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**Impact of primary  
formaldehyde in the  
MCMA**

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# Impact of primary formaldehyde on air pollution in the Mexico City Metropolitan Area

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## Abstract

Formaldehyde (HCHO) is a radical source that plays an important role in urban atmospheric chemistry and ozone formation. The Mexico City Metropolitan Area (MCMA) is characterized by high anthropogenic emissions of HCHO (primary HCHO), which together with photochemical production of HCHO from hydrocarbon oxidation (secondary HCHO), lead to high ambient HCHO levels. The CAMx chemical transport model was employed to evaluate the impact of primary HCHO on its ambient concentration, on the RO<sub>x</sub> radical budget, and on ozone (O<sub>3</sub>) formation in the MCMA. Important radical sources, including HCHO, HONO, and O<sub>3</sub>-olefin reactions, were constrained by measurements from routine observations of the local ambient air monitoring network and the MCMA-2003 field campaign. Primary HCHO was found not only contributing significantly to the ambient HCHO concentration, but also enhancing the radical budget and O<sub>3</sub> production in the urban atmosphere of the MCMA. Overall in the urban area, total daytime radical production is enhanced by up to 10% and peak O<sub>3</sub> concentration by up to 8%. While primary HCHO contributes predominantly to the ambient HCHO concentration between nighttime and morning rush hours, significant influence on the radical budget and O<sub>3</sub> production starts early morning, culminates at mid-morning and is sustained until early afternoon.

## 1 Introduction

Formaldehyde (HCHO) is the most abundant carbonyl compound in both urban areas and the remote troposphere (Lurmann and Main, 1992; Ho et al., 2002; Hellen et al., 2004). It can be directly emitted from incomplete combustion processes (primary HCHO), such as combustion engines and biomass burning, or produced by photooxidation of hydrocarbons (secondary HCHO). Small amounts of HCHO can also be emitted directly from vegetation (Kesselmeier et al., 1997). The major loss processes of HCHO are through photolysis and reaction with the hydroxyl radical (OH). HCHO

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5 serves as an important primary source for the hydroperoxy radical ( $\text{HO}_2$ ) and contributes to other odd hydrogen radicals ( $\text{RO}_x = \text{OH} + \text{HO}_2 + \text{RO}_2$ ) through the radical propagation processes, which leads to ozone ( $\text{O}_3$ ) production in the presence of nitrogen oxides ( $\text{NO}_x$ ). Because of its widespread presence and its role in  $\text{O}_3$  and radical photochemistry, HCHO is an essential component for assessing photochemical processes and radical budget on local, regional and global scales. Unlike most primary volatile organic compounds (VOCs), photolysis of primary HCHO does not consume radicals, which makes primary HCHO a unique radical source. HCHO is a known carcinogen (Seinfeld and Pandis, 1998; Molina and Molina, 2002; IARC, 2004); exposure to high levels of ambient HCHO is detrimental to human health and to the ecosystem.

10 High concentrations of HCHO have been measured in the Mexico City Metropolitan Area (MCMA) (Molina and Molina, 2002). Grutter et al. (2005) and Volkamer et al. (2005) report that the monthly average concentrations range from 4–9 ppb with monthly maxima up to 35 ppb in recent years, which are comparable or higher than those in many US urban cities (EPA, 2005). For example, the annual average concentrations of HCHO were 2.0 ppb in Chicago, 7.2 ppb in Los Angeles, 4.4 ppb in St. Louis and 7.9 ppb in Houston in 2005. The high ambient level of HCHO in the MCMA is partially attributed to the direct emissions from mobile and industrial sources (Garcia et al., 2006). According to the emission estimates constructed from the official emissions inventory for the year 2002 in the MCMA (CAM, 2004), mobile and industrial sources are responsible for total HCHO emissions of about 2050 tons/yr in the MCMA, of which mobile emissions account for about 50%. There is evidence that the mobile emission rates of HCHO in the MCMA and the HCHO/ $\text{CO}_2$  emission ratio are much higher than in the US urban areas (Kolb et al., 2004; Zavala et al., 2006). This is probably due to the differences in vehicle fleet characteristics (e.g. fleet age and emission control technology) (Zavala et al., 2006) and the combustion efficiency attributed to high altitude (2.2 km a.s.l. in Mexico City). The high emissions of HCHO lead us to expect that the primary HCHO may play an important role not only in the ambient HCHO concentrations, but also in the radical and  $\text{O}_3$  formation chemistry in the MCMA.



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Employing a statistical regression analysis, Garcia et al. (2006) estimate the contribution of primary HCHO to the ambient HCHO concentration, finding that a significant amount of HCHO observed in the MCMA is associated with primary HCHO. On a 24-h average, the contributions of primary, secondary and unaccounted sources (background) to ambient HCHO concentrations are 42, 37, and 21%, respectively, with the primary HCHO dominating at night and during early morning hours.

A detailed analysis of radical sources in the MCMA is presented by Volkamer et al. (2007) using a box model featuring the Master Chemical Mechanism constrained by an extensive array of measurements. These authors find that contributions of various radical sources ( $O_3$  photolysis, HCHO photolysis, HONO photolysis, alkene ozonolysis, OVOC photolysis) are fairly even in the MCMA. Using the HCHO partitioning results of Garcia et al. (2006), Volkamer et al. (2007) estimate that primary HCHO accounts for about 10% of the total radical production before 10 a.m., and contributes significantly to photochemical oxidants in mid-morning.

In this study, we employ the 3-D chemical transport model, the Comprehensive Air Quality Model with extensions (CAMx) (ENVIRON 2006), to investigate the impact of primary HCHO on the photochemistry in the MCMA, with important radical precursors and/or sources constrained by measurements from a local ambient air monitoring network and the MCMA-2003 campaign (Molina et al., 2007). The objective is to examine the influence of primary HCHO on the odd hydrogen radical budget and  $O_3$  formation in the MCMA's atmosphere.

## 2 Methodology

### 2.1 Model and input

CAMx v4.40 with the SAPRC-99 gas phase chemical mechanism (Carter, 2000) was employed in this study. The model configuration and model domain are described in detail in Lei et al. (2007). Briefly, the model domain covers  $52 \times 52$  grids with a grid

resolution of 3 km centered in Mexico City; there are 15 vertical layers extending from the surface to about 5 km a.g.l with the bottom model layer interface of about 64 m a.g.l.

The model was driven by hourly meteorological output fields from the Pennsylvania State University/National Center for Atmospheric Research Mesoscale Model System (MM5, Grell et al., 1995), as described in de Foy et al. (2006). Gaseous emissions were estimated in two steps. First, spatially and temporally resolved and chemically speciated emission fields were constructed based on the official emissions inventory for the year 2002 in the MCMA (CAM, 2004) using the procedures and an updated database described in Lei et al. (2007); these emission fields are referred as the initial emission estimates henceforth. Second, the initial emission estimates were then adjusted based on observations from the Mexico City Ambient Air Monitoring Network (RAMA) (SIMAT, 2003) and the MCMA-2003 field measurements (Lei et al., 2007). Model runs with varying emissions were carried out and simulated morning rush hour (6–9 a.m.) speciated VOC (as well as total odd nitrogen ( $\text{NO}_y$ ) and CO) concentrations were compared with measurements until a good agreement was reached. Chemical initial and boundary conditions were similar to those used in West et al. (2004) and were examined and adjusted using measurements taken at the boundary sites. Photolysis frequencies for clear sky under typical aerosol loading in the MCMA were precomputed using TUV model (Madronich and Flocke, 1998) and were corrected for the effects of clouds using the algorithm of Chang et al. (1987). Details of the emission estimation and adjustments, as well as other model inputs, are described in Lei et al. (2007).

The simulation episode selected was 13–15 April 2003, for which Lei et al. (2007) has characterized the ozone formation and response in the MCMA. The base case (with primary HCHO) was similar to the reference case in Lei et al. (2007) except a new version of CAMx (v4.40 vs v4.03) was used here and the CMAQ scheme (Byun, 1999) was used to reconstruct the vertical diffusivity fields ( $k_v$ ). Because of the changes to the vertical diffusion algorithm in the new version (Greg Yarwood, personal communication, 2007) and because CMAQ scheme overestimates  $k_v$  values (de Foy et al., 2007), the vertical diffusivity inputs were adjusted. By comparing  $k_v$  values with the results of the

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O'Brien scheme (1970) used in Lei et al. (2007) and by comparing concentrations of observed primary pollutants (mainly CO, NO<sub>y</sub>), a day-to-day varying scaling factor of 0.2–0.3 was applied uniformly (spatially) to the original  $k_v$  values.

The photochemical impact of primary HCHO is identified by turning on and off the HCHO emissions. As such, the effects of primary HCHO in HCHO concentration and photochemistry include not only the influence of the directly emitted HCHO (direct effects), but also the influence from the addition of photochemical HCHO produced through the enhanced photooxidation of hydrocarbons due to the addition of the primary HCHO (indirect effects). It should be noted that the effect (or impact, contribution, etc.) of primary and secondary HCHO defined here is different from those reported in Garcia et al. (2006) and Volkamer et al. (2007); we bracket the indirect effect in the primary term, whereas the other articles include it in the secondary term.

## 2.2 Measurements and model constraints

One aspect of the complexity in urban photochemistry is the presence of various important radical sources in the urban atmosphere, which include O<sub>3</sub>, O<sub>3</sub> precursors such as VOCs and NO<sub>x</sub>, heterogeneous sources of HONO, and alkene-O<sub>3</sub> reactions in the case of the MCMA (Volkamer et al., 2007). A critical aspect for successfully quantifying the impact of primary HCHO depends on whether these radical sources, besides primary HCHO, in the urban areas are accurately captured in the simulation.

The emissions of CO, NO<sub>x</sub>, and speciated VOCs used in the model were constrained by concurrent measurements, as described in Lei et al. (2007). Briefly, simulated CO, NO<sub>x</sub> and O<sub>3</sub> were compared with RAMA observations; concentrations of alkanes and alkenes were compared with measurements obtained from canister sampling analyzed by Gas Chromatography/Flame Ionization Detection (GC/FID) at various sites during the MCMA-2003 campaign (Velasco et al., 2007); emissions of aromatics and formaldehyde were evaluated and adjusted by comparing with long-path Differential Optical Absorption Spectroscopy (DOAS) measurements at the campaign supersite CENICA (Volkamer et al., 2005). The DOAS data also included HONO concentrations.

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Olefin measurements using a Fast Isoprene Sensor (FIS) calibrated with a propylene standard at CENICA (Velasco et al., 2007) were also used in this study.

By comparing the simulated with the measured concentrations of HCHO and considering findings from previous studies on the mobile emission rate of HCHO in Mexico City (Kolb et al., 2004; Zavala et al., 2006), a factor of 7 was needed to scale the initial emission estimates of HCHO (from 2050 tons/yr to 13 920 tons/yr) in the MCMA in order to reproduce the measured HCHO concentrations. The factor of 7 is also in accordance with the findings from previous studies on the mobile emission rate of HCHO in the MCMA (Kolb et al., 2004; Zavala et al., 2006). A map showing the spatial distribution of HCHO emissions is presented in Fig. 1, which also shows the locations of the CENICA supersite and the “urban region” – an area of 30×36 km<sup>2</sup> encompassing the MCMA urban center and containing most of the RAMA monitoring stations. Figure 2 provides a comparison of simulated (using adjusted HCHO emissions) and observed HCHO concentrations at CENICA. The model reproduced well the magnitudes and diurnal variations of HCHO concentration using the adjusted HCHO emissions, except that it overpredicted HCHO concentrations by 40% during late afternoon and nighttime (from 16 p.m. to 5 a.m. next day). The overprediction is probably due to underestimated mixing, rather than emissions, since the model overestimation during this time window also occurred for CO and NO<sub>y</sub> (Lei et al., 2007), and morning rush hour concentrations of HCHO were well reproduced. The HCHO detection limit of DOAS (1 ppb) may also contribute to the discrepancy since during this time window HCHO ambient concentrations were only a few ppbs (Fig. 2a). For the rest of the time, simulated HCHO were in excellent agreement with the measurements. As discussed later, the overprediction will affect the HCHO partitioning during late afternoon and nighttime, but should have little effect on the photochemistry, because photochemical influence of primary HCHO occurs only significantly in the morning and early afternoon.

In the MCMA, 85% of radical sources are produced from photochemical reactions (Volkamer et al., 2007), and light absorbing organic aerosol reduces the amount of sunlight that reaches the ground, lowering radical production from photochemical sources

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such as HCHO, HONO, O<sub>3</sub>, and OVOC photolysis (Barnard et al., 2008). To account for the effects of aerosol on the radiation using a first-order approximation, the aerosol optical depth at 340 nm was set to 0.8 for Mexico City in the TUV computation of photolysis frequency, conforming to the concurrent LIDAR aerosol extinction measurements reported during the 2003 campaign (Frey et al., 2004; Simeonov et al., 2004). In addition, a wavelength-independent value of aerosol single scattering albedo (SSA) in the urban area was set to 0.90. Barnard et al. (2008) report morning hour SSA values as low as 0.78 at 368 nm in the MCMA and SSA is wavelength dependent. We examined the simulated J-values in the urban area, and they were in good agreement with those measured by spectroradiometry during MCMA-2003 (Volkamer et al., 2005); for example, JNO<sub>2</sub> was about 30 hr<sup>-1</sup> at noon. It should be noted although the near surface J-values were well simulated using a SSA value of 0.90 combined with other aerosol parameters, the assumption of aerosol's smaller absorptivity would lead to an overestimate of J-values aloft, which in turn may lead to an overestimate of radical production.

Heterogeneous chemistry is a major source for nighttime HONO (Platt et al., 1980a; Kleffmann et al., 1998; Finlayson-Pitts et al., 2003; Stutz et al., 2004). However, since the formation mechanism is still not well understood, a direct emission of HONO was artificially included in the model as the surrogate for the heterogeneous source. The magnitude and temporal variation of the estimated HONO emissions were based on the NO emissions and were constrained by the DOAS HONO measurements; i.e. the temporal variation of HONO emissions were adjusted until the simulated HONO agreed with the measurements. A comparison of the simulated and observed HONO concentrations is shown in Fig. 3, which illustrates good agreement between the two.

Volkamer et al. (2007) find that alkene ozonolysis contributes significantly (~18%) to the radical production during morning hours in the MCMA. We did not have direct constraints on this radical source. Instead, this source was indirectly constrained by evaluating the simulations of O<sub>3</sub> and VOCs. Figure 4 shows the comparison of simulated and observed diurnal variations of surface concentrations of O<sub>3</sub> and alkenes at

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CENICA averaged over the simulation episode. The alkene (OLE) concentration shown in the figure is the propene-equivalent alkene concentration averaged over 14–15 April measured by the FIS. The OLE comparison did not include 13 April, which had anomalously high measured VOC concentrations. For the simulated values, concentrations of different olefin model species were weighted based on their FIS response factors and their contributions to the standard VOC mixture used in the SAPRC99 mechanism (Velasco et al., 2007). As shown in the figure, the simulated morning hour concentrations of O<sub>3</sub> and OLE agree well with the observations (within 1σ level). This suggests that the precursors of this radical source were well constrained, and demonstrates that the O<sub>3</sub>-OLE reaction is well represented in the model.

NO<sub>3</sub>-alkene reactions can also be an important source for nighttime peroxy radicals in both marine boundary layer and urban atmosphere (Platt et al., 1980b; Geyer et al., 2003; Lei et al., 2004). Volkamer et al. (2007) report the first direct evidence for the presence of up to 50 ppt NO<sub>3</sub> inside a megacity, and the relative contribution of this source strongly depends on altitude. Indeed Lei et al. (2004) find that NO<sub>3</sub>-alkene reactions contribute substantially to nighttime organic radicals in the residual layer in Houston, while their impact is negligible at ground level. In this study there were no constraints on this source.

### 3 Results and discussion

#### 3.1 HCHO partitioning

Primary emissions, secondary photochemical formation of VOC oxidation, and background HCHO all contribute to the simulated concentrations of HCHO. The background HCHO represents the portion that is not accounted for by either the emissions or the in situ secondary photochemical formation. In this study, the background concentration was assumed to be the episode-averaged lowest HCHO concentration at night and early morning when there were no HCHO emissions, which was 1.5 ppb. Figure 5

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shows the simulated contributions of different sources to HCHO at CENICA. The contribution of primary HCHO was obtained as the difference between the run with primary emissions (base case) and the other control run without primary emissions. As pointed out earlier, the contribution of primary HCHO includes the contribution not only from directly emitted HCHO, but also from the feedback of secondary HCHO that are produced through the enhanced photooxidation of hydrocarbons due to the addition of the emitted HCHO (indirect effects). Table 1 summarizes the contributions of primary and secondary (not including primary HCHO's indirect contribution) HCHO as a function of the time of the day. It can be seen that primary HCHO contributes significantly to the ambient HCHO concentration at night and early morning (>69%), and culminates at morning traffic rush hours. On the other hand, secondary HCHO dominates the ambient HCHO in the afternoon (~50%). On a 24-h basis, the contributions from primary, secondary and background sources are 57, 24 and 19%, respectively. A correction to the 40% model overprediction of HCHO between 16 p.m. to 5 a.m. (see Sect. 2.2 and Fig. 2b) would modify the corresponding contributions to 52, 27, and 21%, respectively (assuming the background concentration of HCHO does not change).

Garcia et al. (2006) estimate the partitioning of HCHO in MCMA using a statistical regression analysis, and find that the contributions of the primary, secondary, and background (unaccounted) sources are 42, 38, and 21%, respectively, on a 24-h basis. Note the definitions of primary and secondary sources are different from Garcia et al. (2006), where the indirect effect of emitted HCHO is bracketed in the secondary term. We have not quantified the indirect effect, but according to Volkamer et al. (2007), the indirect effect accounts for about 10% of the primary HCHO. Taking this into consideration, the contributions of primary, secondary and background sources to ambient HCHO in Garcia et al. (2006) would be 47, 32, and 21% respectively. These corrections bring the results of Garcia et al. (2006) and this study to a good agreement (within 5%), even though different methods and time coverage were employed.

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## 3.2 Impact on radical budgets

Photolysis of HCHO directly produces HO<sub>2</sub>. HCHO can also affect OH and RO<sub>2</sub> (organic peroxy radicals) through radical cycling processes. To estimate the overall effects of HCHO on radical concentrations and initiation rate (or primary radical production rate), the term OH-equivalent (denoted as ΣOH, in unit of ppb/hr) is used, which takes into account the propagation efficiency of the HO<sub>2</sub>→OH and RO<sub>2</sub>→OH conversions. Analogous to Sheehy et al. (2008), the conversion efficiencies of HO<sub>2</sub>→OH, γ<sub>HO<sub>2</sub></sub>, and RO<sub>2</sub>→OH, γ<sub>RO<sub>2</sub></sub>, are the portion of HO<sub>2</sub> and RO<sub>2</sub> participating in the radical propagation process that convert to OH during the propagation, respectively, which are defined as following in this study,

$$\gamma_{\text{HO}_2} = \frac{\text{HO}_2 \rightarrow \text{OH}}{\text{total HO}_2 \text{ reacted}} \quad (1)$$

$$\gamma_{\text{RO}_2} = \gamma_{\text{HO}_2} \frac{\text{RO}_2 \rightarrow \text{HO}_2}{\text{total RO}_2 \text{ reacted}} \quad (2)$$

Where HO<sub>2</sub> → OH and RO<sub>2</sub> → HO<sub>2</sub> are the propagation rates of HO<sub>2</sub> to OH and RO<sub>2</sub> to HO<sub>2</sub>, respectively. As such,

$$\Sigma\text{OH}_{\text{new}} = \gamma_{\text{HO}_2} \bullet \text{HO}_{2\text{new}} + \gamma_{\text{RO}_2} \bullet \text{RO}_{2\text{new}} + \text{OH}_{\text{new}} \quad (3)$$

Where OH<sub>new</sub>, HO<sub>2new</sub> and RO<sub>2new</sub> are the radical initiation rates of OH, HO<sub>2</sub> and RO<sub>2</sub> (in unit of ppb/hr), respectively.

Figure 6 and Table 2 show the contributions of primary HCHO to surface radical concentrations and radical initiation rates in the MCMA urban region. It is evident that primary HCHO contributes significantly to the radical budget, particularly in the morning and early afternoon hours in the urban area. For example, on the episode-average basis, the contribution of primary HCHO to OH concentration increases from 7% in the early morning to 16% in the late morning and early afternoon, culminating

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to about 20% at 9–11 a.m., and enhances peak OH concentration by 7%. For HO<sub>2</sub>, the primary HCHO contribution increases from 11% in early morning to 31% in late morning and early afternoon, and enhances peak concentration by 16%. The contribution to the OH-equivalent primary radical production rate ( $\Sigma \text{OH}_{\text{new}}$ ) is similar to that of OH concentration, but the  $\Sigma \text{OH}_{\text{new}}$  peaks much earlier. On the 24-h basis, primary HCHO enhances OH, HO<sub>2</sub> and  $\Sigma \text{OH}_{\text{new}}$  by 8, 11 and 5%, respectively. The contributions of primary HCHO to daytime (06:00–18:00 LT) OH, HO<sub>2</sub>, and  $\Sigma \text{OH}_{\text{new}}$  are 8, 18, and 9%, respectively. Unlike the contribution to ambient HCHO concentrations, which dominates at night and early morning but decreases significantly after late morning, the significant contributions of primary HCHO to radical concentrations and production continue into early afternoon.

Using box model with the Master Chemical Mechanism constrained by comprehensive measurements, Volkamer et al. (2007) quantified the radical sources in the MCMA. One of their findings is that primary HCHO (including the indirect effect) contributes to  $\Sigma \text{OH}_{\text{new}}$  up to 10% in the morning and 7% for the 06:00–18:00 LT average (9 and 6% respectively if excluding the indirect effect). Our results yield about 35% higher primary HCHO contributions; some of this discrepancy may be due to the assumption of aerosol's smaller absorptivity used in the TUV calculation, which would lead to an overestimate of UV radiation aloft, resulting in an overestimate of the relative contribution from primary HCHO, even though the total radical production would also be overestimated. Another reason is that in Volkamer et al. (2007) the HCHO source attribution for VOC classes and oxidants was evaluated by setting all but one class of VOC or oxidant to zero, which would lead to an upper limit radical production from secondary HCHO. A third reason is that our results are concluded from a 3-day average while Volkamer et al. (2007) use median constraints for the entire MCMA-2003. Despite these, the agreement is still reasonable. The 06:00–12:00 LT average production rate of  $\Sigma \text{OH}_{\text{new}}$  is 6.0 ppb/hr, which is in excellent agreement with 6.1 ppb/hr reported by Volkamer et al. (2007).

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### 3.3 Impact on radical flow

Radicals are formed from the photolysis of O<sub>3</sub>, aldehydes, and other species; subsequently they undergo propagation reactions, and eventually are removed from the system by radical-NO<sub>x</sub> reactions (e.g. formation of HNO<sub>3</sub>, PANs, and other organic nitrates) and radical-radical reactions (which lead to the formation of peroxides). The addition of primary HCHO to a system modifies these radical initiation-propagation-removal processes (radical flow). By tracking the influences of primary HCHO on the radical flow, we can identify the roles of primary HCHO in the radical chemistry.

The effect of primary HCHO on the radical flow in the MCMA is illustrated in Fig. 7, where the numbers by each arrow indicate the percentage change of radical chemical tendency that follows each pathway accumulated over the entire simulation episode and over the urban region. As primary HCHO is added, new OH radicals produced from O<sub>3</sub> photolysis and alkene ozonolysis increase by 9 and 4%, respectively, as a result in O<sub>3</sub> concentration. In contrast, the radical formation from the net HONO source (HONO photolysis minus OH+NO → HONO) decreases by 5%. This decrease is due to the larger magnitude of the OH+NO → HONO reaction over the photolysis in early morning (7–9 a.m.) when primary HCHO is included, which leads to a marginal increase in HONO concentration (not shown), consistent with the HONO source apportionment during morning hours reported by Volkamer et al. (2007). Initiation rates of HO<sub>2</sub> and RO<sub>2</sub> are increased by 17 and 5%, respectively, which are attributed to the increase in HCHO and other species directly from emissions and indirectly from the additional VOC photooxidation. The interconversions between different radicals increase significantly (9–18%). The radical removal processes are also enhanced: 9% for HNO<sub>3</sub>, 15% for organic nitrates, and 11% for peroxides. The changes in the interconversion rates are basically equal to the changes in radical removal rates, implying that the catalytic efficiency of radicals in O<sub>3</sub> formation remains largely unchanged.

In summary, primary HCHO significantly enhances radical initiation, propagation and termination. The impact of primary HCHO on radical budgets described in the previous

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section is the ultimate consequence of the impact of primary HCHO on the radical flows.

### 3.4 Impact on O<sub>3</sub> formation

Due to the changes in radical budgets, primary HCHO is expected to influence O<sub>3</sub> photochemical formation in the MCMA. Figure 8 and Table 3 shows the time series of simulated surface O<sub>3</sub> concentration averaged over the urban region, with and without primary HCHO emissions. Primary HCHO increases the surface peak O<sub>3</sub> concentration by 4% to 10% (corresponding to changes of 4–17 ppb), varying from day to day, with 8% on average. Moreover, the increase of peak O<sub>3</sub> concentration due to the primary HCHO is more evident and magnified at locations registered with high O<sub>3</sub> levels (not shown). The significance of an 8% contribution of primary HCHO to O<sub>3</sub> formation can be seen by considering that a 50% reduction in emissions of both VOC and NO<sub>x</sub> leads to the decrease of urban surface peak O<sub>3</sub> concentrations by 19% (Lei et al., 2007). The most evident impact of primary HCHO on surface O<sub>3</sub> occurs at mid morning and during the early afternoon (09:00–13:00 LT), where primary HCHO leads to an increase of O<sub>3</sub> concentration by 18% on average (over the episode) in the urban region. After 16:00, the contribution of primary HCHO decreases rapidly. In the case of the radicals, the significant impact of primary HCHO on O<sub>3</sub> continue into the afternoon.

Finally, it should be noted that our current understanding of the radical production process is incomplete (Volkamer et al., 2007; Sheehy et al., 2008). Radical production fluxes in early morning are uncertain by about a factor of two. In the lack of an understanding of the underlying physico-chemical processes that are causing this mismatch, our discussion of primary HCHO does not attempt to account for this effect. Any additional radical flux from sources that are currently unidentified will reduce the estimates of the contributions of primary HCHO to ozone formation, as well as the radical budget.

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## 4 Conclusions

A distinguished feature of Mexico City metropolitan Area is the high emissions of formaldehyde from anthropogenic sources, in particular from mobile exhaust. By employing the CAMx chemical transport model for a case run on 13–15 April 2003, the impact of primary HCHO on the ambient HCHO concentration, radical budget and O<sub>3</sub> formation in the MCMA was examined. Important radical sources, including HCHO, heterogeneous HONO, alkene ozonolysis and other radical precursors, were constrained by measurements from the MCMA-2003 campaign and the routine monitoring network.

Primary HCHO contributes significantly to the ambient HCHO concentration (up to 50% on daily basis); primary HCHO dominates ambient HCHO at night and in the morning (accounting for up to 80%), and decreases to 32% or less in the afternoon.

Primary HCHO contributes significantly to the radical budget, such as OH, HO<sub>2</sub>, and radical initiation rate  $\Sigma OH_{new}$ , particularly in the morning and early afternoon hours in the urban area. The contribution of primary HCHO to radical formation becomes significant in the early morning, culminates at 9–11 a.m., and continues throughout the early afternoon. It enhances daily OH, HO<sub>2</sub> and total radical initiation rate  $\Sigma OH_{new}$  by 8, 11 and 5%, respectively, while enhancing daytime OH, HO<sub>2</sub>, and  $\Sigma OH_{new}$  by 8, 18, and 9%, respectively. Through its direct effects (radical formation from primary HCHO itself) and indirect effects (radical formation from enhanced VOC oxidations by primary HCHO), primary HCHO influences the radical initiation, propagation, and termination, which leads to the increase of OH, HO<sub>2</sub> and  $\Sigma OH_{new}$ .

Primary HCHO also significantly influences surface O<sub>3</sub> formation in the MCMA. As the case for radical budget, the influences and enhancements of O<sub>3</sub> formation by primary HCHO kicks-in in the early morning, culminates at mid-morning, and continues through the early afternoon. It not only increases the morning–early afternoon hour surface O<sub>3</sub> concentration (up to 19%), but also increases surface peak O<sub>3</sub> concentration (8% on average). Moreover, the increase and enhancement of peak O<sub>3</sub> concentration due to the primary HCHO is more evident and magnified at locations registered with

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high O<sub>3</sub> levels.

The conclusions presented in this study are based on one case study, which covers a three day episode, and the model constraints on important radical precursors, such as HCHO, HONO, alkene, and O<sub>3</sub> heavily rely on measurements at a specific location (CENICA). More studies are needed in order to comprehensively characterize the photochemical impact of primary HCHO with more spatial coverage and broader spatial coverage for measurement constraints. In particular it is vital to have an accurate estimate of HCHO emissions, which demands larger measurement datasets. We plan to further our modeling studies using the much larger and comprehensive datasets from the 2006 MILAGRO Campaign (Molina et al., 2008). In addition, it will be interesting to examine the influence of primary HCHO on the O<sub>3</sub>-NO<sub>x</sub>-VOC sensitivity chemistry.

*Acknowledgements.* This work was supported by the Mexican Metropolitan Commission of Environment (CAM) and the US National Science Foundation (ATM-0528227). We would like to thank E. Velasco for assistance in processing the FIS data. CAMx is made publicly available by ENVIRON.

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**Table 1.** Contributions of emissions and secondary formation to ambient HCHO at CENICA.

Time	Primary (%)	Secondary (%)
0–6, 19–24	71	3
7–10 (rush hours)	76	8
11–18	33	51
daily	57 (47)*	24 (32)*

\* Numbers in the parenthesis are the results of Garcia et al. (2006) aligned to same definitions.

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**Table 2.** Percentage increases of radical concentrations and initiation rates due to primary HCHO.

Time	$\Delta[\text{HO}_2]$ , %	$\Delta[\text{OH}]$ , %	$\Delta\Sigma\text{OH}_{\text{new}}$ , %
7–9	11	7	5
9–13	31	16	19
13–16	20	8	7
16–20	10	4	3
6–18	18	8	9
Daily	11	8	5

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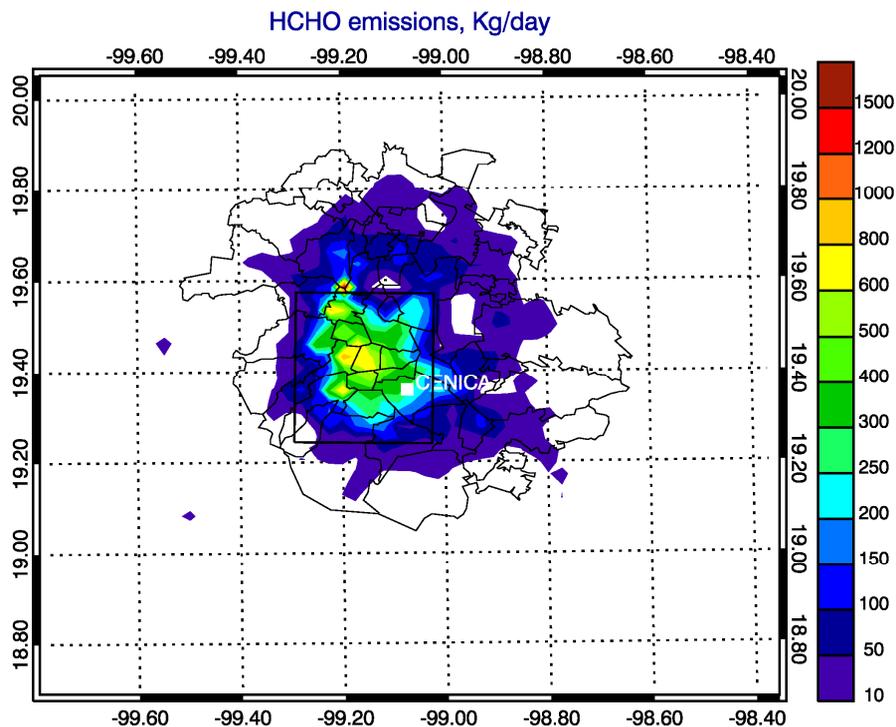
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Time	$\Delta[\text{O}_3]$ , %
7–9	9
9–13	18
13–16	9
16–20	3
Daily	11
Peak O <sub>3</sub>	8

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**Fig. 1.** Spatial distribution of HCHO emissions in the CAMx model domain. The daily emissions have been adjusted from 5,615 kg/day in the estimate of 2002 EI to 38,140 kg/day used in this study. The inner black rectangle designates the “urban region” used in the text. Also shown in the figure is the MCMA-2003 campaign supersite CENICA (white square).

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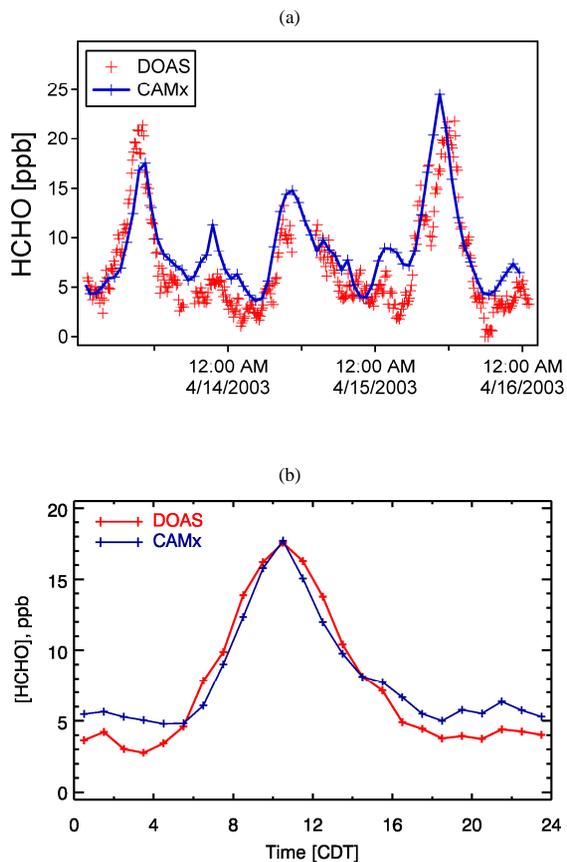
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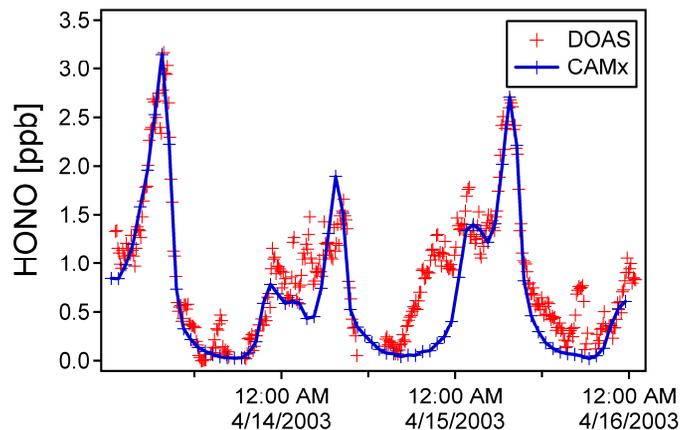


**Fig. 2.** Comparison of measured and simulated of **(a)** day-to-day variation and **(b)** episode-averaged (13–15 April) diurnal variation of surface HCHO concentrations at CENICA. DOAS measurements are denoted as red crossed line, while simulated values are denoted as blue crossed line.

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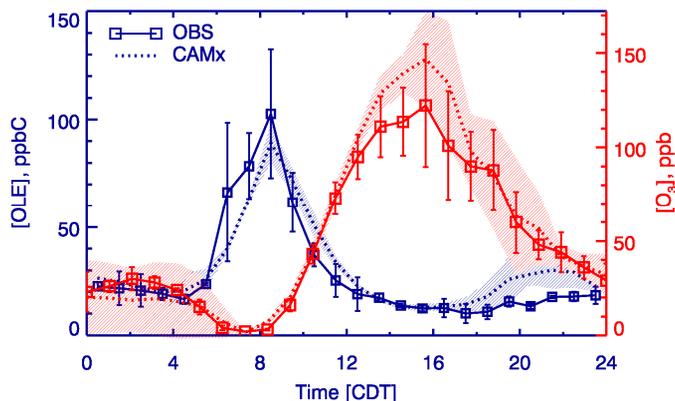


**Fig. 3.** Comparison of measured and simulated time series of surface HONO concentrations at CENICA. DOAS measurements are denoted as red cross, while simulated values are denoted as blue crossed line.

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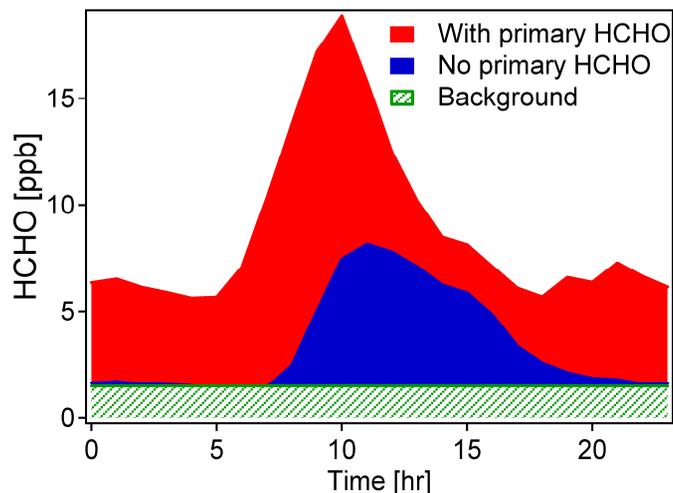


**Fig. 4.** Comparison of simulated and measured diurnal variations of surface alkene (OLE) in blue and O<sub>3</sub> concentrations in red at CENICA. Measurements in solid lines and simulations in dash lines. Error bars represent  $\pm 1$  standard deviations of measurements, and hatched areas represent  $\pm 1$  standard deviations of simulations.

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**Fig. 5.** Partitioning of HCHO to sources of primary (including the indirect effect), secondary and background at CENICA. The red area denotes the contribution of primary HCHO to the HCHO concentration, blue area denotes the contribution of secondary HCHO when there are no HCHO emissions, and the hatched green area represents background contributions (set to 1.5 ppb).

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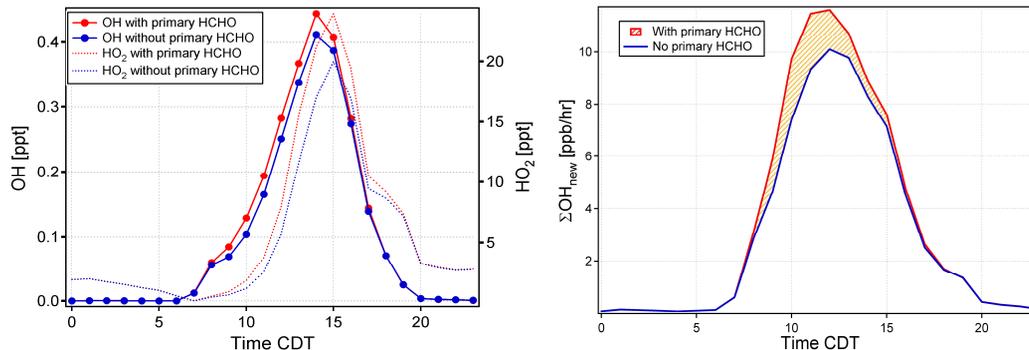
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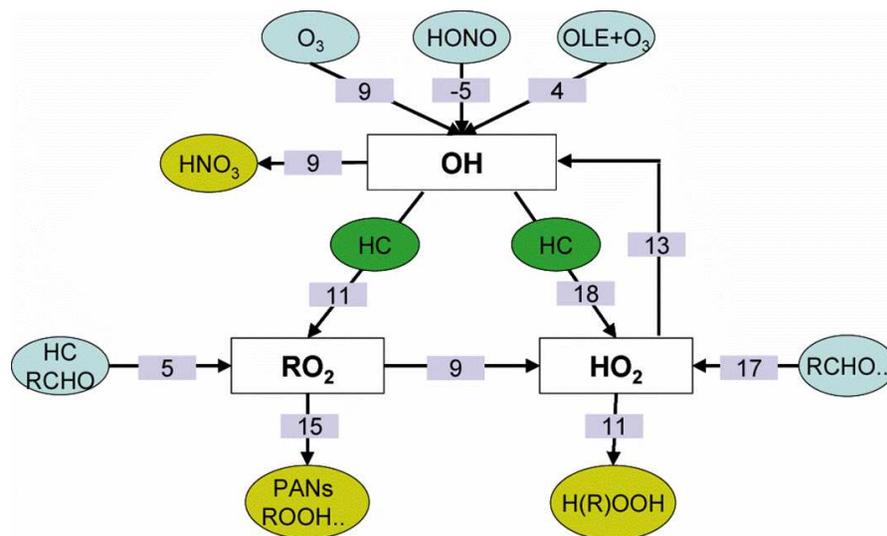


**Fig. 6.** Effects of primary HCHO on (left) radical concentrations and (right) radical production in the urban region averaged over 13–15 April 2003. In the left panel, solid lines represent the diurnal variations of OH concentrations, and dashed lines represent the diurnal variations of HO<sub>2</sub> concentrations. Inclusions of HCHO emissions in red color, while exclusions of HCHO emissions in blue color.

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**Fig. 7.** Effects of primary HCHO on the radical flows in the urban region. The numbers by each arrow indicate the percentage change of radical chemical tendency that follows each pathway accumulated over the entire simulation episode and over the urban region. RCHO includes HCHO.

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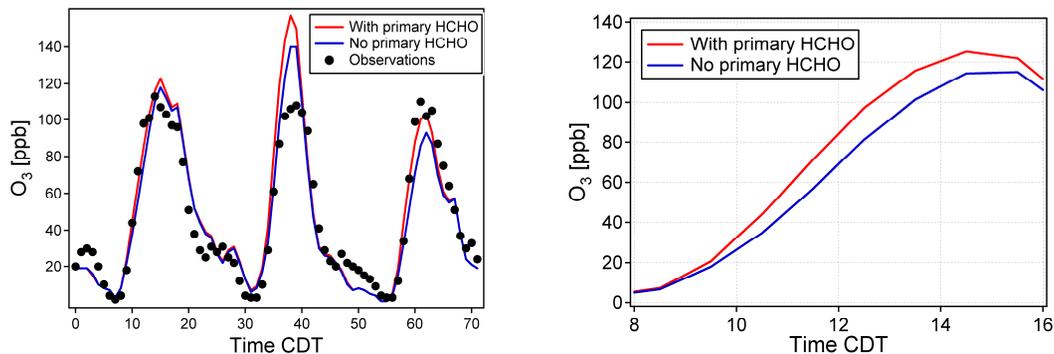
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**Fig. 8.** Effects of primary HCHO on surface O<sub>3</sub> concentrations in the urban region. RAMA measurements in black dots, simulations with primary HCHO in red lines, and simulations without primary HCHO in blue lines. The left panel shows the time series over the whole simulation episode, while the right panel focuses on the morning and afternoon hour O<sub>3</sub> averaged over the episode.

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