Evaluation of the volatility basis-set approach for the simulation of organic aerosol formation in the Mexico City metropolitan area

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Abstract

New primary and secondary organic aerosol modules have been added to PMCAMx, a three dimensional chemical transport model (CTM), for use with the SAPRC99 chemistry mechanism based on recent smog chamber studies. The new modeling framework is based on the volatility basis-set approach: both primary and secondary organic components are assumed to be semivolatile and photochemically reactive and are distributed in logarithmically spaced volatility bins. This new framework with the use of the new volatility basis parameters for low-NO$_x$ and high-NO$_x$ conditions tends to predict 4–6 times higher anthropogenic SOA concentrations than those predicted with older generation of models. The resulting PMCAMx-2008 was applied in Mexico City Metropolitan Area (MCMA) for approximately a week during April of 2003. The emission inventory, which uses as starting point the MCMA 2004 official inventory, is modified and the primary organic aerosol (POA) emissions are distributed by volatility based on dilution experiments. The predicted organic aerosol (OA) concentrations peak in the center of Mexico City reaching values above 40 µg m$^{-3}$. The model predictions are compared with Aerosol Mass Spectrometry (AMS) observations and their Positive Matrix Factorization (PMF) analysis. The model reproduces both Hydrocarbon-like Organic Aerosol (HOA) and Oxygenated Organic Aerosol (OOA) concentrations and diurnal profiles. The small OA underprediction during the rush hour periods and over-prediction in the afternoon suggest potential improvements to the description of fresh primary organic emissions and the formation of the oxygenated organic aerosols respectively, although they may also be due to errors in the simulation of dispersion and vertical mixing. However, the AMS OOA data are not specific enough to prove that the model reproduces the organic aerosol observations for the right reasons. Other combinations of contributions of primary, aged primary, and secondary organic aerosol production rates may lead to similar results. The model results suggest strongly that during the simulated period transport of OA from outside the city was a significant contributor to the observed OA levels. Future simulations should use a larger domain
in order to test whether the regional OA can be predicted with current SOA parameterizations. Sensitivity tests indicate that the predicted OA concentration is especially sensitive to the volatility distribution of the emissions in the lower volatility bins.

1 Introduction

Anthropogenic air pollution is an increasingly serious problem for public health, global climate, and ecosystems. Organic aerosol (OA) contributes approximately 20–50% to the total fine particulate mass at continental mid-latitudes (Saxena and Hildemann, 1996; Putaud et al., 2004; Murphy et al., 2006; Zhang et al., 2007). Approximately half of the total aerosol mass in Mexico City is organic (Chow et al., 2002; Edgerton et al., 1999; Salcedo et al., 2006; DeCarlo et al., 2008; Aiken et al., 2009). PM$_{2.5}$ in urban Mexico City during March 1999 had an average organic carbon (OC) concentration of 10 µg m$^{-3}$ (Chow et al., 2002). These levels are comparable to those observed in Los Angeles (Schauer et al., 1996; Docherty et al., 2008) and in three Chinese megacities, Beijing, Shanghai, and Guangzhou (Feng et al., 2006). Please note that all concentrations in this paper are under ambient pressure and temperature conditions. Although OA accounts for a large fraction of the PM$_{2.5}$ concentration, the contributions of primary and secondary organic aerosol have been difficult to quantify (e.g. Hallquist et al., 2009; de Gouw and Jimenez, 2009b). Organic aerosol originates from many different natural and anthropogenic sources and processes. Primary organic aerosol (POA) has been traditionally defined as the OA emitted into the atmosphere in particle form, e.g., from fossil fuel and biomass combustion, while secondary organic aerosol (SOA) is formed from gaseous precursors through gas-phase (Jacobson et al., 2000; Seinfeld et al., 2003; NARSTO, 2003), particle phase (Jang et al., 2002), or aqueous-phase reactions (Claeys et al., 2004; Blando, 2000). Due to their different origins and formation mechanisms, fresh POA and SOA usually have different chemical and microphysical properties (Mircea et al., 2002; Kerminen et al., 2000; Cruz et al., 1997; Kavouras et al., 2002; Zhang et al., 2005a; Aiken et al., 2008). Therefore, to design effective
fine particle control strategies and to better evaluate the roles of organic aerosols in regional and global climate we must understand the concentrations, properties, and sources of these two organic aerosol types (NARSTO, 2003).

Spectroscopic techniques, including Fourier transform infrared (FTIR) spectroscopy (Allen et al., 1994; Blando et al., 1998) and nuclear magnetic resonance (NMR) (Dece-sari et al., 2000), have been used to characterize the functional group composition of bulk aerosol organics or their water-soluble fraction. Mass spectrometry techniques have been widely used in aerosol analysis because of their universal, extremely sensitive, and rapid detection of aerosol components (McKeown et al., 1991; Suess and Prather, 1999). Among these, the Aerodyne Aerosol Mass Spectrometer (AMS) (Jayne et al., 2000; Jimenez et al., 2003) is the most commonly used during the last few years. It is capable of quantitatively measuring the size-resolved mass concentrations of organic aerosols with a time resolution of minutes (e.g., Allan et al., 2003a; Takegawa et al., 2005; Jimenez et al., 2003; Zhang et al., 2005b). Good correlation between the mass concentrations of organic aerosols measured by an AMS and the organic carbon concentrations measured by thermal-optical Carbon Analyzers has been observed in various locations, including Pittsburgh (Zhang et al., 2005b), Tokyo (Takegawa et al., 2005), and off the New England coast (Bates et al., 2005; de Gouw et al., 2005).

Zhang et al. (2005a) developed a custom principal component analysis of AMS organic spectra that can identify and quantify broad organic aerosol “classes” that have different temporal and mass spectral signatures, and quantified two types of organic aerosols, hydrocarbon-like (HOA) and oxygenated (OOA), which together accounted for almost all the OA mass measured by the AMS during the PAQS study in Pittsburgh. HOA has similar AMS mass spectra to those of hydrocarbon mixtures in fresh primary OA, while OOA has high oxygen content and correlates with secondary tracers (Zhang et al., 2005a). In addition, recent work using the positive matrix factorization (PMF) method (Paatero and Tapper, 1994; Paatero, 1997) has allowed the identification of additional detail on primary and secondary sources/components at urban locations in Europe (Lanz et al., 2007) and North America (Ulbrich et al., 2009; Aiken et al., 2008,
Chemical transport models (EPA, 2009; Environ, 2008) have traditionally treated POA emissions as non-volatile and non-reactive, while SOA compounds are modeled as semi-volatile products of the oxidation of volatile precursors (Chung and Seinfeld, 2002; Kanakidou et al., 2005). With few exceptions, further oxidation of either POA or SOA, if treated at all, is modeled with an ad-hoc constant timescale for conversion of hydrophobic to hydrophilic material irrespective of oxidant availability and particle reactivity (Cooke et al., 1999). However, POA is clearly semi-volatile and undergoes gas-particle partitioning in the atmosphere as a function of its volatility, background OA concentrations (Robinson et al., 2007; Lipsky et al., 2006) and temperature (Kuhn et al., 2005; Huffman et al., 2009a, b). In addition, several recent field studies have shown that SOA formed downwind of metropolitan areas may be strongly underestimated by current models based on “traditional” SOA precursors and chamber yields (de Gouw et al., 2005; Volkamer et al., 2006; Kleinman et al., 2008; Docherty et al., 2008; Matsui et al., 2009; Dzepina et al., 2009). The formation of SOA in Mexico City is similar to that observed at other locations such as the Northeast US, Tokyo, or the Po Valley (Kleinman et al., 2008; de Gouw et al., 2009a; de Gouw and Jimenez, 2009b). The “traditional” secondary organic precursors include biogenic compounds (monoterpens, sesquiterpenes, and isoprene) and anthropogenic compounds (mainly aromatics). In addition, recent work has suggested that chemical aging of semivolatile and intermediate volatile organic compounds (SVOCs and IVOCs) either emitted directly or resulting from the evaporation of particles (Robinson et al., 2007), or generated from VOCs (Lane et al., 2008a) may be an important and previously neglected pool of precursors for SOA formation and growth as well. Products with high vapor pressures can be oxidized to species with lower vapor pressures that can condense into the aerosol phase (Donahue et al., 2006). These chemical reactions can lead to continued SOA growth after complete precursor consumption as products undergo further oxidation (Kroll et al, 2006; Ng et al., 2006).

Shrivastava et al. (2008) used the chemical transport model PMCAMx to investigate
the effects of gas-particle partitioning and photochemical aging of primary emissions on organic aerosol concentrations in the Eastern United States. Lane et al. (2008a, 2008b) used a new framework for modelling the secondary organic aerosol formation in the Eastern United States based on the SOA volatility basis-set approach (Donahue et al., 2006; Stanier et al., 2008) instead of the two-product approach (Odum et al., 1996) used in existing models. Nevertheless there are no reported efforts of combining all these new findings in a single CTM and applying it in a polluted area with high concentrations of both fresh and aged secondary and primary organic aerosols. Trying to compare the results of such an application with the analysis of the AMS measurements can help evaluate the current state of understanding of the organics and at the same time can assist in the interpretation of measurements from field campaigns.

In this work we explicitly simulate the volatility of all organic compounds, including both primary emissions and secondary reaction products, and also model gas-phase reactions of semi-volatile material. Each reaction time step alters the volatility distribution and thus the total organic aerosol mass. NO$_x$-dependent SOA yields based on smog chamber studies are also included in the updated SOA module (Lane et al., 2008a). The traditional terminology used to describe the major OA components needs to be extended to be compatible with the proposed modeling framework. We will be using the term POA to describe primary organic aerosol material that did not undergo chemical reactions during its atmospheric lifetime. Oxidized primary OA (OPOA) will be the organic material emitted with saturation concentration initially less or equal than $10^2$ µg m$^{-3}$ (all volatilities in this paper are at 298 K) which moved to the gas phase, was oxidized and re-condensed to the aerosol phase. The current model does not simulate heterogeneous oxidation (reaction of gas-phase oxidants with particle-phase molecules) which is often also referred to as OPOA. Traditional SOA will be the OA formed in the atmosphere from the oxidation of the volatile organic compounds (traditional SOA precursors with $C^* > 10^6$ µg m$^{-3}$). Finally non-traditional SOA (NT-SOA) will be the OA formed in the atmosphere from the oxidation of intermediate volatility species (non-traditional SOA precursors with $10^3 \leq C^* \leq 10^6$ µg m$^{-3}$). The oxidation
products of all compounds that remained in the gas phase can be further oxidized and can condense in the aerosol phase. Therefore the model simulates three types of oxygenated OA based on the initial volatility of the corresponding precursor compounds: OPOA ($C^* \leq 10^2 \text{ µg m}^{-3}$), non-traditional SOA ($10^3 \leq C^* \leq 10^6 \text{ µg m}^{-3}$) and traditional SOA ($C^* > 10^6 \text{ µg m}^{-3}$).

The model is applied in the Mexico City Metropolitan Area for approximately a week during 12–16 April 2003, as part of the MCMA-2003 field campaign (Molina et al., 2007). The model predictions for this period are presented and are compared with measurements taken from the CENICA supersite by Salcedo et al. (2006). Moreover, in order to evaluate our current state of understanding the formation and the composition of the organic mass, we compare PMCAMx predictions of OA components against AMS analysis results. Finally the sensitivity of the proposed organic aerosol framework to the volatility distribution of the emissions is investigated.

2 PMCAMx-2008 description

PMCAMx is a three-dimensional chemical transport model which uses the framework of CAMx (Environ, 2003) and models the processes of horizontal and vertical advection, horizontal and vertical dispersion, wet and dry deposition, and gas phase chemistry. Dry deposition is modeled using the resistance model of Wesely (1989), assuming a Henry’s law constant for all the organic condensable gasses equal to $2.7 \times 10^3 \text{ M/atm}$. In addition, three detailed aerosol modules are used: inorganic aerosol growth (Gaydos et al., 2003; Koo et al., 2003), aqueous phase chemistry (Fahey and Pandis, 2001), and SOA formation and growth. These modules employ a sectional approach that dynamically models the size evolution of each aerosol constituent across 10 size sections varying from 40 nm to 40 µm.

The chemical mechanism used is based on the SAPRC99 mechanism (Carter, 2000; Environ, 2003) and includes 211 reactions of 56 gases and 18 free radicals. The version of SAPRC99 used here has five lumped alkanes, two lumped olefins, two lumped
aromatics, isoprene, a lumped monoterpene, and a lumped sesquiterpene species. Only the two highest molecular weight alkane species are considered SOA precursors because the other three consist of smaller hydrocarbons (Pandis et al., 1991). OLE1 contains all the terminal alkenes, while OLE2 consists of all the internal alkenes and cyclic alkenes. Table 1 lists the lumped VOC classes used in SAPRC99 the major compounds for each VOC class and the nine SAPRC99 surrogate VOCs that are considered SOA precursors.

2.1 Organic aerosol modeling

Partitioning of primary emissions: Emission inventories and models currently treat POA as non-reactive and non-volatile. However, the POA mass is highly sensitive to ambient conditions, including dilution and temperature (Lipsky and Robinson, 2006; Hildemann et al., 1989). The critical attribute controlling organic compound partitioning is volatility. The modified PMCAMx-2008 accounts for partitioning of primary emissions using the same module used to calculate partitioning of any semivolatile organic species (Koo et al, 2003) assuming that the bulk gas and particle phases are in equilibrium and that all condensable organics form a pseudo-ideal solution (Odum et al., 1996). Nine surrogate species with saturation concentrations at room temperature ranging from $10^{-2}$ to $10^6 \mu g m^{-3}$ are used following the approach of Shrivastava et al. (2008).

Traditional Secondary Organic Aerosol Formation: The modeling framework used in this work is based on the SOA volatility basis-set approach (Lane et al., 2008a) instead of the two-product approach used in existing models. This approach includes four SOA species for each VOC using the basis set for their effective saturation concentrations at 300 K: 1, 10, 100, 1000 $\mu g m^{-3}$. The SOA module in PMCAMx has been updated in order to include anthropogenic aerosol yields, based on laboratory results from recent smog-chamber experiments (Ng et al., 2006; Hildebrandt et al., 2009). Moreover, the updated SOA module incorporates NO$_x$-dependent SOA yields (Table 2) (Lane et al., 2008b). Under low-NO$_x$ conditions, the RO$_2$ radicals react with other peroxy radicals to form a distribution of products with lower volatilities, resulting in higher SOA yields.
At high-NO\textsubscript{x} conditions, the SOA yields are lower because aldehydes, ketones, and nitrates dominate the product distribution. Dzepina et al. (2009) report that the low-NO\textsubscript{x} pathway was negligible in downtown Mexico City during a case study from MCMA-2003, however this is likely not the case outside the city. The enthalpy of vaporization is assumed to be independent of the NO\textsubscript{x} level due to the lack of relevant experimental data at high-NO\textsubscript{x} conditions.

**Chemical Aging Reactions:** Chemical reactions that change the volatility of the organics in the gas phase will change the organic aerosol mass by influencing their partitioning. In this new approach all species (primary and secondary) are treated as chemically reactive. Primary organic gases (POG), formed due to evaporation of POA in the atmosphere, are assumed to react with OH radicals reducing their volatility. The products of this oxidation (aged primary gases) are allowed to partition between gas and particle phase according to their volatilities. This resulted in the formation of oxidized primary organic aerosols (OPOA).

Intermediate volatility species (IVOC) that are co-emitted with the POA but are never in the particle phase during the emission process also age in the same way to form non-traditional SOA (NT-SOA) (Robinson et al., 2007).

Chemical aging of organic condensable gases (OCG) generated from VOCs that are traditional SOA precursors is an important source of OA as well. For both cases, aging is modeled with a gas-phase OH reaction with a rate constant of $4 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003). Each reaction is assumed to reduce the volatility of the vapor material by one order of magnitude (i.e., shifting material from a C$^*$ of 100 to 10 µg m$^{-3}$), with a small net increase in mass (7.5%) to account for added oxygen. The proposed chemical aging is confined to the gas-phase according to the reactions below:

\begin{align*}
\text{POA}_i(p) &\leftrightarrow \text{POG}_i(g) \quad \text{(R1)} \\
\text{POG}_i(g) + \text{OH} &\rightarrow 1.075 \text{ OPOG}_{i-1}(g) \quad \text{(R2)} \\
\text{OPOG}_{i-1}(g) &\leftrightarrow \text{OPOA}_{i-1}(p) \quad \text{(R3)}
\end{align*}
IVOC\textsubscript{i}(g) + OH → 1.075 IVOC\textsubscript{i-1}(g) \quad \text{(R4)}

IVOC\textsubscript{i-1}(g) ← NT–SOA\textsubscript{i-1}(p) \quad \text{(R5)}

\text{VOC}(g) + OH → \sum_{i=1}^{n} a_i \text{OCG}_i(g) \quad \text{(R6)}

\text{OCG}_i(g) + OH → 1.075 \text{OCG}_{i-1}(g) \quad \text{(R7)}

\text{OCG}_{i-1}(g) ← \text{SOA}_{i-1}(p) \quad \text{(R8)}

where \( i \) is the corresponding volatility bin. Heterogeneous and condensed-phase reactions are not simulated explicitly in this framework but they could also play a role. The formation of SOA from glyoxal may be important in Mexico City (Volkamer et al., 2007; 2009; Dzepina et al., 2009), but is not considered explicitly in this study.

\textbf{2.2 Volatility-resolved OA emission inventory}

The emission inventory used is constructed based on the official emissions inventory for the MCMA for 2004 (CAM, 2006) which includes PM mass emissions but without chemical speciation. Mobile sources are the most significant contributors to primary fine particle mass in MCMA. The direct impact of biogenic VOCs in the urban area is small, although recent results suggest that the transport of biogenic SOA formed in the coastal mountain ranges may be an important source of regional SOA that impacts Mexico City (Hodzic et al., 2009), which would be represented here as part of the boundary condition OA. The official emission estimates of PM mass used in this study were obtained using the bottom-up approach that combines source-specific emissions and activity factors (CAM, 2006). The PM emissions from biogenic, mobile, point, and area sources were spatially and temporally distributed following the techniques described in Lei et al. (2007). Updated fine resolution population maps, road, street and highway digital data along with the digitalization of point sources and
most of the area emission sources considered in the emissions inventory were combined with a Geographical Information System to construct spatially distributed gridded emission maps. The mass of PM from the official emissions inventory was partitioned using the PMF analysis of rush-hour measurements taken during the MCMA-2003 and MILAGRO/MCMA-2006 field campaigns using periods of high HOA and minimum secondary formation. In order to account for partitioning of primary organic emissions, the emission inventory for PMCAMx-2008 must include the emitted primary organic aerosols before their dilution in the atmosphere. However, the current emission inventory, as described above, is based on ambient measurements at an urban background site (as opposed to a roadside site) and according to the volatility theory, some of the emitted POA has already evaporated and is not included in the official emission fluxes. Ambient organic aerosols in Mexico City are heavily impacted by primary emissions from motor vehicles and at times also biomass combustion (Stone et al., 2008; Aiken et al., 2009). Laboratory experiments, in which diesel exhaust and wood smoke emissions were measured at different levels of dilution, have shown that the measured primary organic aerosols in ambient conditions represent 15–40% of the primary organic aerosol actually emitted, depending on the ambient organic aerosol concentration and temperature (Lipsky and Robinson, 2006). Thermal denuder measurements in Mexico City during MILAGRO (Huffman et al., 2009b; Dzepina et al., 2009) have also shown that the POA volatility in Mexico City was of the same order of magnitude as that reported by Lipsky and Robinson (2006). The average concentration of the organic aerosols in Mexico City was in the range of 20 µg m⁻³ during the MCMA-2003 campaign (Salcedo et al., 2006). In this range of organic aerosol ambient concentrations the measured organic PM is approximately one third of the total emitted organic aerosols (Fig. 1a of Robinson et al., 2007). Therefore, in order to estimate the total semivolatile organic emissions, the OA particulate inventory is multiplied by a factor of 3. Source test data for wood combustion, gasoline vehicles, and diesel vehicles which used a sample train of quartz filters in combination with denuders and/or sorbents (Schauer et al., 1999; Schauer et al., 2001; Schauer et al., 2002) has shown
that the mass of missing IVOC vapors is between 0.25 to 2.8 times the existing primary OA emissions. In this work, the OA emissions were distributed by volatility (Table 3) using the volatility distributions of Shrivastava et al. (2008). This distribution derived by fitting gas particle partitioning data for diesel exhaust and wood smoke assuming that the mass of missing IVOC emissions is equivalent to 1.5 times the primary organic aerosol emissions. The amount of new material introduced in the model as evaporated POA and IVOCs is poorly constrained as these species have not been measured in Mexico City. However Sheehy et al. (2008) and Dzepina et al. (2009) report that the new material introduced in this way is compatible with the observations of total OH-reactivity and integrated C-H stretches measured with FTIR during MCMA-2003 and in fact does not yet close the gap between the sum of speciated contributions and the total integrated measurements in both cases. The result was a gridded emission inventory (Fig. 1) of nine lumped non-oxidized primary species (POA) and intermediate volatility species (IVOC) corresponding to volatility bins ranging from $10^{-2}$ to $10^6$ µg m$^{-3}$ at 300 K (Fig. 2). This distribution includes “nonvolatile” ($C^* \leq 10^{-1}$ µg m$^{-3}$), “semivolatile” (SVOC; $10$ µg m$^{-3} \leq C^* \leq 10^2$ µg m$^{-3}$), and “intermediate-volatility” (IVOC; $10^3$ µg m$^{-3} \leq C^* \leq 10^6$ µg m$^{-3}$) organic compounds. The majority of these emissions have a $C^* \geq 10^3$ µg m$^{-3}$ and therefore exist largely in the gas phase at typical atmospheric conditions. Nevertheless, they might be important NT-SOA precursors as their oxidation can produce compounds with lower vapor pressures. The effective saturation concentration, molecular weights, and enthalpies of vaporization of these nine lumped species are listed in Table 3, based on fits of diesel and woodsmoke partitioning data (Lipsky and Robinson, 2006; Shrivastava et al., 2006).

3 Model application

PMCAMx is applied in the Mexico City Metropolitan Area for approximately a week during 12–16 April 2003. The Mexico City Metropolitan Area (MCMA) is situated inside a basin at 2200 m altitude. The basin is surrounded by high mountains on three sides as
shown in Figure 3. The model domain covers a 156×156×6 km region in the MCMA with 3×3 km grid resolution and 15 vertical layers. The first day of the simulation has been excluded from the analysis to limit the effect of the initial conditions on the results. The values of the OA concentrations at the boundaries of the domain, approximately 7 µg m\(^{-3}\) in the west, 10 µg m\(^{-3}\) in the east, 6 µg m\(^{-3}\) in the south and 5.5 µg m\(^{-3}\) in the northern boundary, were chosen based on results of the GISS-II’ global CTM for April (Racherla et al., 2006). 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 µg m\(^{-3}\) (Fast et al., 2009). These boundary condition values are consistent with the ground measurements in T2 during MILAGRO (very close to the northern boundary of the domain) by Doran et al. (2007) who reported average OA concentrations of approximately 8 µg m\(^{-3}\) (assuming an OM/OC ratio of 1.6) for the month of March 2006. 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. The organic mass transported into the domain is assumed to be a mixture of aged primary and secondary organic aerosols (Zhang et al., 2007; DeCarlo et al., 2008) and is referred to hereinafter as “long range transport oxygenated OA”.

Inputs to the model include horizontal wind components, temperature, pressure, water vapor, vertical diffusivity, clouds, and rainfall, all based on the work of de Foy et al. (2005) using the meteorological model MM5 (Grell et al., 1995). The simulated month, April, is a transition month between the hot dry season and the wet season (Jauregui, 1988). The first two days of simulation had unperturbed westerlies with weak anticyclonic conditions to the south and a strong subtropical jet just to the north of the MCMA. The remaining days are dominated by a low level anticyclonic circulation over central southern Mexico and westerly winds in the north. This leads to subsidence over the Mexico basin with weak surface winds favorable to the development of thermally driven circulations (de Foy et al., 2005).
4 Predicted Organic Aerosol concentrations

The average predicted OA ground concentration during 13–16 April is depicted in Fig. 4. Because of the high boundary condition concentrations assumed in the base-case simulation the average predicted OA levels in the area exceed everywhere 6 µg m\(^{-3}\). The average concentrations of OA peak in the centre of Mexico City with values in the range of 20 µg m\(^{-3}\). Hourly concentrations peak as high as 40 µg m\(^{-3}\). The predicted OM consists of POA, OPOA, SOA (traditional and non-traditional from the oxidation of IVOCs). The corresponding fractional and average contributions of these components to the organic mass are shown in Figs. 5 and 6. POA represents on average on third of the predicted OA in the center of the city with concentrations up to 8 µg m\(^{-3}\), but its contribution drops rapidly to 10% or less of the total (concentration less than 1 µg m\(^{-3}\)) in the edges of the urban area. OPOA is predicted to be the dominant OA component in the modelling domain (Fig. 5b); however a significant fraction of OPOA is predicted to be the result of transport from areas outside the city including biomass burning (Fig. 6b and d). The concentration of OPOA produced from locally emitted POA is around 1 µg m\(^{-3}\) inside the city and less than that outside. Finally, SOA contributes on average roughly half of the OA inside the city and one third of the OA outside of it. The SOA produced from locally emitted organic vapors has concentrations around 7 µg m\(^{-3}\) in the centre of Mexico City and is dominated by SOA produced from aromatic hydrocarbons (Fig. 7). On average, 19% of total SOA (sum of traditional SOA and NT-SOA) is the result of oxidation of ARO1 (toluene, benzene, ethyl benzenes, etc), 28% of ARO2 (xylenes, ethyl toluenes, dimethyl and trimethyl benzenes, etc.), 1% of ALK4, 12% of ALK5 (large alkenes), 4% of OLE1, 15% of OLE2, 3% of TERP, 0.5% of ISOP, 1.5% of SESQ, and 16% of IVOCs. Overall, this new framework with the use of the new volatility basis parameters for low-NO\(_x\) and high-NO\(_x\) conditions (Fig. 10 in Hildebrandt et al, 2009), which far exceed the historical parameters used in previous models (Koo et al., 2003; Volkamer et al., 2006), predicts 4–6 times higher anthropogenic SOA concentrations inside Mexico City than those predicted with older
generation of models such as Koo et al. (2003). The importance of transported OA is depicted in Fig. 6d. It dominates as expected the area outside the city, but even within the urban area it represents a significant component of OA. Obviously, its fractional contribution decreases significantly during the periods with high OA levels inside the city and in these cases it represents less than one quarter of the total OA. The sensitivity of these results to the boundary conditions for OA is discussed in more detail in a subsequent section.

5 Model performance evaluation for organic PM

Model predictions were compared with measurements that took place during the Mexico City Metropolitan Area field campaign at a highly instrumented “Supersite” located at the “Centro Nacional de Investigacion y Capacitacion Ambiental” (CENICA), in Southeast Mexico City (Salcedo et al., 2006, 2007; Volkamer et al., 2006, 2007; Johnson et al., 2008; Dzepina et al., 2009). CENICA is located in a mixed commercial-residential area with relatively few industries or congested road networks, and was thus assumed to be representative of ambient urban conditions. During the MCMA-2003 campaign, an Aerodyne Quadrupole Aerosol Mass Spectrometer (Q-AMS) was deployed at CENICA, measuring the size-resolved aerosol chemical composition of non-refractory species in particles smaller than about 1 µm (NR-PM$_1$) with 4 min time resolution (Jayne et al., 2000; Jimenez et al., 2003). Positive matrix factorization (PMF) of AMS organic spectra allowed the separation of ambient urban OA mass into several components (Ulbrich et al., 2009).

Total Organic Aerosol mass: According to the measurements the average PM$_1$ OA concentration during 13–16 of April 2003 was 15 µg m$^{-3}$ (Fig. 8) at CENICA. OM measurements show high daily variation and peak values mainly during the morning rush hour and the early afternoon. The first peak is associated with primary organic aerosols while the second with the afternoon photochemistry and the formation of the secondary organic aerosols. The comparison of PMCAMx-2008 predictions with hourly average
measurements during the same period is encouraging (Fig. 8) with the exception of
the 13th of April when PMCAMx tends to overpredict the OM concentration during the
afternoon. In order to investigate if PMCAMx is predicting the total organic mass for
the right reasons, the predicted components of the total organic mass are compared
against the corresponding results of the AMS-PMF analysis in the next section focusing
on the diurnal average profiles of the components of the organic mass.

Local Primary Organics: According to laboratory and field studies the AMS HOA is
typically associated with combustion exhaust (Alfarra et al., 2004; Zhang et al., 2004,
2005a; Canagaratna et al., 2004; Allan et al., 2003; Ulbrich et al., 2009; Dzepina et
al., 2009; Aiken et al., 2009). HOA often increases during the rush hours in urban
areas. In addition, the size distribution of HOA in urban areas almost always displays
a prominent ultrafine mode that is clearly associated with vehicular emissions (Zhang
et al., 2004, 2005a; Alfarra, 2004; Canagaratna et al., 2004; Allan et al., 2003). In
view of these facts HOA appears to be an AMS mass spectral fingerprint for primary
combustion particles from urban sources, and also including particles from other rela-
tively reduced sources such as meat cooking and trash (plastic) burning (Mohr et al.,
2009). Therefore the AMS HOA is compared with PMCAMx POA which is the fraction
of the emissions that is in the aerosol phase without undergoing any chemical reaction
(Fig. 9). Both PM$_1$ HOA and POA values always exceed 2 $\mu$g m$^{-3}$ and increase sig-
nificantly during the rush hour with a peak value at 09:00 a.m. The AMS HOA is higher
than the POA by 0.3 $\mu$g m$^{-3}$ on average with the highest discrepancy at 08:00 a.m.
This encouraging agreement between the diurnal patterns indicates that the new ap-
proach for the primary organics combined with the volatility-based emission inventory
is in general consistent with the AMS technique of estimating the local primary OA.
The reasonable agreement of modelled vs. measured POA is consistent with the mod-
elling results of Fast et al. (2009) using WRF-CHEM and of Hodzic et al. (2009) using
CHIMERE for MILAGRO-2006.

Oxygenated Organic Aerosol: OOA is an important fraction of the organic particles
in Mexico City. It 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 SOA, NT-SOA, OPOA, and transported oxygenated OA (Fig. 10). Both profiles suggest that the oxygenated organic aerosol concentration always exceeds 7 µg m$^{-3}$ on average and increases in the afternoon when photochemistry is more intense. PMCAMx suggests that there is a relatively high background highlighting the potential importance of sources outside Mexico City for the average conditions, and consistent with the results of Hodzic et al. (2009). AMS and PMCAMx give high oxygenated organic aerosol concentrations in the early afternoon with the highest at 03:00 p.m. Generally, PMCAMx reproduce well the AMS OOA values in the morning while in the afternoon the model predictions exceed the AMS values. The correlation between the two patterns suggests that the volatility theory and parameters along with the new higher SOA anthropogenic yields are in general consistent with the AMS OOA levels in Mexico City for this period. However it is important to note that the AMS measurements lack the specificity to distinguish between traditional SOA, NT-SOA, and OPOA, and that the amounts of precursors for OPOA and NT-SOA are poorly constrained. Thus the reasonable agreement observed here should not be over-interpreted, as it mainly indicates that the combination of amounts, yields, and reaction rates of the mix of SOA and OPOA precursors used here can produce an amount of OOA consistent with the measurements, but confirming the partitioning between the different fractions requires much additional research.

6 Sensitivity to changes in emissions and boundary conditions

Uncertain inputs for the model include the volatility distribution for the existing primary organic aerosol emissions, the amount of the missing intermediate volatile organic
compound emissions and the boundary conditions. Three different simulations were conducted in order to bound the model predictions for plausible ranges of these parameters. A low volatility case, where the emissions in the low volatility bins (C*:10^{-2}–10^{2} \mu g m^{-3}) are doubled and the emissions in the high volatility bins are set to 0, a high volatility case, where the emissions of the additional IVOCs in the high volatility bins (10^{4}–10^{6} \mu g m^{-3}) are doubled (Table 3), and a low boundary condition case where the boundary conditions are reduced by half.

Using the low volatility distribution, the partitioning of the emissions favors the particulate phase. In this case, PMCAMx predicts that the fraction of the emissions that did not undergo any chemical reaction, POA, is two times higher than using the basecase distribution. The model in this case overpredicts the estimated HOA (not shown). Moreover, in the low volatility case, the vapor material that is produced from the partitioning of the emissions is lower (expecting less OPOA) but at the same time is distributed in lower volatility bins and consequently its oxidation will favor the OPOA formation. These opposite effects results in an almost zero change of OPOA. PMCAMx does not produce any NT-SOA as in the low volatility case there are no IVOC emissions. The absence of these emissions can potentially increase the formation of SOA as there are more oxidants available to react with the SOA precursors (consistent with the results of Sheehy et al., 2008 who estimated that SVOCs and IVOCs contribute about 10% of the OH reactivity during MCMA-2003). PMCAMx predicts that the magnitude of this SOA increase is almost 0.5 \mu g m^{-3}.

For the high volatility case, there are less oxidants available, due to the increase of the additional IVOCs, resulting in a decrease of SOA by approximately 0.3 \mu g m^{-3}. The extra IVOC emissions result in 0.5 \mu g m^{-3} more NT-SOA than the basecase predictions. Finally, there is no change predicted in the concentrations of POA and OPOA as in the high volatility case the emissions and their distribution in the volatility bins with saturation concentration up to 10^{3} \mu g m^{-3} remained unchanged. The sensitivity of OA and its components to this change is therefore relatively small.

In the third sensitivity simulation, the 50% reduction of the boundary conditions re-
sulted in an almost linear response of the background organic concentration. In particular the average background organic concentration of the entire domain in the base case simulation was predicted to be \(6 \mu g m^{-3}\), while in the low boundary conditions case is predicted to be approximately \(3 \mu g m^{-3}\). Figure 11 shows the comparison between the measured and the predicted total organic mass concentrations at CENICA for lower boundary conditions during 13–16 April 2003. In this case the model underpredicts the observed OA especially during the nighttime. During this period the primary organic aerosol emissions are limited and the photochemical processes are not active. This was not the case in the basecase simulation (Fig. 8). Therefore, the higher values of the boundary conditions used in the basecase simulation appear to be more consistent with the observed OA at CENICA. 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 CENICA.

### 7 Conclusions

In this work, the effects of the semi-volatile nature of primary organic emissions and photochemical aging of primary and secondary organics on OA levels in MCMA were simulated using a modified 3-D Chemical Transport Model PMCAMx. The primary organic aerosol emissions were distributed among a set of volatility bins based on the fits to measured partitioning behaviour of diesel exhaust and wood smoke data. The modified PMCAMx model allowed the primary emissions to partition in the atmosphere according to the absorptive partitioning theory. Gas phase low-volatility organics from partitioning of SOA and POA were photo-chemically aged in the atmosphere via reaction with the OH radical. Aging was assumed to shift the organic mass to lower volatility bins generating condensed phase oxidized primary organic aerosol (OPOA), traditional and non traditional SOA.

The model predictions are compared with PMF analysis of Aerodyne Aerosol Mass Spectrometry (AMS) observations from the MCMA 2003 campaign. The comparison
of the predicted and measured component organic mass diurnal profiles is encouraging. There is a small missing part during the rush hours and an overprediction during the afternoon. According to this comparison there is a relatively high background highlighting the importance of the boundary conditions around Mexico City for at least this period. Thereby, in order to eliminate the effect of the boundaries, the model domain should be expanded for the future applications. The new approach indicates that the volatility distribution of the aerosols is important suggesting that instead of measuring fixed POA emission factors one must measure the volatility distribution of the emissions. The IVOC emissions play an important role not only to the formation of NT-SOA but of traditional SOA too, as they can affect the amount of the available oxidants. Finally, the distribution of OA emissions to the low volatility bins appears to be extremely important for the predicted POA as it has great impact to the initial partitioning between the aerosol and the gas phase. Measurements of the amounts and speciation of primary SVOCs and IVOCs, as well as more specific measurements of the sources of SOA are needed to further constrain and evaluate the model results.

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resolved chemical composition of submicron particles in Pittsburgh Implications for aerosol
2005b.
species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlati-
### Table 1. Major compounds for each lumped VOC within SAPRC99.

<table>
<thead>
<tr>
<th>Species</th>
<th>Major Components</th>
<th>SOA precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALK1</td>
<td>Ethane, Methyl Formate</td>
<td>No</td>
</tr>
<tr>
<td>ALK2</td>
<td>Propane, Cyclobutane, Ethyl Formate, Methyl Acetate</td>
<td>No</td>
</tr>
<tr>
<td>ALK3</td>
<td>(n)-Butane, Ethanol, Isobutane, Dimethyl Butane, Dimethyl Pentane</td>
<td>No</td>
</tr>
<tr>
<td>ALK4</td>
<td>(n)-Pentane, (n)-Hexane, Branched C(_5)-C(_6) Alkanes, Cyclopentane, Trimethyl Butane, Trimethyl Pentane, Isopropyl Alcohol, (n)-Propyl Alcohol</td>
<td>Yes</td>
</tr>
<tr>
<td>ALK5</td>
<td>C(<em>7)-C(</em>{22}) (n)-Alkanes, C(<em>5)-C(</em>{16}) Cycloalkanes, Branched/Unspeciated C(<em>6)-C(</em>{18}) Alkanes</td>
<td>Yes</td>
</tr>
<tr>
<td>OLE1</td>
<td>Propene, C(<em>4)-C(</em>{15}) Internal Alkenes</td>
<td>Yes</td>
</tr>
<tr>
<td>OLE2</td>
<td>Isobutene, C(<em>4)-C(</em>{15}) Internal Alkenes, C(<em>6)-C(</em>{15}) Cyclic or di-olefins, Styrenes</td>
<td>Yes</td>
</tr>
<tr>
<td>ARO1</td>
<td>Toluene, Benzene, Ethyl Benzene, C(<em>9)-C(</em>{13}) Monosubstituted Benzenes</td>
<td>Yes</td>
</tr>
<tr>
<td>ARO2</td>
<td>Xylenes, Ethyl Toluenes, Dimethyl and Trimethyl Benzenes, Ethylbenzenes, Naphthalene, C(<em>8)-C(</em>{15}) Di-, Tri-, Tetra-, Penta-, Hexa-substituted Benzenes, Unspeciated C(<em>{10})-C(</em>{12}) Aromatics</td>
<td>Yes</td>
</tr>
<tr>
<td>TERP</td>
<td>(\alpha)-Pinene, (\beta)-Pinene, Limonene, Carene, Sabinene, other monoterpenes</td>
<td>Yes</td>
</tr>
<tr>
<td>ISOP</td>
<td>Isoprene</td>
<td>Yes</td>
</tr>
<tr>
<td>SESQ</td>
<td>Sesquiterpenes</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Table 2. SOA yield scenarios using a four-product basis set with saturation concentrations of 1, 10, 100, and 1000 µg m\(^{-3}\) at 300 K.

<table>
<thead>
<tr>
<th>SOA precursors</th>
<th>Aerosol Yield(^1)</th>
<th>High-NO(_x) Parameterization</th>
<th>Aerosol Yield Low-NO(_x) Parameterization</th>
<th>Molecular Weight (g mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOC</td>
<td>1</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000 120</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.038</td>
<td>0.000</td>
<td>0.075 150</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000 120</td>
</tr>
<tr>
<td>ALK4</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000 120</td>
</tr>
<tr>
<td>ALK5</td>
<td>0.000</td>
<td>0.150</td>
<td>0.000</td>
<td>0.000 150</td>
</tr>
<tr>
<td>OLE1</td>
<td>0.01</td>
<td>0.005</td>
<td>0.005</td>
<td>0.009 120</td>
</tr>
<tr>
<td>OLE2</td>
<td>0.003</td>
<td>0.026</td>
<td>0.023</td>
<td>0.044 120</td>
</tr>
<tr>
<td>OLE3</td>
<td>0.003</td>
<td>0.165</td>
<td>0.435</td>
<td>0.075 150</td>
</tr>
<tr>
<td>ARO1</td>
<td>0.002</td>
<td>0.165</td>
<td>0.435</td>
<td>0.075 150</td>
</tr>
<tr>
<td>ARO2</td>
<td>0.02</td>
<td>0.195</td>
<td>0.435</td>
<td>0.075 150</td>
</tr>
<tr>
<td>ISOP</td>
<td>0.07</td>
<td>0.150</td>
<td>0.900</td>
<td>0.075 250</td>
</tr>
<tr>
<td>SESQ</td>
<td>0.075</td>
<td>0.750</td>
<td>0.900</td>
<td>0.075 250</td>
</tr>
<tr>
<td>TERP</td>
<td>0.012</td>
<td>0.201</td>
<td>0.500</td>
<td>0.107 180</td>
</tr>
</tbody>
</table>

\(^1\) The SOA yields are based on an assumed density of 1.5 g cm\(^{-3}\).
Table 3. Parameters used to treat partitioning of POA emissions.

<table>
<thead>
<tr>
<th></th>
<th>C* at 298 K(µg m⁻³)</th>
<th>0.01</th>
<th>0.1</th>
<th>1</th>
<th>10</th>
<th>10²</th>
<th>10³</th>
<th>10⁴</th>
<th>10⁵</th>
<th>10⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction of emissions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Basecase)</td>
<td></td>
<td>0.03</td>
<td>0.06</td>
<td>0.09</td>
<td>0.14</td>
<td>0.18</td>
<td>0.30</td>
<td>0.40</td>
<td>0.50</td>
<td>0.80</td>
</tr>
<tr>
<td>(Low volatility case)</td>
<td></td>
<td>0.06</td>
<td>0.12</td>
<td>0.18</td>
<td>0.28</td>
<td>0.36</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(High volatility case)</td>
<td></td>
<td>0.03</td>
<td>0.06</td>
<td>0.09</td>
<td>0.14</td>
<td>0.18</td>
<td>0.30</td>
<td>0.60</td>
<td>1.00</td>
<td>1.60</td>
</tr>
<tr>
<td>Molecular weight (g mol⁻¹)</td>
<td></td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>ΔH (kJ mol⁻¹)</td>
<td></td>
<td>112</td>
<td>106</td>
<td>100</td>
<td>94</td>
<td>88</td>
<td>82</td>
<td>76</td>
<td>70</td>
<td>64</td>
</tr>
</tbody>
</table>
Fig. 1. Total primary organic aerosol emission rates (kg d\(^{-1}\) km\(^{-2}\)) spatial distribution. These are assumed to be semivolatile in PMCAMx (their saturation concentration range from \(10^{-2}\) to \(10^{6}\) µg m\(^{-3}\)) and a significant fraction of them evaporates after emission and dilution.
**Fig. 2.** Volatility distribution of primary organics. The non-volatile POA emissions are those used in the traditional non-volatile POA framework. The white bars are the estimated emissions in the volatility basis set framework as described in the text. The sum of the white bars is 55 tons d$^{-1}$. 

The bar chart shows the distribution of emission rates for non-volatile primary and volatile organics as a function of saturation concentration $C^*$ ($\mu$g m$^{-3}$). The non-volatile primary emissions are depicted in black, and the volatile organics in white bars. The sum of the white bars indicates the total emissions under the volatility basis set approach, quantified as 55 tons d$^{-1}$. 

The x-axis represents the saturation concentration range, while the y-axis indicates emission rates in tons per day.
Fig. 3. Modelling domain used for the simulation.
Fig. 4. Predicted average ground level concentrations of PM$_1$ organic mass (µg m$^{-3}$) during 13–16 of April 2003.
Fig. 5. Predicted average ground level fractions of (a) POA, (b) OPOA, (c) sum of traditional SOA and NT-SOA during 13–16 of April 2003. Different scales are used for better illustration of the spatial variation of the corresponding concentrations.
Fig. 6. Predicted average ground level concentrations ($\mu g m^{-3}$) of (a) POA, (b) OPOA produced from locally emitted POA, (c) SOA (traditional and non-traditional) from locally emitted VOCs and IVOCs and (d) OA transported into the domain from other areas (assumed to be OOA and SOA) during 13–16 of April 2003. Different scales are used for better illustration of the spatial variation of the corresponding concentrations.
Fig. 7. Predicted average ground level fractional contribution of anthropogenic SOA to PM$_1$ total traditional SOA during 13–16 of April 2003.
**Fig. 8.** Comparison of model predictions with hourly measurements for total PM$_1$ organic mass concentration taken during the MCMA campaign in 13–16 of April 2003 at Cenica.
Fig. 9. Comparison of model diurnal predictions for PM$_1$ local primary organic aerosols against AMS-HOA taken during the MCMA campaign in 13–16 of April 2003 at Cenica.
**Fig. 10.** Comparison of model diurnal predictions for PM$_1$ oxygenated organic aerosols (sum of Long Range Transport Oxygenated OA, Traditional SOA, NT-SOA, and OPOA) against AMS-OOA taken during the MCMA campaign in 13–16 of April 2003 at Cenica.
**Fig. 11.** Comparison of model predictions in the low boundary conditions case with hourly measurements for total PM$_1$ organic mass concentration taken during the MCMA campaign in 13–16 of April 2003 at Cenica.