



Received: 15 October 2010 – Accepted: 4 November 2010 – Published: 15 November 2010

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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**Sources and  
production of organic  
aerosol in Mexico  
City**

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## Abstract

Urban areas are large sources of organic aerosols and their precursors. Nevertheless, the contributions of primary (POA) and secondary organic aerosol (SOA) to the observed particulate matter levels have been difficult to quantify. In this study the three-dimensional chemical transport model PMCAMx-2008 is used to investigate the temporal and geographic variability of organic aerosol in the Mexico City Metropolitan Area (MCMA) during the MILAGRO campaign that took place in the spring of 2006. The organic module of PMCAMx-2008 is based on the volatility basis-set approach: both primary and secondary organic components are assumed to be semi-volatile and photochemically reactive and are distributed in logarithmically spaced volatility bins. The MCMA emission inventory is modified and the POA emissions are distributed by volatility based on dilution experiments. The model predictions are compared with observations from four different types of sites, an urban (T0), a suburban (T1), a rural (T2), and an elevated site in Pico Tres Padres (PTP). The performance of the model in reproducing organic mass concentrations in these sites was encouraging. The average predicted  $\text{PM}_{10}$  OA concentration in T0, T1, and T2 was  $18 \mu\text{g m}^{-3}$ ,  $11.7 \mu\text{g m}^{-3}$ , and  $10.5 \mu\text{g m}^{-3}$  respectively, while the corresponding measured values were  $17.2 \mu\text{g m}^{-3}$ ,  $11 \mu\text{g m}^{-3}$ , and  $9 \mu\text{g m}^{-3}$ . The average predicted fresh primary OA concentrations were  $4.4 \mu\text{g m}^{-3}$  at T0,  $1.2 \mu\text{g m}^{-3}$  at T1 and  $1.7 \mu\text{g m}^{-3}$  at PTP in reasonably good agreement with the corresponding PMF analysis estimates based on the AMS observations of 4.5, 1.3, and  $2.9 \mu\text{g m}^{-3}$  respectively. The model reproduced reasonably well the average oxygenated OA (OOA) levels in T0 ( $7.5 \mu\text{g m}^{-3}$  predicted versus  $7.5 \mu\text{g m}^{-3}$  measured), in T1 ( $6.3 \mu\text{g m}^{-3}$  predicted versus  $4.6 \mu\text{g m}^{-3}$  measured) and in PTP ( $6.6 \mu\text{g m}^{-3}$  predicted versus  $5.9 \mu\text{g m}^{-3}$  measured). Inside Mexico City, the locally produced OA is predicted to be on average 53% fresh primary (POA), 11% semi-volatile (S-SOA) and intermediate volatile (I-SOA) organic aerosol, and 36% traditional SOA from the oxidation of VOCs (V-SOA). The long range transport from biomass burning activities and other sources in Mexico is predicted to contribute on average almost as much as the local sources during the MILAGRO period.

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## 1 Introduction

The Mexico City Metropolitan Area (MCMA) is the largest megacity in North America and is one of the five largest cities in the world with over 20 million people living in an area of 1500 km<sup>2</sup>. The MCMA has a history of severe air quality problems due to a large number of pollution sources with uneven levels of emission control, which can be further exacerbated by the topography and meteorology of the basin. The tropical location (19° N) and high altitude (2200 m above sea level) result in high UV radiation fluxes and intense photochemistry. The basin is surrounded by mountains on three sides, reducing ventilation of pollutants, especially at night and in the early morning (Molina and Molina, 2002).

Fine particulate matter (PM) is one of the most serious air quality problems in Mexico City (Molina et al., 2007). Pollution from megacities and large urban areas, such as MCMA, is important not only for its local effects on health (Pope and Dockery, 2006), visibility (Watson, 2002), and ecosystems/crops (Bytnerowicz and Fenn, 1996), but also because of its potential influence on regional scale atmospheric chemistry and radiative forcing. Organic species account for a large fraction of the fine aerosol mass at most locations (Zhang et al., 2007) and are poorly understood. The MILAGRO (Megacity Initiative: Local and Global Research Observations) field campaign, which took place during March 2006, used multiple sites and mobile platforms to assess pollutant emissions, and evolution in and around Mexico City (<http://www.eol.ucar.edu/projects/milagro>), providing a unique dataset to study the formation of organic aerosols. The MILAGRO field experiment involved more than 400 researchers from over 120 institutions in the USA, Mexico, and several other countries (Molina et al., 2010). The campaign included coordinated aircraft and ground-based measurements supported by extensive modeling and satellite observations. Three main sites were chosen to characterize the transport and transformation of the pollutants carried from the urban area of the city to its surroundings; one in the urban area of Mexico City designated T0 located in Northeast Mexico City at the Instituto

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showed a strong correlation with water soluble OC (WSOC) and was considered to be secondary in nature. Yokelson et al. (2007) also found high biomass burning emissions suggesting that the fires from forests near Mexico City could produce as much as 80–90% of the primary fine particle mass generated in the Mexico City area. The 50 ± 30% of the “aged” fine particle mass in the March 2006 Mexico City outflow could be from these fires. Moreover, Crouse et al. (2009) found that fires contribute more than half of the organic aerosol mass and submicron aerosol scattering. DeCarlo et al. (2010) reported that during periods of high forest fire intensity near the basin, OA arising from open BB represents around 65% of the OA mass in the basin and contributes similarly to OA mass in the outflow. Aiken et al. (2010) estimated that during the low regional fire periods, 38% of organic carbon (OC) in the Mexico City center was from non-fossil sources, suggesting the importance of urban and regional non-fossil carbon sources other than the fires, such as food cooking and regional biogenic SOA. They also showed that, by properly accounting for the non-BB sources of K, the fires from the region near the MCMA are estimated to contribute 15–23% of the OA. Finally, De Gouw et al. (2009) investigated the diurnal variations of hydrocarbons, elemental carbon (EC) and hydrocarbon-like organic aerosol (HOA) which were dominated by a high peak in the early morning. In comparison, diurnal variations of species with secondary sources such as OOA and WSOC stayed relatively high in the afternoon indicating strong photochemical formation.

Chemical transport models (CTMs) that can accurately and efficiently describe the physical and chemical atmospheric transformations of pollutants have been also used to estimate the chemical composition and the concentration of the aerosols in the MCMA (e.g., Karydis et al., 2010; Tsimpidi et al., 2010; Hodzic 2009, 2010). Fast et al. (2009) assessed the uncertainties in predicted POA during MILAGRO before testing and evaluating the performance of secondary organic aerosol (SOA) treatments. Modeled POA was consistently lower than the measured OA at the ground sites, which is consistent with the expectation that SOA should be a large fraction of the total organic matter mass. Other studies have reported large discrepancies in the measured vs.

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modeled OOA mass concentrations in both urban and regional polluted atmospheres (Heald et al., 2005; de Gouw et al., 2005; Johnson et al., 2006; Volkamer et al., 2006; Kleinman et al., 2008). Hodzic et al. (2009) found fairly good agreement between predicted and observed POA within the city but large discrepancies were encountered for SOA, suggesting that less than 15% of the observed SOA within the Mexico City can be explained by the oxidation of the traditional SOA precursors. These results are in agreement with the findings of Dzepina et al. (2009) where the traditional SOA precursors (mainly aromatics) by themselves failed to produce enough SOA to match the observations by a factor of 7. Hodzic et al. (2010) applied the CHIMERE model to estimate the potential contribution to SOA formation of recently identified semi-volatile and intermediate volatility organic precursors (Robinson et al., 2007) in and around Mexico City. The results showed a substantial enhancement in predicted SOA concentrations (2–4 times) both within and downwind of the city leading to much reduced discrepancies with the total OA measurements.

Robinson et al. (2007) proposed two major amendments to the current treatment of OA: (1) accounting for the volatility and gas particle partitioning of POA; and (2) explicit representation of gas-phase oxidation of all low-volatility vapors in SOA production mechanisms. These amendments were implemented in a 3D-CTM, PMCAMx, resulting in the PMCAMx-2008 version (Lane et al., 2008a, b; Shrivastava et al., 2008; Tsimpidi et al., 2010). Tsimpidi et al. (2010) applied PMCAMx-2008 in MCMA during the MCMA-2003 campaign (Molina et al., 2007), reducing significantly the discrepancies between the measured and the modeled OOA. However, that study was limited by the availability of organic aerosol measurements in only one site.

The current study is based on the insights of the work of Tsimpidi et al. (2010) and its goal is to assess further the temporal and geographic variability of organic mass compounds during the 2006 MILAGRO campaign using PMCAMx-2008. The geographic variability of the OA concentration is evaluated by comparing the model predictions against measurements taken at an urban site in Mexico City, two peripheral sites located on the outskirts of the metropolitan area, and an elevated site located at Pico de

Tres Padres (PTP). This study aims to provide a concrete understanding of the sources of organic mass in Mexico City and a complimentary analysis of oxygenated organic aerosol formation and growth.

## 2 Model description

PMCAMx-2008 simulates advection, dispersion, gas-phase chemistry, emission, wet/dry deposition, aerosol dynamics and aqueous-phase chemistry of atmospheric compounds (Gaydos et al., 2007; Karydis et al., 2007). Following Tsimpidi et al. (2010), a volatility distribution is applied to the emitted POA species with ten simulated volatility bins, ranging from 0 to  $10^6 \mu\text{g m}^{-3}$  saturation concentration (all effective saturation concentrations in the VBS are at 298 K). This simulation also includes emissions of intermediate volatility organic compounds (IVOCs), which are distributed among the  $10^4$ ,  $10^5$ , and  $10^6 \mu\text{g m}^{-3}$  saturation concentration bins with emissions rates equal to 0.2, 0.5, and 0.8 times the original non-volatile POA emission rate, respectively. The gas-phase chemical mechanism in use, SAPRC-99, includes 77 gas-phase species (not including the gas- and particulate-phase organic species added for this study) and 217 reactions (Carter, 2000). SOA is split between aerosol formed from the condensation of the oxidation products of the volatile organic compounds (V-SOA), intermediate volatile organic compounds (I-SOA), and semi-volatile organic compounds (S-SOA). The V-SOA is simulated with 4 volatility bins (1, 10, 100,  $1000 \mu\text{g m}^{-3}$ ), and 10 size bins (diameters range from 0.04 to  $40 \mu\text{m}$ ). I-SOA and S-SOA are described with 10 volatility bins (0 and  $10^{-2}$ – $10^6 \mu\text{g m}^{-3}$ ) and 10 size bins. The V-SOA yields used in PMCAMx-2008 are based on the  $\text{NO}_x$ -dependent stoichiometric yields of Lane et al. (2008a). The corresponding parameters affecting V-SOA partitioning and removal processes, including effective Henry's law constants, molecular weights and enthalpies of vaporization, are taken from Lane et al. (2008b). Those parameters for the S-SOA and I-SOA are obtained from Shrivastava et al. (2008). Further gas-phase oxidation of SOA vapors (chemical aging) is modeled using a second-order reaction with hydroxyl

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radicals. To express the decrease of volatility with aging, products of this reaction are shifted down one volatility bin (factor of 10 reduction in effective saturation concentration). The base-case simulation ages S-SOA, I-SOA and V-SOA from anthropogenic sources using a rate constant  $k(298\text{ K}) = 40 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  for S-SOA and I-SOA and  $k(298\text{ K}) = 10 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  for V-SOA. No biogenic SOA aging is simulated based on both the available laboratory studies (Ng et al., 2006; Presto et al., 2006) and the results of Lane et al. (2008b). Overall, the model, apart from the fresh primary organic aerosols (POA), simulates three types of oxygenated organic aerosols based on the initial volatility of the corresponding precursor compounds: S-SOA ( $C^* \leq 10^2 \mu\text{g m}^{-3}$ ), I-SOA ( $10^3 \leq C^* \leq 10^6 \mu\text{g m}^{-3}$ ), and V-SOA ( $C^* > 10^6 \mu\text{g m}^{-3}$ ). A more comprehensive description of the organic aerosol module used by PMCAMx-2008 can be found in Tsimpidi et al. (2010), Lane et al. (2008a, b) and Shrivastava et al. (2008).

### 3 Model application

This study uses PMCAMx-2008 to simulate March 2006 for the Mexico City Metropolitan Area. The first three days of the simulation are used for initialization and are not included in the results presented here. The modeling domain covers a  $210 \times 210 \text{ km}$  region in the Mexico City Metropolitan Area with  $3 \times 3 \text{ km}$  grid resolution and fifteenth vertical layers totaling 6 km (Fig. 1). This is a much larger domain than that used by Tsimpidi et al. (2010) and includes the industrial area of Tula to the north of Mexico City (Song et al., 2010). Inputs to the model include horizontal wind components, temperature, pressure, water vapor, vertical diffusivity, clouds, and rainfall; all created using the Weather Research and Forecast (WRF) model.

*Emission inventory.* The emission inventory has been updated in order to include the anthropogenic emissions from the refineries, power plants and chemical companies in the Tula area located north of Mexico City (Fig. 1), the biogenic emissions emitted from the forests northeast of the model domain, and a semi-empirical HONO

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“source” (0.8% of the  $\text{NO}_x$  emissions based on Aumont et al., 2003; Li et al., 2010). In order to account for partitioning of primary organic emissions, the emission inventory was modified following the recommendations of Tsimpidi et al. (2010). Table 1 shows the amount of the emitted organic material within the limits of the modeling domain.

Anthropogenic and biogenic VOC emissions serve as anthropogenic and biogenic V-SOA precursors respectively. Semivolatile (SVOC;  $1 \leq C^* \leq 10^2 \mu\text{g m}^{-3}$ ) primary organic emissions partition between the aerosol and the gas phase. The material that remains in the aerosol phase and did not undergo chemical reactions during its atmospheric lifetime is fresh POA while the gas phase material is considered as S-SOA precursor. Finally, intermediate-volatility (IVOC;  $10^3 \mu\text{g m}^{-3} \leq C^* \leq 10^6 \mu\text{g m}^{-3}$ ) organic compounds exist largely in the gas phase at typical atmospheric conditions and are important I-SOA precursors as their oxidation can produce compounds with lower vapour pressures.

*Boundary conditions.* The values of the OA concentrations at the boundaries of the domain, approximately  $8 \mu\text{g m}^{-3}$  in the west,  $11.5 \mu\text{g m}^{-3}$  in the east,  $7 \mu\text{g m}^{-3}$  in the south and  $5 \mu\text{g m}^{-3}$  in the northern boundary, were chosen based on results of the GISS-II' global CTM for March (Racherla et al., 2006). Please note that all concentrations in this paper are under ambient pressure and temperature conditions. These levels represent the average OA concentrations over the Central Mexican Plateau approximately 50 km outside Mexico City and should not be confused with the larger-scale background concentrations of Mexico (reflecting concentrations over the lower to middle troposphere over the Pacific Ocean) of much less than  $0.5 \mu\text{g m}^{-3}$  (DeCarlo et al., 2008; Fast et al., 2009). Because the biomass burning emissions are not included in the current inventory, they are implicitly provided to the model as a part of the boundary conditions. These relatively high boundary condition values are consistent with the findings of Yokelson et al. (2007) suggesting that the fires in the mountainous forests around Mexico City (MC) could produce as much as 80–90% of the primary fine particle mass generated in the MC area. Crouse et al. (2009) estimated that biomass burning contributed two thirds of the organic aerosol to the study area in

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March 2006. Subsequent atmospheric oxidation of co-emitted hydrocarbons can yield low vapor pressure compounds that condense on the existing particulate forming secondary organic aerosol. Therefore, the organic mass transported into the domain is assumed to be a mixture of aged primary and secondary organic aerosols, and is referred to hereinafter as “long range transport oxygenated OA”. The model assumes that V-SOA, I-SOA and S-SOA form a pseudo-ideal solution together with the long range transport oxygenated OA and, therefore, are allowed to partition into this pre-existing organic aerosol.

*Ground observations.* The model predictions were compared against measurements which were carried out from 10 to 29 March 2006 (Doran et al., 2007; Aiken et al., 2009), at the T0, T1, T2, and PTP (900 m above city ground) monitoring stations (Fig. 1) in order to evaluate the predicted geographic variability of organic mass.

The T0 monitoring station was located to the northwestern part of the basin of Mexico City. It is an urban background site influenced by road traffic fresh emissions (300 m from four major roads surrounding it), domestic and residential emissions, but also potentially influenced by local industrial emissions and from the Tula industrial area (60 km to the north-northwest, in the Hidalgo State). T1 is an suburban background site located around 50 km to the north of Mexico City, in an area isolated from major urban agglomerations but close to small populated agglomerations, and around 500 m from the closest road. T2 is a regional background site located around 90 km to the north of the city of Mexico, in the surroundings of a farm isolated from major urban agglomerations, and around 2 km from the closest road. Finally, the Aerodyne Mobile Laboratory was located to the north part of Mexico City urban area on an elevated site of Pico Tres Padres (PTP, 900 m above city ground).

#### 4 Overview of model predictions

The predicted average ground-level concentration of PM<sub>1</sub> organic mass over the period of March 2006 is shown in Fig. 2. The organic mass peak values (approximately

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20  $\mu\text{g m}^{-3}$ ) are in the center of Mexico City and in the Tula industrial area. The predicted organic mass concentration is the sum of the predicted concentration of primary organic aerosols which have been emitted in the atmosphere as particles (fresh POA) (Fig. 3a) and the predicted concentrations of the oxygenated organic aerosol (Fig. 3b) that has been created in the atmosphere through chemical reactions and corresponds to the sum of PMCAMx-2008 S-SOA, I-SOA, and V-SOA. The primary organic aerosol concentration is high in the center of Mexico City and in Tula, while it decreases rapidly from its sources mainly due to dilution and evaporation. As an example in the T0 urban site the predicted average fresh primary organic concentration is  $4.4 \mu\text{g m}^{-3}$  while in the T1 suburban site it decreases to  $1.2 \mu\text{g m}^{-3}$  and in the T2 rural site is lower than  $1 \mu\text{g m}^{-3}$ . On the contrary, the predicted oxygenated organic aerosol concentration has a relatively more uniform spatial distribution with high values in the entire domain (Fig. 3b). The highest values are predicted in the center of Mexico City (up to  $7.5 \mu\text{g m}^{-3}$ ), coming mainly from anthropogenic sources, and in the northeast corner of the domain, mainly from biogenic sources. In the suburban and rural areas, such as T1 and T2, the predicted oxygenated OA is also high, with concentrations around  $6 \mu\text{g m}^{-3}$ . Anthropogenic V-SOA, I-SOA, and S-SOA, are predicted to be more photochemically processed and less volatile downwind of the Mexico City center. In particular at T0 OA consists of 60% POA and 40% OOA. At T1 and T2, POA corresponds to 40% and 15% of total OA respectively.

## 5 Model performance evaluation

The results of the comparison of model predictions with the OA observations are depicted in Fig. 4. The model does a reasonable job most of the time reproducing the observations in the T0 site, which is located in the urban center of Mexico City (Fig. 4a). Nevertheless, the model is missing a few major spikes which appear early in the morning such as during the 11th, 18th, and 21st of the month and are associated with biomass burning events (Aiken et al., 2009). Therefore, these underpredictions

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The predicted concentrations of biogenic V-SOA were compared against daily average measurement-based estimates of biogenic SOA at T0 and T1 sites (Stone et al., 2009). Overall, the PMCAMx predictions tend to be lower than the Stone et al. (2009) V-SOA estimates in both sites. The simulated biogenic V-SOA concentrations range from 0.1 to 1.1  $\mu\text{g m}^{-3}$  at T0 and from 0.1 to 1.4  $\mu\text{g m}^{-3}$  at T1. The measurement-based estimates range from 0.4 to 1.8  $\mu\text{g m}^{-3}$  at T0 and from 0.4 to 2.2  $\mu\text{g m}^{-3}$  at T1. These results suggest that biogenic SOA levels in the Mexico City region are far from negligible. In particular, the relative contribution of fresh biogenic V-SOA to total OA is predicted to be up to 15% north of Mexico City. The PMCAMx-predicted contribution of fresh biogenic V-SOA to fresh total SOA (sum of V-SOA, I-SOA, and S-SOA) is 20–30% within the city and up to 70% at the surrounding areas. Hodzic et al. (2009) estimated the relative contribution of biogenic SOA to the predicted monthly levels of SOA, to be more than 30% at the city center and up to 65% at the regional scale. The biogenic V-SOA contribution to total OA is predicted by PMCAMx to vary from 5 to 15% (Fig. 5).

## 5.1 Diurnal average profiles

The predicted and measured diurnal average OA concentration profiles at T0, T1, and T2 sites during MILAGRO are depicted in Fig. 6. These averages depend less on the day to day variability of the meteorology and the emissions and more on the major processes affecting the OA concentrations. In all cases, the model predictions are in agreement within experimental error with the measurements. The diurnal profile at the urban site T0 (Fig. 6a) has two peaks; the major one during morning, related to the primary emissions, and a second less pronounced peak in the afternoon, mainly due to photochemical processes. The same peaks appear in the diurnal profile of OA at the suburban site T1 (Fig. 6b), the levels of which are smaller compared to those in the T0 site. The first peak is related to the local sources while the peak in the afternoon is caused by the OA which was transported there from the urban center and the local photochemistry. Finally, both the measured and the predicted organic mass at the

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rural site T2 (Fig. 6c), increase slightly late in the afternoon mainly due to transport of emissions and also photochemistry. As expected, there is no morning peak, given the absence of local sources in the area around and immediately upwind of T2.

## 5.2 Comparison with PMF analysis

The AMS spectra were analyzed with the PMF technique (Paatero and Tapper, 1994) as described by Ulbrich et al. (2009) and Aiken et al. (2009) separating total organic aerosol (OA) into hydrocarbon-like organic aerosol (HOA, a POA surrogate), oxidized organic aerosol (OOA, a surrogate for SOA) and biomass burning organic aerosol (BBOA) for three locations in Mexico City: T0, T1, and PTP.

This specification allows a more in-depth evaluation of modeled OA components as they have different temporal emission and formation patterns. HOA appears to have the AMS mass spectral fingerprint for primary combustion particles from urban sources, and also includes particles from other relatively reduced sources such as meat cooking and trash (plastic) burning (Mohr et al., 2009). Therefore the AMS fresh HOA can be compared with the PMCAMx-2008 POA which is the fraction of the emissions that is in the aerosol phase without having undergone any chemical reactions (Fig. 7). At T0, PMCAMx-2008 successfully reproduces the observed HOA variation characterized by an early morning peak associated with traffic (Fig. 7a). Both, the average predicted POA concentration and the AMS-HOA concentration during March 2006 at T0 are close to  $4.5 \mu\text{g m}^{-3}$ . The agreement is still reasonable at T1 where the average POA and AMS-HOA concentrations are approximately  $1.3 \mu\text{g m}^{-3}$ . However the predicted morning POA peaks 2 h later than observed (Fig. 7b). At PTP, larger discrepancies between observed and modeled POA values are found. The average predicted POA concentration during March 2006 is  $1.7 \mu\text{g m}^{-3}$  while the PMF analysis resulted in  $2.9 \mu\text{g m}^{-3}$  HOA during the same periods at PTP. The predicted morning POA peaks 2 h earlier than observed (Fig. 7c). The late arrival of the measured pollutants over the elevated PTP site is associated with the growth of the PBL above 900 m (station's altitude). Therefore, this discrepancy suggests potential problems in describing the vertical mixing in the complex terrain around PTP in the early morning hours.

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OOA often contains a more volatile and less processed oxygenated OA fraction which shows high correlation with photochemical products such as  $O_3$ ,  $O_x$ , glyoxal, and ammonium nitrate (Volkamer et al., 2006, 2007; Aiken et al., 2008, Lanz et al., 2007; Ulbrich et al., 2009; Dzepina et al., 2009). However, a significant fraction of the OOA consists of more oxygenated organics (Aiken et al., 2008) which are assumed here to have initially formed far from Mexico City. Therefore, the AMS OOA is compared with the sum of the PMCAMx-2008 S-SOA, I-SOA, V-SOA, and transported oxygenated OA. Figure 8 presents the comparison of average diurnal profiles of predicted oxygenated organic components and the PMF-estimated OOA at the 3 locations, T0, T1 and PTP. The shape of the OOA diurnal profile features a strong enhancement in concentrations during the morning associated with an active photochemical production of oxygenated organic aerosols close to the emissions (i.e. T0, PTP). The diurnal variability is less pronounced at the peripheral T1 station and displays a more gradual increase of concentrations during the day. Figure 8 confirms that the predicted oxygenated organic aerosol values and their associated variability range are in reasonable agreement with the observed ones. Both predicted and observed OOA levels gradually decrease downwind of the city with monthly average concentrations ranging from  $7.5 \mu\text{g m}^{-3}$  at T0 respectively to  $6.3 \mu\text{g m}^{-3}$  and  $4.6 \mu\text{g m}^{-3}$  at T1 respectively. At T0 and PTP the predicted formation of OOA during the early morning hours is not as rapid as the PMF estimates. This discrepancy can be partially attributed to the predicted OH levels as they are slightly underestimated during early morning even though they are reasonably reproduced by the model during the rest of the day (not shown). A sensitivity study to the HONO emissions used by the model (see Sect. 6) suggests that the HONO production and emissions are relatively important for the production of OH and SOA in the early morning. The comparison at T1 and PTP suggests a model tendency to overpredict OOA concentration during early afternoon. At PTP the average monthly predicted OOA concentration is  $6.6 \mu\text{g m}^{-3}$  while the PMF analysis resulted in  $5.9 \mu\text{g m}^{-3}$  OOA on average during the same period.

Overall, the predicted chemical composition of OA is generally consistent with the PMF analysis results. However, PMCAMx-2008 tends to predict higher oxygenated OA than the PMF analysis. Given that the AMS PMF results are also subject to error this comparison of the predictions of these two methods is quite encouraging. Future simulations though, should use a larger domain along with an accurate biomass burning emission inventory in order to increase the precision not only of the estimated BBOA but also of the SOA produced from fire emitted VOCs, I-VOCs, and S-VOCs. Moreover, this study does not estimate explicitly the formation of SOA from very volatile precursors such as glyoxal (Volkamer et al., 2007; Ng et al., 2008). Finally, aqueous phase reactions in clouds (Wameck, 2003; Lim et al., 2005; Liu et al., 2009) and the oligomerization processes of particle-phase semivolatile material (Jang et al., 2002; Kalberer et al., 2004; Iinuma et al., 2004) that can lead to continued SOA growth are also not taken into account.

## 6 Sensitivity analysis

Uncertain inputs for the organic aerosol module include the volatility distribution for the organic aerosol emissions and the rate constant used for the aging reactions of SOA vapors with hydroxyl radicals. A simulation based on a low emissions' volatility case, where the emissions in the low volatility bins ( $C^*:10^{-2}-10^2 \mu\text{g m}^{-3}$ ) are doubled and the emissions in the high volatility bins are set to 0, was conducted in order to investigate the sensitivity of the model predictions to changes on the volatility distribution of the OA emissions. Using the low volatility distribution, the partition of the emissions favors the particulate phase. In this case, PMCAMx predicts that the fresh POA (emissions that did not undergo any chemical reaction) is two times higher than using the basecase distribution (Fig. 9). In particular, POA increases from  $4.4 \mu\text{g m}^{-3}$  to  $8.5 \mu\text{g m}^{-3}$  at T0, from  $1.2 \mu\text{g m}^{-3}$  to  $2.2 \mu\text{g m}^{-3}$  at T1, and from  $0.25 \mu\text{g m}^{-3}$  to  $0.5 \mu\text{g m}^{-3}$  at T2. The corresponding measurements were  $4.5 \mu\text{g m}^{-3}$  at T0 and  $1.3 \mu\text{g m}^{-3}$  at T1. These discrepancies between the two simulations indicate that the assumed volatility distribution

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of the emissions has a significant impact on the predicted POA concentrations. Using the low volatility distribution, the model significantly overpredicts the HOA concentrations at T0 and T1, indicating that the basecase distribution is more appropriate for the description of the primary organic aerosols in the Mexico City Basin.

5 The sensitivity of the predicted OOA to the aging reaction constant was investigated by using a rate constant equal to  $k(298\text{ K}) = 10 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  for S-SOA, I-SOA and V-SOA. The higher oxidation constant used resulted in higher OOA concentrations by 20% in Mexico City and Tula vicinity (Fig. 10). At T0, OOA increased from  $7.5 \mu\text{g m}^{-3}$  to  $9.1 \mu\text{g m}^{-3}$  resulting in an overprediction of OOA, compared to PMF  
10 analysis results, during the afternoon (Fig. 11). This increase is due more to increased S-SOA and I-SOA levels (three times higher concentrations than the base case) and less at V-SOA (increased by 10%). This result suggests that the potential of the I-VOC and S-VOC to form SOA is high and the rate constant of their photochemical aging is quite important. Nevertheless, the S-SOA and I-SOA are only a small portion of the  
15 predicted total OA (5–10%) in MCMA. Therefore, even if their concentration tripled after using the higher oxidation constant, the total OA increased by 15% at T0.

To examine the effect of the HONO emissions used in this application (as discussed in Sect. 3) on the predicted OOA, a simulation excluding these emissions was conducted. The results of this sensitivity analyses indicate that the inclusion of HONO to the emissions inventory is indirectly responsible for 3% and 10% of the predicted OOA  
20 in the Mexico City center and the Tula area respectively. Nevertheless, the HONO emissions and formation appeared to be relatively important for the production of the OOA in the center of Mexico City as it photodissociates upon sunrise to inject a pulse of OH into the early morning atmosphere. At T0, the model, taking into account the HONO  
25 emissions, predicts that the formation of OOA starts to be significant at 07:00 a.m., while excluding these emissions, the formation of OOA is delayed for one hour and starts at 08:00 a.m. (Fig. 12). The increase of the predicted OOA during 07:00 a.m. to 12:00 p.m. after the inclusion of HONO to the emission inventory is 25% on average at T0.

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The sensitivity of the results to the boundary conditions of OA and the corresponding long range transport was also tested. A 50% reduction of the OA boundary conditions resulted in an almost linear response of the background organic concentration, which is not surprising since this OA is assumed to be non-reactive and nonvolatile. The influence of the long range transport concentration remains significant for the low boundary condition case as it represents approximately 20% of the total organic aerosol concentration at Mexico City center. Figure 13 shows the comparison between the measured and the predicted total organic mass concentrations at T0, T1, and T2 for lower boundary conditions during March 2006. In this case, the model tends to underpredict the observed OA on 18–21 March in all three sites, while the agreement improves for 24–29 March. During the first period, high biomass activities were observed, while during the latter, the fire emissions were the lowest of the month. Therefore, each set of boundary conditions performs better in different time periods, and probably an accurate biomass burning emission inventory is necessary, or at least, the boundary conditions should be variable in time. Overall, the model using the base case boundary conditions set has a better performance in all three measurement sites than using the lower boundary conditions set. In particular, the base case set results in an overprediction of OM with mean bias  $1.9 \mu\text{g m}^{-3}$ ,  $0.8 \mu\text{g m}^{-3}$ , and  $1.5 \mu\text{g m}^{-3}$  at T0, T1, and T2 sites respectively. On the other hand, the lower boundary conditions set underpredicts the OM with mean bias  $-2.3 \mu\text{g m}^{-3}$ ,  $-3.5 \mu\text{g m}^{-3}$ , and  $-2.7 \mu\text{g m}^{-3}$  at T0, T1, and T2 sites respectively.

## 7 Conclusions

In this work PMCAMx-2008, which accounts for volatility partitioning and aging of primary and secondary organic aerosols, was applied in Mexico City Metropolitan Area during the MILAGRO-2006 campaign. The model performance was evaluated against measurements from four different types of sites. The urban site (MILAGRO site T0) was located in downtown Mexico City and was selected to characterize fresh aerosols generated in the metropolitan area. The suburban site (MILAGRO site T1), was selected



composition of OA is generally consistent with the PMF analysis results suggesting that the depiction in the model of the corresponding processes is not inconsistent with the observations.

Overall, PMCAMx-2008 predicts that the background concentration of OA is a significant fraction of the total OA in Mexico City center. In particular, only approximately half of the average OA consists of fresh emitted POA and local SOA, while the rest is coming mainly from the forest fires in the surrounding area either in the form of SOA or in the form of biomass burning OA. These results are also in agreement with the findings of Crouse et al. (2009) who estimated that biomass burning contributes 66% of the organic aerosol to the study area in March 2006. Moreover, biogenic emissions also have a significant contribution to total SOA (up to 70%) and total OA (up to 15%). Even in the center of Mexico City, the predicted contribution of biogenic SOA to total SOA is approximately 20–30%. The predictions of PMCAMx-2008 for biogenic SOA are lower than the results of Hodzic et al. (2009) who predicted that the relative contribution of biogenic SOA to total SOA in the city center is up to 40%. This could be due to the lower predicted anthropogenic SOA concentrations in that modeling study.

The distribution of OA emissions to the low volatility bins appears to be important for the predicted POA as it has great impact to the initial partitioning between the aerosol and the gas phase. Increasing the aging reaction constant by one order of magnitude resulted in 20% higher OOA concentrations. Finally, including HONO emissions to the inventory used by the model, appear to be important for the production of OOA during the early morning hours, resulting in an increase of 25% during morning.

*Acknowledgements.* The authors thank Sihee Song for assistance with the biogenic emissions and Guohui Li for valuable comments. This research was supported by the European Union and the 7th Framework Programme under the project MEGAPOLI (Grant agreement no.: 212520) and NSF ATM 0732598. A. P. Tsimpidi, V. A. Karydis, M. Zavala were supported by scholarships from the Molina Center for Energy and the Environment. L. T. Molina acknowledges support from NSF ATM 0528227 and ATM 0810931.

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Organic compound	Emission rate (tons d <sup>-1</sup> )
Anthropogenic VOCs	2572
Biogenic VOCs	954
Intermediate volatile compounds	217
Semi-volatile compounds	55

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**Fig. 1.** The modeling domain for the Mexico City Metropolitan Area during the MILAGRO campaign. Also shown, the locations of the monitoring stations during the campaign.

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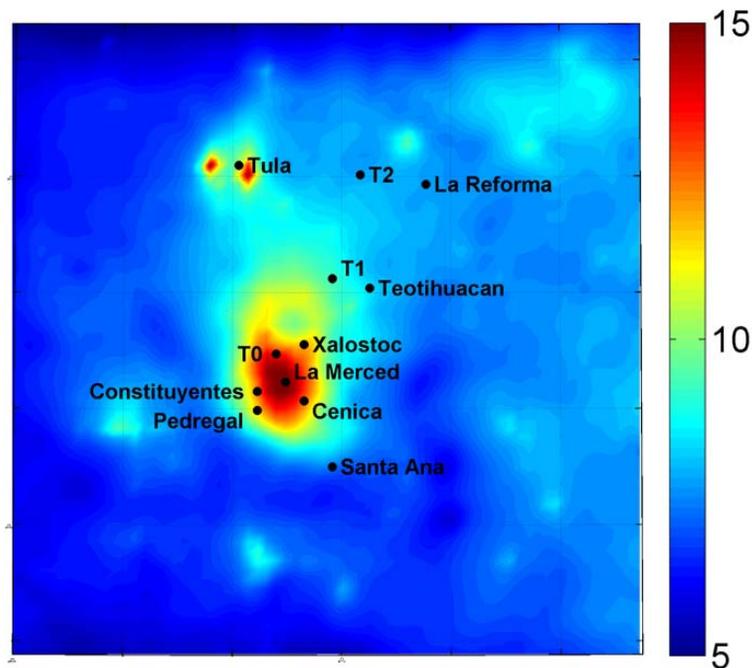
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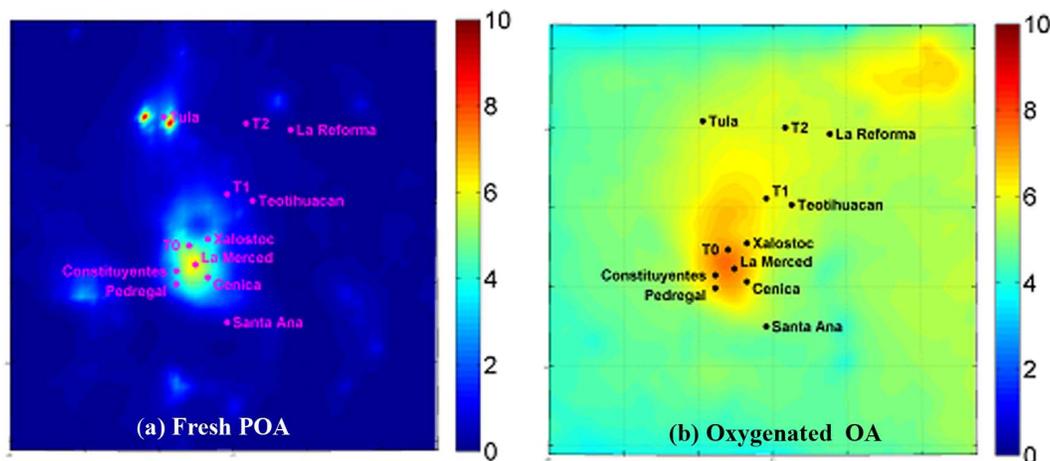
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**Fig. 2.** Predicted average ground level concentrations of PM<sub>1</sub> organic mass ( $\mu\text{g m}^{-3}$ ) during 4–30 March 2006.

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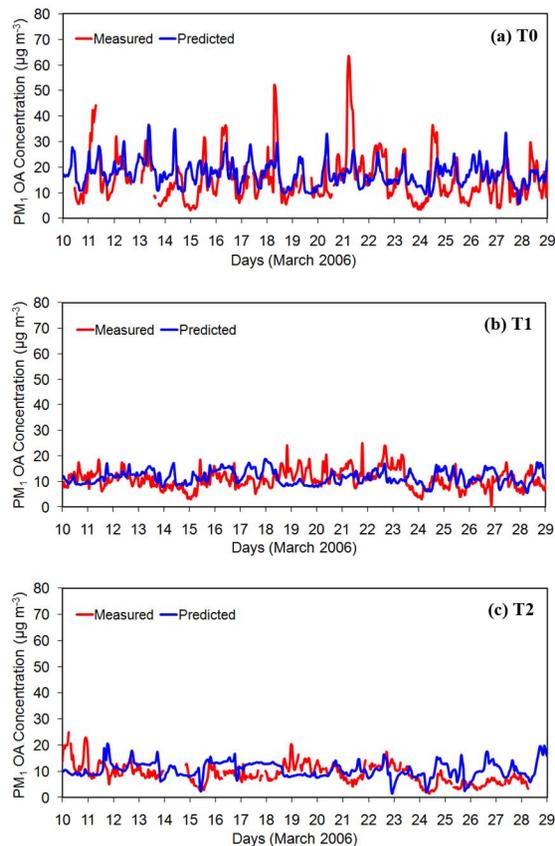


**Fig. 3.** Average predicted PM<sub>1</sub> (a) primary and (b) oxygenated organic aerosol concentrations ( $\mu\text{g m}^{-3}$ ) at the ground level.

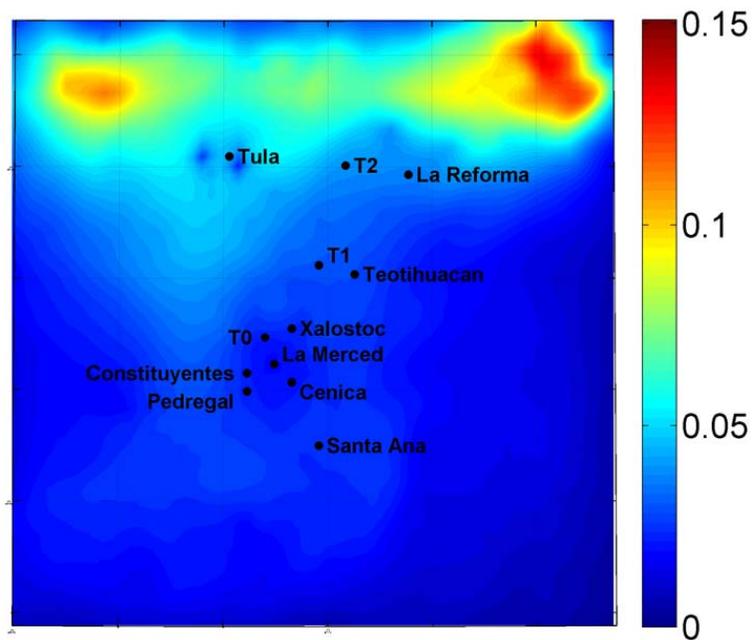
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**Fig. 4.** Comparison of model predictions with hourly measurements for total PM<sub>1</sub> organic mass concentration taken during the MILAGRO campaign in March 2006 at **(a)** T0 (urban site), **(b)** T1 (suburban site), and **(c)** T2 (rural site) on ground level.



**Fig. 5.** Fractional contribution of fresh biogenic SOA to total OA at the ground level.

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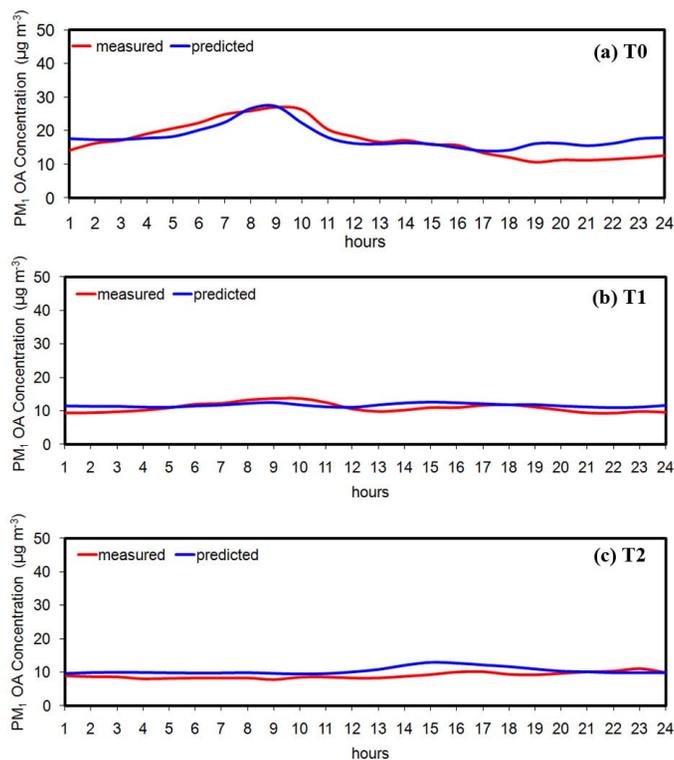
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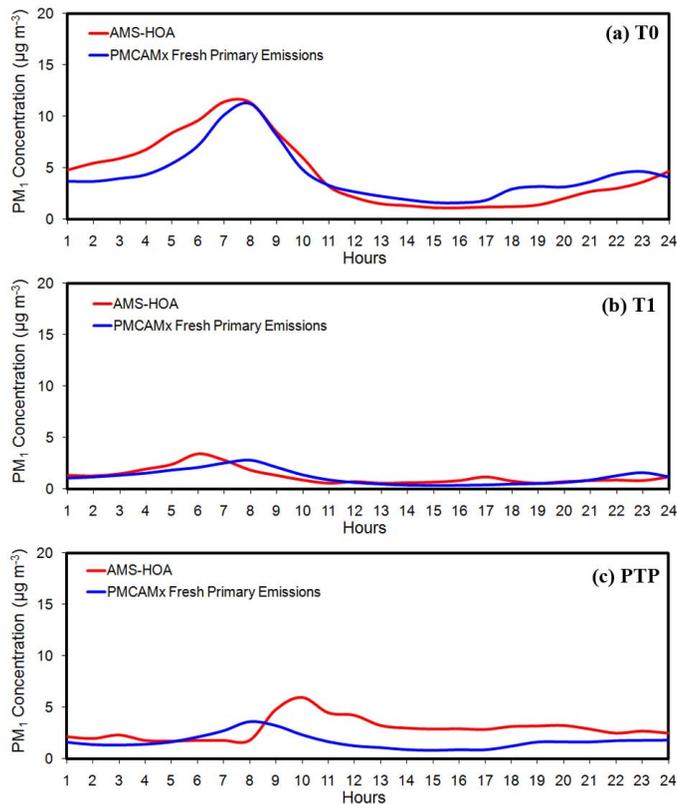


**Fig. 6.** Comparison of model diurnal predictions with hourly measurements for total PM<sub>1</sub> organic aerosols against measurements taken during the MILAGRO campaign in March 2006 at **(a)** T0 (urban site), **(b)** T1 (suburban site), and **(c)** T2 (rural site) on ground level.

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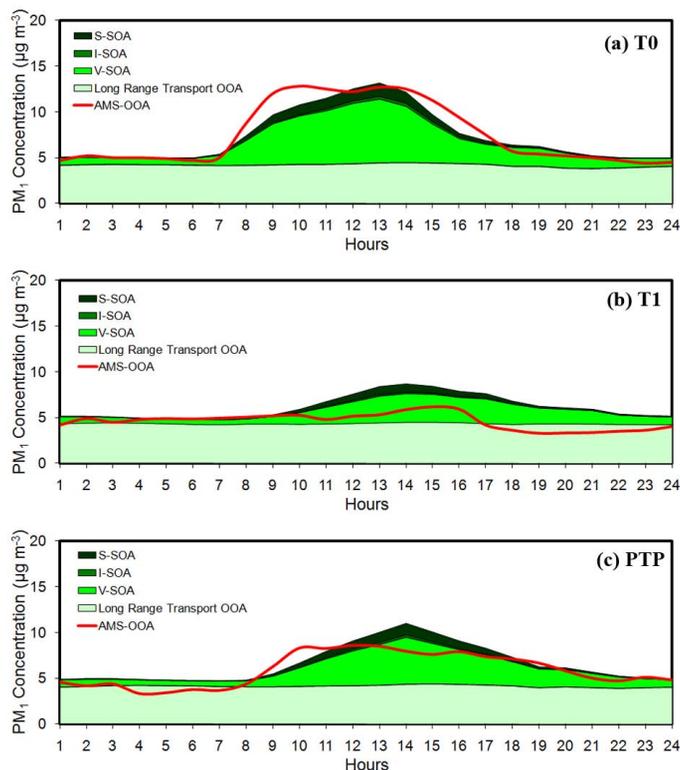
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**Fig. 7.** Comparison of model episode average diurnal predictions for PM<sub>1</sub> local primary organic aerosols against AMS-HOA taken during the MILAGRO campaign in 4–30 March 2006 at **(a)** T0, **(b)** T1 and **(c)** PTP.

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**Fig. 8.** Comparison of model episode average diurnal predictions for  $PM_1$  oxygenated organic aerosols (sum of Long Range Transport Oxygenated OA, V-SOA, I-SOA, and S-SOA) against AMS-OOA taken during the MILAGRO campaign in 4–30 March 2006 at **(a)** T0, **(b)** T1 and **(c)** PTP.

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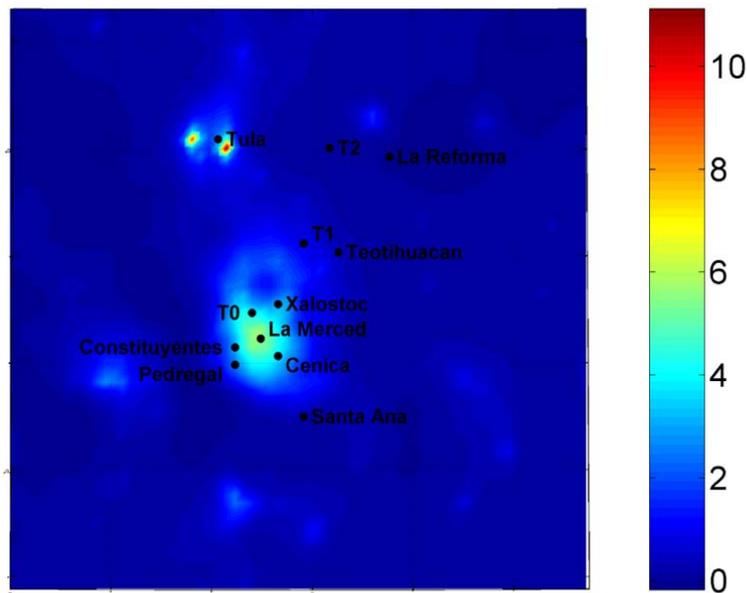
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**Fig. 9.** Predicted change in ground-level concentrations ( $\mu\text{g m}^{-3}$ ) of the  $\text{PM}_{10}$  POA after using a lower volatility distribution of OA primary emissions. A positive change corresponds to an increase.

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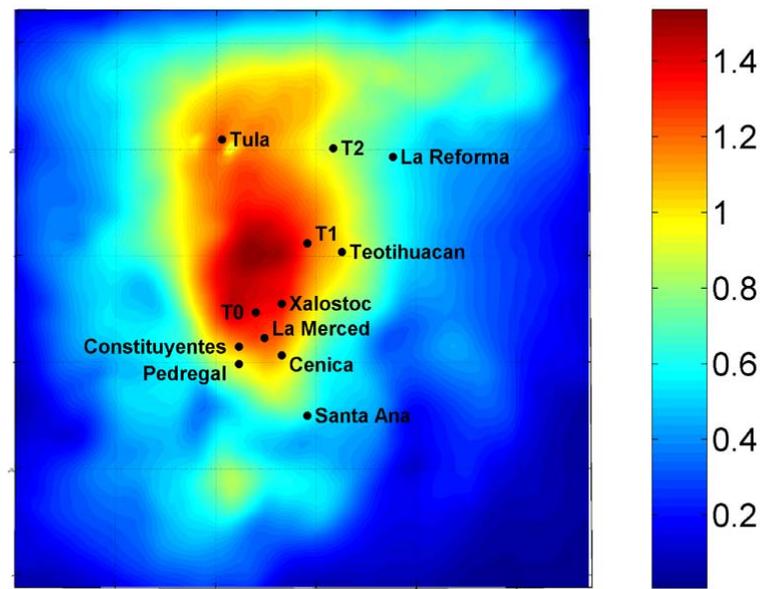
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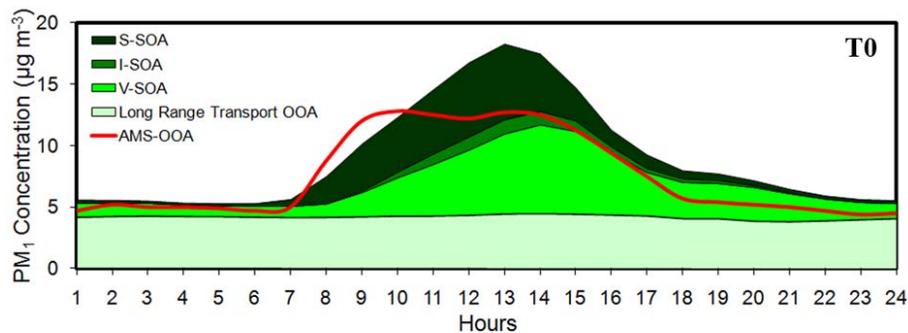
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**Fig. 10.** Predicted change in ground-level concentrations ( $\mu\text{g m}^{-3}$ ) of the  $\text{PM}_1$  OOA after using a ten times higher constant rate for the aging reactions. A positive change corresponds to an increase.

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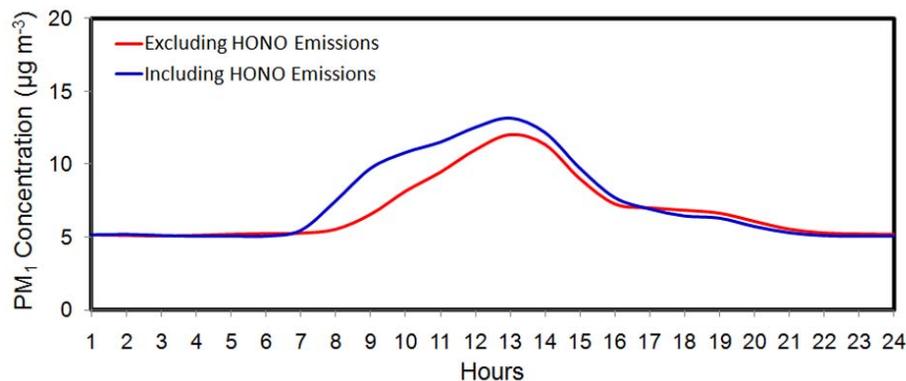
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**Fig. 11.** Comparison of model episode average diurnal predictions in high aging reaction case for PM<sub>1</sub> oxygenated organic aerosols (sum of Long Range Transport Oxygenated OA, V-SOA, I-SOA, and S-SOA) against AMS-OOA taken during the MILAGRO campaign in 4–30 March 2006 at T0.

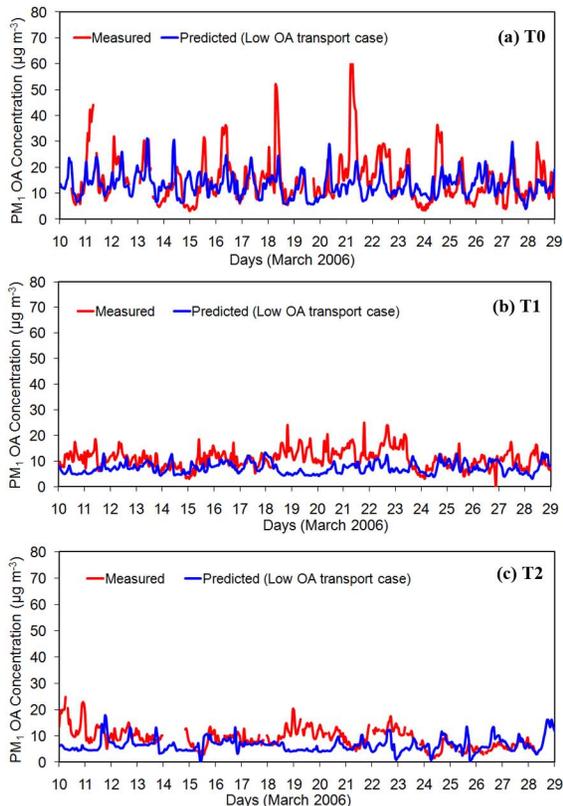
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**Fig. 12.** Comparison of model episode average diurnal predictions for PM<sub>1</sub> oxygenated organic aerosols at T0 using an emission inventory with HONO emissions (red line) and without HONO emissions (blue line).

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**Fig. 13.** Comparison of model predictions in the low boundary conditions case with hourly measurements for total  $PM_1$  organic mass concentration taken during the MILAGRO campaign in March 2006 at **(a)** T0 (urban site), **(b)** T1 (suburban site), and **(c)** T2 (rural site) on ground level.

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