IMPACT OF GAS-PHASE CHEMISTRY ON WRF/CHEM PREDICTIONS OF O_3 AND $PM_{2.5}$: MECHANISM IMPLEMENTATION AND COMPARATIVE EVALUATION

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1. INTRODUCTION

Gas-phase chemistry provides important oxidants and gaseous precursors for secondary aerosol formation. Different gas-phase chemical mechanisms may lead to different gaseous and aerosol predictions. Simulating gas-phase chemistry, in particular, chemistry of volatile organic compounds (VOCs), on the other hand, poses major challenges due to a large number of reactants and non-stable intermediate products as well as uncertainties in reaction kinetics (e.g., products, yields, and rate constants). In order to achieve reasonable compromise between accuracy and computational cost/storage in three dimensional (3-D) air quality modeling, lumped approaches for VOCs are often used in gas-phase chemical mechanisms. A number of intercomparisons of gas-phase mechanisms have been conducted based on theories (e.g., Dodge (2000)), box models (e.g., Kuhn et al. (1998), Zaveri and Peters (1999), Tonnesen and Luecken (2001), and Jimenez et al. (2003)), and 3-D air quality models (AQMs) (e.g., Byun et al. (2006), Arnold and Dennis (2007), Luecken et al. (2008), Faraji et al. (2008), and Sarwar et al. (2008)).

Previous gas-phase mechanism comparison studies in 3-D AQMs, however, were largely conducted in offline models. In this study, an online modeling system, i.e., the Weather Research and Forecasting Model with Chemistry (WRF/Chem) is used to intercompare three gas-phase mechanisms that are coupled with the same aerosol module. WRF/Chem allows physically-realistic feedbacks between meteorology and chemistry; therefore enabling a simulation of changes in radiation and meteorology due to different gaseous and fine particulate matters ($PM_{2.5}$) predictions resulted from different gas-phase mechanisms.

The three gas-phase mechanisms included in this study include the Carbon Bond Mechanism-Z (CBM-Z) (Zaveri and Peters, 1999), the 2005 version of Carbon Bond Mechanism (CB05) (Yarwood et al., 2005; Sarwar et al., 2008), and the 1999 version of Statewide Air Pollution Research Center mechanism (SAPRC99) (Carter, 2000). CBM-Z was implemented into WRF/Chem and coupled with the Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) by Fast et al. (2006). CB05 was implemented into WRF/Chem v2.1 and v2.2 by Pan et al. (2008) using a generic gas-phase chemistry solver, i.e., the Kinetic PreProcessor (KPP) of Salzmann (2007). Both Hu et al. (2008a) and Pan et al. (2008) have coupled CBM-Z and CB05 with the Model of Aerosol Dynamics, Reaction, Ionization, and Dissolution (MADRID 1) of Zhang et al. (2004) and Hu et al. (2008b) to simulate $PM_{2.5}$ species including sulfate, nitrate, ammonium, sodium, chloride, black carbon (BC), and primary organic matters (POM). Secondary organic aerosol (SOA) module in MADRID 1, however, was inactivated in both studies. In this study, SAPRC99 has been implemented into WRF/Chem v2.2 using KPP and coupled with MADRID 1. Following Hu et al. (2008a) and Pan et al. (2008), SOA module in MADRID 1 is also inactivated in this study to allow an intercomparison of the impacts of different gas-phase mechanisms on secondary inorganic aerosols, as the first step of this comparative evaluation. Also, all simulations are conducted without aqueous-phase chemistry. Intercomparison of simulations with MADRID 1 SOA module activated as well as aqueous-phase chemistry will be conducted in the future.

WRF/Chem-MADRID 1 simulations have been conducted for July 1-31, 2001 over the continental U.S. at a horizontal resolution of 36 km with three gas-phase mechanisms: CBM-Z, CB05, and SAPRC99. Simulation results are compared

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and evaluated against surface and satellite observations. The likely causes of discrepancies between observations and simulations are examined. The sensitivity of gaseous and $PM_{2.5}$ (except for SOA) predictions to various gas-phase mechanisms is assessed through comparative evaluations of major gases, oxidants, and $PM_{2.5}$ species.

2. MODEL DEVELOPMENT

CBM-Z and CB05 are two variants of CBM-IV. Compared with CBM-IV that was developed for urban applications (Gery et al., 1989), CBM-Z treats additional reactions under low NO_x conditions for regional and global applications (Zaveri and Peters, 1999), while CB05 includes explicit treatments of additional reactions involving higher aldehydes, oxygenated products, and terpene chemistry that can better simulate boigenics, toxics, PM formation, and acid deposition under pristine, wintertime, and high altitude conditions (Yarwood et al., 2005). Higher aldehydes and terpene chemistry are also included in SAPRC99, but not in CBM-Z. Compared with CB05, SAPRC99 includes more chemical species (e.g., ketones, acetone, and aromatic aldehydes) and more detailed categories of peroxy radicals, peroxy-acetyl nitrate (PAN) analogues, isoprene products, organic acids, and alkanes. In WRF/Chem, CBM-Z includes 175 reactions for 66 gas-phase species, which can be divided into 4 major categories: background troposphere, urban, rural continental, and remote marine. The 11 species in 32 remote marine reactions, however, are not activated in this study, consistent with CB05 and SAPRC99. CB05 includes 156 reactions for 58 species, while SAPRC99 treats 210 reactions for 74 species.

The implementation of a new gas-phase mechanism into WRF/Chem using KPP requires definition of species and reactions in KPP mechanism and WRF registry, the modifications of WRF/Chem drivers of initialization, emissions, and dry deposition, as well as the development of new subroutines for reading boundary conditions and emissions. The coupling of a new gas-phase mechanism with MADRID 1 requires modifications of WRF/Chem drivers of initialization, emissions, photolysis, dry and wet deposition, aerosol processes, and cloud chemistry, as well as a mapping of gas-phase species to MADRID 1. Since MADRID 1 and MOSAIC share some modules (e.g., aerosol initialization, radiation feedback, and deposition), additional changes are needed in these modules in MOSAIC.

3. EVALUATION AND DISCUSSIONS

Simulation results are evaluated against surface networks including the Clean Air Status and Trends Network (CASTNET), the Speciation Trend Network (STN), the Aerometric Information Retrieval System-Air Quality Subsystem (AIRS-AQS), the Interagency Monitoring of Protected Visual Environments (IMPROVE), and the Southeastern Aerosol Research and Characterization Study Experiment (SEARCH), as well as satellite data including the Global Ozone Mapping Experiment (GOME), the Total Ozone Mapping Spectrometer/Solar Backscattered Ultra Violet (TOMS/SBUV), and the Moderate Resolution Imaging Spectroradiometer (MODIS).

3.1 Meteorological Fields

This study uses the same meteorological configuration as that of Pan et al. (2008), which provides satisfactory predictions of temperature and relative humidity at 2-meter height, compared with observations from CASTNET, STN, and SEARCH. Wind speeds at 10-meter height are overestimated by 0.51 m s^{-1} to 1.53 m s^{-1}, with normalized mean biases (NMBs) of 28.1%-77.5%.

The direct aerosol-radiation feedback is turned on in WRF/Chem-MADRID 1 simulations, and therefore meteorological predictions in this study are slightly different when different gas-phase mechanisms are used in the simulations.

3.2 Gaseous Concentrations

Evaluation of surface gaseous concentrations is conducted against CASTNET, AIRS-AQS, and SEARCH. All the WRF/Chem-MADRID 1 simulations under- or over-predict max 1-hr O_3 (with NMBs of -1.9% to 42.5%) and CO (with NMBs of -1.3 to 37.6%), overpredict max 8-hr O_3 (with NMBs of 2.6%-53%), NO_2 (with NMBs of 20.6-34.9%), SO_2 (with NMBs of 62%-83.1%), and HNO_3 (with NMBs of 50.3%-207%), and underpredict NO (with NMBs of -91.8 to -85.9%). All simulations show the highest biases in simulated max 8-hr O_3 at SEARCH sites, with NMBs of 21.4%, 37.9, and 53.0% for CBM-Z, CB05, and SAPRC99, respectively. Likely factors for the model's incapability in reproducing O_3 in urban/suburban areas in the southeastern U.S. may include uncertainties in model inputs (e.g., overestimations of precursor emissions) and model treatments (e.g., poor representations of meteorological characteristics in urban areas),

which are subject to further investigation. Fig. 1 shows the monthly average overlay of spatial distribution of surface max 1-hr and max 8-hr O_3 mixing ratios.

Compared with surface observations, CBM-Z gives the best predictions of O_3 and CO, but the worst predictions of NO_2 and HNO_3 (Figures are not shown for CO, NO_2, and HNO_3). Predictions with CB05 and SAPRC99 are more similar in spatial patterns of most gases than either of them with CBM-Z, largely because their inclusion of higher aldehydes, which leads to much higher O_3 and PAN predictions than CBM-Z. The inclusion of methacrolein and aromatic aldehydes in SAPRC99 leads to even higher O_3 and PAN formation than CB05. As a result of different VOC reactions, reactive nitrogen species (i.e., NO_y, defined as a sum of NO, NO_2, NO_3, N_2O_5, HNO_2, HNO_3, HNO_4, PAN, and other organic nitrates) exist more as HNO_3 in CBM-Z but more as PAN and PAN analogues in CB05 and SAPRC99. Since PAN and PAN analogues have shorter lifetimes than HNO_3, CB05 and SAPRC99 tend to give higher O_3 predictions than CBM-Z. The inclusion of higher aldehydes also leads to higher predictions of some radicals (e.g., acetylperoxy and higher acyperoxy radicals), which causes more conversions of NO to NO_2, therefore also contributing to higher O_3 predictions in CB05 and SAPRC99.

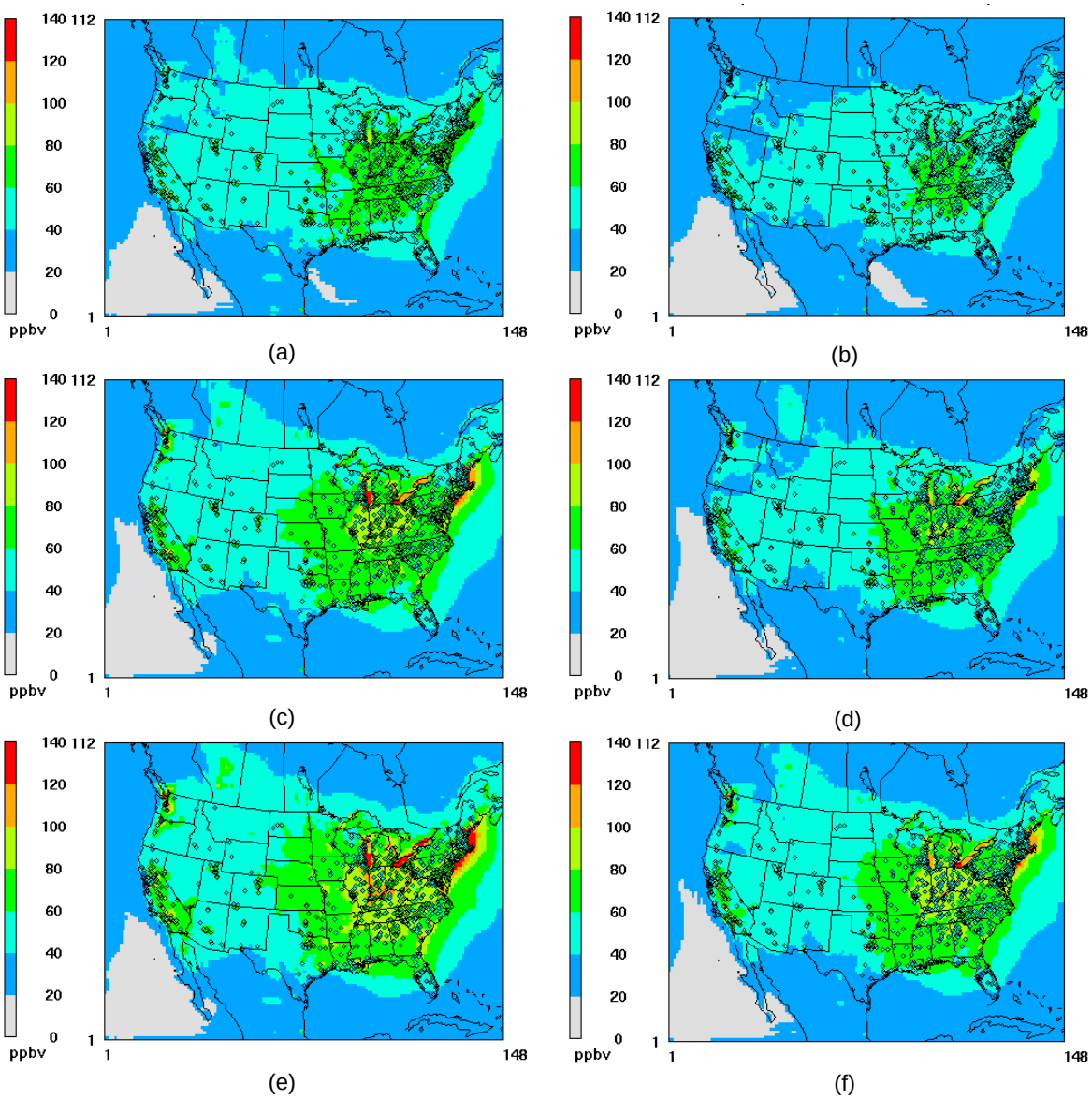


Fig. 1. Overlay plots of monthly average simulated surface max 1-hr (left column) and max 8-hr (right column) O_3 mixing ratios vs. observations from CASTNET, AIRS-AQS, and SEARCH: CBM-Z/MADRID 1 ((a) and (b)); CB05/MADRID 1 ((c) and (d)); and SAPRC99/MADRID 1 ((e) and (f)).

CBM-Z predicts the highest HNO_3, which implies that the NO_2 + OH terminal reaction dominates over the OH + OH terminal reaction in CBM-Z than in CB05 and SAPRC99. Consequently, CBM-Z predicts the lowest H_2O_2 and the highest OH radical in the gas-phase. The highest OH radical mixing ratios in CBM-Z lead to the highest oxidizing rate of SO_2 and thus the lowest prediction of SO_2.

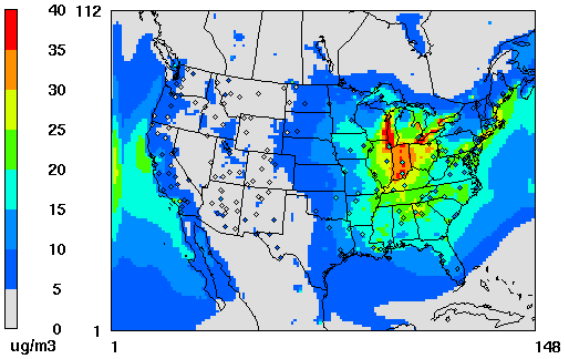
All the WRF/Chem-MADRID 1 simulations give fairly good agreement for tropospheric NO_2 column abundance, against GOME observations, but significantly underestimation of tropospheric ozone residual (TOR), as compared with data from TOMS/SBUV.

3.3 Particulate Matters (PM)

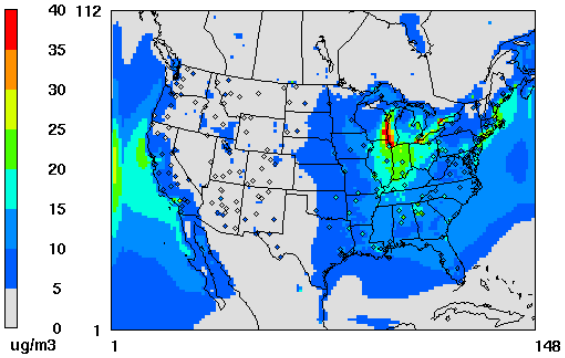
Evaluation of surface $PM_{2.5}$ and its components is conducted against observations from STN, IMPROVE, and SEARCH. All the WRF/Chem-MADRID 1 simulations predict reasonable $PM_{2.5}$ (with NMBs of -19.5% to 46.6%), and SO_4^{2-} (with NMBs of -45.4% to 40.2%), but significantly overestimate NO_3^- (with NMBs of 87.6%-973%). CB05 and SAPRC99 also give reasonable NH_4^+ (with NMBs of -31.7% to –2.6%), whereas CBM-Z significantly overestimates NH_4^+ (with NMBs of 23%-155%). Different gas-phase mechanisms affect primary and secondary aerosol formation including SO_4^{2-}, NH_4^+, and NO_3^-. Fig. 2 shows the monthly average overlay of spatial distribution of surface $PM_{2.5}$. Note that SOA module in MADRID 1 is inactivated in the simulations; therefore $PM_{2.5}$ shown here only includes inorganic species and POM.

CB05 and SAPRC99 are also more similar in terms of spatial patterns of most PM species predictions than either of them with CBM-Z. With the highest SO_2 oxidation rate, CBM-Z gives the highest SO_4^{2-} (with NMBs of 27.6%-46.6%), which leads to the highest NH_4^+ prediction, due to the neutralization of SO_4^{2-} by NH_4^+. Over- or under-predictions of NH_4^+ are associated exactly with over- or under-predictions of SO_4^{2-}. Meanwhile, CBM-Z also gives the highest NO_3^- due to the highest prediction of HNO_3.

Aerosol optical depths (AODs) are evaluated against MODIS (Figure not shown). All the three simulations are able to capture regions with higher AODs in eastern U.S, but fail to capture those along the west coast. Different gas-phase mechanisms give different PM predictions, therefore different AOD predictions.



(a)



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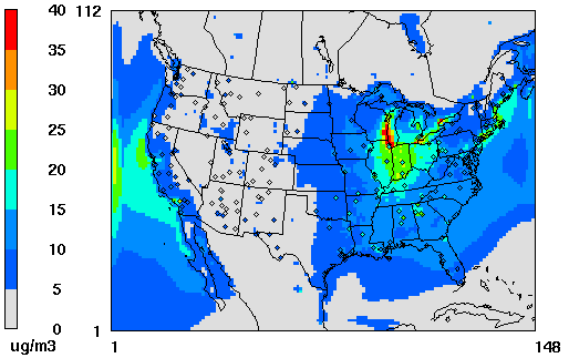

(c)

Fig. 2. Overlay plots of monthly average simulated surface 24-hr average $PM_{2.5}$ vs. observations from STN, IMPROVE, and SEARCH: CBM-Z/MADRID 1 (a); CB05/MADRID 1 (b); and SAPRC99/MADRID 1 (c).

4. SUMMARY

SAPRC99 has been successfully implemented into WRF/Chem using KPP and coupled with MADRID 1. WRF/Chem simulations with three gas-phase mechanisms: CBM-Z, CB05, and SAPRC99 that are coupled with MADRID 1 are conducted for July 1-31, 2001 over the continental U.S. Meteorological and chemical predictions are evaluated against surface and satellite observations.

All the WRF/Chem-MADRID 1 simulations give very similar meteorological predictions, with satisfactory temperature and relative humidity but overestimated wind speed. CB05 and SAPRC99 are more similar in spatial patterns of gaseous and aerosol predictions than either of them is with CBM-Z. The inclusion of higher aldehydes in CB05 and SAPRC99 leads to higher PAN predictions, and therefore lower HNO_3 and higher O_3 mixing ratios. CBM-Z predicts the highest HNO_3 and consequently the lowest H_2O_2 but highest OH radical. Discrepancies in simulated gaseous mixing ratios can explain those in secondary inorganic aerosol species predictions. For example, the highest OH radical prediction in CBM-Z leads to the highest oxidizing rate of SO_2, causing the highest SO_4^{2-} prediction, and thus the highest NH_4^+ prediction. The highest HNO_3 mixing ratio in CBM-Z leads to the highest NO_3^- prediction.

CB05 and SAPRC99 with KPP have been re-implemented in the latest version of WRF/Chem (i.e., v3.0). The SOA module in MADRID 1 of Pun et al. (2006) with inclusion of 25 SOA species has also been implemented into WRF/Chem v3.0. 6 reactions have been modified and 11 additional reactions have been added in CB05 and SAPRC99 to produce 25 SOA precursors for MADRID 1 SOA module, they, however, are not added in CBM-Z because CBM-Z is hard-wired with a numerical solver (instead of KPP) in WRF/Chem and its modification cannot be easily made by users without significant efforts. WRF/Chem simulations with SOA module are being conducted. The impacts of different gas-phase mechanisms on SOA formation will be examined. In addition, MADRID 2 of Pun et al. (2002) that provides a mechanistic treatment of SOA will be implemented into WRF/Chem v3.0. Simulations with the same gas-phase mechanism (e.g., CB05) but different aerosol modules (e.g., MOSAIC, MADRID 1, and MADRID 2) will be conducted in the future.

5. ACKNOWLEDGEMENTS

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