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Modeling the impacts of biomass burning on air quality in and around Mexico City

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Abstract

The local and regional impacts of open fires and trash burning on ground-level ozone (O_3) and fine carbonaceous aerosols in the Mexico City Metropolitan Area (MCMA) and surrounding region during two high fire periods in March 2006 have been evaluated using WRF-CHEM model. The model captured reasonably well the measurement-derived magnitude and temporal variation of the biomass burning organic aerosol (BBOA), and the simulated impacts of open fires on organic aerosol (OA) were consistent with many observation-based estimates. We did not detect significant effects of open fires and trash burning on surface O_3 concentrations in the MCMA and surrounding region. In contrast, they had important influences on OA and elemental carbon (EC), contributing about 60, 22, 33, and 22 % to primary OA (POA), secondary OA (SOA), total OA (TOA), and EC, respectively, on both the local and regional scales. Although the emissions of trash burning are substantially lower than those from open fires, trash burning made slightly smaller but comparable contributions to OA as open fires did, and exerted an even higher influence on EC. SOA formation due to the open fires and trash burning enhanced the OA concentration by about 10 and 5 % in the MCMA, respectively. On the annual basis and taking the biofuel use emissions into consideration, we estimated that biomass burning contributed about 60, 30, and 25 %, respectively, to the loadings of POA, SOA and EC in both the MCMA and its surrounding region, with about 35, 18, and 15 % from open fires and trash burning. The estimates of biomass burning impacts in this study may contain considerable uncertainties due to the uncertainties in their emission estimates, extrapolations and the nature of spot comparison. More observation and modeling studies are needed to accurately assess the impacts of biomass burning on tropospheric chemistry, regional and global air quality, and climate change.

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1 Introduction

Biomass burning (BB), generally defined as open or quasi-open combustion of any non-fossilized vegetative or organic fuel, such as open fires in forests, savannas, agricultural lands, and biofuel burning (Akagi et al., 2011), is the largest source of primary carbonaceous aerosols and the second largest source of trace gases in the global troposphere (Andreae, 1991; Andreae and Merlet, 2001; Bond et al., 2004), contributing 20–40 % of CO, NO_x and non-methane hydrocarbons, and > 35 % of particulate organic carbon (OC). The trace gases and particulates emitted by or formed in the biomass burning plumes adversely affect human health and have important impacts on tropospheric chemistry, regional and global air quality, and climate change.

The air quality and atmospheric chemistry in the Mexico City Metropolitan Area (MCMA) is frequently affected by open biomass burning in the nearby mountains and savannas surrounding the city (Molina et al., 2010; Yokelson et al., 2011). Previous studies indicated that biomass burning can be an important contributor to fine particulate matter (PM) in the MCMA during the dry season (Bravo et al., 2002; Molina et al., 2007), particularly to organic aerosol (OA), which comprises approximately half of the total fine PM (Salcedo et al., 2006; DeCarlo et al., 2008; Kleinman et al., 2008; Aiken et al., 2009). Extensive multi-platform measurements during the MILAGRO (Megacity Initiative: Local And Global Research Observations) campaign in 2006 in the MCMA and the surrounding areas further demonstrated the important role of BB in OA loading and its air quality and climate impacts (Molina et al., 2010). The estimated BB influences on OA using different apportionment techniques from the multi-platform measurements during MILAGRO are highly variable. Using potassium (K^+) as the BB tracer, Moffet et al. (2008) reported that BB contributed 40 % to the submicron particle (PM_1) number observed at the urban supersite (T0) using aerosol time-of-flight mass spectrometry (ATOFMS). Based on a chemical mass balance (CMB) analysis of molecular marker species (levoglucosan) measured from ground-based filter samples, Stone et al. (2008) found that BB contributed 5–26 % (average 11 %) to particulate OC mass

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in the urban area and 7–39 % (average 16 %) in the suburban area of Mexico City. Querol et al. (2008) estimated about a 5–15 % contribution of BB to $PM_{2.5}$ (fine particles below 2.5 µm in aerodynamic diameter) (9–27 % to OA) concentrations in Mexico City according to their ground-based filter PM measurements and chemical analysis. Liu et al. (2009) reported a lower limit of 8 % contribution of BB to submicron PM in the Mexico City urban area based on a Positive Matrix Factorization (PMF) analysis of FTIR and X-ray Fluorescence (XRF) measurements of organic functional groups and elemental composition. From the same data set, Gilardoni et al. (2009) further estimated that BB contributed an upper limit of about 30–40 % to OC using non-soil *K* as the biomass burning tracer. de Gouw et al. (2009) estimated that the BB contribution to OC lied between 7 % and 39 % (mostly below 30 %) on the ground in the suburban supersite (T1) based on the correlation between the enhancement ratio of acetonitrile (CH_3CN) to CO and a CMB analysis. Aiken et al. (2009, 2010) used PMF analysis of Aerosol Mass Spectrometer (AMS) data measured at T0 and determined that BB contributed 15–23 % of the OA in general in Mexico City during MILAGRO and 23–31 % during the high fire periods. Marley et al. (2009) and Aiken et al. (2010) employed measurements of modern carbon (^{14}C) to estimate the impacts of BB on OC. Although there was a significant discrepancy in the reported ^{14}C estimates, both groups found that OC was enhanced by ∼ 13 % during high BB periods.

Aircraft observations around the MCMA during MILAGRO-2006 reported relatively higher contributions of BB to OA than surface measurements; this could be due to the afternoon aircraft sampling time and the major BB being forest fires above the Mexico City basin. Yokelson et al. (2007) estimated that mountain fires surrounding the MCMA contributed about 50 ± 30 % of $PM_{2.5}$ in the outflow based on aircraft measurements of HCN and CO and also by coupling fire emission factors with estimated biomass consumption and comparing to the official MCMA emission inventory. Crounse et al. (2009), using aircraft measurements of BB and urban emission tracers (hydrogen cyanide (HCN) and ethyne (C_2H_2), respectively) over and around the Mexico City basin, estimated that BB contributed about two- thirds of the OA (and one-third of CO,

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benzene and NO_y) in the MCMA outflow, while at the surface the BB contribution to the OA was reduced to about 25 %. DeCarlo et al. (2010) applied PMF analysis to high time resolution AMS OA data acquired on the C-130 flying over the MCMA and the Central Mexico Plateau during MILAGRO, and reported that BB accounted about 66 % of the total OA mass during a high fire event in this region.

To date model-based studies of the BB impact on PM and other pollutants in the MCMA have been limited. Emmons et al. (2010) used tagged tracers in a global modeling study and concluded that open fires did not make a dominant contribution to CO, NO_x and O_3 in this region, but they did not assess the impact of fires on PM. Fast et al. (2009) considered open fire emissions and compared their modeled POA to airborne measurements of POA. They concluded that the BB emissions of some large fires may be overestimated and that the timing of the biomass burning OA was not well simulated. Thus, the BB impact was not quantified with a bounded range. The model overestimation may also be due to biases in the placement of the fire smoke injection altitude or/and the transport of the smoke plumes. Hodzic et al. (2010a) predicted the contribution of BB to total OA in the MCMA, but they had large discrepancies with the observations in both the magnitude and temporal-spatial variation, particularly the timing. Thus, they did not attempt to definitively quantify the BB contribution to carbonaceous aerosols. Aiken et al. (2010) used particle dispersion analysis (FLEXPART) to qualitatively investigate the BB impact, and found that a later starting time for smoldering emissions improved the prediction of fire impacts, and that local fires were the dominant source for in situ biomass burning organic aerosols (BBOA) with small contributions from distant fires. Yokelson et al. (2009) noticed that distant fires (e.g. from the Yucatan) could make higher contributions to the Mexico City basin aerosol during El-Nino years.

The above measurement results, as summarized in Table 1, show that BB could be an important contributor to fine PM and especially OA concentrations in Mexico City, with an even larger impact aloft and on the urban outflow. The results also indicate that the BB impact on the atmospheric composition, particularly OA, is highly variable

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with large variations between different estimates. This is likely due to several factors, such as the use of different apportionment approaches and their associated limitations, difficulties in estimating the amount of biomass burned, emission characterization, and emission factors, etc. Also note that different metrics (OA, OC, PM_1, etc.) are used in different estimations. Given the importance of BB to many radiatively and chemically active gases and particulates in this region, it is of great interest to validate a model that can be used to assess the impacts during periods without measurements or to provide an independent estimate of the BB contribution. Validated simulations can also be used to estimate the BB contribution to secondary organic aerosols (SOA), which can be difficult to determine through measurements alone, because of the similarity in chemical characteristics of SOA of BB origin (BBSOA) to SOA from other sources. In addition, there are very few modeling efforts that quantify and assess the BB impact on EC in the MCMA. Finally, to date few studies have assessed the impact of trash burning (TB) on carbonaceous aerosols, which is an important but poorly quantified source of $PM_{2.5}$ in Mexico City and broader scales (Christian et al., 2010; Hodzic et al., 2012), and is also a major source of particulate chloride in the MCMA (Li et al., 2012).

In this study, we employ WRF-CHEM to evaluate the influence of biomass burning on air quality in Mexico City both on the urban and regional scales during MILAGRO, with an emphasis on fine carbonaceous aerosols and ozone. The emissions from open BB fires and trash burning are considered in the model since trash (or garbage) also contains a lot of biomass. The contributions of open fires and trash burning to OA and EC are apportioned. The impacts of TB on total $PM_{2.5}$ and chloride will be addressed in a companion paper (Li et al., 2012). Since the emissions from domestic and industrial use of biomass may be substantial (Christian et al., 2010; Yokelson et al., 2011) and will be considered in future modeling studies, we will attempt to provide a first-order estimation for their impacts, although the emissions of the domestic and industrial biofuel use are not available yet. Section 2 describes the methodology used in this study; Sect. 3 presents and discusses the results; Sect. 4 estimates the overall BB impacts during March 2006 and on the annual basis, and the impacts from the biofuel use, as

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well as discusses the impacts of BB emissions on air quality studies and implications for prescribed fire management; and Sect. 5 summarizes the study.

2 Methodology

2.1 WRF-CHEM model

In this study, we apply an updated version of WRF-CHEM (Grell et al., 2005; Tie et al., 2007) to investigate biomass burning impacts. This version was developed at the Molina Center for Energy and the Environment (Li et al., 2010, 2011). Briefly, the modifications include a new flexible gas phase chemistry module, an accurate and efficient gas-phase chemistry solver, the online Fast Tropospheric Ultraviolet and Visible (FTUV) Radiation for photolysis rate calculation, and an aerosol module based on the EPA CMAQ (version 4.6) aerosol module (Binkowski and Roselle, 2003). In this aerosol model, the most recent advances in our understanding of SOA formation and processing are incorporated, including updated (Ng et al., 2007) and NO_x-dependent (Lane et al., 2008b) SOA yields, the volatility-basis set approach (Robinson et al., 2007; Lane et al., 2008a; Tsimpidi et al., 2010), and the oxidation hypothesis of semivolatile and intermediate volatile organic compounds (S/I VOCs) by Grieshop et al. (2009). In addition, heterogeneous HONO sources, which are important in Mexico City, are also parameterized and included in the model (Li et al., 2010). Details of the modifications are described in Li et al. (2010, 2011).

2.1.1 Model configuration

Two high fire emission periods, 10–14 and 17–21 March 2006, were selected for this study based on the MODIS satellite fire counts, BB emission rates, and the AMS-PMF analysis (Aiken et al., 2010).

The model domain (Fig. 1) covers the MCMA with a 110 × 100 grid at 3 km horizontal resolution and 35 vertical layers extending from the surface to 50 hPa with variable ver-

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tical spacing (the first model layer is about 35 m a.g.l.). The dynamical modeling system uses the Lin microphysics scheme (Lin et al., 1983), QNSE PBL scheme (Sukoriansky et al., 2005), Noah land-surface model (Chen and Dudhia, 2001), Mlawer longwave radiation parameterization (Mlawer et al., 1997), Dudhia shortwave radiation parameterization (Dudhia, 1989), and Kain-Fritsch Cumulus Parameterization (Kain 2004). Meteorological initial and boundary conditions are driven by NCEP $1^{\circ} \times 1^{\circ}$ reanalysis data, and chemical initial and boundary conditions are interpolated from the MOZART 3-h output (Horowitz et al., 2003). The SOA boundary conditions in the boundary layer are set to be $1.4\,\mu g\,m^{-3}$ according to previous studies conducted in the MCMA (Hodzic et al., 2009; Dzepina et al., 2009). Because fire plumes are usually narrow and their local and regional influences are very sensitive to dispersion and transport, we have tested several PBL schemes and found that the Quasi-Normal Scale Elimination (QNSE) parameterization was the most suitable PBL scheme with regards to the PBL wind field and transport in this study compared to other options, such as the YSU and MYJ schemes that are commonly used in WRF modeling.

2.2 Emissions

The emissions considered in this model include fossil fuel combustion (mobile, area and point sources), open burning of biomass and trash, and biogenic sources. The emissions from domestic and industrial use of biomass may also be substantial (Christian et al., 2010; Yokelson et al., 2011). For example, on the national scale, Yokelson et al. (2011) and Christian et al. (2010) estimated that the biofuel use accounted for about 39 % of primary $PM_{2.5}$ and 20 % of NO_x and VOCs emitted from the total BB emissions in 2006. The emissions from domestic and industrial biofuel use (such as food cooking and brick making) are not included in this study, but will be considered in our future modeling studies.

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2.2.1 Fossil fuel combustion

The fossil fuel emissions are defined loosely as anthropogenic emissions, and these two terms will be used interchangeably in this study (strictly speaking a portion of biomass burning emissions comes from human activities). The fossil fuel emissions were constructed from the official emission inventory (EI) for the year 2006 for the MCMA and were adjusted based on field campaign measurements and the MCMA air quality monitoring network (RAMA) observations (Song et al., 2010). The emissions outside of the MCMA were a combination of the official regional emission inventory for point sources and an extrapolation of the MCMA emissions scaled to the population distribution for the mobile and area sources. The emission rates of gaseous species were similar to those in Song et al. (2010), except that we have applied an additional factor of 1.4 to increase the emissions rates of higher aromatics (ARO2) given in Song et al. (2010), because in their study the emission rates of ARO2 remained underestimated after their adjustments.

Primary organic aerosols are semi-volatile and undergo gas-particle partitioning under ambient atmospheric conditions. The evaporated portion of emitted POA particles are conventionally not included in any emission inventories. Following Tsimpdi et al. (2010), the amount of semivolatile VOCs (SVOCs) was estimated to be 2 times the particle-phase POA emitted. In addition, the co-emitted intermediate VOCs (IVOCs) (but are never in particle phase) were equivalent to 1.5 times the primary organic aerosols emitted. The total amount of material (POA + SVOC + IVOC) introduced to the model is 7.5 times the particle-phase POA emissions that are not corrected for the dilution effect (Robinson et al., 2007). Details of the POA emission modification are described in Tsimpdi et al. (2010) and Li et al. (2011).

2.2.2 Open fires

The biomass burning emissions considered in this study are those from open fires surrounding Mexico City (dominantly forest fires) and the trash burning. A product of

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1 km × 1 km for the open fire daily emissions of trace gases and particles was developed following the method described by Wiedinmyer et al. (2006, 2011). The emissions model applied emission factors (EF) measured during the MILAGRO campaign (Yokelson et al., 2007) and used MODIS fire detection data (fire location and timing) (http://maps.geog.umd.edu; Davies et al., 2009). The uncertainty for the fire emissions calculated through this approach is about a factor of 2. A preliminary version of the open fire emissions calculated above (beta version) has been used by Fast et al. (2009) to evaluate the BB impacts on POA in the MCMA.

The daily emissions were temporally resolved to hourly emissions using satellite fire count-based diurnal profiles. A default diurnal profile (*profile_default*) was applied to almost all fire, which was calculated statistically from all fires in the North America subtropical areas in the spring 2003 using the 2003 GOES satellite fire counts (Wiedinmyer, personal communication, 2010). In addition, an alternative diurnal profile (*profile_2*), in which emissions started later and continued into the night time, was applied to consider the effects of some smoldering fires not detected by satellite observations. Figure 2 shows the two sets of diurnal profiles. Note that the start time in the diurnal profiles for individual fires may shift sooner or later. For the majority of the fires, the emissions were allocated evenly in the 2nd and 3rd model layers (up to 250 m), while the emissions of smoldering fires were mostly released in the 1st model layer (90 %). The reason for a lower release height of the smoldering fires is because these fires usually have smaller flames and continue to emit at night where their emissions are usually trapped in the shallow nocturnal boundary layer. More detailed information on the use of the diurnal profile and the release height of fire emissions is presented in Sect 3.1.2.

The emissions of SVOCs from the open fires and trash burning were treated similarly as those in the anthropogenic sources (scaling wise) in this study, while no additional IVOC emissions were included (Grieshop et al., 2009) and the volatility distribution followed the approach of Grieshop et al. (2009) for the wood smoke data.

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2.2.3 Trash burning

The trash burning emissions in the MCMA were estimated based on the garbage fire emissions factors measured during MILAGRO (Christian et al., 2010) and literature (Lemieux et al., 2004; Akagi et al., 2011), in conjunction with a 1 km × 1 km spatial distribution of population and socioeconomic classifications in Mexico City (Hodzic et al., 2012). In the estimation, the daily per capita trash production and percentage trash burned for different socioeconomic classes was assumed following Ojeda-Benıtez et al. (2008). The uncertainty in the estimated TB emissions is about a factor of 2 or more. We also assume the trash burning emissions are time invariant, since no temporal information is available. This is an approximate first-order assumption and needs to be improved through future observational data or model-measurement comparisons of trash burning molecular markers, such as multiple metals pertinent to TB as proposed by Christian et al. (2010) in Mexico City.

The daily emissions from the adjusted anthropogenic sources (fossil fuel combustion), open fires and trash burning in the MCMA during MILAGRO are presented in Fig. 3; the domain-wide average daily emissions from these sources during the entire MILAGRO and simulation period are shown in Table 2. Compared to the anthropogenic emissions we have estimated based on the MCMA-2006 emission inventory (Song et al., 2010), both in the MCMA and the model domain-wide, biomass burning is a minor source for CO, VOCs and NO_x (less than 10 %). In contrast, open fires are the major source for POA in the MCMA and domain-wide during the dry season (130 and 170 % relative to the anthropogenic emissions, respectively, and even higher during the simulation period), and the open fire contribution is highly variable with time. In the high fire events, open fires dominate the anthropogenic sources, accounting for 3–6 times of the anthropogenic emissions for POA. Trash burning contributes to the emissions of POA at about 45 % of the anthropogenic counterpart in the MCMA and 15 % domain-wide. The contribution to the EC emissions from the open fires is also highly variable with an average of 22 % of the anthropogenic sources in the MCMA (27 % domain-

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wide), which is less significant compared to POA. Garbage burning contributed about 15 % as much EC as the anthropogenic sources in the MCMA.

The TB emissions outside the MCMA are not available and are not included in this study. Therefore it should be noted that the estimation of the TB impact will only be restricted to the MCMA, and the model-estimated "regional" impact of TB is in fact the influence of the MCMA TB emissions on the regional environment.

The total emissions of POA from open fires and trash burning in the MCMA and in the model domain exceed those from the fossil fuel use in March 2006. This is consistent with the measurement-based calculations by Yokelson et al. (2011), who estimated that about 175 $Tg\,yr^{-1}$ of biomass, biofuel and garbage are burned in a typical year in Mexico nationwide.

2.3 Measurements

The simulated OA concentrations are compared with the MILAGRO High-Resolution Aerosol Mass Spectrometer (AMS) OA measurements at the urban (T0) and the suburban (T1) supersites (Molina et al., 2010). The "measured" biomass burning OA (BBOA) component was derived from the Positive Matrix Factorization (PMF) analysis of the AMS data (Aiken et al., 2009, 2010). The AMS-PMF analysis, which has an uncertainty of about 35 %, also identifies hydrocarbon-like OA (HOA) and oxygenated OA (OOA, mostly secondary OA or SOA). Note that the AMS-PMF BBOA is dominantly the primary organic aerosol (POA), and BB SOA is included in OOA due to similar spectra of the two.

Simulated EC concentrations are compared with the EC data measured using an Aethalometer and an aerosol absorption photometer at T0 and T1 (Marley et al., 2009a, b). Simulated CO and O_3 concentrations are compared with the measurements from the RAMA monitoring stations.

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2.4 Estimation of the simulated BB impacts

The BB impacts are calculated by conducting simulations with and without BB emissions. The difference in the scenarios with and without the BB emissions is attributed to BB. Contributions from a specific burning type, such as open fires and trash burning, are estimated using similar method. The percentage change is the difference relative to the scenario with all emissions included.

3 Results and discussions

3.1 Model performance

3.1.1 Carbon monoxide and ozone

Figure 4 shows the comparisons of measured and simulated near surface CO and O_3 hourly concentrations averaged over the RAMA stations (about 18 stations with available observation data during the simulation periods with majority located in the urban area), and Table 3 presents the statistical performance for O_3, CO and carbonaceous aerosols. In the simulations, the biomass burning emissions are included. During the two 5-day episodes, in general the model captured the diurnal variations of CO and O_3 reasonably well, with the index of agreement (IOA) reaching 0.88 and 0.96 for CO and O_3 respectively. The days with inferior O_3 agreement are usually coincident with the days of inferior CO agreement, such as on 10 and 11 March when both CO and O_3 were under predicted. 10–12 March was an "O_3-North" episode (de Foy et al., 2008) followed by a transition to an "O_3-South" episode starting on 15 March. 18–21 March was another "O_3-North" period. The "O3-North" event features a convergence zone that forms inside the basin and proceeds to the north and northeast during the daytime, causing the urban pollution plume to move towards the north and northeast progressively. The under-predictions of CO and O_3 on these two days are

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probably because the simulated daytime southerly winds were too strong and caused the northward transport to be too fast and too strong, as illustrated in Fig. 5. The four-dimensional data assimilation (FDDA) technique, not used in this study, could improve the meteorological fields for this episode (Song et al., 2010).

3.1.2 Primary Organic Aerosol from Biomass Burning (BBPOA)

The PMF-derived AMS BBOA is mainly primary BBOA (BBPOA), with the SOA produced from the BB activities (BBSOA) detected mostly as OOA (oxygenated OA). Figure 6 shows the comparison of the PMF-AMS and simulated BBPOA at T0 during 10–14 March and at T0 and T1 during 17–21 March (there were no AMS measurements at T1 before 14 March). Two emission scenarios are presented in the simulation – "*default*" and "*adj*". In the "*default*" scenario, the default diurnal profile was used for all open fires (see Fig. 2). In the "*adj*" simulation for the episode of 10–14 March, the profile_2 was used for the fires located south of T0 within 60 km on 10–11 March. In the "*adj*" simulation for the episode of 17–21 March, the profile_2 was applied to the open fires located in the southeast of T0 within 60 km on 17 March, the fires in the south of T0 with 60 km on 18 March, and three large fires in the southwest close to T0 on 20–21 March. The fires with the profile_2 diurnal profile were distributed in the model's bottom layer; all other fires were distributed in the 2nd and 3rd model layers. The rationales for the adjustment of the diurnal profile of sectional or individual fires were based on the evening-nighttime transport conditions, fire locations and their potential direct hits at T0 (as will be shown later in Figs. 7 and 8). The range of 60 km was chosen based on Aiken et al. (2010) who found that the open fires within 60 km of T0 dominated the BB influences to T0. We have conducted several additional scenarios to examine the sensitivity of the simulated BB impacts at T0 and T1 to the BB diurnal profile, smoke injection altitude, and transport condition (through different PBL schemes); we found that the simulated BB impacts at specific locations were most sensitive to meteorology, quite sensitive to the diurnal profile, but less sensitive to the injection altitude.

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Figure 6 shows that with the adjusted BB emissions, the model captures both the magnitude and temporal variation of the BBPOA concentrations at T0 quite well, particularly during 10–14 March. During this period, the AMS BBOA concentrations started at very high levels on 11 March ($\sim 28\,\mu g\,m^{-3}$) and decreased progressively with time and very low BB effects were found on 14 March, which the model captures the inter-diurnal variation very well. The simulated BBPOA was highly variable temporally, ranging between as low as a few tenth $\mu g\,m^{-3}$ and as high as over $20\,\mu g\,m^{-3}$. BBPOA was observed generally high in the early morning, decreased during the daytime when the mixing and transport became stronger, and started to accumulate at late evening when the afternoon emissions increased and the nocturnal PBL set in. This diurnal variation is also well captured by the model, although there are some biases in the exact timing. On 11 March, a very high BBPOA peak was observed in the early morning, but the model precedes the peak by about 4–5 h, probably due to rapid transport in the model. During 17–21 March, the model captures reasonably well the diurnal and inter-diurnal variability of the BBOA. Except for the two extremely high early morning BBPOA peaks detected by the AMS on 18 and 21 March (~ 20 and $30\,\mu g\,m^{-3}$), the model simulates reasonably well the BBPOA concentrations and the diurnal variation at T0, with the IOA of 0.60 (see Table 3) and a model's underprediction of 28 % (average concentrations of $4.4\,\mu g\,m^{-3}$ in observations vs. $3.2\,\mu g\,m^{-3}$ in simulations during the simulation episodes). We also note that there is a significant bias in the simulation (with the RMSE value larger than the averages), suggesting a significant uncertainty in the modeling; however, it could also be reflecting the real high variability in the BB activities. The model underprediction could be attributed to the uncertainties in both the AMS and PMF analysis and modeling, and could also be attributed to the fact that some small fires were not detected by satellites and were not registered as hotspots (Yokelson et al., 2011). If the two extreme events are removed in the comparison, the average concentrations would become $3.1\,\mu g\,m^{-3}$ from observation and $2.8\,\mu g\,m^{-3}$ from simulation, and the IOA would improve to 0.76 with the RMSE reducing to $2.8\,\mu g\,m^{-3}$. At T1, the model was able to predict the magnitude of BBPOA concentration, but failed

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to reproduce the diurnal variability. In addition, there were limited observation data on OA, which makes the comparison more difficult.

Aiken et al. (2010) attributed the two peaks (on 18 and 21 March) to the nearby smoldering fire plumes that directly "hit" T0. They applied FLEXPART to estimate the fire impact factor (FIF) and found that using a diurnal profile similar to the *profile_2* increased the overall agreement between AMS BBOA and FIF, but the improvement for the 21 March peak was still very limited. We examined these two peaks with various hypothetical diurnal profiles of the BB emissions, and found that only limited improvements can be achieved in reproducing the two observed peaks. Furthermore, whenever the nighttime and early morning BBPOA were better simulated at T0 using different BB diurnal profiles, the BBPOA concentrations at T1 would be significantly overestimated. Simulated spatial distributions of BBPOA and its nighttime evolution, as illustrated in Fig. 7, show that if a BB plume hits T0 at night, it would also hit T1 because of the proximity of T0 and T1, and the weak but consistent southerly nighttime wind field that confines yet horizontally broadens the nighttime BB plume within the shallow PBL. The observed BBPOA concentrations were not correlated to each other at T0 and T1, but the simulated BBPOA were correlated to some extent, particularly at night. This discrepancy is probably due to that the satellite-based BB emission inventory may not capture the emissions of some small local fires as mentioned above. In addition, Aiken et al. (2010) claimed that the increase of AMS BBOA at 5:00–8:00 p.m. on 20 March at T0 was due to the hit of the smoldering fire. Our simulations show that the evening spike of BBPOA on 20 March did not have to be attributed from the smoldering fires (note that the default case was also able to reproduce this spike). If the smoldering fire hit T0 starting at 5:00–6:00 p.m. on 20 March, it would most likely remain hitting T0 throughout the nighttime due to the constant weak wind pattern, and would be less likely to circumvent T0 from 8:00 p.m.–4:00 a.m. next day and resurge after 4:00 a.m. without affecting T1. It is probable that some local burnings could contribute to the two extreme early morning peaks on 18 and 21 March. The possible local burnings are less likely from cooking sources, which are an important source for OA (Christian et al.,

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2010; Mohr et al., 2011) in the urban areas, but would not exert significant impacts until later hours. However, it cannot be ruled out that meteorology may play a critical role in the occurrence of the two peaks, since the transport and disperse of a BB plume is sensitive to the meteorological conditions. Figure 7 also shows that BBPOA is spatially highly variable, with maximum concentrations occurring near the fire location and its immediate downwind area at night.

3.1.3 Primary Organic Aerosol (POA) and Secondary Organic Aerosol (SOA)

The comparisons of AMS-derived and simulated surface OA concentrations at T0 are shown in Fig. 8. Note that in this comparison, BBPOA is included in POA, since the AMS-PMF BBOA is dominantly the primary organic aerosol; the SOA in the measurements is represented by the AMS-PMF OOA component, which is the SOA surrogate. No comparisons at T1 are presented in this study due to the limited availability of AMS OA measurement data as mentioned above. For the two episodes (10–14 March and 17–21 March), the POA concentrations and their intra- and inter-diurnal variations simulated with the BB emissions agree well with the observations with the IOA of 0.70. On the other hand, SOA at T0 tended to be systematically overestimated even without the BB influence (6.9 vs. 8.2 $\mu g\,m^{-3}$ in observed and predicted averages, and the IOA of 0.66; see Table 3), especially during 10–14 March. The systematic overestimation of SOA is probably associated with the meteorological conditions. We were also aware that in the SOA simulation, we have assumed that the OH- initiated oxidations of intermediate and semi-volatile VOCs did not consume OH because OH would be recycled at the end. The OH non-consuming aging processes can enhance the daytime SOA formation by more than 10 % (Li et al., 2011). A more reasonable scenario might be a partial consumption of OH in the aging processes.

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3.1.4 Elemental carbon

As shown in Fig. 9, the model captured both the magnitude and temporal variations of the EC concentration at T0 very well, except during a few days when the observed EC levels were very high (such as on 10, 11 and 13 March). Other than that, no systematic biases were found; the IOA at T0 is 0.76 (0.73 and 0.79 during 10–14 March and 17–21 March, respectively). On the other hand, EC at T1 was systematically underestimated by about 42 % in the model, especially during the second episode, although the temporal variation was reasonably predicted. The IOA at T1 is 0.53 (0.37 and 0.66 during the two periods respectively). The underestimation at T1 could be due to the underestimation of EC emissions in the local and surrounding areas. For instance, Christian et al. (2010) observed high EC emissions from several brick kilns near T1.

3.2 Evaluation of simulated BB impacts at urban and regional scales

Figures 4, 8, 9 and Table 4 illustrate the BB impacts on ground-level O_3, POA (including BBPOA), SOA and EC in the MCMA urban and surrounding areas. Biomass burning has, from this study, relatively small effects on the surface O_3 concentration both in the MCMA urban and suburban areas (with an average of −0.2 % contribution), due to its comparatively low contribution to total emissions of VOCs and NO_x (less than 10 % of the total MCMA emissions) and the compensating effects of the emitted aerosol precursors and aerosols on the O_3 production. The BB contribution to POA is significant, consistently about 33 % at T0 in the two episodes, and much higher at T1 of about 63 %. The BB contributions to SOA are smaller than that to POA, with similar contributions of 22 % and 24 % at T0 and T1, respectively. The BB contributions to the total organic aerosols (TOA) are about 30 % and 40 % at T0 and T1, respectively. Note that important temporal variation exists in all numbers as indicated in the standard deviations. Exclusion of the observed extreme BB events (11, 18 and 21 March) does not change much the BB contributions. The BB influence on EC is minor at T0 (∼ 9 %), but

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becomes significant at T1 (29 %). However, as noted above, the model underestimation of EC at T1 probably contributes to this result.

The BB influences on the surface O_3 concentrations are also minor (−1.3 and 0.2 %, respectively) when averaged over the MCMA (urban scale) and the model domain (regional scale). The regional O_3 impact (0.2 %) is likely underestimated, because of the probable underestimation of the BB VOC emissions. The BB VOC emissions are usually estimated by projected biomass burned and the emissions factors for VOC species detected by available instrumentation; however, only about 50 % of VOCs are identified on the mass basis (Yokelson et al., 2008; Akagi et al., 2011), most of those unidentified are high mass reactive compounds, and not all identified species have measured EFs. The relative contribution of BB to the total VOC emissions in our study is about 4 % domain-wide, much lower than the global average of 20–40 % (Andreae, 1991; Andreae and Merlet, 2001). On the other hand, O_3 production in the fire plumes are typically NO_x-limited (Jaffe and Widger, 2012), therefore photochemical modeling is needed to examine how exactly the VOC underestimation will affect O_3 production. Observations of the excess ratio of $\Delta O_3/\Delta CO$ in the fire plumes have been used to characterize the BB O_3 production in smoke plumes (Jaffe and Wigder, 2012). Using ΔO3/ΔCO value of 0.15 in aged fires (after several hours) in Central Mexico, and noting the 10 % contribution of BB CO to the anthropogenic CO emissions (Table 2), we estimate that the BB contribution to O_3 would increase to about 1.5 %, which is not significant. The underestimation of BB VOC emissions would probably have even smaller effects on the BB O_3 impact in the MCMA due to the overwhelming dominance of anthropogenic VOC emissions (> 98 %).

The BB exerts a dominant impact on POA concentration (∼ 60 %) on the urban and regional scale, which is consistent with its dominance in the POA emissions. The BB exerts a slightly higher impact on SOA in the MCMA (27 %) than on the regional scale (20 %), similar to its contributions at T0 and T1. This indicates that the BB's impacts on SOA are quite spatially uniform. The impacts of BB on EC concentrations are about

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20 % on both the urban and regional scales, but as mentioned above, this contribution may be overpredicted.

These simulated contributions of biomass burning to OA are much lower than their fractional contributions to the emissions (see Sect. 2.2 and Table 2), mainly due to the difference of emission diurnal profiles in the anthropogenic and BB sources, where a large portion of anthropogenic components is emitted in the morning hours when the pollutants are trapped in the PBL, while the majority of BB components is released in the afternoon when the meteorology is conductive. On the other hand, the simulated BB contributions to OA are higher than many of the observation-based estimates (where most lie below 20 %, see Table 1). This is probably because the simulated BB effects include the BBSOA contributions and the trash burning impacts while the observation-based estimates do not (or only include a very small portion), which we will discuss further later.

It is interesting to note, as shown in Table 4, that the BB impacts in the MCMA are similar to those at T1, the suburban site, but are different (particularly for POA) to those at T0, the urban site. This difference is probably mainly due to the high heterogeneity of the anthropogenic emissions in the MCMA, suggesting that measurement or simulation at one site (or a limited number of sites) may not represent the overall conditions of an urban area.

The simulated BB impacts are not significantly affected by the observation-derived BB extremities in the early morning of 11, 18 and 21 March, since the model did not capture the last two extreme events very well. The exclusion of the observed extreme events in the early morning of 11, 18 and 21 March would alter the simulated BB contributions to OA and EC by less than 2 % both in the MCMA and domain-wide.

3.3 Partitioning of simulated BB impacts

We have conducted case studies to estimate the contributions of open fires and trash burning to ground-level OA and EC through the Brute Force method. Table 3 shows the partitioning of the contributions from sources of open fires (OF), TB and other sources

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(anthropogenic and biogenic combined) to OA and EC at T0 and T1. During the two high BB periods, at T0, the open fires, trash burning, and other emission sources contribute about 20, 14, and 66 % to POA, 13, 10, and 78 % to SOA, and 4, 5 and 91 % to EC, respectively; their contributions to T0 OA are 17, 12, and 70 %, respectively. At T1, the contributions from the open fires and TB to SOA are similar to those at T0 (15 and 9 %, respectively), while their impacts on POA enhance importantly (reaching 31 and 33 %, respectively), and their impacts on EC enhance even more, by a factor of 3 (reaching 12 and 18 %, respectively). The impacts of open fires and TB on TOA account for about 23 and 18 % at T1, respectively.

There are several noticeable results in the estimates. First, the BB emissions make important impacts on the ground-level concentrations of POA and TOA in the MCMA, accounting for about one-third of POA and TOA at T0 and 40–60 % of POA and TOA at T1, while their influences on SOA are much smaller. Second, the influence of TB on OA is surprisingly comparable to that of open fires in both the urban and suburban areas, and even higher contributions to EC, although the total emissions of POA and EC from the TB are much lower than the counterparts of the open fires during high BB periods. As discussed above, this is probably attributed to the difference of the emission temporal profiles coupled with the meteorological characteristics. Finally, the simulated impact of open fires on TOA at T0 (17 %) is consistent with many observation-based estimates. For example, the average BB contribution to OA is estimated to be about 11 % by Stone et al. (2008), 18 % by Querol et al. (2008), 19 % by Aiken et al. (2010), and 20 % by Gilardoni et al. (2009) (see Table 1). However, the simulated contribution is lower than the estimate of 27 % by Aiken et al. (2010) during high fire periods, which is mainly due to the fact that the model failed to capture the extremely high BBPOA concentrations observed in the early morning on 18 and 21 March.

The tracer- or PMF-based observation estimations of BB impacts usually do not include the TB influence. Furthermore, most observation-based estimations do not include SOA formed from the biomass burning (BBSOA) either. If BBSOA is included, according to our simulations, the contribution of open fires to OA would be additional

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8 % and 11 % at T0 and T1, respectively, while BBSOA from TB contributes about 5 % to TOA in the suburban area. This is contrast to the findings of Aiken et al. (2010) who reported very minor contributions of BB to SOA. Their estimates on the BBSOA effects were based on the change of SOA during high and low fire periods, and thus may be subject to the probable differences in meteorological conditions during different periods.

We further estimate the BB partitioning on the MCMA-local and regional scales (Table 5b). For POA, the contribution from open fires increases from 37 % in the local scale to 54 % on the regional scale; on the other hand, the TB contribution decreases from 23 % in the MCMA to 8 % on the regional scale. Similar to the case at T0 and T1, the impact of open fires on SOA is similar on the local and regional scales (18–21 %), but the TB has a smaller influence on the regional scale (2 % vs. 6 %). On both the local and regional scales, the open fires have consistent influences on TOA (~ 30 %), although open fires contribute relatively smaller within the MCMA. For EC, the contributions to the EC concentrations from the open fires and TB in the MCMA are similar, in contrast to the much higher EC emissions from the open fires. On the regional scale, open fires have relatively much higher impacts on EC compared to TB (16 % vs. 4 %). Nevertheless, other emission sources, such as fossil fuel consumption, dominate the EC concentrations.

4 Broader BB impacts

4.1 Extrapolation of BB's monthly and annual impacts

In the previous section, we have calculated the BB impacts during the two high-fire periods. A more general question of interest is what are the BB's overall impacts monthly or even annually. In this section, we will estimate the longer-term impacts based on the simulations of the two events and the BB emissions for a longer time period, assuming that the BB impacts can be linearly scaled according to the BB emissions.

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Both within the MCMA and on the regional scale, the BB emissions (open fires + TB) accounted for 75 % to the total POA emissions and 35 % to the total PEC emissions during the simulation period, while the BB emissions accounted for about 65 % and 25 %, respectively, to the total POA and PEC emissions in March 2006. During the simulation period, BB contributes 60 % to the POA concentrations in the MCMA and on the regional scale, and about 20 % to the EC concentrations. Assuming the BB impact (on POA and EC) is proportional to its emissions, we can estimate that BB contributes about 50 % and 15 % to POA and EC, respectively, on both local and regional scales in March 2006. Similarly, we estimate that the BB contributes 20 % to SOA in March 2006. On the annual basis, according to the MODIS hotspot data for the year 2006 in Mexico, the hotspot number during March accounted about 9 % of the total. Assuming a linear relation between the BB emissions and the fire counts, we expect that the contribution of BB to POA, SOA and EC on the annual basis would be about 90 % ($\approx 1/12/0.09 \times 100$) of those in March, i.e. 45, 18 and 14 %, respectively, both on the local and regional scales.

4.2 Estimation of the impacts of biofuel use

Due to the unavailability of the emission inventory for the domestic and industrial biofuel use, we have not directly calculated the impacts of the biofuel use on OA. However, it is possible to estimate its influence in a first-order approximation by combining the simulation results above and the emission amounts from the biofuel use with some assumptions. Christian et al. (2010) and Yokelson et al. (2011) estimated that on the annual basis, the emissions from the domestic and industrial biofuel use account for about 39 % of the total BB emissions for $PM_{2.5}$ (open fires accounting for 52 %) in Mexico. Assuming that the biofuel emissions and transformations behave similarly as the open fires and TB do in affecting the air quality and photochemistry, we estimate, on the annual basis, that the biofuel use emissions would contribute about 25, 12, and 10 %, respectively, to the total concentrations of POA, SOA, and EC in both MCMA and its surrounding region, while the open fires and TB emissions combined would

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contribute about 35, 18, and 15 %, respectively (note here the total concentrations include the contribution from the biofuel use, i.e. the denominator changes). The annual contributions to POA, SOA and EC loadings from all the BB sources (open fires, TB and biofuel use) would then be 60 %, 30 %, and 25 %, respectively. We are aware that there may exist large uncertainties in this estimation, which originated from the emission estimation, temporal variations of the emissions and the linear-response scaling approach, however, this is the best assessment we are able to obtain with the information available.

4.3 Implications of the BB emissions on air quality and prescribed fire control

Open fire emissions are generally estimated from the total biomass consumptions and the temporal-spatial distribution is typically retrieved from satellite detection of hotspots and/or burned areas) in conjunction with field-measured emission factors. Due to the inherent limitations of the satellite detection technique (such as low frequency overpass and difficulties in detecting small size and short duration fires, as well as the meteorological factors), the retrieved biomass consumption estimate and fire distribution are highly uncertain (Wiedinmyer et al., 2011). The BB field-measured emission factors also vary considerably from fire to fire due to factors such as burning type (smoldering vs. flaming) and meteorological conditions (Yokelson et al., 2007, 2011). The TB emission estimates contains even higher uncertainties (Christian et al., 2010), due to the difficulty in accurately estimating the amount of garbage generated, amount of garbage burned, and the composition of garbage, etc. Nevertheless, the BB emission estimates are likely underestimated in Mexico City (Yokelson et al., 2011; Christian et al., 2010). Therefore the BB emissions presented at Table 1 and the BB impacts shown above are not the upper limits of the BB effects in Mexico City. BB is a major emitter of POA in the MCMA and at regional scales, surpassing the anthropogenic sources. On the national scale, Yokelson et al. (2011) estimate that BB emissions are large enough to be of major importance for particulates and many gaseous species in Mexico.

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The BB emissions and their impacts on air quality in the MCMA and at regional scales have important implications in urban and regional air quality studies. First, any PM modeling studies should include the BB emissions, which are generally severely underestimated in the official emission inventories. On the other hand, the impact of BB on O_3 concentrations is mostly likely negligible in the MCMA and the surrounding region despite probable underestimates of the BB emissions, due to their moderate contributions to the O_3 precursors (VOCs and NO_x) and the offset effects of BB-originating aerosols on O_3 formation. This is in contrast to the BB's important role (~38 %) in tropospheric O_3 at the global scale (Andreae, 1991; Levine et al., 1995).

As pointed out previously, the BB impact is sensitive to the temporal profile of the BB emissions, with higher influences for biomass burned at nighttime (from evening to early morning next day) with significantly reduced influences for daytime fires. This provides important information for the management of planned or prescribed fires that are conducted to reduce fuels and wildfire hazards before the fire season start. It will be beneficial to conduct the prescribed fires during the daytime, best in the early afternoon when the meteorological conditions are conductive. The same management also holds for garbage burning.

The BB impact on elemental carbon, as illustrated in this study, is moderate in the MCMA (9 %), but becomes more important at the regional scale (~30 %). Considering the higher hygroscopicity and relatively short lifetime of the BB-produced EC (BBEC) compared with that of the fossil fuel-origin EC (Petters et al., 2009), the local and regional climate warming effect induced by BBEC is probably not significant in Mexico City.

4.4 Comparison to other model studies of TB

This model exercise uses similar open fire and TB emissions to another recent model-based study focused on TB impacts (Hodzic et al., 2012). As a result, the contributions of TB to MCMA OA are similar in both studies in general, except a slightly higher TB impact from our study. However, the general agreement does not indicate a high

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level of certainty in the TB or even BB impacts. Much of the uncertainty stems from the approximate factor of two uncertainties in anthropogenic POA and VOC, BBPOA and VOC, and even higher uncertainty in TB POA and VOC. SOA production is most studied from the anthropogenic source and has been found to be highly variable for reasons that are poorly understood. SOA from the other sources is less studied (BB) or completely unmeasured/unstudied (TB). The measurements of OOA, HOA, BBOA, etc., are based on simplifying algorithms applied to complex mass spectra. The derived quantities are useful, but have non-negligible error that may be incompletely characterized in some complex environments. The actual controlled quantity from an air quality perspective is $PM_{2.5}$. The MCMA has prodigious emissions of NO_x and SO_2 which will convert to $PM_{2.5}$ in ways that depend on meteorology and a changing mix of co-emitted species. The arid climate of the MCMA and the nearby agriculture lead to a large dust component to the aerosol presenting another challenge. Antimony (Sb) has been used to estimate TB impacts as upper limits (Christian et al., 2010) or for lower central estimates (Hodzic et al., 2012), but Sb is also produced by vehicle brake pads and other sources such as metal processing (Christian et al., 2010). The brake pad source, unlike TB, also produces large amounts of Ba, but in varying ratios to Sb in different studies (Sternbeck et al., 2002; Schauer et al., 2006). Thus as proposed by Christian et al. (2010) a multi-species analysis based on a suite of metals with locally measured source profiles for TB, vehicles, and any smelters or other Sb sources would likely offer the best way forward to quantify the impacts. In addition, most of the intensive measurement campaigns in the MCMA have been made in the springtime and it would be worthwhile to implement large-scale efforts at other periods of the year.

5 Conclusions

Biomass burning (open fires and trash burning) contributes substantially to the OA emissions in the MCMA and its surrounding areas, while their contributions to the aerosol precursors are relatively minor compared to the anthropogenic sources. In the

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present study, the emissions of aerosols and aerosol precursors from the open fires were calculated based on emission factors and emission ratios measured during the MILAGRO campaign in conjunction with the MODIS fire detection data, whereas the trash burning emissions were estimated based on the garbage fire emissions factors measured during MILAGRO combined with literature values and a spatial distribution of population and socioeconomic classifications in Mexico City. We have employed WRF-CHEM during two high fire periods to assess the impacts of open fires and garbage burning on the air quality in and around the MCMA, with emphases on O_3, organic aerosols and elemental carbon. The model has captured reasonably well the measurement-derived magnitude and temporal variation of the biomass burning OA in and near Mexico City, with no systematic biases found at the T0 urban site, while a higher bias exists in the T1 suburban site.

From this study while we did not detect significant effects of open fires and trash burning on ground-level O_3 concentrations in the MCMA and surrounding region, they make important contributions to the ground-level OA and EC in and around the MCMA, contributing about 34 %, 22 %, 30 %, and 9 % to POA, SOA, total OA (TOA), and EC respectively at T0, and contributing even higher at T1, with 63 %, 24 %, 41 %, and 29 % to POA, SOA, TOA, and EC respectively during the high fire events. It is noted that the BB impacts on OA are highly variable temporally and spatially, consistent with the measurements. Trash burning makes slightly smaller contributions to OA than open fires in the MCMA, while exerting higher influences to EC compared to the latter, although the TB emissions are much lower than those of open fires during high fire periods. The simulated impacts of open fires on OA at T0 (17 %) are consistent with many observation-based estimates during the MILAGRO campaign. BBSOA from open fires increases TOA by about 8 % and 11 % at T0 and T1, respectively, while BBSOA from TB contributes about 5 % to TOA in both sites. SOA formation due to the BB emission enhances the OA concentration by about 10 % in and around the MCMA.

Extrapolating the simulations to the entire month of March 2006 based on the emissions of open fires and trash burning during this month, we estimate that the open fires

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and trash burning contribute about 50, 20, and 15 %, respectively, to the ambient concentrations of POA, SOA and EC in and around the MCMA. Taking the extrapolation one step further and taking the emissions from the biofuel use into consideration, we estimate that, on the first- order approximation, biomass burning contributes about 60, 30 and 25 %, respectively, to the loading of POA, SOA and EC in and round the MCMA, of which open fires and trash burning account for 35, 18, and 15 % to the total loading of POA, SOA and EC.

It should be noted that although the simulated biomass burning OA are in good agreement with observations, the model-based estimates of the BB impacts may contain significant uncertainties due to the uncertainties in the BB emission estimates, extrapolations and the nature of spot comparison, which is subject to the bias of transport and local emission influences. The impact of the emissions from the biofuel use, a major BB source in Mexico, is implicitly extrapolated instead of explicitly simulated. In addition, TB emissions outside the MCMA are not included in this study, which implies that the TB impacts would otherwise be higher than we estimate on the regional scale. More modeling studies are needed to accurately assess the BB impacts.

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Table 1. Measurement-based estimates of BB contributions to OA in the MCMA and/or its outflow.

Source	Method	Variable	Platform/Site	Contribution (%)
Moffet et al. (2008)	ATOFMS/K-tracer	PM_1 number	T0	40
Stone et al. (2008)	Filter sampling/	OC	T0	5–26
	Tracer CMB		T1	7–39
Querol et al. (2008)	Filter sampling/BB-OC	OA		9–27
	relation in Stone et al. (2008)		T0	
Liu et al. (2009)	FTIR/XRF/PMF	PM_1	T0	8
Gilardoni et al. (2009)	FTIR/XRF/K-tracer	OC	T0	30–40
de Gouw et al. (2009)	ATOFMS/	OC		7–39
	Tracer CMB		T1	
Aiken et al. (2010)	AMS/PMF	OA	T0	15–23
	^{14}C	OC	T0	13
Marley et al. (2009)	^{14}C	OC	T0	13
Yokelson et al. (2007)	Nephelometer/EI	$PM_{2.5}$	Aircraft outflow	20–80
Crounse et al. (2009)	CIMS/BB tracer	OA	Aircraft outflow	66
			surface	25
DeCarlo et al. (2010)	AMS/PMF	OA	Aircraft outflow	66

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Table 2. Emission averages (tons/day) from different sources in the model domain during MILAGRO in March and during the simulation periods.

	March 2006				
	CO	VOCs	NO_x	POA[a]	EC
Anthropogenic	15017.0	4543.6	1465.1	69.4	27.3
Open fire	1477.1	153.4	61.2	119.6	7.4
Trash burning	92.3	20.0	9.4	10.8	1.3
	During the simulation periods				
	CO	VOCs	NO_x	POA[a]	EC
Anthropogenic	13515.2	4089.2	1318.6	62.4	24.6
Open fire	2562.9	282.4	105.3	203.5	12.0
Trash burning[b]	92.3	20.0	9.4	10.8	1.3

[a] Particle-phase.
[b] Not TB emissions outside the MCMA.

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Table 3. Statistical measures of model performance during the two simulated episodes.

	O_3[a] RAMA	CO RAMA	BBPOA T0	POA T0	SOA T0	EC T0	EC T1
Mean obs[b]	71.2	1.18	4.4	10.0	6.9	4.2	2.4
Mean mod[b]	60.1	1.09	3.2	8.3	8.2	4.3	1.4
RMSE[b]	21.1	0.46	5.2	8.5	6.1	2.6	2.1
NB (%)	−13.7	−2.7	1.6	3.6	43.3	11.7	−21.3
NMB (%)	−15.7	−7.3	−28.5	−17.5	18.6	0.10	−41.5
IOA	0.92	0.88	0.60	0.70	0.66	0.76	0.53

[a] The cutoff (threshold) concentrations for O_3 was set at 40 ppb in the statistical calculations.
[b] the units are ppb for O_3, ppm for CO, and $\mu g\,m^{-3}$ for PM.

Note: obs = observation, mod = model, RMSE (root mean square root) = $\left[\frac{1}{N}\sum_{i=1}^{N}(P_i - O_i)^2\right]^{\frac{1}{2}}$,

NB (normalized bias) = $\frac{1}{N}\sum_{i=}^{N}\frac{(P_i-O_i)}{O_i} \times 100\,\%$,

NMB (normalized mean bias) = $\frac{\sum_{i=1}^{N}(P_i-O_i)}{\sum_{i=1}^{N}O_i} \times 100\,\%$,

IOA (index of agreement) = $1 - \frac{\sum_{i=1}^{N}(P_i-O_i)^2}{\sum_{i=1}^{N}(|P_i-\overline{O}|+|O_i-\overline{O}|)^2}$,

where O_i and P_i are observed and predicted concentrations, respectively, $\overline{O}$ are averaged observation concentrations, and N is the sample size.

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Table 4a. Impacts of BB at T0. Numbers listed are the percentage contributions averaged over the simulation periods and the standard deviations.

Episode	O_3*	POA	SOA	TOA	EC
10–14 Mar	−0.2 ± 2.5	34.5 ± 14.8	18.8 ± 18.0	28.8 ± 16.3	9.4 ± 4.9
17–21 Mar	−0.1 ± 1.7	32.9 ± 17.7	25.2 ± 18.2	30.4 ± 17.1	8.4 ± 5.9
Overall	−0.2 ± 2.1	33.7 ± 16.4	22.0 ± 18.5	29.6 ± 16.7	8.9 ± 5.4

* O_3 averaged over the RAMA stations, most of which are located in the MCMA urban area.

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Table 4b. Impacts of BB at T1. Numbers listed are the percentage contributions averaged over the simulation periods and the standard deviations.

Episode	POA	SOA	TOA	EC
10–14 Mar	61.8 ± 18.7	21.8 ± 19.2	37.1 ± 19.7	29.2 ± 12.2
17–21 Mar	64.6 ± 13.9	26.9 ± 18.3	44.1 ± 15.9	29.3 ± 12.0
Overall	63.2 ± 16.5	24.3 ± 18.9	40.6 ± 18.3	29.2 ± 12.1

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Table 4c. Impacts of BB in the MCMA and model domain.

	O_3	POA	SOA	TOA	EC	BBPOA to TOA
MCMA						
10–14 Mar	−1.5 ± 3.5	57.8 ± 15.0	25.9 ± 16.7	41.7 ± 13.5	22.9 ± 10.4	17.6 ± 15.3
17–21 Mar	−1.0 ± 2.2	60.6 ± 16.2	28.7 ± 18.5	45.1 ± 16.1	24.9 ± 12.5	17.4 ± 14.9
Overall	−1.3 ± 2.9	59.2 ± 15.7	27.3 ± 17.7	43.4 ± 15.0	23.9 ± 11.1	17.5 ± 15.1
Domain-wide						
10–14 Mar	0.2 ± 0.7	60.2 ± 14.5	19.2 ± 12.0	28.5 ± 10.8	18.8 ± 7.5	15.8 ± 10.2
17–21 Mar	0.2 ± 0.4	64.0 ± 17.7	21.0 ± 13.2	33.4 ± 13.7	23.0 ± 12.2	15.8 ± 10.7
Overall	0.2 ± 0.6	62.1 ± 16.3	20.1 ± 12.7	31.0 ± 12.6	20.9 ± 10.4	15.8 ± 10.5

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Table 5a. Partitioning of the impacts of different emission sources on OA and EC at T0 and T1.

	POA	SOA	TOA	EC
T0				
Open fires	19.8 ± 18.4	16.9 ± 17.0	19.5 ± 17.5	4.3 ± 5.3
Trash burning	13.9 ± 7.5	5.1 ± 5.3	10.1 ± 5.8	4.6 ± 2.7
Others	66.3	78.0	70.4	91.1
T1				
Open fires	30.5 ± 22.7	18.0 ± 17.2	24.3 ± 18.9	10.3 ± 10.3
Trash burning	32.7 ± 13.8	6.3 ± 7.1	18.9 ± 7.5	18.9 ± 7.5
Others	36.8	75.7	59.4	70.8

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Table 5b. Partitioning of the impacts of different emission sources on OA and EC in the MCMA and domain-wide.

	POA	SOA	TOA	EC
MCMA				
Open fires	36.7 ± 23.1	21.3 ± 16.9	29.3 ± 18.5	12.1 ± 12.0
Trash burning	22.5 ± 9.9	6.0 ± 5.5	14.1 ± 7.0	11.8 ± 4.1
Others	40.8	72.7	56.6	76.1
Domain-wide				
Open fires	53.8 ± 20.4	18.1 ± 11.8	27.5 ± 13.1	16.5 ± 10.9
Trash burning	8.4 ± 5.1	2.0 ± 1.6	3.5 ± 1.7	4.4 ± 1.8
Others	37.9	79.9	69.0	79.1

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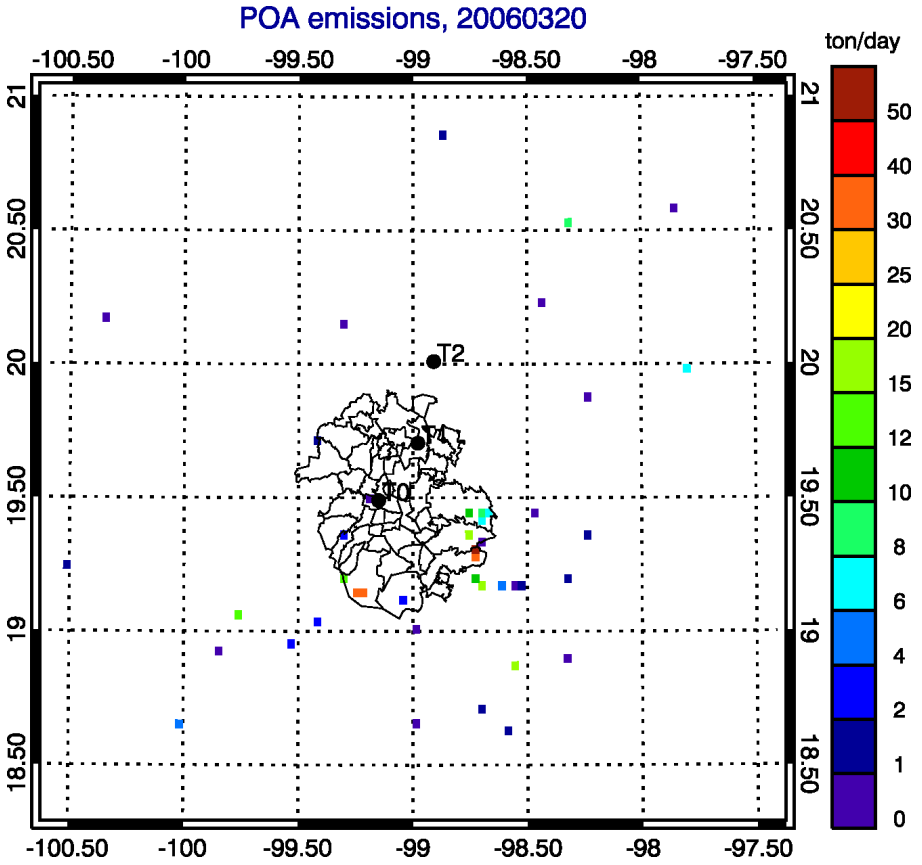

Fig. 1. Model domain and the geographical distribution of forest fire emissions of POA on 20 March 2006 in the domain. The curves are the MCMA delegation political borderlines. The MILAGRO supersites T0, T1 and T2 are indicated as dots.

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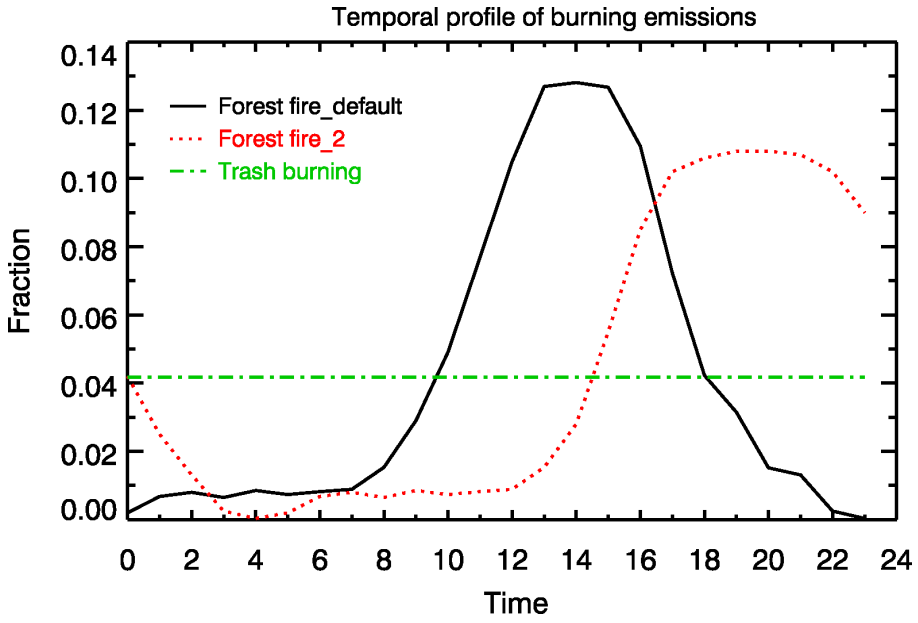

Fig. 2. Diurnal profiles of emissions from forest fire and garbage burning.

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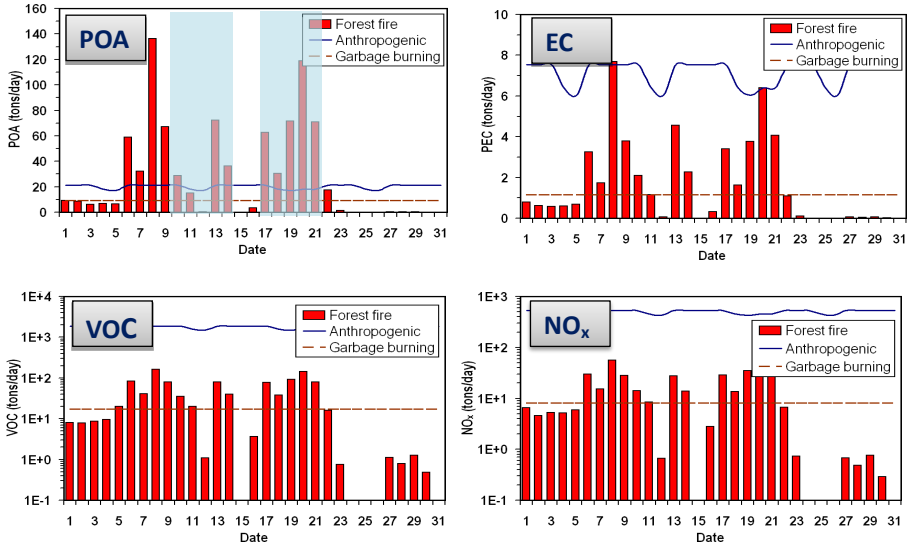

Fig. 3. Emissions of anthropogenic, open fires and trash burning in the MCMA during the MILAGRO campaign. The red bars denote the daily emissions of open fires (dominantly forest fires), the blue line denotes the emissions from the fossil fuel use, and the brown dash line denotes the garbage burning emissions. The blue bars indicate the simulation periods.

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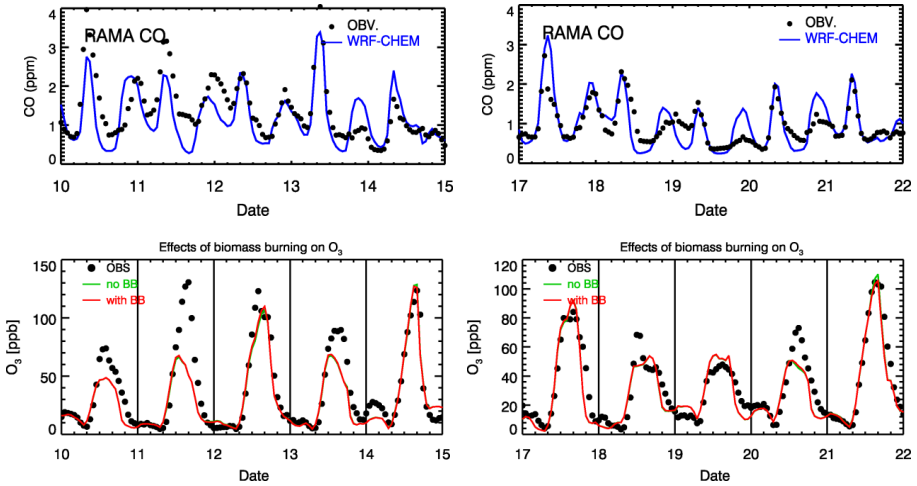

Fig. 4. Comparisons of measured and simulated CO and O_3 averaged over the RAMA stations during 10–14 March and 17–21 March 2006. Dots represent observations, and lines represent simulations. Two cases for O_3 simulations are presented: excluding BB (no BB) and including BB (with BB) emissions.

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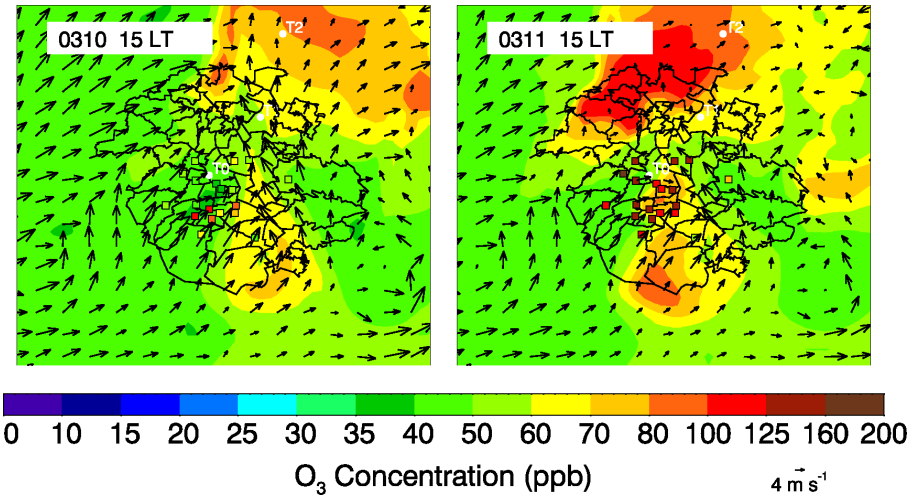

Fig. 5. Spatial distribution of ground O_3 concentration at 15:00 LT on 10 and 11 March. Colored squares represented RAMA observations, and colored contour and black arrows are simulated O_3 and wind fields, respectively.

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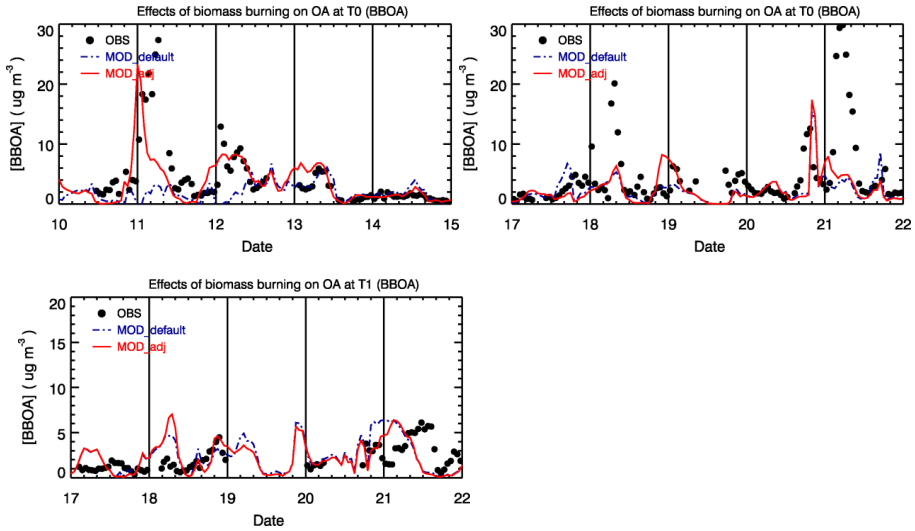

Fig. 6. Comparisons of AMS-derived and simulated BBPOA concentrations at T0 during 10–14 March and at T0 and T1 during 17–21 March. The black dots represent AMS PMF data, the dashed blue lines represent the simulations with the default BB emissions, and the red lines represent the simulations with the adjusted BB emissions. Details of the BB emissions are described in the main text.

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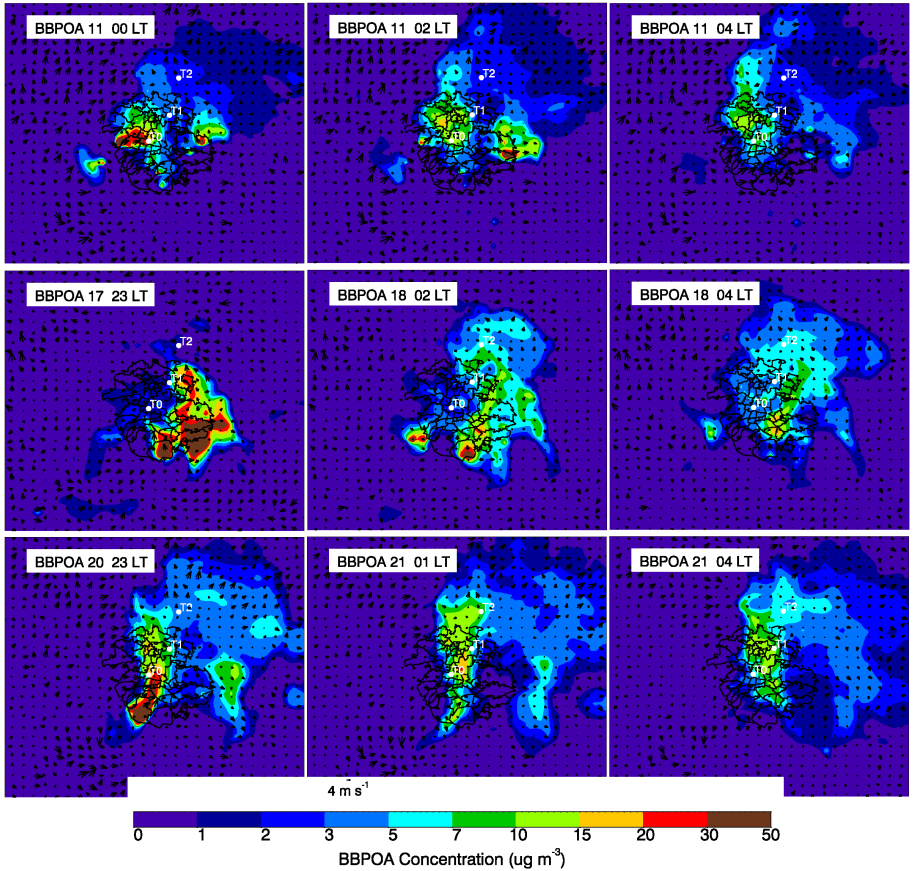

Fig. 7. Simulated BBPOA spatial distributions and their evolutions at nighttime. The date and local time is shown in the caption (e.g. 11 02 LT means 11 March 2:00 a.m.).

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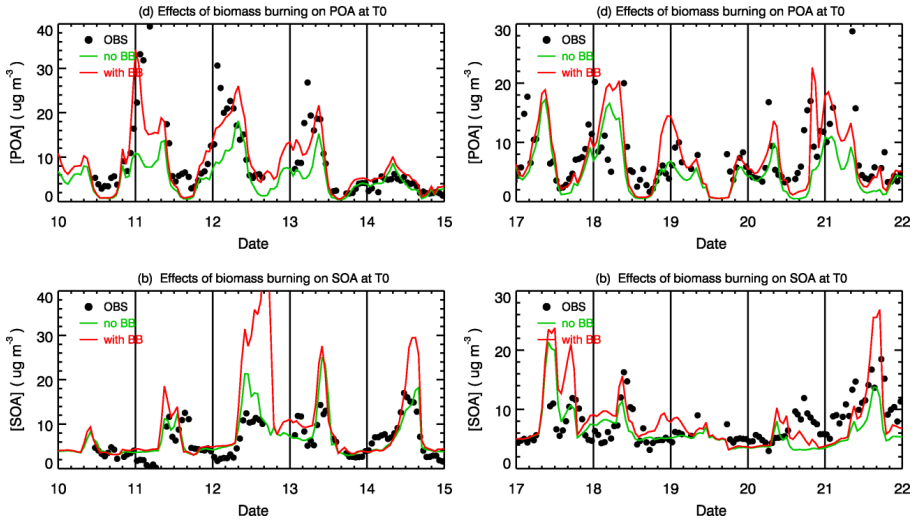

Fig. 8. Comparisons of observed and simulated POA (top panels) and SOA (bottom panels) at T0. Green lines denote the case without the BB emissions, while red lines denote the case with the BB emissions.

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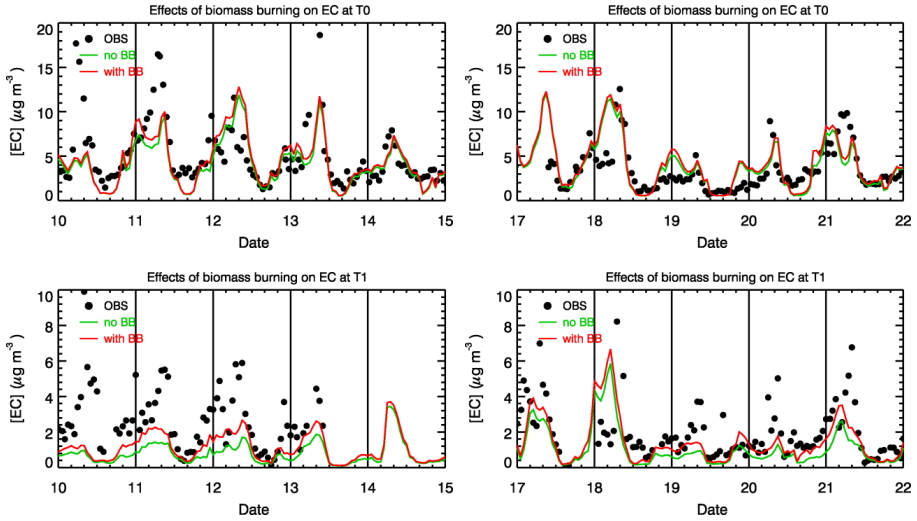

Fig. 9. Comparisons of observed and simulated elemental carbon particulates at T0 and T1. The adjusted BB emissions were used in the simulations.

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