

High Resolution Air Quality Modeling for the Mexico City Metropolitan Zone using a Source-Oriented CMAQ model – Part I: Emission Inventory and Base Case Model Results

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1. INTRODUCTION

Degradation of air quality in the urban areas can directly harm the health of a large population, adversely affect the built and natural environment of the surrounding regions, and contribute to global climate change. In this aspect, the rapid growth of megacities (urban areas with a population of over 10 million) in the developing world being a major source of atmospheric pollution is a cause for concern.

The Mexico City Metropolitan Zone (MCMZ) is situated on an elevated basin 2240 m above sea level. MCMZ has a population of around 20 million inhabitants, around 4 million vehicles, and over 40,000 industries that contribute to atmospheric pollution. The MCMZ (Figure 1) covers an area of approximately 7700 km² that is constrained by mountain ridges. The surrounding mountains tend to trap pollutants within the MCMZ basin. The high altitude and temperate climate lead to intense sunlight that aids the photochemical processes of ozone and other oxidants.

Several different models have been used in the past to help understand the formation of air pollutants in the MCMZ, including the offline CAMx/MM5 (Lei et al., 2008) and WRF-Chem (Zhang et al., 2009). Horizontal grid resolution up to 3 km have been used these studies. Although the modeling domains in these studies typically cover MCMZ and surrounding regions, most of the studies did not include anthropogenic emissions of gaseous and PM pollutants from sources outside the MCMZ, the PM emissions due to windblown dust and SO₂ emissions from Popocatepetl, an active volcano 70 km southeast of Mexico City, although several individual studies have shown

that these sources could all contribute significantly to the observed concentrations in the MCMZ. In addition, the MCMZ anthropogenic emissions used in these studies are generally outdated and could not represent the actual emissions during the modeling episodes.

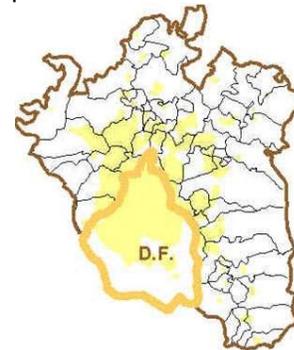


Figure 1 Mexico City Metropolitan Zone

The objectives of this study are to 1) develop a modeling emission inventory for the MCMZ and surrounding areas that utilizes the most updated information and includes all major sources that could potentially affect air quality in the MCMZ, and 2) evaluate the emission inventory by comparing 3D air quality model predictions with all available observation data.

2. MODEL APPLICATION

In this study, a source-oriented Community Multiscale Air Quality Model (CMAQ) based on CMAQ v4.7.1 is applied to model air quality in the MCMZ and surrounding regions that cover an area of 200x200 km² during a six-day air quality episode from March 2-7, 2006 with 1 km spatial resolution. Figure 1 shows the surface elevation of the domain and the location of the monitoring stations for meteorology and air pollutants. The gas phase mechanism SAPRC-99 and the aerosol module AERO5 are used for this study.

The initial and hourly boundary conditions are generated using the GEOS-Chem model for the nested North America domain with 0.5x0.666 grid

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consumptions records and sulfur content of the fuel oil used by the power plant. Several errors in the original MNEI for the thermoelectric power plant, including stack height, stack diameter and number of stacks, are also corrected using the data acquired directly from the plant. Moreover, the SO₂ emissions from Popocatepetl, an active volcano 70 km southeast of Mexico City are included. Area and mobile sources outside the MCMZ were not included in the current model emission inventory.

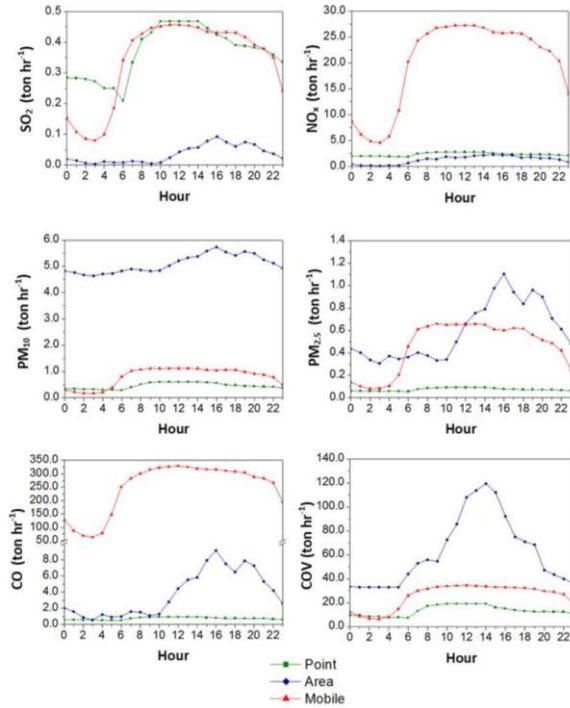


Figure 3 Temporal distribution by source and specie obtained from the 2006 emission inventory for the Mexico City Metropolitan Zone by Mexico City's Secretary of Environment.

Windblown dust emissions in the entire domain are predicted based on the model described by Fernando (2008) and Shaw et al. (2008), with slight modifications. In summary, the predicted surface friction velocity and soil moisture from WRF as well as the soil type and land use/land cover information is used to predict the vertical flux of PM10. Emission rate of PM2.5 is set to be 6% of PM10 and windblown dust speciation profiles from SPECIATE 3.2 is used to calculate the emission rates of individual PM2.5 components. More details of the windblown dust model and the contributions of windblown dust to PM2.5/PM10 will be documented elsewhere.

Biogenic emissions were generated using the Biogenic Emissions Inventory System, Version 3 (BEIS3) included in the SMOKE distribution. The 1-km resolution BELD3 and cover data with 230 different cover types were used to estimate emissions from vegetation and soil.

4. RESULTS AND DISCUSSION

4.1 Meteorology

Figure 4 shows that the WRF model generally captures the diurnal variation of the wind speed in the MCMZ. Wind speed is highest in the later afternoon and lower at night and early morning hours. The WRF predictions are slightly higher than the observations. The predicted wind directions agree better with observations when wind speed is higher but there are larger differences when the wind speed is low. The differences in the wind directions are not likely to significantly affect air quality model results because of the slower wind speed.

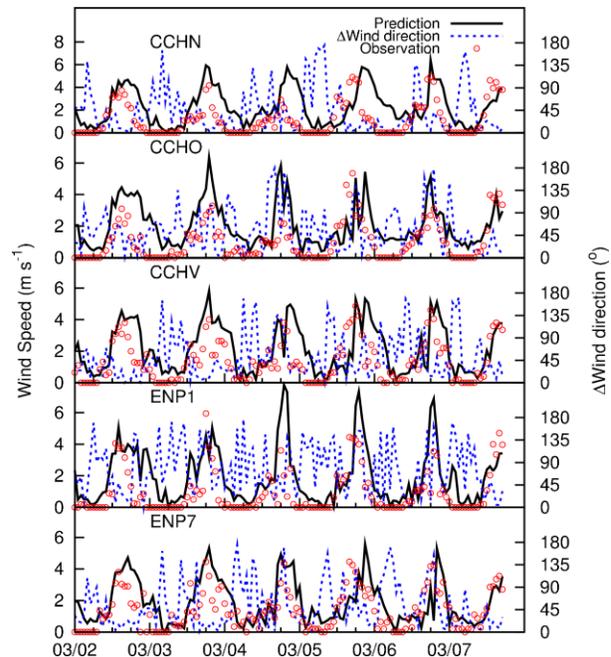


Figure 4 Predicted and observed surface wind speed and the difference between the observed and predicted wind direction.

Figure 5 shows that the predicted temperature and relative humidity agrees well with observations. The WRF model seems to over-predict relative humidity at all stations on the morning of March 5th and 7th by approximately 20% but otherwise the predictions are reasonably well.

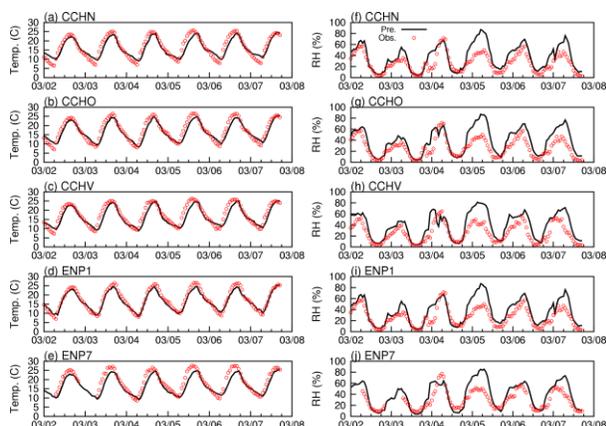


Figure 5 Predicted and observed surface temperature and relative humidity.

4.2 Gas Phase Pollutants

Figure 6 shows the predicted O₃ concentrations at 10 observation stations. The locations of the stations can be seen in Figure 1. The base case results are based on the default CMAQ initial and boundary conditions. The dash lines represent predictions using boundary conditions generated from the GEOS-Chem simulation as discussed before. Both sets of simulations agree well with observations although peak O₃ concentrations are under-predicted on a few days. The simulation using GEOS-Chem boundary conditions predicts slightly higher O₃ than the default boundary conditions. The under-prediction of O₃ peaks are likely caused by the overestimation of NO_x emissions coupled with the underestimation of VOC emissions (see Figure 7 and Figure 8 below).

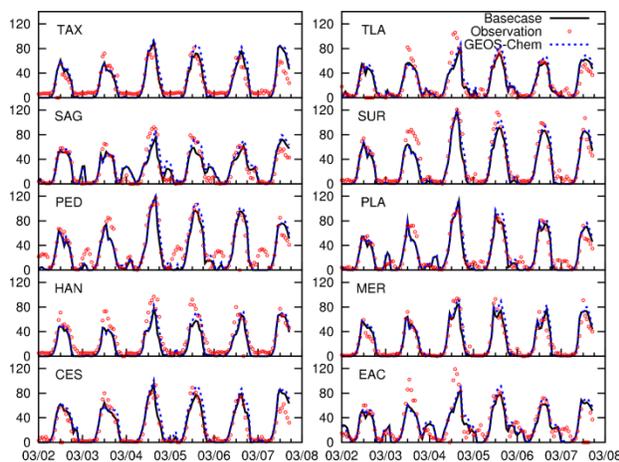


Figure 6 Time series of predicted and observed O₃ concentrations. Units are ppb.

Figure 7 shows that although the model correctly captures the diurnal variation of NO_x concentrations at all stations, the morning peaks

of NO_x are over-predicted, especially for stations in the northern part of DF. The over-prediction problem is not likely caused by insufficient vertical mixing as the minimal vertical diffusion coefficients were calculated based on urban fraction and a minimum value of 2.0 m² s⁻¹ is used for 100% urban regions, such as most part of DF. It has been reported that NO_x emissions from MOBILE5 can be over-estimated by a factor of 2 (Singh and Sloan, 2006). Thus, the overestimation is likely caused by uncertainties in the MOBILE5 model. Overestimation of NO_x emissions will enhance the titration of O₃ during the day, leading to under-predictions of O₃ and over-predictions of NO₂. The NO₂ concentrations are indeed over-predicted (not shown). CO concentrations in the urban center stations are also over-predicted. Further experimental and modeling studies to validate/correct the MOBILE5-Mexico emission estimates of mobile source emissions are necessary to provide more confidence in the mobile source emissions.

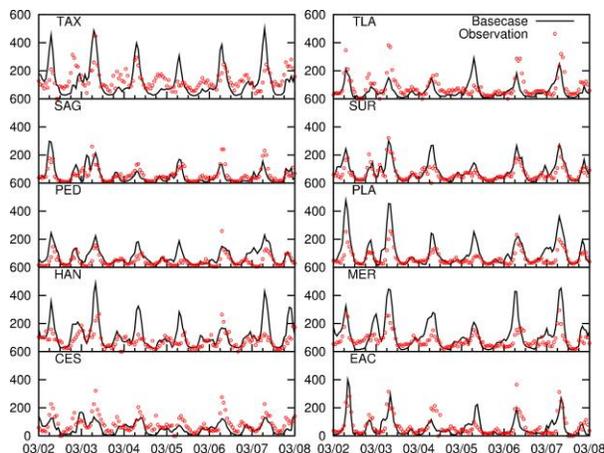


Figure 7 Time series of predicted and observed NO_x concentrations. Units are ppb.

Figure 8 shows the box-and-whisker plot of the ranges of the ratio of the observed SAPRC-99 VOC concentrations (based on 54 individual PAMS VOC species) to the predicted SAPRC-99 VOC concentrations. 24-hour average samples were taken at 5 monitoring stations every 6 days. The data shown here is based on an extended modeling exercise for March 2nd to March 31st with 19 data points for each VOC species. Light alkanes and alkenes are under-predicted by a factor of 2-5 while aromatics and larger alkanes are under-predicted by approximately an order of magnitude. The under-prediction of aromatics and long chain alkanes (ALK5) could have significant impacts on the SOA predictions.

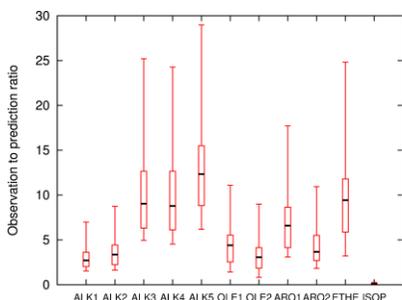


Figure 8 Observation to prediction ratio of VOC species. Median, minimum, maximum and 25% to 75% quartiles are shown on the plot.

Figure 9 shows the predicted and observed SO₂ concentrations. The model does not predict the SO₂ well and under-predicts high SO₂ concentrations on several instances. A regional SO₂ peak occurs on the morning of March 4th while none of the simulations are able to capture, although the GEOS-Chem simulation appears to yield better results, suggesting the regional increase of SO₂ might occur in an area larger than the current domain. Back trajectories analysis shows that air masses are coming from the north when the high SO₂ concentrations occur, thus rule out the possibility of the contributions from the Popocatepetl volcano.

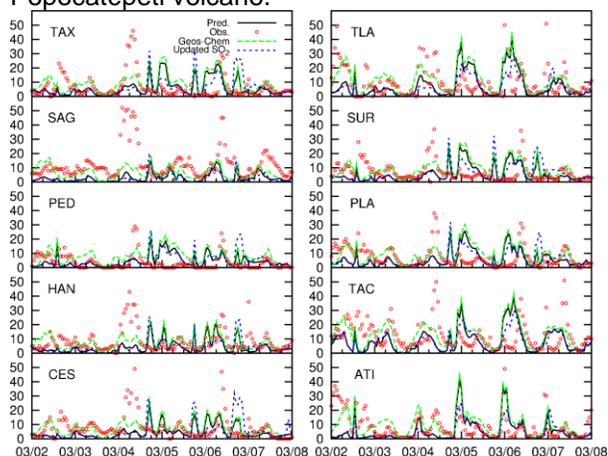


Figure 9 Time series of predicted and observed SO₂ concentrations. Units are ppb. Base case results are based on the default MNEI 1999 with SO_x emissions reduced by 40%. Updated SO₂ case uses the SO₂ emissions based on daily oil-fuel consumption and fuel sulfur content from the Francisco Pérez Ríos thermoelectric power plant in the Tula industrial complex.

Episode-average regional distribution of SO₂ shown in Figure 10(a) clearly shows the locations of the two major SO₂ sources, the Tula industrial complex to the northwest and the Popocatepetl volcano to the southeast. Hour 1200-1300 is

selected because the highest SO₂ concentration in the MCMZ occurs at this hour. The emissions from the Tula industrial complex have greater impacts on the MCMZ than the volcano during this episode. Other sources outside MCMZ do not contribute significantly. Back trajectories calculated using the HYSPLIT model (with the same meteorology files used to drive the CMAQ model) are shown in Figure 10(b). Significant amount of trajectories pass through the downwind regions of the Tula industrial complex. There are fewer trajectories pass through the areas influenced by the volcano during this episode.

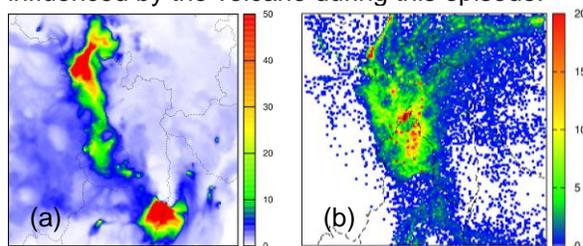


Figure 10 (a) Episode averaged distribution of predicted surface SO₂ at 1200-1300 LST. Units are ppb. The maximum concentration is set to 50 ppb to better show the spatial distribution of SO₂. (b) Frequency distribution of 24-hour back-trajectories ending at all monitoring stations at all hours throughout the episode. Maximum at trajectory end points should be 144 but is scaled to better show the spatial distributions.

The difficulty in SO₂ predictions in MCMZ is that most of the SO₂ is not produced locally but arrives at MCMZ through long range transport. Gas flow rate and exhaust exit temperatures are key parameters that determines the plume rise and the dispersions of SO₂ but are generally not monitored. The parameters used in the current study are based default US EPA data.

4.3 Secondary Organic Aerosol

Both SOA and odd oxygen (O_x=NO₂+O₃) are formed as products of VOCs oxidation. Figure 11 shows the correlation between SOA and O_x along 12-hour back trajectories ending at all monitoring stations during March 2nd to 7th. O_x concentrations reach as high as 170 ppb. The slope of a linear fit between O_x and SOA using data points with O_x greater than 70 ppb is 24.1 μg m⁻³ / ppm O_x. The predicted peak SOA concentrations are a factor of 3-10 lower than AMS measurements (Wood et al., 2010) while the O_x concentrations are also under-predicted. While it is possible that the under-prediction of SOA could be caused by under-predictions of VOC precursors as shown in Figure 8, further investigation is necessary to determine

the causes of the gap between predictions and observations.

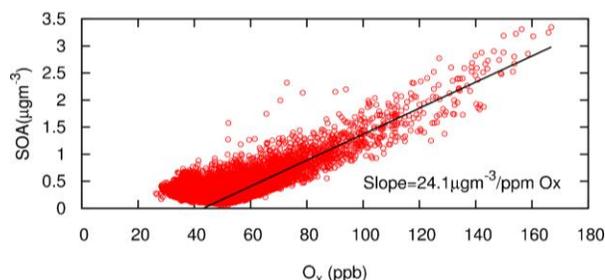


Figure 11 Correlation of SOA and O_x

Figure 12 shows the regional distributions of episode-average SOA concentrations. Alkanes and aromatic compounds are major anthropogenic contributors to SOA while isoprene and monoterpenes are major contributors to biogenic SOA. In addition, oligomerized biogenic SOA contributes to approximately $0.2 \mu\text{g m}^{-3}$. It should be noted that these estimations are likely low by an order of magnitude because of under-predictions of VOC precursors.

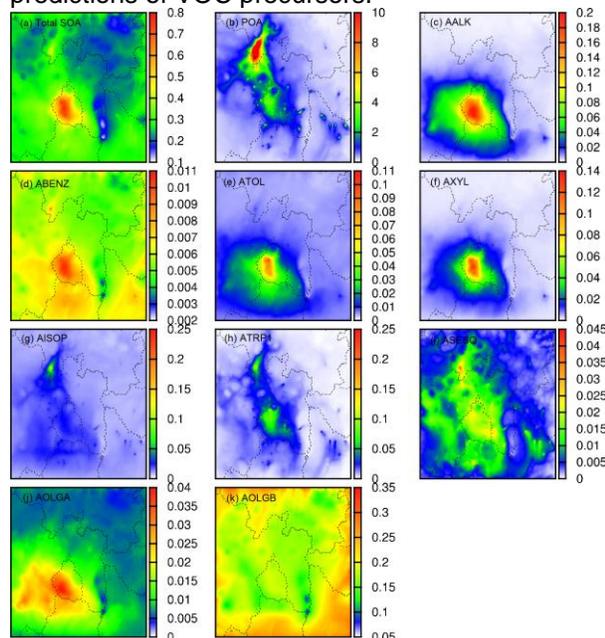


Figure 12 Episode average of regional distribution of SOA and SOA components. POA is the PM_{2.5} primary organic aerosol.

ACKNOWLEDGMENT

This research is funded by TAMU-CONACyT collaborative research program, project #2009-0055. IVC is also supported by an exchange student fellowship from CONACyT for her visit at TAMU. The authors also would like to thank Ing. Jorge Sarmiento, Magdalena Armenta, Patricia Camacho, and Francisco Hernández from the

Mexico City Secretary of Environment for providing the 2006 emission inventory and Pablo Sánchez, A. from the Environmental Pollution Section, CCA-UNAM for his help in the project.

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