 of the Supplement.

Several statistical measures were calculated for validation while using the hourly simulated and observed concentrations

Table 1

Comparison of the biomass burning and anthropogenic gaseous emissions in Greece for selected periods of August 2007.

Pollutant	23 August to 31 August 2007			25 August 2007		
	Emissions (kt)		Emission ratio (biomass burning/anthropogenic)	Emissions (kt)		Emission ratio (biomass burning/anthropogenic)
	Biomass burning	Anthropogenic		Biomass Burning	Anthropogenic	
CO	171.8	20.3	8.5	79.7	2.0	39.9
NOx (as N)	2.6	1.7	1.5	1.2	0.2	6.0
SO ₂	1.1	3.1	0.4	0.5	0.3	1.7
NH ₃	7.1	0.2	35.5	3.3	0.02	165.0
NMVOCs	20.8 ^a	4.7 ^b	4.4	9.7 ^a	0.5 ^b	19.4
Ethene (C ₂ H ₄)	2.5	0.4	6.3	1.2	0.04	30.0
Propene (C ₃ H ₆)	1.7	0.1	17.0	0.8	0.01	80.0
Formaldehyde (HCHO)	2.3	0.2	11.5	1.1	0.02	55.0
Ethane (C ₂ H ₆)	1.2	0.1	12.0	0.5	0.01	50.0

^a Sum of methanol, ethanol, ethane, propane, higher alkanes (C ≥ 4), ethene, propene, higher alkenes (C ≥ 4), isoprene, terpenes, toluene lumped (benzene, toluene, xylene), formaldehyde, acetaldehyde, acetone, and dimethyl sulfide emissions.

^b Sum of alcohols, ethane, propane, butanes, pentanes, hexanes and higher alkanes, ethene, propene, ethyne, other alk(adi)enes and alkynes, benzene, toluene, xylenes, trimethylbenzene, other aromatics, esters, ethers, formaldehyde, other aldehydes, ketones, acids, and other NMVOCs emissions.

of NOx and O₃. CAMx results for CO were not compared with observations because during the simulation period CO was only measured in stations of urban characterization. The statistical measures calculated for each station are described in the Supplement. These measures are commonly used to assess how effectively the model reproduces the pollutants observed concentration levels (i.e. comparison of the observed and simulated mean and mean daily maximum values, estimation of bias) and the pollutants observed concentration variability (i.e. comparison between the standard deviations of observed and simulated values). The Index of Agreement is a standardized measure of the degree of model prediction error. These indicators are described in the model validation methodology that has been developed in the framework of the EU FP7 project “Promote Air Quality Services integrating Observations – Development Of Basic Localised Information for Europe (PASODOBLE)” and they have been also used in recent studies for the Eastern Mediterranean (Im et al., 2011b; Im et al., 2010.).

3. Results

3.1. CAMx evaluation results

Table 3 presents the mean and median values of the statistical measures calculated for all stations presented in Table S1. In the supplement, Table S2 shows the validation scores for each monitoring station separately.

Tables 3 and S2 indicate that the CAMx results for O₃ are satisfactory both for the mean and the mean maximum values. According to Table 3, the mean and median bias for O₃ takes small negative values and the ratios of the simulated to observed mean and mean daily maximum values are close to 1. The mean and median values of the standard deviation of the simulated O₃ concentrations (σ_s) are lower than but comparable with the corresponding ones of the observed values (σ_o). Table S2 reveals that the model errors in mean and mean maximum O₃ values are negative for most stations. According to the US Environmental Protection Agency (US EPA), model errors for O₃ in the order of ±15% suggest a good model performance for O₃ (Ziomas et al., 1998). In this study, for all stations, the errors in mean O₃ values are small to moderate ranging in absolute values from 0.5% to 24%. The errors in mean maximum O₃ values are up to 24% in absolute values; however, for most of the stations these errors are below the US EPA limit. According to Table S2, for all stations except for Finokalia, the standard deviations of the simulated O₃ concentrations are lower than those of the observed O₃ values but comparable to them for most stations. Also, for most of the stations the IOA is 0.6 and higher. The model evaluation scores for O₃ presented in this study are comparable with those in previous modeling studies focusing on the Eastern Mediterranean area (i.e. Hodnebrog et al., 2012; Im et al., 2011a; Poupkou et al., 2009).

In Table 3, the mean and median bias for NOx takes small values and the ratios of the simulated to observed mean and

Table 2

Biomass burning emissions for different European countries and regions.

Reference area	Reference period	Emissions (ktn)					Reference
		CO	NOx	SO ₂	NH ₃	NMVOCs	
Greece	23 to 31 August 2007	171.8	5.5	1.1	7.1	20.8	This study
	July 2000	157.8	5.4	1.1	1.2	14.2	
	Portugal	456.0	21.0	–	–	32.0	
Portugal	2003 fire season	137.0	7.0	–	–	10.0	Martins et al. (2012)
	2004 fire season	230.0	11.0	–	–	16.0	
	2005 fire season	30.0	–	–	–	–	
Russia (European)	June 2010	1830.0	–	–	–	–	Konovalov et al. (2011)
	July 2010	7850.0	–	–	–	–	
	August 2010	102.6	3.2	0.5	–	7.6	
Turkey and the Eastern Mediterranean	31 July to 5 August 2008	102.6	3.2	0.5	–	7.6	Baldassarre et al. (2013)

Table 3

Mean and median values of the statistical measures estimated for the monitoring stations in the Eastern Mediterranean for the period 23 to 31 August 2007.

Statistical measures ^a	O ₃		NOx	
	Mean	Median	Mean	Median
Observed mean	95.1	91.6	21.2	22.4
Simulated mean	88.1	86.1	17.7	21.4
Observed mean daily maximum	131.9	128.1	54.2	55.3
Simulated mean daily maximum	114.5	119.2	41.1	50.8
Standard deviation σ_{O}	28.4	32.4	19.0	20.0
Standard deviation σ_{S}	22.2	21.2	12.9	15.9
Bias	−6.9	−10.4	−3.5	−0.1
IOA	0.5	0.6	0.5	0.5

^a All measures are expressed in $\mu\text{g}/\text{m}^3$ except for the IOA which is unit less.

mean daily maximum values are close to 1. This is due to the fact that the model may both overestimate and underestimate the NOx values measured in the stations. As derived from Table S2, the model errors in mean NOx values have a rather wide range. In half of the stations, the errors (mostly positive) are small to moderate ranging in absolute values from 13% to 33%. In the remaining stations, the errors are mostly negative and take absolute values that can be higher than 55%. The performance of the model in reproducing the mean daily maximum NOx values is better, since in five out of the eight stations measuring NOx, the model errors (mostly positive) are small ranging in absolute values from 2% to 16%. The comparison of the standard deviations of the simulated and observed NOx concentrations indicates a tendency of the model to moderately underestimate the variability of the observed NOx values. For all stations, the IOA is moderate ranging from 0.4 to 0.6. The above suggest a rather satisfactory overall model performance for NOx. Better air quality model performance for O₃ with respect to NOx is identified in Vautard et al. (2009).

3.2. Impact on air quality

Following, the non-radiative impact of the biomass burning emissions on the gas-phase atmospheric composition in the Eastern Mediterranean is presented (the impact of temperature and radiation changes due to biomass burning on the air quality cannot be accounted for while using the off-line coupled models MM5 and CAMx).

Fig. 3 shows the differences in the mean computed levels of gaseous pollutants (CO, NOx and O₃) between the emission scenarios with and without biomass burning emissions. In Fig. 3a,b,c, mean concentrations were calculated from the first model layer hourly results averaged for the period extended from 23 to 31 August 2007. Similar are the Fig. 3d,e,f which refer to differences in concentrations averaged in the model layers up to ~2 km agl in which biomass burning emissions were injected in CAMx runs and which can be considered as representative of the boundary layer.

Fig. 3a reveals that the biomass burning results to an increase of the spatially resolved mean CO values over the whole modeling domain which can range from +0.09 ppm to +0.28 ppm over the fire hot spots. NOx levels are enhanced over the greater part of the study domain (Fig. 3b). Over the areas influenced by the biomass burning emissions, mean NOx concentrations are increased by up to +1.5 ppb while over the areas burnt the increase may be up to +7 ppb. The maximum

CO and NOx increases are over the Peloponnesus fires. Because of the biomass burning events, the domain-wide near surface mean concentration is higher by +6% for CO (change from 0.126 ppm to 0.133 ppm) and by +11% for NOx (change from 0.37 ppb to 0.41 ppb).

Over the fire hot spots in Peloponnesus and Evia, O₃ levels are generally slightly reduced (reduction down to −3 ppb) (Fig. 3c). Over the areas that are under the influence of the fire plumes, there is a small enhancement of mean O₃ levels ranging from +2% to +10%. The highest O₃ increases (up to about +5.3 ppb) are found in the maritime area southwest of Peloponnesus being downwind of the wild forest fires and over there additional O₃ is chemically produced from the fire emitted precursors.

The impact of the biomass burning events on the CO and NOx concentrations in the boundary layer in the Eastern Mediterranean is comparable with that on the near surface concentrations over the greater part of study domain except for the fire hot spots over which the impact is less pronounced compared to that near the surface. Over the forest fires in Peloponnesus, the enhancement in the vertically averaged values is up to +0.14 ppm for CO and +3.4 ppb for NOx (Fig. 3d and e). The impact of biomass burning emissions on the mean O₃ levels in the boundary layer is similar with that near surface (Fig. 3f). The maximum O₃ enhancement is about +5.1 ppb and is located in the maritime area southwest of Peloponnesus.

Fig. 4 shows, in different atmospheric layers, the effect of the biomass burning events on the air quality in the Eastern Mediterranean on the 26th August 2007 since on that day the air quality impact has been estimated to be more pronounced.

On the 26th August 2007, the influence of fire emissions on the air quality is identified mostly over Albania, western and southern Greece and the maritime area southwest of Peloponnesus. The plume of the fires in southern Bulgaria is tracked over the Aegean Sea. Over the large forest fires in Peloponnesus the increase is more than +0.7 ppm up to +1.1 ppm for CO and greater than +15 ppb up to +29 ppb for NOx (Fig. 4a,b). Because of the biomass burning events, the domain-wide near surface mean concentration is higher by +11% for CO (change from 0.128 ppm to 0.142 ppm) and by +19% for NOx (change from 0.42 ppb to 0.50 ppb).

Over the fire hot spots in Peloponnesus, a significant reduction in surface mean O₃ levels down to −34% (about −12 ppb) was estimated which is due to O₃ titration by NOx (Fig. 4c). However, over the greater part of the modeling domain, mean O₃ levels have been increased. The highest O₃

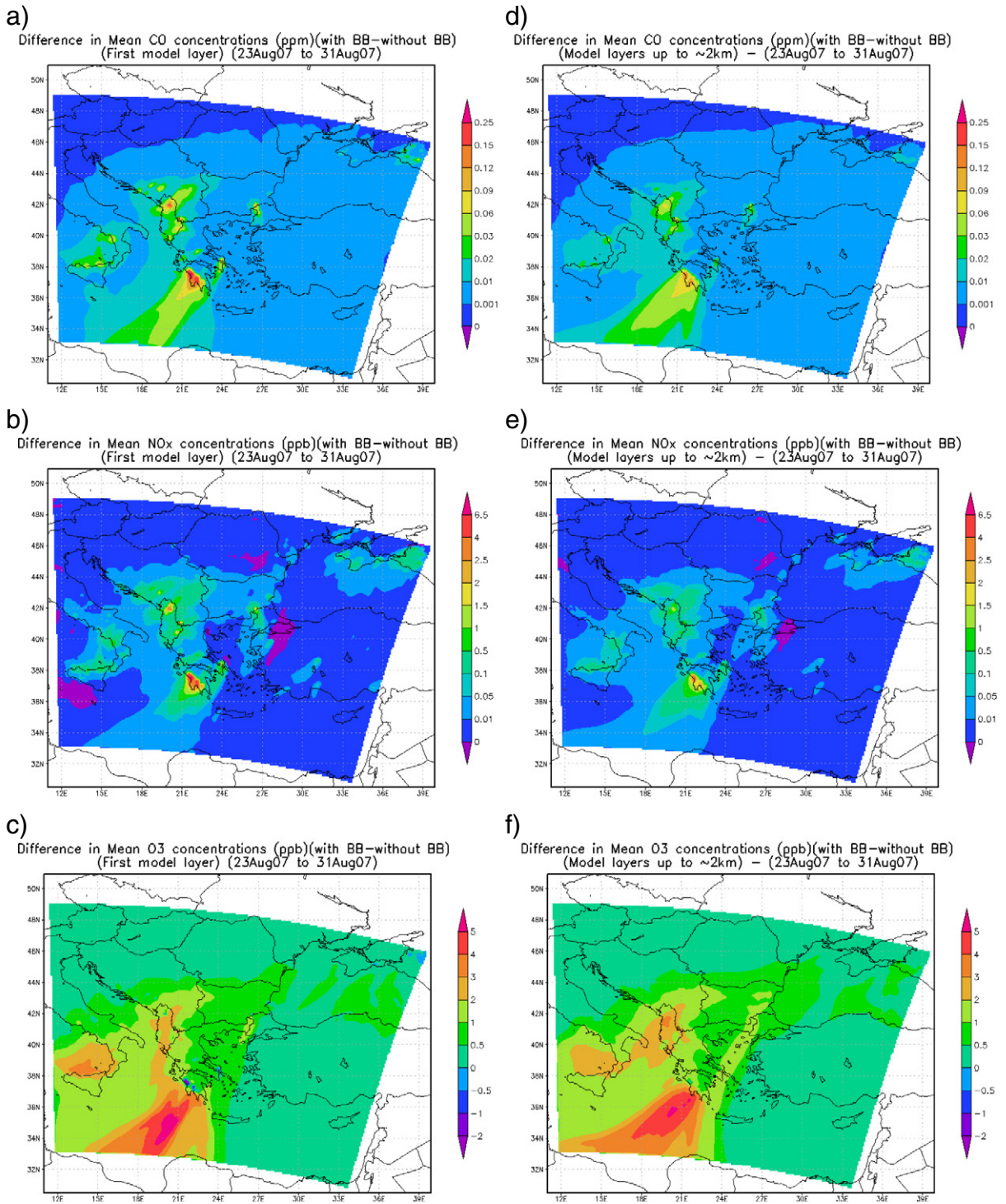


Fig. 3. The non-radiative impact of biomass burning on the air quality in the lower troposphere in the Eastern Mediterranean for the period 23 August to 31 August 2007.

increases, ranging from +20% to +52% (about +10 ppb to +27 ppb), are found over the maritime area southwest of Peloponnese which was downwind the large forest fires.

The influence of the biomass burning emissions on the atmospheric chemical processes can be identified above the

boundary layer, in different tropospheric model layers for the different pollutants as shown in Fig. 4d,e and f which depict the ratios of the pollutant mean concentrations estimated for the scenarios with and without biomass burning emissions. The Peloponnese fire plume and generally the increases in

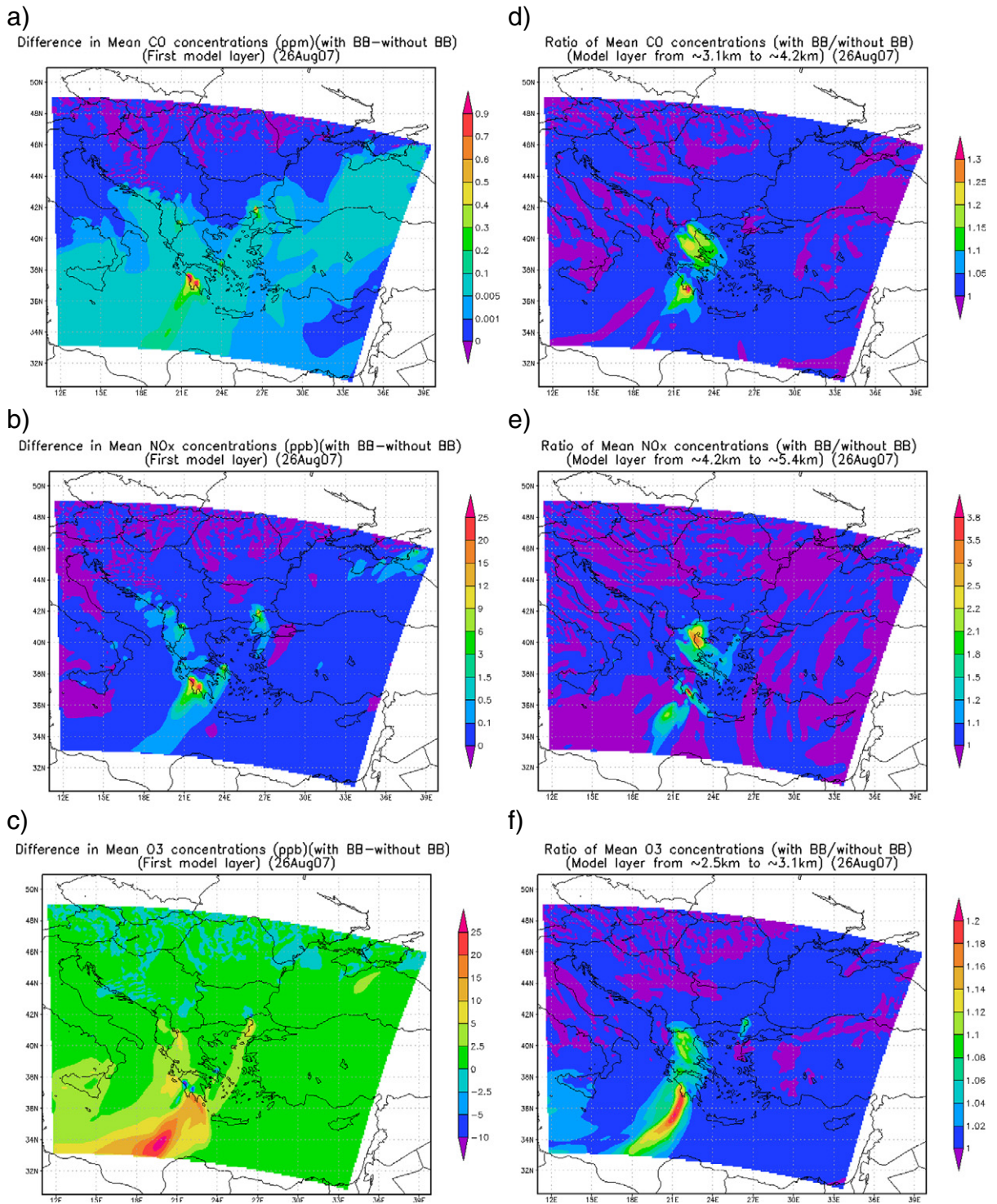


Fig. 4. The non-radiative impact of biomass burning on the air quality in different atmospheric layers in the Eastern Mediterranean for the 26th August 2007.

mean pollutant levels due to biomass burning are more evident up to about 3 km agl for O₃, 4 km agl for CO and 5.5 km agl for NO_x. The differences in heights are attributed to the generally high background of O₃ and CO levels in contrast to the low NO_x background values in the free troposphere.

4. Discussion

In this section, we analyze the atmospheric processes that determine the air quality in the Eastern Mediterranean on the 26th August 2007 focusing mainly on O₃. The 26th August

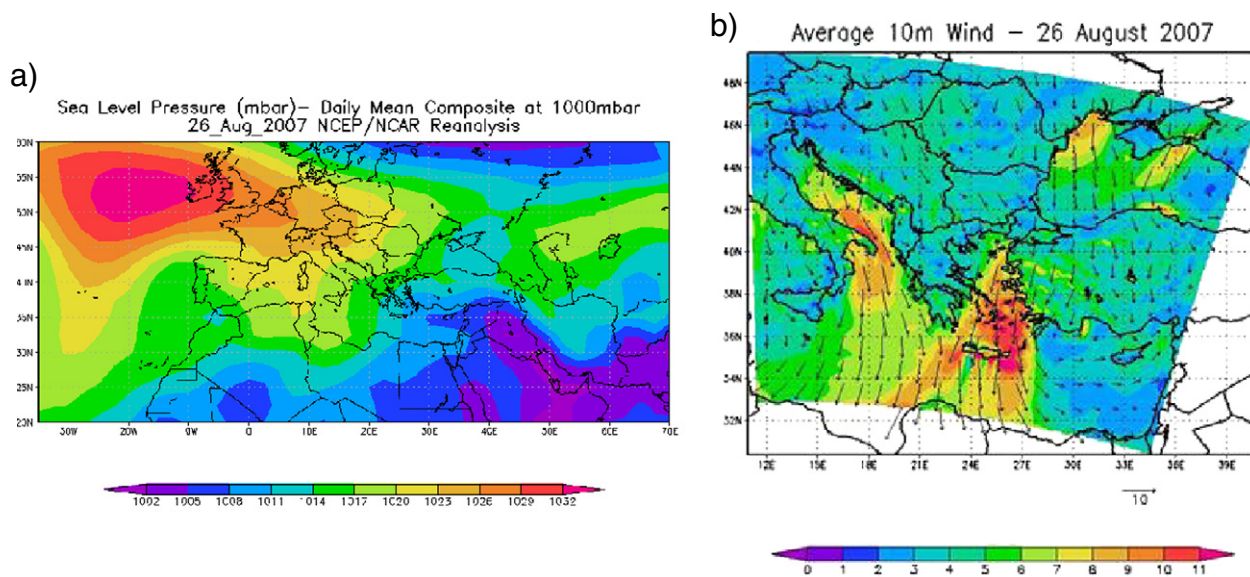


Fig. 5. a) Sea level pressure over Europe and Middle East and b) Daily 10 m-wind field from the MM5 model results in the Eastern Mediterranean, on the 26th August 2007.

2007 was selected because on that day the fire events were most severe (also on the 25th August 2007). For both emission scenarios (“with BB” and “without BB”), the CAMx Process Analysis (PA) tool was applied. The CAMx PA tool is designed to provide in-depth analysis of the physical and chemical processes and to help the understanding of the complex interactions of the different processes and the better explanation of simulated results within the context of the model formulation (ENVIRON, 2010).

The 26th August 2007 was characterized by a low pressure area above Iraq and Middle East and an anticyclone centered over North Atlantic (Fig. 5a). This pressure pattern resulted in strong north sector winds above Greece (the Etesian winds) enhancing the fire propagation (Fig. 5b).

4.1. Analysis of atmospheric processes

In the following, process rate information is provided for the following processes: 1) Deposition (dry and wet) (Dep), 2) Gas-Phase Chemistry (Gas Chem), 3) Heterogeneous Chemistry (Hetero Chem), 4) Emissions (area and point) (Emis), 5) Top Boundary Advection and Diffusion (Top Bnd) and 6) Lateral Boundaries Advection and Diffusion (Lateral Bnd). The process analysis area represents the Eastern Mediterranean simulation domain extended up to about 2 km agl.

Fig. 6 shows for the two emission scenarios the time series of the contributions of the atmospheric processes to the determination of O_3 levels in the area of interest on the 26th August 2007. A positive flux always tends to increase the cell concentration. Top boundary advection and diffusion (mostly advection) results in positive changes in O_3 levels during the greater part of the day due to entrainment of high O_3 concentrations from the free troposphere. According to Zanis et al. (2014), an important factor for the area of Eastern Mediterranean during summertime is the existence of a free tropospheric ozone pool due to downward transport from

the upper troposphere and lower stratosphere associated with enhanced subsidence and limited outflow transport that dominates the summertime Eastern Mediterranean/Middle East circulation. The lateral boundaries advection might contribute to hourly increases or decreases of O_3 concentrations depending on the balance between the O_3 that is imported from the north boundary and exported from the south one. The influence on O_3 of the east and west boundaries advection is minor. As discussed before, mainly north-sector winds were blowing over the Eastern Mediterranean on the 26th August 2007 transporting pollutants to the south. For both emission scenarios examined, on an hourly basis, the import of O_3 to the study area from the north boundary is the same. However, when fire emissions are accounted for in the CAMx simulation, more O_3 is produced and exported to the south. As a result, either higher O_3 hourly decreases or lower O_3 hourly increases because of the lateral boundaries advection are estimated during the day, compared to those when fire emissions are not included in the CAMx run. Deposition (mostly dry) represents an O_3 loss process being more influential during daytime. Gas chemistry is a source for O_3 during daytime when biomass burning emissions are accounted for. When biomass burning emissions are omitted in the CAMx run, the photochemical production of O_3 is more limited while from 10 to 12 UTC the gas chemistry acts as an O_3 sink. Daytime O_3 photochemical destruction rates are linked to low daytime NO_x levels being less than 120 ppt indicating a photochemical destruction regime for O_3 (Zanis et al., 2000). Comparing the hourly changes in O_3 concentrations due to all the processes between the two emission scenarios examined, higher daytime and lower nighttime O_3 increases are identified when biomass burning emissions are included in model runs mainly because of the more enhanced daytime photochemical O_3 production and the greater nighttime O_3 export from the south boundary of the domain.

Fig. 7 compares the total changes (sum of the hourly changes) in O_3 , CO, NO $_x$ and HNO $_3$ concentrations in the Eastern Mediterranean up to 2 km agl on the 26th August 2007 due to the different atmospheric processes for the two emission scenarios studied. The O_3 total increase due to the gas phase chemistry is about 7 times higher when accounting for the open biomass burning emissions. The CO concentration total increase because of the emissions is about 16 times more in the “with BB” scenario compared to the “without BB” scenario. When biomass burning emissions are excluded from the CAMx run, the import of O_3 and CO from the north boundary (+17.6 ppb and +35.3 ppb respectively) and the export from the south one (−15.3 ppb and −32.8 ppb respectively) results in an enhancement of about +2.0 ppb

for O_3 and an almost no change for CO (including also the concentration changes induced by the east and west boundaries being minor though). In the case of the “with BB” scenario, this balance becomes almost zero for O_3 and −14.6 ppb for CO mainly due to more O_3 and CO transported from the south out of the domain (Fig. 7a and b). This is in agreement with Turquety et al. (2009) according to which, the emissions from the large fires in the Peloponnese were rapidly transported across the Mediterranean towards North Africa (Libya and Tunisia) by strong north-easterly winds above Greece. Biomass burning in the “with BB” scenario results in a 2 times higher NO $_x$ increase due to emissions but enhances also the gas phase destruction of NO $_x$ by 70% and the gas phase production of HNO $_3$ by 53% (NO $_x$ are partly converted to HNO $_3$)

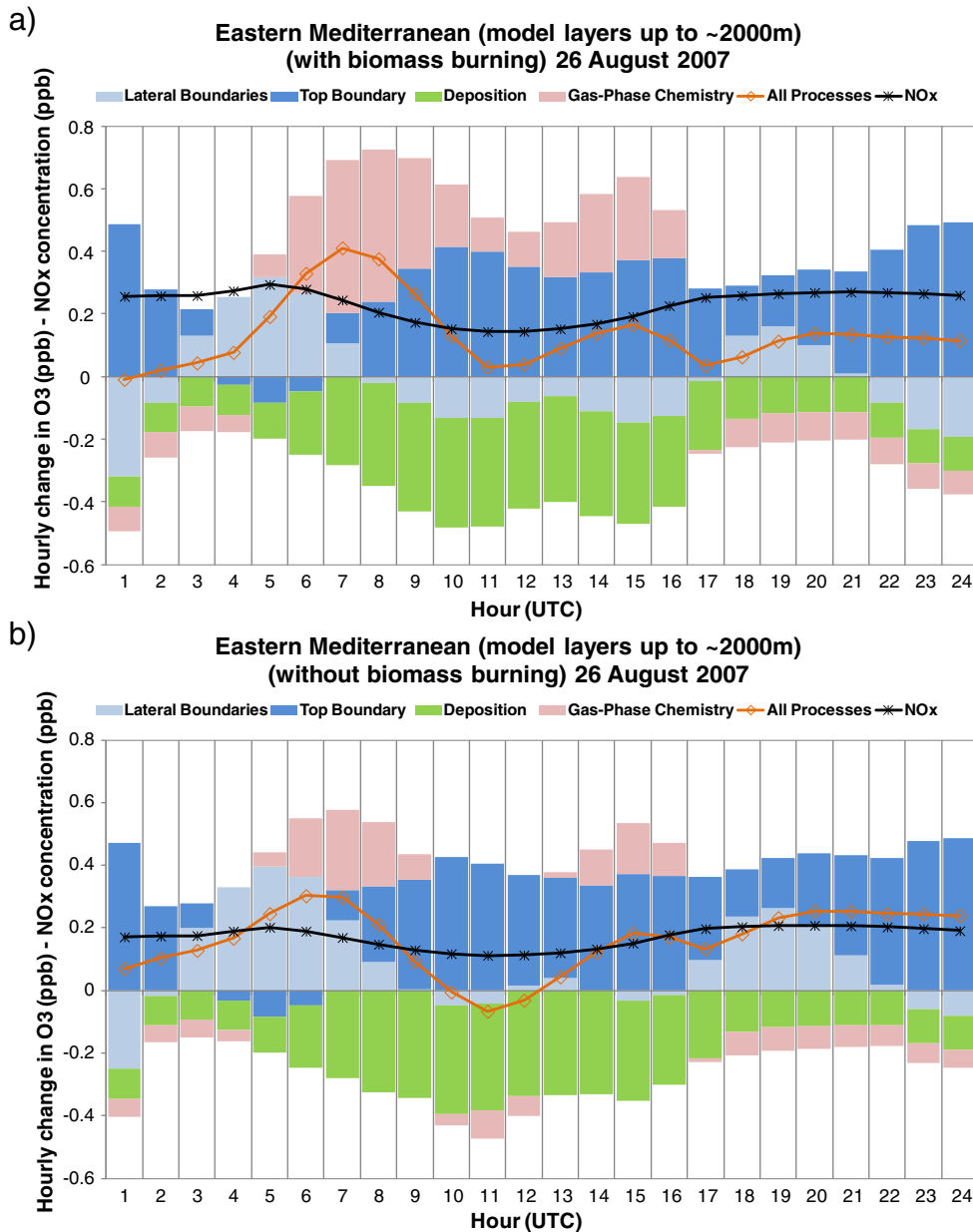


Fig. 6. Time series of the contributions of atmospheric processes to the determination of O_3 levels in the Eastern Mediterranean on the 26th August 2007.

(Fig. 7c and d). As with O_3 and CO, more HNO_3 is exported from the south boundary in the case of the “with BB” scenario resulting in an increase of HNO_3 concentration due to the lateral boundaries which is less pronounced compared to that in the “without BB” scenario.

On the 26th August 2007, for both emission scenarios, the changes of the pollutant concentrations due to all the processes are in almost all cases positive. The concentrations of the pollutants shown in Fig. 7 are higher (or almost equal e.g. for NOx) at the end of the day than in the beginning meaning that pollution is built up in the Eastern Mediterranean during the 26th August 2007.

4.2. Chemical process analysis

In this section, we identify the geographic areas that are “VOC-sensitive” or “NOx-sensitive” with respect to O_3 production and investigate the non-radiative impact of biomass burning on the oxidizing capacity of the atmosphere in the Eastern Mediterranean on the 26th August 2007. The time period selected for the analysis was chosen to coincide with the hours of photochemical O_3 production, i.e. 6 UTC to 16 UTC (as shown in Fig. 6). The results of the chemical process analysis were vertically averaged up to about 2 km agl.

One of the methods that have been proposed for differentiating the O_3 sensitivity to precursors (NOx and VOCs) based on chemical indicators is the ratio of the production rates of hydrogen peroxide and nitric acid ($PH_2O_2/PHNO_3$ indicator). This method is implemented in the CAMx chemical process analysis and was used to determine grid cells as VOC-sensitive or NOx-sensitive by defining $PH_2O_2/PHNO_3$ of 0.35 and higher as the NOx-sensitive regime.

Fig. 8 presents the mean value of the $PH_2O_2/PHNO_3$ indicator as calculated for the time period extending from 6 UTC to 16 UTC of the 26th August 2007 while running CAMx

for the “with BB” scenario. The close areas where the wild forest fires were burning in Peloponnesus are identified as VOC-sensitive areas while the remaining modeling domain is characterized as NOx-sensitive. In a corresponding figure depicting the mean value of the $PH_2O_2/PHNO_3$ indicator for the first model layer (not shown here), in addition to the VOC-sensitive burnt areas in Peloponnesus, a transition from VOC-sensitivity in the high NOx emission urban areas, mainly Istanbul and Athens greater areas, to NOx-sensitivity in the lower NOx emission rural areas has been revealed. The differences between both figures are associated with the difference in the vertical distribution of the anthropogenic emissions released in the first model layer (except for the point sources) and the biomass burning emissions injected up to 2000 m agl. The plume of the Peloponnesus fires is NOx sensitive and produces additional O_3 as it is advected over the maritime area south-west of Peloponnesus.

The biomass burning emissions cause an overall small enhancement in the oxidizing capacity of the boundary layer (up to 2 km agl) in the Eastern Mediterranean. The domain wide hydroxyl radical (OH) mean concentration on the 26th August 2007 from 6 to 16 UTC changes from 0.106 ppt to 0.112 ppt that is an increase of about +6%. The corresponding concentration of hydroperoxy radical (HO_2) is enhanced by approximately +4% due to biomass burning (from 19.67 ppt to 20.45 ppt). However, the spatially resolved changes can be much more pronounced. Fig. 9 shows the spatial distribution of the differences in OH and HO_2 mean concentrations on the 26th August 2007 from 6 to 16 UTC due to biomass burning emissions. Increases in OH mean levels are found over the greater part of the modeling domain being maximum over the Peloponnesus forest fires. There, the OH increases are up to +0.25 ppt and are mainly due to the production of OH from the conversion of the highly available NO to NO_2 by HO_2 and alkyl peroxy radicals (RO_2).

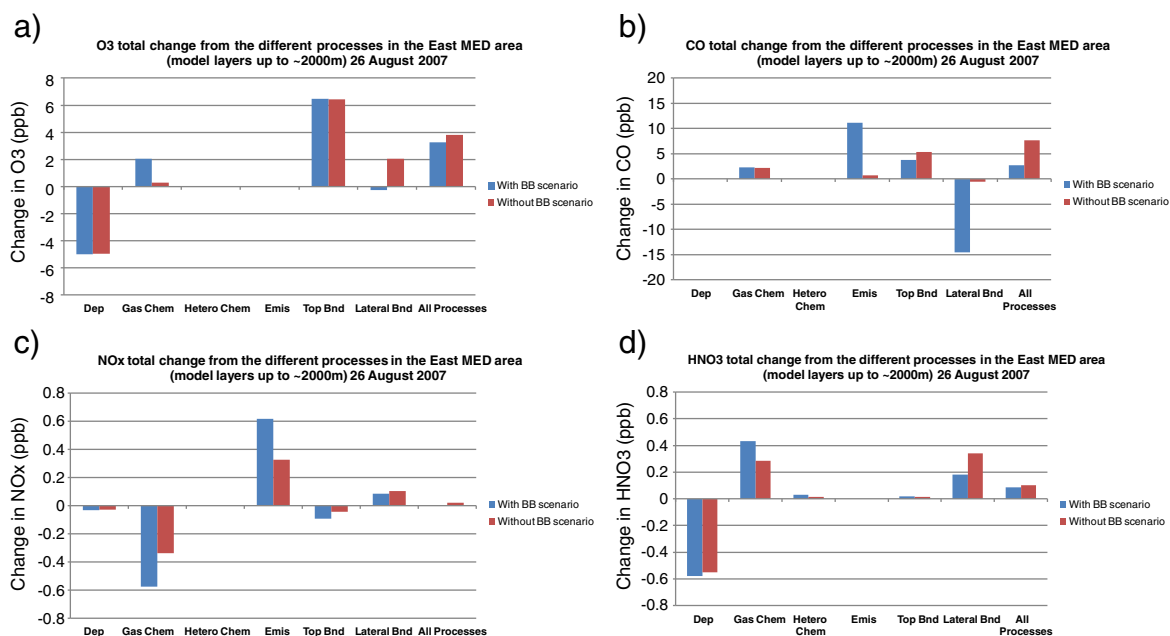


Fig. 7. Comparison of the total changes in O_3 , CO, NOx and HNO_3 concentrations in the Eastern Mediterranean up to 2 km agl on the 26th August 2007 due to the atmospheric processes for the two emission scenarios studied.

In the Peloponnese wildfire plume downwind the forest fires, the enhancements in OH concentrations may be associated to the increases in O₃ levels due to biomass burning that contribute to OH production via the photolysis of O₃ and reaction of O(¹D) with H₂O. These chemical pathways seem to overwhelm the OH reduction caused because of its reaction with CO and VOCs. The HO₂ mean levels are reduced over the Peloponnese large forest fires due to high NO_x levels (reduction down to about –13 ppt). In the downwind plume increases in HO₂ mean concentrations are identified, ranging from +6 ppt to +12 ppt, due to decreasing downwind NO_x concentrations (e.g. due to dilution plus oxidation of NO_x to HNO₃) that limit the HO₂ to OH conversion and allow the HO₂ to increase, in combination also with its formation from the reaction of OH with CO and VOCs.

5. Conclusions

The MM5–CAMx modeling system was applied in the Eastern Mediterranean in high spatial and temporal resolution in order to assess the spatial distribution of the non-radiative impact on the lower troposphere gas phase air quality (CO, NO_x and O₃ levels) of the intense biomass burning events (i.e. large fires in Peloponnese, Evia and Albania) that took place at the end of August 2007 (fires were most severe on the 25th and 26th of August). Two emission scenarios have been used in CAMx; with and without biomass burning emissions. Process analysis was performed for the 26th August 2007 so as to examine for both emission scenarios the atmospheric processes that determined the O₃ values in the boundary layer (i.e. in the model layers up to about 2 km agl) of the study area and how biomass burning might have affected the atmospheric processes configuring the O₃, NO_x, CO and HNO₃ levels. The results of the chemical process analysis for the same day were used to differentiate

the O₃ sensitivity to its precursors (NO_x and VOCs) and to investigate how the oxidizing capacity of the boundary layer in the Eastern Mediterranean was altered due to biomass burning.

Biomass burning resulted to an enhancement of the CO and NO_x values over almost the entire modeling domain which was more pronounced over the burnt areas and maximum over the Peloponnese wild forest fires. The 23 to 31 August 2007 average near surface pollutant concentrations over the Peloponnese fires were increased by +0.28 ppm for CO and +7 ppb for NO_x due to biomass burning emissions. On the 26th August 2007, the corresponding increases were stronger (up to +1.1 ppm for CO and +29 ppb for NO_x), while the domain-wide near surface mean concentration was higher by +11% for CO and by +19% for NO_x. Near surface O₃ values were reduced over the fire hot spots due to NO_x titration. On the 26th August 2007, the maximum O₃ concentration reduction (–34% i.e. about –12 ppb) was found over Peloponnese. However, on the same day, over the greater part of the modeling domain, mean O₃ levels were increased. The highest O₃ increase (+52% i.e. about +27 ppb) was found over the maritime area southwest of Peloponnese which was downwind the large forest fires at a distance of about 500 km.

The time series of the contributions of the atmospheric processes to the determination of O₃ levels in the boundary layer in the Eastern Mediterranean on the 26th August 2007 revealed that gas chemistry was a source for O₃ during daytime when biomass burning emissions were accounted for in the application of the photochemical model. When biomass burning emissions were omitted, the daytime photochemical production of O₃ was more limited while during some daytime hours the gas chemistry acted as an O₃ sink because of low NO_x levels (less than 120 ppt) indicative of a photochemical destruction regime for O₃ in the Eastern Mediterranean. Comparing the hourly changes in O₃ concentrations due to all the processes

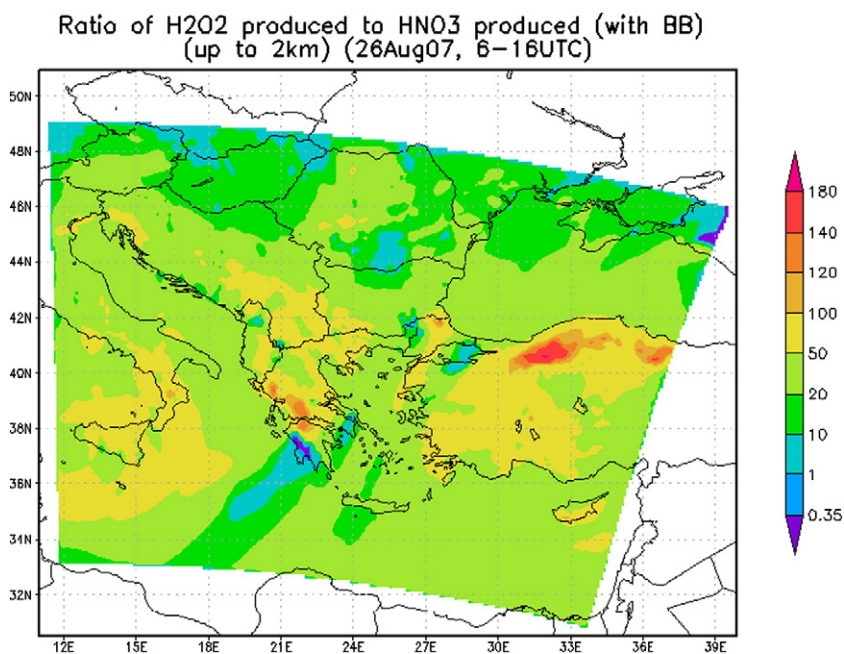


Fig. 8. VOC and NO_x sensitivity with respect to O₃ formation.

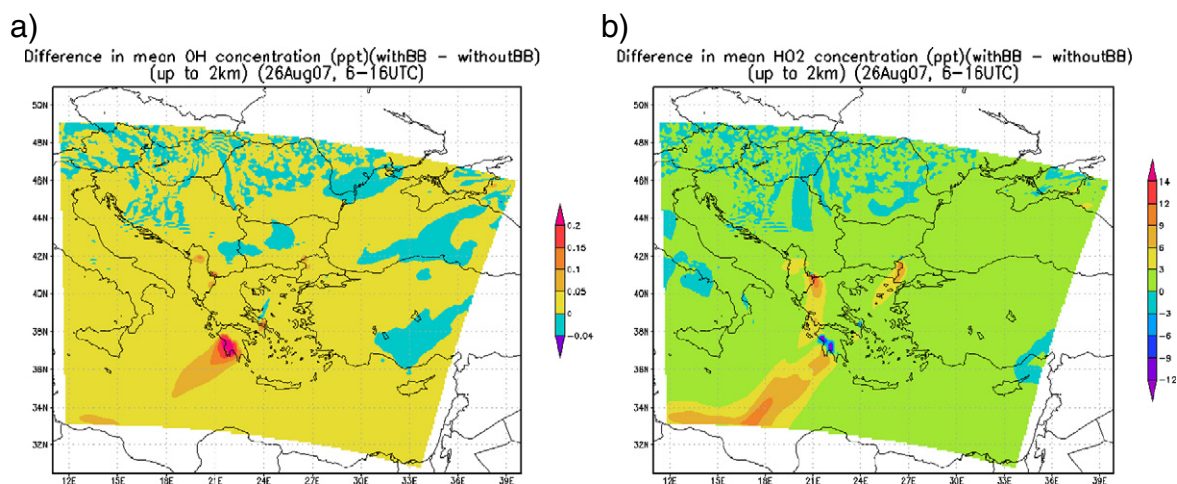


Fig. 9. The non-radiative impact of biomass burning on the oxidizing capacity of the boundary layer in the Eastern Mediterranean on the 26th August 2007.

between the two emission scenarios examined, higher daytime and lower nighttime O_3 increases were estimated when biomass burning emissions were included in model runs mainly because of the more enhanced daytime photochemical O_3 production and the greater nighttime O_3 export from the south boundary of the domain.

The chemical process analysis on the 26th August 2007 during the hours of photochemical O_3 production suggested that the O_3 photochemistry in the boundary layer was VOC-sensitive only in the areas close to the Peloponnesus forest fires. The O_3 photochemistry occurring in the downwind fire plumes was limited by the NO_x availability. In addition, the influence of the biomass burning emissions on the oxidizing capacity of the boundary layer was found to be characterized by a rather small overall enhancement of the domain wide OH and HO_2 concentrations. However, the spatially resolved impact was revealed to be much more pronounced; increases up to +0.25 ppt in the OH mean values and decreases down to approximately –13 ppt in the HO_2 mean levels over the Peloponnesus fires, while in the downwind plume the increases in the HO_2 mean concentrations were up to +12 ppt.

The above results suggest that the intense open biomass burning events, although episodic, may have important effects on the photochemistry in the Eastern Mediterranean and biomass burning emissions are necessary to be considered while applying chemical transport models in the southeastern Europe. In addition, the results of the present study should be regarded under the future perspective of climate change. Southeastern Europe is expected to be more affected by the biomass burning in the future (Amiridis et al., 2012). Future scenarios on climate change indicate that the already hot and semi-arid climate of southeastern Europe is expected to become warmer and drier (Tolika et al., 2012) and such climate conditions may trigger increased fire occurrence frequency (Giannakopoulos et al., 2009, 2011) which could increase further the air pollution levels. An issue that needs to be considered in future relevant scientific work is the radiative impact of biomass burning emissions on the gas-phase atmospheric composition. There is no study to address this issue with a focus on the Eastern Mediterranean. In Hodzic et al. (2007), the radiative impact of wildfire emissions on O_3

formation in Europe is assessed. Hodzic et al. (2007) used the chemical transport model CHIMERE in order to investigate the effects of wildfire emissions on air quality in Europe in the summer 2003, including the heat-wave episode in the first half of August 2003 which was characterized by the most intense fire activity (especially in Portugal from 3 to 5 August 2003). According to the study, during the polluted period from 3 to 8 August 2003, the calculated $J[NO_2]$ and $J[O_3(1D)]$ values were reduced from 10 to 30% over a large part of Europe due to the presence of smoke. The decrease in photolysis frequencies suggested a decrease in the surface O_3 levels of comparable magnitude and explained the model overestimation of O_3 concentrations over Northern Europe during the heat-wave period, since the aerosol indirect feedback on O_3 formation was not included in CHIMERE runs. Under this view, on-line modeling in the Eastern Mediterranean will provide additional results about the impact of biomass burning emissions on the air quality of this area.

Acknowledgments

This work was supported by the FP7 EU projects CityZen (megaCITY-Zoom for the Environment: Grant agreement no. 212095), MACC (Monitoring Atmospheric Composition and Climate: Grant agreement no 218793) and MACC II (Monitoring Atmospheric Composition and Climate Interim Implementation: Grant agreement no 283576). We would like to thank the Research Committee of the Aristotle University of Thessaloniki for supporting this work with a 2011 Post-Doctoral Scholarship. The results presented in this research paper have been produced using the EGI and HellasGrid infrastructures. The authors would like to acknowledge the support provided by the Scientific Computing Center at the Aristotle University of Thessaloniki throughout the progress of this research work. We thank Dr G. Kouvarakis and Professor N. Mihalopoulos for the Finokalia data availability.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.atmosres.2014.05.015>.

References

- Akagi, S.K., Yokelson, R.J., Wiedinmyer, C., Alvarado, M.J., Reid, J.S., Karl, T., Crouse, J.D., Wennberg, P.O., 2011. Emission factors for open and domestic biomass burning for use in atmospheric models. *Atmos. Chem. Phys.* 11, 4039–4072.
- Amiridis, V., Melas, D., Balis, D.S., Papayannis, A., Founda, D., Katragkou, E., Giannakaki, E., Mamouri, R.E., Gerasopoulos, E., Zerefos, C., 2007. Aerosol Lidar observations and model calculations of the planetary boundary layer evolution over Greece, during the March 2006 total solar eclipse. *Atmos. Chem. Phys.* 7, 6181–6189.
- Amiridis, V., Giannakaki, E., Balis, D.S., Gerasopoulos, E., Pytharoulis, I., Zanis, P., Kazadzis, S., Melas, D., Zerefos, C., 2010. Smoke injection heights from agricultural burning in Eastern Europe as seen by CALIPSO. *Atmos. Chem. Phys.* 10, 11567–11576.
- Amiridis, V., Zerefos, C., Kazadzis, S., Gerasopoulos, E., Eleftheratos, K., Vrekoussis, M., Stohl, A., Mamouri, R.E., Kokkalis, P., Papayannis, A., Eleftheriadis, K., Diapouli, E., Keramitsoglou, I., Kontoes, C., Kotroni, V., Lagouvardos, K., Marinou, E., Giannakaki, E., Kostopoulou, E., Giannakopoulos, C., Richter, A., Burrows, J.P., Mihalopoulos, N., 2012. Impact of the 2009 Attica wild fires on the air quality in urban Athens. *Atmos. Environ.* 46, 536–544.
- Andreae, M.O., Merlet, P., 2001. Emission of trace gases and aerosols from biomass burning. *Glob. Biogeochem. Cycles* 15, 955–966.
- Asthitha, M., Kallos, G., Katsafados, P., 2008. Air pollution modeling in the Mediterranean region: analysis and forecasting of episodes. *Atmos. Res.* 89, 358–364.
- Baldassarre, G., Pozzoli, L., Kaiser, J.W., Schmidt, C.C., Unal, A., Kindap, T., 2013. Estimation of biomass burning emissions over Turkey using SEVIRI fire characterization data: the Antalya fire, August 2008. Electronic proceedings of the Presented at the 12th Annual CMAS Conference, Chapel Hill, NC, October 28–30, 2013.
- Carvalho, A., Monteiro, A., Flannigan, M., Solman, S., Miranda, A.I., Borrego, C., 2011. Forest fires in a changing climate and their impacts on air quality. *Atmos. Environ.* 45, 5545–5553.
- Coheur, P.-F., Clarisse, L., Turquety, S., Hurtmans, D., Clerbaux, C., 2009. IASI measurements of reactive trace species in biomass burning plumes. *Atmos. Chem. Phys.* 9, 5655–5667.
- Dentener, F., Kinne, S., Bond, T., Boucher, O., Cofala, J., Generoso, S., Ginoux, P., Gong, S., Hoelzemann, J.J., Ito, A., Marelli, L., Penner, J.E., Putaud, J.P., Textor, C., Schulz, M., van der Werf, G.R., Wilson, J., 2006. Emissions of primary aerosol and precursor gases in the years 2000 and 1750 prescribed datasets for AeroCom. *Atmos. Chem. Phys.* 6, 4321–4344.
- Drori, R., Dayan, U., Edwards, D.P., Emmons, L.K., Erlick, C., 2012. Attributing and quantifying carbon monoxide sources affecting the Eastern Mediterranean: a combined satellite, modelling, and synoptic analysis study. *Atmos. Chem. Phys.* 12, 1067–1082.
- EC, 2008. Forest Fires in Europe 2007. European Commission, Joint Research Centre, Institute for Environment and Sustainability. JRC Scientific and Technical Reports, Report No 8, EUR 23492 EN ISSN 1018-5593.
- EEA, 2000. CORINE Land Cover technical guide – Addendum 2000. European Environment Agency Technical Report no. 40 (May 2000) prepared by: M. Bossard, J. Feranec and J. Otahel.
- ENVIRON, 2010. User's Guide CAMx Comprehensive Air Quality Model with Extensions, Version 5.30. ENVIRON International Corporation, (December 2010).
- Founda, D., Giannakopoulos, C., 2009. The exceptionally hot summer of 2007 in Athens, Greece – a typical summer in the future climate? *Global Planet. Chang.* 67, 227–236.
- Freitas, S.R., Longo, K.M., Chatfield, R., Latham, D., Silva Dias, M.A.F., Andreae, M.O., Prins, E., Santos, J.C., Gielow, R., Carvalho Jr., J.A., 2007. Including the sub-grid scale plume rise of vegetation fires in low resolution atmospheric transport models. *Atmos. Chem. Phys.* 7, 3385–3398.
- Giannakopoulos, C., Le Sager, P., Bindi, M., Moriondo, M., Kostopoulou, E., Goodess, C.M., 2009. Climatic changes and associated impacts in the Mediterranean resulting from a 2 °C Global Warming. *Global Planet. Chang.* 68, 209–224.
- Giannakopoulos, C., Kostopoulou, E., Varotsos, K.V., Tziotziou, K., Plitharas, A., 2011. An integrated assessment of climate change impacts for Greece in the near future. *Reg. Environ. Chang.* 11, 829–843.
- Grell, G.A., Dudhia, J., Stauffer, D.R., 1994. A description of the fifth-generation Penn State/NCAR mesoscale model (MM5). NCAR Technical Note, NCAR/TN-398 + STR.
- Hodnebrog, Ø., Solberg, S., Stordal, F., Svendby, T.M., Simpson, D., Gauss, M., Hilboll, A., Pfister, G.G., Turquety, S., Richter, A., Burrows, J.P., Denier van der Gon, H.A.C., 2012. Impact of forest fires, biogenic emissions and high temperatures on the elevated Eastern Mediterranean ozone levels during the hot summer of 2007. *Atmos. Chem. Phys.* 12, 8727–8750.
- Hodzic, A., Madronich, S., Bohn, B., Massie, S., Menut, L., Wiedinmyer, C., 2007. Wildfire particulate matter in Europe during summer 2003: meso-scale modeling of smoke emissions, transport and radiative effects. *Atmos. Chem. Phys.* 7, 4043–4064.
- Im, U., Markakis, K., Unal, A., Kindap, K., Poupkou, A., Incecik, S., Yenigün, O., Melas, D., 2010. Study of a winter PM episode in Istanbul using the high resolution WRF/CMAQ modeling system. *Atmos. Environ.* 44, 3085–3094.
- Im, U., Markakis, K., Poupkou, A., Melas, D., Unal, A., Gerasopoulos, E., Daskalakis, N., Kanakidou, M., 2011a. The impact of temperature changes on summer time ozone and its precursors in the Eastern Mediterranean. *Atmos. Chem. Phys.* 11, 3847–3864.
- Im, U., Poupkou, A., Markakis, K., Unal, A., Kindap, T., Incecik, S., Yenigün, O., Melas, D., 2011b. The impact of anthropogenic and biogenic emissions on surface ozone concentrations in Istanbul. *Sci. Total Environ.* 409, 1255–1265.
- Im, U., Markakis, K., Kocak, M., Gerasopoulos, E., Daskalakis, N., Mihalopoulos, N., Poupkou, A., Kindap, T., Unal, A., Kanakidou, M., 2012. Summertime aerosol chemical composition in the Eastern Mediterranean and its sensitivity to temperature. *Atmos. Environ.* 50, 164–173.
- Inness, A., Baier, F., Benedetti, A., Bouarar, I., Chabrillat, S., Clark, H., Clerbaux, C., Coheur, P., Engelen, R.J., Errera, Q., Flemming, J., George, M., Granier, C., Hadji-Lazarou, J., Huijnen, V., Hurtmans, D., Jones, L., Kaiser, J.W., Kapsomenakis, J., Lefever, K., Leita, O.J., Razinger, M., Richter, A., Schultz, M.G., Simmonds, A.J., Suttie, M., Stein, O., Thepaut, J.-N., Thouret, V., Vrekoussis, M., Zerefos, C., the MACC team, 2013. The MACC reanalysis: an 8 yr data set of atmospheric composition. *Atmos. Chem. Phys.* 13, 4073–4109.
- Junquera, V., Russell, M.M., Vizuete, W., Kimura, Y., Allen, D., 2005. Wildfires in eastern Texas in August and September 2000: emissions, aircraft measurements, and impact on photochemistry. *Atmos. Environ.* 39, 4983–4996.
- Kaiser, J.W., Boucher, O., Doutriaux-Boucher, M., Flemming, J., Govaerts, Y.M., Gulliver, J., Heil, A., Jones, L., Lattanzio, A., Morcrette, J.-J., Perrone, M.R., Razinger, M., Roberts, G., Schultz, M.G., Simmonds, A.J., Suttie, M., Wooster, M.J., 2009. Smoke in the air. *ECMWF NewsL.* 119, 9–15.
- Kaiser, J.W., Heil, A., Schultz, M.G., Stein, O., van der Werf, G.R., Wooster, R.M.J., Xu, W., 2011. Final report on implementation and quality of the D-FIRE assimilation system. MACC deliverable D-D-FIRE 7, European Centre for Medium-Range Weather Forecasts (ECMWF) (http://gmes-atmosphere.eu/documents/deliverables/d-fire/D-FIRE_final_report_v7.pdf).
- Kaiser, J.W., Heil, A., Andreae, M.O., Benedetti, A., Chubarova, N., Jones, L., Morcrette, J.-J., Razinger, M., Schultz, M.G., Suttie, M., van der Werf, G.R., 2012. Biomass burning emissions estimated with a global fire assimilation system based on observed fire radiative power. *Biogeosciences* 9, 527–554.
- Kaskaoutis, D.G., Kharol, S.K., Sifakis, N., Nastos, P.T., Sharma, A.R., Badarinath, K.V.S., Kambezidis, H.D., 2011. Satellite monitoring of the biomass-burning aerosols during the wildfires of August 2007 in Greece: climate implications. *Atmos. Environ.* 45, 716–726.
- Katragkou, E., Kioutsioukis, I., Poupkou, A., Lisaridis, I., Markakis, K., Karathanasis, S., Melas, D., Balis, D., 2007. An air quality study for Greece with the MM5/CAMx modelling system. European Space Agency, (Special Publication) ESA SP, Issue SP-636, July 2007, 5p, Envisat Symposium 2007; Montreux; Switzerland; 23 April 2007 through 27 April 2007; Code 70666.
- Keywood, M., Kanakidou, M., Stohl, A., Dentener, F., Grassi, G., Meyer, C.P., Tørseth, K., Edwards, D., Thompson, A.M., Lohmann, U., Burrows, J., 2013. Fire in the air: biomass burning impacts in a changing climate. *Crit. Rev. Environ. Sci. Technol.* 43, 40–83.
- Konovalov, I.B., Beekmann, M., Kuznetsova, I.N., Yurova, A., Zvyagintsev, A.M., 2011. Atmospheric impacts of the 2010 Russian wildfires: integrating modelling and measurements of an extreme air pollution episode in the Moscow region. *Atmos. Chem. Phys.* 11, 10031–10056.
- Kuenen, J., van der Gon, H.D., Visschedijk, A.J.H., van der Brugh, H., van Gijlswijk, R., 2011. MACC European Emission Inventory Database for the years 2003–2007. The Netherlands Organisation, TNO report TNO-060-UT-2011-00588, March 2011.
- Langmann, B., Duncan, B., Textor, C., Trentmann, J., van der Werf, G.R., 2009. Vegetation fire emissions and their impact on air pollution and climate. *Atmos. Environ.* 43, 107–116.
- Lavoue, D., Liousse, C., Cachier, H., Stocks, B.J., Goldammer, J.G., 2000. Modeling of carbonaceous particles emitted by boreal and temperate wildfires at northern latitudes. *J. Geophys. Res.* 105, 26871–26890.
- Lazaridis, M., Latos, M., Aleksandropoulou, V., Hov, Ø., Papayannis, A., Tørseth, K., 2008. Contribution of forest fire emissions to atmospheric pollution in Greece. *Air Qual. Atmos. Health* 1, 143–158.
- Liu, Y., Kahn, R.A., Chaloulakou, A., Koutrakis, P., 2009. Analysis of the impact of the forest fires in August 2007 on air quality of Athens using multi-sensor aerosol remote sensing data, meteorology and surface observations. *Atmos. Environ.* 43, 3310–3318.

- Markakis, K., Giannaros, T., Poupkou, A., Melas, D., Sofiev, M., Soares, J., 2009. Evaluating the impact of particle emissions from natural sources in the Balkan region. European Aerosol Conference, 6–11 September 2009, Karlsruhe, Germany.
- Markakis, K., Poupkou, A., Melas, D., Zerefos, C., 2010a. A GIS based anthropogenic PM10 emission inventory for Greece. *Atmos. Pollut. Res.* 1, 71–81.
- Markakis, K., Poupkou, A., Melas, D., Tzoumaka, P., Petrakakis, M., 2010b. A computational approach based on GIS technology for the development of an anthropogenic emission inventory of gaseous pollutants in Greece. *Water Air Soil Pollut.* 207, 157–180.
- Markakis, K., Im, U., Unal, A., Melas, D., Yenigun, O., Incecik, S., 2012. Compilation of a GIS based high spatially and temporally resolved emission inventory for the greater Istanbul area. *Atmos. Pollut. Res.* 3, 112–125.
- Markakis, K., Katragkou, K., Poupkou, A., Melas, D., 2013. MOSESS: a new emission model for the compilation of model-ready emission inventories-application in a coal mining area in northern Greece. *Environ. Model. Assess.* 18, 509–521.
- Martins, V., Miranda, A.I., Carvalho, A., Schaap, M., Borrego, C., Sá, E., 2012. Impact of forest fires on particulate matter and ozone levels during the 2003, 2004 and 2005 fire seasons in Portugal. *Sci. Total Environ.* 414, 53–62.
- Monks, P.S., Granier, C., Fuzzi, S., Stohl, A., Williams, M.L., Akimoto, H., Amann, M., Baklanov, A., Baltensperger, U., Bey, I., Blake, N., Blake, R.S., Carslaw, K., Cooper, O.R., Dentener, F., Fowler, D., Fragkou, E., Frost, G.J., Generoso, S., Ginoux, P., Grewe, V., Guenther, A., Hansson, H.C., Henne, S., Hjorth, J., Hofzumahaus, A., Huntrieser, H., Isaksen, I.S.A., Jenkin, M.E., Kaiser, J., Kanakidou, M., Klimont, Z., Kulmala, M., Laj, P., Lawrence, M.G., Lee, J.D., Liousse, C., Maione, M., McFiggans, G., Metzger, A., Mieville, A., Mousiopoulos, N., Orlando, J.J., O'Dowd, C.D., Palmer, P.L., Parrish, D.D., Petzold, A., Platt, U., Pöschl, U., Prevot, A.S.H., Reeves, C.E., Reimann, S., Rudich, Y., Sellegri, K., Steinbrecher, R., Simpson, D., tenBrink, H., Theloke, J., van der Werf, G.R., Vautard, R., Vestreng, V., Vlachokostas, C., von Glasow, R., 2009. Atmospheric composition change – global and regional air quality. *Atmos. Environ.* 43, 5268–5350.
- Morris, G.A., Hersey, S., Thompson, A.M., Pawson, S., Nielsen, J.E., Colarco, P. R., McMillan, W.W., Stohl, A., Turquetly, S., Warner, J., Johnson, B.J., Kucsera, T.L., Larko, D.E., Oltmans, S.J., Witte, J.C., 2006. Alaskan and Canadian forest fires exacerbate ozone pollution over Houston, Texas, on 19 and 20 July 2004. *J. Geophys. Res.* 111, D24S03. <http://dx.doi.org/10.1029/2006JD007090>.
- Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura, K., Segers, A., Kanakidou, M., 2011. In-cloud oxalate formation in the global troposphere: a 3-D modeling study. *Atmos. Chem. Phys.* 11, 5761–5782.
- NATAIR, 2007. Improving and applying methods for the calculation of natural and biogenic emissions and assessment of impacts to the air quality. Final activity report of the EU FP6 project NATAIR, contract No. 513699, August 2007.
- Pfister, G.G., Wiedinmyer, C., Emmons, L.K., 2008. Impacts of the fall 2007 California wildfires on surface ozone: integrating local observations with global model simulations. *Geophys. Res. Lett.* 35. <http://dx.doi.org/10.1029/2008GL034747> L19814.
- Pizzigalli, C., Cesari, R., D'Isidoro, M., Maurizi, A., Mircea, M., 2012. Modelling wildfires in the Mediterranean area during summer 2007. *Nuovo Cimento C* 35 (C), 137–146.
- Poupkou, A., Melas, D., Kioutsioukis, I., Lissaridis, I., Symeonidis, P., Balis, D., Karathanasis, S., Kazadzis, S., 2006. Regional air quality forecasting over Greece within PROMOTE. European Space Agency, (Special Publication) ESA SP, Issue 628, July 2006, 6p, 1st Atmospheric Science Conference; Frascati; Italy; 8 May 2006 through 12 May 2006; Code 68136.
- Poupkou, A., Melas, D., Ziomas, I., Symeonidis, P., Lissaridis, I., Gerasopoulos, E., Zerefos, C., 2009. Simulated summertime regional ground-level ozone concentrations over Greece. *Water Air Soil Pollut.* 196, 169–181.
- Poupkou, A., Giannaros, T., Markakis, K., Kioutsioukis, I., Curci, G., Melas, D., Zerefos, C., 2010. A model for European biogenic volatile organic compound emissions: software development and first validation. *Environ. Model. Softw.* 25, 1845–1856.
- Poupkou, A., Zanis, P., Nastos, P., Papanastasiou, D., Melas, D., Tourpali, K., Zerefos, C., 2011. Present climate trend analysis of the Etesian winds in the Aegean Sea. *Theor. Appl. Climatol.* 106, 459–472.
- Schultz, M.G., Heil, A., Hoelzemann, J.J., Spessa, A., Thonicke, K., Goldammer, J., Held, A.C., Pereira, J.M.C., 2008. Global emissions from wildland fires from 1960 to 2000. *Global Biogeochem. Cycles* 22, GB2002. <http://dx.doi.org/10.1029/2007GB003031>.
- Sofiev, M., Vankevich, R., Lotjonen, M., Prank, M., Petukhov, V., Ermakova, T., Koskinen, J., Kukkonen, J., 2009. An operational system for the assimilation of the satellite information on wild-land fires for the needs of air quality modeling and forecasting. *Atmos. Chem. Phys.* 9, 6833–6847.
- Symeonidis, P., Poupkou, A., Gkantou, A., Melas, D., Yay, O.D., Pouspourika, E., Balis, D., 2008. Development of a computational system for estimating biogenic NMVOCs emissions based on GIS technology. *Atmos. Environ.* 42, 1777–1789.
- Tolika, C.K., Zanis, P., Anagnostopoulou, C., 2012. Regional climate change scenarios for Greece: future temperature and precipitation projections from ensembles of RCMs. *Global Nest J.* 14, 407–421.
- Turquetly, S., Hurtmans, D., Hadji-Lazarou, J., Coheur, P.-F., Clerbaux, C., Josset, D., Tsamalis, C., 2009. Tracking the emission and transport of pollution from wildfires using the IASI CO retrievals: analysis of the summer 2007 Greek fires. *Atmos. Chem. Phys.* 9, 4897–4913.
- Van der Werf, G.R., Randerson, J.T., Giglio, L., Collatz, G.J., Kasibhatla, P.S., Arellano Jr., A.F., 2006. Interannual variability in global biomass burning emissions from 1997 to 2004. *Atmos. Chem. Phys.* 6, 3423–3441.
- van der Werf, G., Randerson, J., Giglio, L., Collatz, J., Kasibhatla, P., Morton, D., DeFries, R., 2010. The improved Global Fire Emissions Database (GFED) version 3: contribution of savanna, forest, deforestation, and peat fires to the global fire emissions budget. *Geophys. Res. Abstr.* 12 (EGU2010-13010, 2010 EGU General Assembly 2010).
- Vautard, R., Schaap, M., Bergstrom, R., Bessagnet, B., Brandt, J., Buitjes, P.J.H., Christensen, J.H., Cuvelier, C., Foltescu, V., Graff, A., Kerschbaumer, A., Krol, M., Roberts, P., Rouil, L., Stern, R., Tarrason, L., Thunis, P., Vignati, E., Wind, P., 2009. Skill and uncertainty of a regional air quality model ensemble. *Atmos. Environ.* 43, 4822–4832.
- Wang, J., Christopher, S.A., Nair, U.S., Reid, J.S., Prins, E.M., Szykman, J., Hand, J.L., 2006. Mesoscale modeling of Central American smoke transport to the United States: 1. “Top-down” assessment of emission strength and diurnal variation impacts. *J. Geophys. Res.* 111, D05S17. <http://dx.doi.org/10.1029/2005JD006416>.
- Wiedinmyer, C., Akagi, S.K., Yokelson, R.J., Emmons, L.K., Al-Saadi, J.A., Orlando, J.J., Soja, A.J., 2011. The fire inventory from NCAR (FINN): a high resolution global model to estimate the emissions from open burning. *Geosci. Model Dev.* 4, 625–641.
- Yarwood, G., Rao, S., Yocke, M., Whitten, G.Z., 2005. Updates to the carbon bond chemical mechanism: CB05. Final Report prepared for US EPA, RT-04-00675 (http://www.camx.com/publ/pdfs/CB05_Final_Report_120805.pdf).
- Zanis, P., Monks, P.S., Schuepbach, E., Carpenter, L.J., Green, T.J., Mills, G.P., Bauguitte, S., Penkett, S.A., 2000. In situ ozone production under free tropospheric conditions during FREETEX '98 in the Swiss Alps. *J. Geophys. Res.* 105, 24223–24234.
- Zanis, P., Katragkou, E., Kanakidou, M., Psiloglou, B., Karathanasis, S., Vrekoussis, M., Gerasopoulos, E., Lysaridis, I., Markakis, K., Poupkou, A., Amiridis, V., Melas, D., Mihalopoulos, N., Zerefos, C., 2007. Effects on surface atmospheric photo-oxidants over Greece during the total solar eclipse event of 29 March 2006. *Atmos. Chem. Phys.* 7, 6061–6073.
- Zanis, P., Kapsomenakis, I., Philandras, C., Douvis, K., Nikolakis, D., Kanellopoulou, E., Zerefos, C., Repapis, C., 2009. Analysis of an ensemble of present day and future regional climate simulations for Greece. *Int. J. Climatol.* 29, 1614–1633.
- Zanis, P., Hadjinicolaou, P., Pozzer, A., Tyrlis, E., Dafka, S., Mihalopoulos, N., Lelieveld, J., 2014. Summertime free tropospheric ozone pool over the Eastern Mediterranean/Middle East. *Atmos. Chem. Phys.* 14, 115–132.
- Zhang, M., Uno, I., Carmichael, G.R., Akimoto, H., Wang, Z., Tang, Y., Woo, J.-H., Streets, D.G., Sachse, G.W., Avery, M.A., Weber, R.J., Talbot, R.W., 2003. Large-scale structure of trace gas and aerosol distributions over the western Pacific Ocean during the Transport and Chemical Evolution Over the Pacific (TRACE-P) experiment. *J. Geophys. Res.* 108 (D21), 8820. <http://dx.doi.org/10.1029/2002JD002946>.
- 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, 2313–2321.