Application of WRF/Chem over North America under the AQMEII Phase 2: Part II. Evaluation of 2010 Application and Responses of Air Quality and Meteorology-Chemistry Interactions to Changes in Emissions and Meteorology from 2006 to 2010

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Abstract

The Weather Research and Forecasting model with Chemistry (WRF/Chem) simulation with the 2005 Carbon Bond (CB05) gas-phase mechanism coupled to the Modal for Aerosol Dynamics for Europe (MADE) and the Volatility Basis Set (VBS) approach for secondary organic aerosol (SOA) (MADE/VBS) are conducted over a domain in North America for 2006 and 2010 as part of the Air Quality Model Evaluation International Initiative (AQMEII) Phase 2 project. This Part II paper focuses on comparison of model performance in 2006 and 2010 as well as analysis of the responses of air quality and meteorology-chemistry interactions to changes in emissions and meteorology from 2006 to 2010. In general, emissions for gaseous and aerosol species decrease from 2006 to 2010, leading to a reduction in gaseous and aerosol concentrations and associated changes in radiation and cloud variables due to various feedback mechanisms. Compared to 2006, the performance for most meteorological variables in 2010 gives lower normalized mean biases (NMBs) but higher normalized mean errors (NMEs) and lower correlation coefficients (Corr). This indicates some compensation in over- and underpredictions against observations. The worse meteorological performance in 2010 is likely

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due to inaccurate chemistry feedbacks resulted from less accurate emissions in 2010 as the values of Corr are higher and NMEs are lower for the 2010 WRF only simulation than those for the 2010 WRF/Chem simulation. The model also shows worse performance for most chemical variables in 2010. This could be attributed to underestimations in emissions of some species such as primary organic aerosol in some areas of the U.S. in 2010, inaccurate meteorological predictions, as well as the use of a coarse grid resolution. The effects of the decrease in emissions and changes in meteorology between 2006 and 2010 result in complex changes in model predictions in 2010 due to chemistry-meteorology feedbacks. The inclusion of chemical feedbacks to meteorology, clouds, and radiation reduces model biases in meteorological predictions in 2010; however, it increases model errors and weakens correlations. Sensitivity simulations comparing WRF and WRF/Chem simulations for 2006 and 2010 show that for 2006, the performance of meteorological variables is comparable between both but for 2010, WRF/Chem performs slightly worse than WRF. These results indicate a need to further improve the accuracy of the model representations of SOA, meteorology for extreme events, and chemistry-meteorology feedbacks in the online-coupled models.

Keywords: AQMEII, Emission variation, WRF/Chem, Meteorology-chemistry Interactions, SOA, model responses to changes in emissions and meteorology from 2006 to 2010

1. Introduction

Changes in meteorology, climate, and emissions affect air quality (e.g., Hogrefe et al., 2004; Leung and Gustafson, 2005; Zhang et al., 2008; Dawson et al., 2009; Gao et al., 2013; Penrod et al., 2014). As federal, state, and local environmental protection agencies enforce the

anthropogenic emission control programs, ambient air quality is expected to be continuously improved. However, such an improvement may be compensated by adverse changes in climatic or meteorological conditions (e.g., increases in near surface temperature, solar radiation, and atmospheric stability, or reductions in precipitation) that are directly conducive to the formation and accumulation of air pollutants and that may result in higher biogenic emissions. It is therefore important to examine changes in both meteorology/climate and emissions as well as their combined impacts on air quality. The Air Quality Model Evaluation International Initiative (AQMEII) Phase 2 was launched in 2011 to intercompare online-coupled air quality models (AQMs) in their capabilities in reproducing atmospheric observations and simulating air quality and climate interactions in North America (NA) and Europe (EU) (Alapaty et al., 2012). The simulations over NA and EU with multi-models by a number of participants have been performed for two years (2006 and 2010) that have distinct meteorological conditions. Compared with 2006, 2010 is characterized by warmer summer conditions in eastern U.S. and less precipitation over NA (Stoeckenius et al., 2014; Pouliot et al., 2014). In addition, the emissions of key pollutants are reduced in 2010 relative to 2006, e.g., emissions of NO_x and SO_2 are reduced by 10-30% and 40-80% for many regions in NA (Pouliot et al., 2014). Comparison of 2010 and 2006 simulations will thus provide an opportunity to examine the success of the emission control programs and the impacts of meteorological/climatic variables on air quality. Compared to model intercomparison during AQMEII Phase 1 (Rao et al., 2012) in which offline-coupled models were used, the use of online-coupled AQMs models during AQMEII Phase 2 allows for study of the interactions between meteorology and chemistry through various direct and indirect feedbacks among aerosols, radiation, clouds, and chemistry (Zhang, 2008; Baklanov et al., 2014). The two year simulations further enable an examination of the responses of air

quality and meteorology-chemistry interactions to changes in emissions and meteorology from 2006 to 2010 that was not possible with offline-coupled models.

Similar to offline AQMs, large uncertainties exist in online-coupled AQMs, which will affect the model predictions and implications. Such uncertainties lie in the meteorological and chemical inputs such as emissions, initial and boundary conditions (ICONs and BCONs), model representations of atmospheric processes, and model configurations for applications such as horizontal/vertical grid resolutions and nesting techniques. Several studies examined the uncertainties in emissions (e.g., Reid et al., 2005; Zhang et al., 2014) and BCONs (e.g., Hogrefe et al., 2004; Schere et al., 2012). There are also uncertainties in the various chemical mechanisms and physical parameterizations used in AQMs such as gas-phase mechanisms (Zhang et al., 2012), aerosol chemistry and microphysical treatments (Pun et al., 2003; Zhang et al., 2010), microphysical parameterizations (van Lier-Walqui et al., 2014), convective parameterizations (Yang et al., 2013), boundary layer schemes (Edwards et al., 2006), and land surface models (Jin et al., 2010). Due to the complex relationships in online-coupled AQMs among the emissions, ICONs and BCONs, and model processes that may be subject to inherent limitations, it is difficult to isolate the contributions of model inputs or the representations of atmospheric processes to the model biases. In mechanistic evaluation (also referred to as dynamic evaluation), sensitivity simulations are performed by changing one or a few model inputs or process treatments, while holding others constant. This approach can help diagnose the likely sources of biases in the model predictions.

The Weather Research and Forecasting model with Chemistry (WRF/Chem) version 3.4.1 with the 2005 Carbon Bond (CB05) gas-phase mechanism coupled with the Modal for Aerosol Dynamics for Europe (MADE) and the Volatility Basis Set (VBS) approach for

93 secondary organic aerosol (SOA) (hereafter WRF/Chem-CB05-MADE/VBS) has been recently
94 developed by Wang et al. (2014). The applications of WRF/Chem-CB05-MADE/VBS to 2006
95 and 2010 in the Part I paper (Yahya et al., 2014) and this work use the same model physical and
96 chemical parameterizations but different emissions, meteorological ICONs and BCONs, and
97 chemical ICONs and BCONs. The mechanistic evaluation by comparing WRF/Chem-CB05-
98 MADE/VBS predictions for the two years would help understand the sensitivity of the model
99 predictions and performance to different model inputs, and that by comparing WRF/Chem-
100 CB05-MADE/VBS and WRF only predictions would quantify the impacts of chemistry-
101 meteorology feedbacks on the meteorological predictions. A comprehensive evaluation of the
102 2006 simulation has been presented in Part I paper. In this Part II paper, the differences in
103 emissions, meteorological and chemical ICONs/BCONs, and meteorology between 2010 and
104 2006 are first examined. The model performance in 2010 is then evaluated and compared with
105 that in 2006. Finally, the responses of air quality and meteorology-chemistry interactions to
106 changes in emissions and meteorology from 2006 to 2010 are analyzed. The main objectives of
107 this Part II paper are to examine whether the model has the ability to consistently reproduce
108 observations for two separate years, as well as to examine whether the trends in air quality and
109 meteorology-chemistry interactions are consistent for both years. Stoeckenius et al. (2014)
110 carried out an extensive analysis of the trends in emissions and observations of meteorological
111 variables, O_3, SO_2 and $PM_{2.5}$ concentrations between 2006 and 2010. This Part II paper
112 complements the work of Stoeckenius et al. (2014) by examining the changes in WRF/Chem
113 predictions and chemistry-meteorology feedbacks in 2010 relative to 2006. Similar evaluations
114 of 2010 and 2006 are performed for the coupled WRF-CMAQ system (Hogrefe et al., 2014).

115 Unlike the coupled WRF-CMAQ system used in AQMEII Phase 2 that only simulates aerosol
116 direct effects, WRF/Chem used in this work simulates both aerosol direct and indirect effects.
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118 **2. Differences in Emissions and ICONs/BCONs between 2006 and 2010**

119 **2.1 Emission Trends**

120 The emission variation trends are examined for major precursors for ozone (O_3) and
121 secondary particulate matters (PM) (i.e., sulfur dioxide (SO_2), oxides of nitrogen (NO_x),
122 ammonia (NH_3), volatile organic compounds (VOCs) including both anthropogenic and biogenic
123 VOCs) and primary PM species (elemental carbon (EC) and primary organic aerosol or carbon
124 (POA or POC)). Comparing to annual mean emissions in 2006, the annual emissions of SO_2 and
125 NO_x decrease significantly in 2010, especially at the point sources (Figure A1), with similar
126 variation patterns in all seasons (Figure not shown). The annual emissions of NH_3 decrease over
127 most areas but increase in some areas in California (CA) and Midwest. Unlike the changes in the
128 emissions of SO_2 and NO_x, NH_3 and VOCs emissions exhibit strong seasonal variations in the
129 emission trends, as shown in Figure 1. In JFD, NH_3 emissions decrease over southeastern and
130 Midwest U.S., while NH_3 emissions increase significantly over northeastern U.S. and in parts of
131 CA due to increased livestock emissions (EPA, 2004). For the other seasons, NH_3 emissions
132 generally decrease over the whole of continental U.S. (CONUS). VOC emissions largely
133 decrease in March, April, May (MAM) and January, February, and December (JFD), and
134 increase in June, July, August (JJA) and September, October, and November (SON), especially
135 in southeastern U.S. Although anthropogenic VOC emissions decrease over CONUS for all
136 seasons (Figure not shown), the VOC emissions increase in the southeast, which is dominated by
137 enhanced biogenic emissions from vegetation as a response to temperature increases

(Stoeckenius et al., 2014). The total annual emissions of EC and POA also decrease but to a smaller extent over most areas of the continental U.S. The changes in annual and seasonal emissions of those species between 2010 and 2006 will affect simulated air quality and meteorology-chemistry interactions.

2.2 Differences in Chemical and Meteorological ICONs/BCONs

Large differences exist in the chemical and meteorological ICONs/BCONs used in 2006 and 2010 simulations. For example, Stoeckenius et al. (2014) reported large differences between 2006 and 2010 in chemical BCONs extracted from a global model simulations, e.g., the mid-tropospheric seasonal mean O_3 mixing ratios are generally lower by several ppbs in 2010 as compared to 2006, especially during spring and summer. Figure 2 shows the differences for JFD and JJA 2010 – 2006 in averaged meteorological ICONs and BCONs of skin temperature and soil moisture fraction 100 to 200 cm below ground extracted from the National Center of Environmental Prediction's (NCEP). The JFD skin temperatures show a significant decrease of up to -8 ºC over eastern and central U.S. and a moderate increase over western U.S. The JJA skin temperatures show a moderate overall increase over eastern and southern U.S. and a moderate decrease in western and northwestern U.S. The soil moistures show more variability from 2010 to 2006. General trends include an increase in soil moisture over southeastern and central U.S. and a decrease over the northeastern and northwestern U.S. for JFD. For JJA, soil moisture mainly decreases over eastern U.S. except for parts of Georgia, Alabama, and Mississippi. Large increases in soil moisture are found over northern U.S. and parts of Canada and Mexico. Soil moisture and temperature are important variables in regulating the sensible and latent heat fluxes from the ground to the atmosphere, affecting wind speeds and planetary boundary layer height

(PBLH). The accuracy of soil moisture initialization is important as latent heat fluxes are very sensitive to variations of soil moisture. Latent heat fluxes tend to be overestimated when soil moisture is high (Hong et al., 2009).

3. Model Performance in 2010 and Its Comparison with 2006

Model predictions in 2010 respond to changes in emissions, BCONs, and meteorology. The model performance for both meteorological and chemical predictions in 2010 is evaluated and compared with that in 2006. Major differences in model performance between the two years and their associations with changes in emissions, BCONs, and meteorology are discussed below.

3.1 Differences in Meteorological Predictions for 2006 and 2010

Table 1 shows the annual mean observed and simulated values as well as correlation coefficients (Corr) between the observed and simulated meteorological variables from the 2010 WRF/Chem and WRF simulations. Similar statistics from the 2006 WRF/Chem and WRF simulations can be found in Table 1 in Yahya et al. (2014). The trends in simulated variables are generally consistent with the trends in observations from 2006 to 2010 except for WS10. Both observed and simulated temperatures at 2-m (T2) at the CASTNET sites increase by ~4 ºC from 2006 to 2010. While observed T2 at the SEARCH sites increases by 0.25 ºC from 2006 to 2010, the simulated T2 only increases by 0.02 ºC. For downward shortwave radiation (SWDOWN), both observed and simulated values at the CASTNET and SEARCH sites decrease from 2006 to 2010. The observed wind speed at 10-m (WS10) remains similar at both CASTNET and SEARCH sites in both years. While simulated WS10 at the CASTNET sites are similar between the two years, the simulated WS10 at the SEARCH sites decreases by 0.37 m s^{-1} from 2006 to

2010. Observed and simulated precipitation (Precip) from GPCC both increase slightly from 2006 to 2010. Observed Precip from NADP shows a larger increase from 2006 to 2010 than GPCC, but simulated Precip at the NADP site decreases, which is the opposite to the observed Precip trend.

To examine changes in meteorology between 2010 and 2006 predicted by WRF only simulations without considering chemistry feedbacks, Figure 3 compares the seasonal changes in several meteorological variables that affect air pollution including SWDOWN, T2, WS10, PBLH, and Precip. Large changes occur in those variables between the two years, e.g., 10-50 W m^{-2} increases in SWDOWN in western and Midwest in JJA, generally warmer in JJA and SON over most areas but cooler by 3-10 ºC in eastern U.S. in JFD, and reduced Precip in eastern or southeastern U.S. in JJA and SON but increased Precip in northwestern U.S. in MAM and JJA and in western U.S. in JFD. ICONs and BCONs for skin temperatures shown in Figure 2 greatly influence T2 shown in Figure 3 for JFD and JJA. Differences in the changes in meteorological variables for WRF/Chem between 2006 and 2010 that accounts for meteorology-chemistry feedbacks will be presented in Section 4.3.

Figure 4 shows normalized mean bias (NMB) vs. normalized mean error (NME) plots for several meteorological variables by seasons against several observational networks for 2006 and 2010. In general, the correlation coefficients (Corr) for 2006 are better than those of 2010, as the correlations between mean observed and simulated values for all meteorological variables are higher for 2006 compared to 2010. However, the biases are smaller for T2 (against CASTNET), SWDOWN, WS10, Precip (against NADP), CF, and CDNC for 2010 compared to 2006. T2 in general increases from 2006 to 2010 for both mean observed and simulated values at the CASTNET sites and increases slightly at the SEARCH sites. T2 is underpredicted against

CASTNET and SEARCH for both 2006 and 2010. The seasonal mean NMBs for both 2006 and 2010 (except for JFD 2006) are < 15%, with annual mean NMBs of -7.7% and -4.9%, respectively. With the exception of JFD 2006 against CASTNET, T2 predictions in the other seasons in 2006 for both CASTNET and SEARCH have lower NMEs (< 25%) for 2006. All the seasons in 2010 have an NME of > 25% for T2 predictions. For SWDOWN, for both 2006 and 2010, seasonal NMBs range from -10% to 20% with annual mean NMBs of 21.3% and 7.4%, respectively, against CASTNET and 3.0% and 12.4%, respectively, against SEARCH; however the seasonal and annual mean NMEs in 2006 are < 40% while those in 2010 range from 40% to 65%. The CASTNET and SEARCH sites also show an average annual increase for SWDOWN from 2006 to 2010, which is reproduced by WRF/Chem. Although SWDOWN is overpredicted on an annual basis, T2 is underpredicted in all seasons in 2006 and all seasons except for JJA in 2010, as T2 is diagnosed from the skin temperature, which depends on not only SWDOWN but also other variables such as soil properties. The Noah land surface model used in this case calculates the heat fluxes and skin temperatures based on SWDOWN, the land-use type, and soil properties including soil texture, soil moisture, soil conductivity and thermal diffusivity which vary for different soil types (Chen, 2007). Annual mean WS10 is overpredicted for both 2006 and 2010. Seasonal WS10 is overpredicted for 2006 but underpredicted for 2010 with better performance in 2010 (i.e., smaller NMBs in 2010 and comparable NMEs between the two years). While the mean observed and simulated WS10 are closer in 2010 compared to 2006, the values of Corr are higher in 2006 compared to 2010. In this study, the Mass and Owens (2010) surface roughness parameterization is used in WRF and WRF/Chem, which helps reduce typical overpredictions in wind speeds overall in both years. However, Mass and Ovens (2010) also noted that by using this parameterization, the high wind speeds are affected and suggested

switching off this drag parameterization at higher wind speeds. For Precipitation, the model performs consistently well against GPCC for both years with seasonal NMBs within -11% and -12%, and annual NMBs of 0.3% and 1.3%, respectively, for 2006 and 2010. The evaluation against NADP shows larger differences with NMBs of 22.2% and 2.5% and Corr values of 0.43 and 0.1 for 2006 and 2010, respectively. CF is the only meteorological variable with a better performance in terms of all three measures including Corr, NMB, and NME in 2010 than in 2006 against MODIS. The better performance in CF in 2010 may help reduce annual mean NMBs in CDNC, SWDOWN, and T2 in 2010, although their annual mean NMEs increase and annual mean Corr values decrease.

The Part I paper (Yahya et al., 2014) compared and evaluated the full-year WRF and WRF/Chem 2006 simulations with the same physical configurations to analyze the effects of feedbacks from chemistry to meteorology. The results for 2006 show that for the evaluation of SWDOWN, T2 and WS10 against CASTNET and SEARCH, the Corr is almost identical for both WRF/Chem and WRF simulations. For evaluation of precipitation against NADP, WRF has a higher Corr compared to WRF/Chem. Unlike 2006, the 2010 WRF only simulation has higher Corr for all meteorological variables compared to the 2010 WRF/Chem simulation except for Precip against GPCC and CF against MODIS. This means that the emissions and chemistry-meteorological feedbacks play an important role in influencing model performance. Another obvious difference is that the NMBs for the meteorological variables for 2010 are smaller compared to 2006 for all the variables except for Precip against GPCC, while the NMEs are larger for 2010 compared to 2006 for all variables except for Precip against GPCC. A smaller overall averaged NMB but a larger NME may indicate compensation of over- and under-

252 predictions leading to a small bias, but the magnitude of the differences are reflected in the NME
253 values.

254 The same model physics and dynamics options are used for both years. In addition to
255 different emissions, there are characteristic climate differences between the two years that lead to
256 lower Corr and larger NMEs for most meteorological fields in 2010 compared to 2006. 2010 is
257 reported to be the warmest year globally since 1895 according the National Climactic Data
258 Center (http://www.ncdc.noaa.gov/cag/). Even though 2010 has high temperatures compared to
259 previous years, a trend analysis of extreme heat events (EHE) from 1930 to 2010 showed that in
260 2010, there were more than 35 extreme minimum heat events (where temperatures are extremely
261 low) over southeastern U.S. compared to about ~10 extreme minimum heat events in 2006. In
262 fact, the number of extreme minimum heat events is the highest overall for CONUS in 2010
263 compared to all the other years from 1930 onwards (Oswald and Rood, 2014). The IPCC
264 reported that since 1950, there is evidence that weather events have become more extreme likely
265 due to climate change (IPCC, 2012). Grundstein and Dowd (2011) stated that on average, by
266 2010 there would be 12 more days with extreme apparent temperatures than there were in 1949.
267 The implications of these would be that increased temperatures change the weather in
268 unexpected ways with uncertainties in the state of science (Huber and Gulledge, 2011), including
269 models. These high and low temperatures could contribute to the compensation of over- and
270 under-predictions leading to smaller NMBs in general for 2010. To better simulate model
271 extreme heat events, Meir et al. (2013) suggested using a higher domain spatial resolution with a
272 grid size of 12-km or smaller, better sea surface temperature estimates, and enhanced
273 urbanization parameterization. Gao et al. (2012) reported better results in reproducing extreme
274 weather events with WRF over eastern U.S. with a 4-km × 4-km resolution. In this study,

although the urban canopy model is used for both WRF and WRF/Chem simulations, a 36-km × 36-km grid resolution might not be sufficient to reproduce the extreme temperature events (highs and lows) in 2010.

As shown in Figure A2, the spatial distribution of MB values for T2 for JFD 2010 show very large negative MBs over southeastern U.S. compared to JFD 2006. T2 is also generally underpredicted over southeastern U.S. in both years, but with larger negative biases (with the absolute values of NMB > 0.5 ºC) in 2010 than those in 2006 (with the absolute values of NMB < 0.2 ºC). T2 biases also seem to be more extreme for JFD 2010 compared to JFD 2006, with dark red and dark blue colors for the MB markers, indicating large positive and large negative biases, respectively. This could explain the poor correlation for T2 in 2010 compared to 2006 as shown in Table 1. On the other hand, the performances of T2 for JJA 2010 and 2006 are very similar, with MBs ~ -0.1 to 0.1 in eastern U.S., large negative MBs at the sites in Montana and Colorado, and a large positive MB at the site in Wyoming.

3.2 Differences in Chemical Predictions for 2006 and 2010

The lower Corr for 2010 compared to 2006 for meteorological variables has a large influence on the model performance for 2010. As shown in Table 1, all the chemical variables for all networks have lower Corr values in 2010 compared to 2006. As shown in Figures 5-7, O_3 concentrations are underpredicted to a larger extent in 2010 compared to 2006. As shown in Figure 5, O_3 concentrations are especially underpredicted for JFD 2010 over southeastern U.S., which is related to the larger MBs in T2 in JFD in 2010 shown in Figure A2. Rasmussen et al. (2012) conducted a statistical study to analyze O_3 concentration biases as a result of temperature biases using the Geophysical Fluid Dynamics Laboratory (GFDL) Atmospheric Model, and

298 concluded that during the summer temperature biases of up to 5 K can result in maximum O_3
299 biases of up to 10 – 15 ppb. In addition, both NO_x and VOC emissions decrease significantly
300 over the entire CONUS from JFD 2006 to 2010 (Figures not shown), which could also contribute
301 to the large underpredictions in O_3 concentrations in JFD 2010 than in JFD 2006. For JJA 2006
302 and 2010, the spatial distribution of NMB markers shows that the temperature biases for both
303 years are relatively similar. Over northeastern U.S., the temperature bias is generally less than -
304 0.1 ºC for both JJA 2006 and JJA 2010. However, as shown in Figure 6, O_3 concentrations over
305 northeastern U.S. in JJA 2010 have negative biases whereas those over northeastern U.S. in JJA
306 2006 have positive biases. In this case, emissions might play a significant role in the
307 underprediction of O_3 concentrations over northeastern U.S. in JJA 2010. Hourly average surface
308 NO_x emissions decrease significantly over northeastern U.S. in JJA from 2006 to 2010. As
309 shown in Figure 6, in general, for all seasons and against all networks, 2006 model performance
310 for O_3 is generally good for all seasons compared to all networks. For 2010, the model performs
311 better for JJA and worst for JFD with the highest magnitude of negative NMB and NME (~-57%
312 and 58%, respectively). Overall, 2010 simulations seem to underpredict O_3 concentrations to a
313 larger extent compared to 2006.

314 Figure 7 shows diurnal variations of observed and simulated temperatures and O_3
315 concentration from CASTNET in 2006 and 2010. The diurnally averaged observed temperatures
316 decrease slightly from 2006 to 2010 with a very similar performance against T2 measurements at
317 the CASTNETs. This seems to be contradictory to the overall trend of T2 as shown in Table 1.
318 This would be possible if there are very high temperatures at certain locations at certain times
319 which would skew and influence the overall average T2 for the whole year. The model
320 meteorology is reinitialized every 2 days starting from around 7 am, which explains the

closeness of the observed and simulated temperatures from 7 am to about 12 pm. After 12 pm, the model consistently underpredicts temperatures to up to 2 ºC. Underpredictions of temperature, especially in the afternoon where O_3 concentrations are high, would result in underpredictions of O_3 concentrations. The diurnal O_3 plots show that the observed O_3 concentrations from CASTNET do not seem to decrease from 2006 to 2010 even though the temperatures decrease in general. In fact the magnitudes of diurnally averaged observed O_3 concentrations for 2006 and 2010 are almost the same or slightly higher than 2006. The model temperature and O_3 diurnal patterns seem to be more correlated, i.e., a decrease in temperature over the CASTNET sites for 2010 leads to a decrease in O_3 concentrations. However, due to the higher observed O_3 concentrations over the CASTNET sites and lower simulated temperatures and precursor emissions, and lower MACC BCONs of O_3 in 2010, the underprediction in surface O_3 is larger in 2010 compared to 2006. Im et al. (2014) showed that WRF/Chem-CB05-MADE/VBS gives relatively large O_3 dry deposition comparing to other models, which may have contributed to the underpredictions of O_3. They also showed that MACC underpredicts O_3 mixing ratios, particularly in winter and spring during both day and night and in summer and fall during nighttime. As indicated by Wang et al. (2014) and Makar et al. (2014), the inclusion of aerosol indirect effects also tends to reduce O_3 mixing ratios, comparing to the models that simulate aerosol direct effect only or do not simulate aerosol direct and indirect effects (i.e., offline-coupled models).

Figure 8 shows spatial distribution plots of NMBs for $PM_{2.5}$ concentrations for JFD and JJA 2006 and 2010 against IMPROVE, STN, and SEARCH. Overall, JJA 2006 and JJA 2010 have similar spatial distribution patterns of NMBs for all sites over CONUS except for several sites in northwestern U.S. where $PM_{2.5}$ concentrations are underpredicted for JJA 2010 but

overpredicted for JJA 2006. However, many sites have positive NMBs over eastern and central U.S. for JFD 2006, whereas more sites have negative NMBs over eastern and central U.S. for JFD 2010. Statistics from Yahya et al. (2014) and Table 1 show that in general, the simulated concentrations of $PM_{2.5}$ and all $PM_{2.5}$ species decrease from 2006 to 2010, however, the Corr values for $PM_{2.5}$ and $PM_{2.5}$ species become worse in 2010 compared to 2006. As shown in Figure 9, $PM_{2.5}$ concentrations for 2006 can be overpredicted or underpredicted, depending on seasons and networks, with an equal distribution of positive and negative NMBs. However for 2010, $PM_{2.5}$ concentrations tend to be underpredicted for all seasons and for all networks except for JFD against SEARCH. As shown in Figure 10, NMBs for $PM_{2.5}$ species for 2006 at individual monitoring sites range from -40% to 60%, while those for 2010 range from -80% to 80%. The markers are more spread out covering a wider range of NMBs and NMEs for 2010 with more extremes as compared to the markers for 2006 clustered around the zero NMB line. NMEs for $PM_{2.5}$ species in 2006 remain below 100%. NO_3^- concentrations are slightly underpredicted in 2006 against all networks; however, NO_3^- concentrations in 2010 are largely underpredicted, likely due to the large decrease in NO_x emissions from 2006 to 2010 and the increase in the surface temperatures. The NMBs for IMPROVE and SEARCH OC remain low from 2006 to 2010, however, the NMEs increase significantly. For TC against IMPROVE, the NMB and NME in 2010 are larger in magnitudes in 2010 than those in 2006. SO_4^{2-} has lower NMBs but higher NMEs for all networks in 2010 compared to 2006. EC concentrations are generally overpredicted in 2006 for all networks but underpredicted against SEARCH and largely overpredicted against IMPROVE in 2010. NH_4^+ also has higher NMEs in 2010 compared to 2006. Overall, the evaluation in 2010 shows large NMEs and poor correlations for all $PM_{2.5}$ species compared to 2006. Figure 11 shows the time series plots for $PM_{2.5}$, SO_4^{2-} and NO_3^- concentrations against

STN for 2006 and 2010. The observed data are collected more frequently in 2006 compared to 2010. In 2006, the PM data were collected on a daily basis in 2006 but every 3 days in 2010. From the time series plots, the model is able to predict most of the peaks and troughs for 2006 even though the magnitudes of observed and simulated concentrations are significantly different for several days. For 2010, the model does not show large spikes and can reproduce the magnitudes well, although it does not predict the peaks and troughs as well as 2006 for some months (e.g., Jan-March and July-Sept. for $PM_{2.5}$). This could be attributed in part to the poor correlations of meteorological variables in 2010 compared to 2006. For example, poor predictions of WS10 can influence the transport and dry deposition of aerosols. Poor predictions of precipitation can impact the wet deposition of aerosols. In fact, the poor performance for EC for 2010 can be attributed to poor predictions of WS10 and precipitation as EC is a primary pollutant. Poor predictions of T2 can influence PBLH and both can also affect the distribution of aerosol concentrations. NO_3^- concentrations for the winter months are moderately underpredicted in 2006 but largely underpredicted in 2010, likely due to underpredictions in NO_2 concentrations (Yahya et al., 2014).

3.3 SOA Evaluation for 2006 and 2010

The VBS framework in WRF/Chem of Ahmadov et al. (2012) provides a more realistic treatment of SOA compared to previous SOA treatments such as the 2-product model by Odum et al. (1996) used in the Secondary Organic Aerosol Model (SORGAM) of Schell et al. (2001). This is because the VBS approach is able to simulate gas-phase partitioning and multiple generations of gas-phase oxidation of organic vapors (Donahue et al., 2006) and it also addresses the shortcomings of the traditional SOA modeling approach as it can cover the complete

volatility range of OA compounds (Murphy et al., 2009). The SOA from the VBS approach contains both anthropogenic and biogenic SOA. Wang et al. (2014) evaluated SOA and OC concentrations simulated from WRF/Chem-CB05-MADE/VBS and WRF/Chem-CB05-MADE/SORGAM over NA for July 2006 against field campaign data from Offenberg et al. (2011) at the Research Triangle Park (RTP), NC for July 2006. They showed significant improvement in simulating SOA and total organic aerosol (TOA) by VBS than by SORGAM.

In this study, SOA and OC predictions in 2006 and 2010 are evaluated against available field campaign data at RTP, NC from Offenberg et al. (2011), and Pasadena, CA and Bakersfield, CA from Klendienst et al. (2012) and Lewandowski et al. (2013). The RTP site is located in a semi-rural area. Pasadena, CA is located about 11 miles from downtown Los Angeles (LA), and Bakersfield, CA is located about ~100 miles from downtown LA. Both sites are classified as urban/industrial sites. Organic carbon concentrations were measured using an automated, semicontinuous elemental carbon-organic carbon (EC-OC) instrument. The observed SOA masses were determined using laboratory-derived values for the organic mass (OM)–organic carbon (OM/OC) ratio. As shown in Figure 12, the model can better simulate SOA and OC concentrations in 2006 compared to 2010. The model overpredicts SOA but underpredicts OC in 2006. As indicated in Wang et al. (2014), the overpredictions in SOA in 2006 (with an NMB of 76.3%) are likely because the SOA observations from RTP did not include those generated by alkanes and alkenes, which are simulated by the VBS module in WRF/Chem. The VBS underpredicts SOA in 2010 with NMBs of -55.3% and -75.3% at Bakersfield and Pasadena, respectively. The underpredictions in SOA at the two sites in 2010 are mainly due to the omission of SOA formation from POA in the current VBS-SOA module in this version of WRF/Chem, although POA may be evaporated to produce semi-volatile organic compounds that

may be oxidized further in the atmosphere to produce SOA (Jimenez et al., 2009). The model performs better for SOA compared to OC in 2010. However, the model underpredicts OC at RTP in 2006 and significantly underpredicts OC at the two sites in CA in 2010 as shown in Figure 13. The differences in OC performance in both years are caused by different ratios of POC to OC at RTP in 2006 and at the two sites in CA in 2010. SOA to OC ratios at RTP are in the range of 50-80%, whereas they are < 20% at Bakersfield, CA and < 40% Pasadena, CA. OC performance thus largely depends on SOA performance at RTP but on POA performance at the two sites in CA. This is why the OC performance remains poor despite a relatively good performance in SOA at the two sites in CA. Simulated OC concentration is calculated by summing up SOA and POA, and dividing the total OA by 1.4 (Aitken et al., 2008). Figure 14 shows the spatial distributions of the average OC concentrations for the months during which the field data were collected during the periods specified in Figure 12 in 2006 and 2010. 2006 in general has higher OC concentrations compared to 2010. Southeastern U.S., also in general has higher OC concentrations compared to western U.S for both 2006 and 2010. The model severely underestimates OC concentrations over western U.S., with a maximum mean in downtown LA area of 1.5 – 1.8 $\mu g\ m^{-3}$, when the observed OC concentrations for Pasadena and Bakersfield range from 1 to 8 $\mu g\ m^{-3}$. Figure 13 also shows that the simulated OC concentrations do not change much daily with the variations in the observed OC concentrations, but remain low throughout the two months. Also, the observed OC concentrations at both sites in CA are much higher than those of SOA, indicating the dominance of POA for 2010 in western U.S. Although simulated SOA gives relatively better performance against observed SOA, OC is significantly underpredicted mainly because of significant underpredictions of POA (due to underestimate in POA emissions) that dominates OC concentrations. The underpredictions in SOA also contribute

436 in part to the OC underpredictions. There would be additional uncertainties in using 1.4 as the
437 factor for deriving OA concentrations from OC; however, and such uncertainties cannot explain
438 the large discrepancies between the simulated and observed OC concentrations in 2010. In
439 addition, stronger wind speeds from the model in JJA 2010 as shown in Figure 3 can help
440 disperse OC over western U.S. toward further inland compared to the weaker winds over western
441 U.S. in JJA 2006, reducing OC concentrations over western U.S in JJA 2010. Figure 14 also
442 shows the spatial distribution of the concentrations of anthropogenic SOA (ASOA) and total
443 SOA (TSOA) (=ASOA + BSOA) and the ratio of SOA/OA. The ratios for April to December
444 2006 range from 0 to 0.8 with higher ratios in southern U.S. from Nevada in the west to Virginia
445 in the east, while the ratios for May to June 2010 range from 0 to 0.9 with higher ratios in eastern
446 U.S. Table 1 also shows that the 2010 simulation has negative NMBs of -30% and -12% for OC
447 at the IMPROVE and STN sites, respectively. The statistics for CONUS are consistent with the
448 underpredictions of OC at the above sites.
449
450 **3.4 Differences in Aerosol-Cloud Predictions for 2006 and 2010**
451 Figure 15 shows NMBs vs. NMEs of several aerosol and cloud variables for JFD and JJA
452 in 2006 and 2010 against satellite data. Table 1 lists the annual statistics of the aerosol and cloud
453 variables against MODIS for 2010. The trends of NMBs and NMEs are quite similar for both
454 seasons in both years. For JJA 2006 and 2010, all cloud variables are underpredicted. For JJA,
455 the model performs better for 2010 for CF, AOD, and COT in terms of seasonal mean spatial
456 distribution. For JFD, the model performs better for CF and CWP in 2010. In terms of annual
457 statistics, 2010 has lower NMBs for CF and COT compared to 2006. Despite the general worse
458 performance of meteorological and chemical variables in 2010 compared to 2006, performance

of cloud variables do not vary significantly. One possible reason is because the evaluation of aerosol-cloud variables is based on monthly values that are averaged out on a seasonal basis. The meteorological and chemical variables shown earlier are evaluated based on site-specific, and hourly, daily, or weekly data. Another reason is that there are still some limitations of the model in simulating the aerosol-cloud feedbacks from meteorology and chemistry. Finally, the responses of aerosol-cloud feedbacks to changes in meteorology and chemistry are on a smaller scale.

4. Responses of 2010 Predictions to Changes in Emissions and Meteorology

The changes in emissions, boundary conditions, and meteorology between 2010 and 2006 lead to changes in simulated air quality and the chemistry-meteorology feedbacks, which in turn change meteorological and air quality predictions during the next time step, which are described below.

4.1 Air Quality Predictions

Simulated air quality responds nonlinearly to the changes in emissions. Figures 16, 17, A3, and A4 show the seasonal changes between 2010 and 2006 in ambient mixing ratios of gases (SO_2, NO_2, NH_3, O_3, and OH) and concentrations of PM species (SO_4^{2-}, NO_3^-, NH_4^+, OM, EC, POA, ASOA, BSOA, and $PM_{2.5}$). SO_2 and NO_2 concentrations tend to decrease for all seasons at most locations over CONUS due to the decrease in their emissions. The increases in NO_2 concentrations over urban areas in eastern U.S. in MAM in 2010 relative to 2006 could be due to a few reasons including decreased photolytic conversion from NO_2 to NO due to a decrease in SWDOWN and less NO_2 conversion to nitrate radical (NO_3) due to decreased OH

concentrations. The NO_2 hotspots also correlate to the decrease in O_3 concentrations in urban areas. This could indicate an increased titration of O_3 by NO. This is an important result for policy implications, as reducing NO_x emissions may reduce NO_2 concentrations overall for CONUS, but may not reduce NO_2 concentrations in several areas, especially in urban areas due to a combination of titration and complex interplay with local meteorology. NH_3 mixing ratios generally decrease in the U.S., except over eastern U.S. in MAM and SON, where there are increases. NH_3 emissions decrease, however, over eastern U.S. in all seasons. The increase in NH_3 concentrations in MAM and SON could be attributed to a number of reasons including less NH_3 conversion to NH_4^+ to neutralize SO_4^{2-} and NO_3^- and less dispersion of NH_3 concentrations due to decreased wind speeds over eastern and southeastern U.S. in MAM and SON, respectively, in 2010 compared to 2006. In JJA and SON, high OM concentrations in Canada are attributed to the enhanced impacts of BCONs by increasingly convergent flow in this region. OM is made up of both POA and SOA. An increase in VOC emissions in eastern U.S. in MAM and SON leads to increases in OM concentrations. Decreases in VOC emissions in western U.S. for all seasons lead to decreases in OM concentrations. The OM concentrations in some areas do not follow a linear relationship with VOC emissions, however, such as southeastern U.S. in JJA, where VOC emissions increase from 2006 to 2010 but OM concentrations decrease. A decrease in POA concentrations must dominate the overall decrease in OM concentrations, even under increased temperatures and biogenic VOC emissions in this area. $PM_{2.5}$ concentrations decrease for all seasons and most regions of the CONUS, which is attributed mainly to decreases in precursor gases, especially the inorganic precursors SO_2 and NO_x in eastern U.S. Increased $PM_{2.5}$ concentrations in JFD and MAM in the Midwest are due to surface temperature decreases,

dominating in this region (Stoeckenius et al., 2014). This in turn leads to increased particle nitrate concentrations (Campbell et al., 2014).

4.2 Meteorological Predictions

Figures 17 and A7 show the seasonal changes between 2010 and 2006 in several meteorological and cloud variables SWDOWN, T2, WS10, Precip, PBLH, AOD, COT, CF, CWP, and CDNC). Figure A8 compares wind vectors superposed with T2 in 2006 and 2010. The relationships between various meteorological variables have been discussed in Yahya et al. (2014). Comparing to the differences in predictions of SWDOWN, T2, WS10, Precip, and PBLH between 2010 and 2006 WRF only simulation (without chemistry-meteorology feedbacks) shown in Figure 3 and those between 2010 and 2006 WRF/Chem simulations (with chemistry-meteorology feedbacks) (see SWDOWN in Figure 17 and other variables in Figure A7), the differences in those meteorological variables except for SWDOWN do not vary significantly between 2010 and 2006 WRF simulations and between 2010 and 2006 WRF/Chem simulations. As shown in Figure 17, the decrease in SWDOWN from 2006 to 2010 is larger over north-central and north-western U.S. and the increase in SWDOWN is smaller over north-eastern and southwestern U.S. for MAM (WRF/Chem) compared to MAM (WRF). For SON, the increase in SWDOWN from 2006 to 2010 simulated by WRF/Chem is larger over eastern U.S. than that by WRF. The differences between WRF and WRF/Chem are the largest for SWDOWN over northeastern U.S. in JFD with an increase in SWDOWN simulated by WRF but a decrease simulated by WRF/Chem from 2006 to 2010. The differences in SWDOWN are likely due to the differences in CF between the two sets of simulation pairs, as the spatial distribution for CF is consistent with that of SWDOWN.

The increase in SWDOWN from 2006 to 2010 does not necessarily translate to an increase in T2. However, in general, increases in SWDOWN lead to increase in T2, as shown in SON in Figure A7, where SWDOWN generally increases over most of the continental U.S., T2 also increases over most of CONUS. In general, the largest differences in T2 between 2006 and 2010 occur in SON (increase) and JFD (decrease). The decrease in T2 in JFD in north-central U.S. and parts of Canada is significant as it results in a decrease in WS10 and PBLH. For JJA, there is an obvious pattern between SWDOWN and Precip, with an increase in SWDOWN corresponding to a decrease in Precip and vice versa. According to IPCC (2007), in the warm seasons over land, strong negative correlations dominate as increased sunshine results in less evaporative cooling. The largest differences in wind vectors as shown in Figure A8 between 2006 and 2010 are in JJA. JJA 2006 has strong northwesterly winds over the coast in the northwestern portion of the domain while for JJA 2010; over the same area the winds are weak and westerly. Over the coast in the eastern portion of the domain, winds are southerly for JJA 2006 but westerly for JJA 2010. For SON, off the eastern coast, the westerly winds are stronger for 2010 compared to 2006. Other than these obvious differences, the seasonally averaged wind patterns are similar for 2006 and 2010.

As expected, the spatial pattern of SWDOWN changes is anti-correlated with CF changes for all seasons between 2006 and 2010, however, the changes in the spatial pattern of CF do not correlate with changes in CDNC. CF in each grid cell is set to either 0 (no clouds), or to 1 (cloudy) if total cloud water + ice mixing ratio > 1×10^{-6} kg kg^{-1} (Wu and Zhang, 2005). In this study, the monthly CF is then normalized over the total number of time steps and vertical layers, giving a value of CF between 0 and 1 in each grid cell. In contrast, the calculations of CDNC in the model depend on the supersaturation, aerosol concentrations, aerosol hygroscopicity and

updraft velocity (Abdul-Razzak and Ghan, 2004). The changes in CF are controlled by large scale state variables including temperature and relative humidity, while CDNC depends on more complex changes in microphysical variables. The dominant CDNC decrease in MAM, JJA, and SON, is due to lower $PM_{2.5}$ concentrations, which in turn lower the effective number of cloud condensation nuclei. However, exception occurs in southeast U.S. where $PM_{2.5}$ decreases but CDNC increases. This is because CDNC also depends on other variables including the amount of liquid water in the atmosphere. The cloud liquid water path over southeastern U.S. increases, which may explain the increase in CDNC. The spatial pattern for precipitation correlates to that of CF. The spatial pattern of CWP also corresponds to a certain extent with CF. PBLH increases when the ground warms up during the day and decreases when the ground cools so PBLH might be intuitively related to SWDOWN and T2. However, we do not see this consistent trend in the plots. This is because the growth of the PBL in the model also depends on the surface sensible latent and heat fluxes and the entrainment of warmer air from the free troposphere (Chen, 2007).

4.3 Meteorology-Chemistry Feedback Predictions

As shown in Table 1, similar to 2006, comparison of the performance of most meteorological variables between WRF/Chem and WRF for 2010 is improved in terms of NMBs when chemistry-meteorology feedbacks are included. This indicates the importance and benefits of inclusion of such feedbacks in online-coupled models. However, unlike 2006 for which both WRF only and WRF/Chem simulations show similar values of Corrs and NMEs, the 2010 WRF simulations give higher Corr and lower NMEs than the 2010 WRF/Chem simulations. This indicates the impact of worse chemical predictions on chemistry-meteorology feedbacks that can in turn affect meteorological predictions. These results indicate the needs of further improvement

of the online-coupled models in their representations of chemistry-meteorology feedbacks. Yahya et al. (2014) analyzed differences in meteorological performance between WRF/Chem and WRF for 2006. Figure A8 shows absolute differences between the meteorological predictions from WRF/Chem and WRF for 2010. The differences between WRF/Chem and WRF are consistent for both 2006 and 2010. SWDOWN in general is higher for WRF/Chem compared to WRF for all seasons, with larger differences over the eastern portion of the domain compared to the western portion. Other obvious similarities between 2006 and 2010 include the increase in T2 over the northern portion of the domain for MAM, SON and JFD; increase in PBLH over the ocean in the eastern part of the domain for all seasons; and increases over the ocean for CF for all seasons. The reasons for the differences between WRF/Chem and WRF in terms of meteorological variables have been discussed in Yahya et al. (2014).

5. Summary and Conclusions

This study compares model performance in 2010 and 2006 and examines the changes in emissions, boundary conditions, and meteorology, as well as the responses of meteorology, air quality and chemistry-meteorology feedbacks to those changes between 2010 and 2006. Two representative years are simulated using WRF/Chem-CB05-MADE/VBS with the same model configurations but different emissions and meteorological and chemical ICONs and BCONs. In general, the emissions of most gaseous and aerosol species over CONUS decrease from 2006 to 2010 with the exception of NH_3 emissions over several areas in JFD and biogenic VOCs mainly over eastern U.S. in JJA and SON. The increases in biogenic VOCs are caused by increases in temperatures in 2010 in eastern U.S. during these seasons. The simulated meteorological variables are shown to be significantly influenced by initial conditions. Overall, T2 increases

596 from 2006 to 2010, however the spatial distribution of the increase/decrease of T2 and other
597 meteorological variables including SWDOWN, WS10, PBLH, and Precip vary over CONUS.
598 The differences between WRF/Chem and WRF for both years are the largest for SWDOWN.
599 The reduced emissions and changed meteorological conditions result in decreased concentrations
600 in general for gaseous and aerosol species except for species influenced by high BCONs, e.g., for
601 OM concentrations over Canada in MAM and JJA. Due to increases in biogenic emissions, OM
602 concentrations increase over eastern U.S. CDNC generally decreases over the U.S. due to the
603 decreases in $PM_{2.5}$ concentrations and CCN from 2006 to 2010. The spatial distributions of other
604 meteorological and cloud variables are consistent with known processes, e.g., SWDOWN is high
605 and precipitation is low where CF is low. There is no clear spatial correlation between CF and
606 CDNC due to the differences in the inherent prognostic treatments of CF and CDNC. COT
607 corresponds relatively well to AOD, especially for JJA in both years. CWP also corresponds well
608 to COT. In general, the model performs well in terms of Corr and NMEs for almost all
609 meteorological and chemical variables in 2006 but not as well in 2010 despite lower NMBs for
610 most variables in 2010, due likely to uncertainties in emission estimates and inaccuracies in the
611 simulated meteorology in 2010.

612 OC concentrations are significantly underpredicted against field data for 2010 in
613 Bakersfield and Pasadena, CA, due mainly to underestimations in emissions of POA that
614 contributes to most OC and also in part to underestimations in emissions of gaseous precursors
615 of SOA. Another possible reason would be the inaccuracies in the WRF predictions in 2010. The
616 lower correlation and higher errors in most meteorological predictions in 2010 indicate the
617 model's limitation in accurately capturing extreme events. It is important for the model to
618 reproduce meteorological fields correctly as the chemical fields are dependent on the state of the

atmosphere. Comparing to OC performance, SOA concentrations are predicted relatively well in 2006 and 2010, despite overpredictions in 2006 and underpredictions in 2010. The improvements in predictions of SOA can be attributed to the use of the VBS module which simulates successive oxidation of organic vapors, resulting in higher SOA concentrations compared to traditional SOA models. Similar to 2006, the inclusion of chemistry-meteorology feedbacks reduces NMBs for most meteorological variables in 2010. However, unlike 2006, the 2010 WRF simulations give higher Corr and lower NMEs than the 2010 WRF/Chem simulations. These results indicate a need to further improve the accuracy of the model representations of organic aerosols and chemistry-meteorology feedbacks in the online-coupled models.

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chemistry measurements are provided by several U.S. networks (CASTNET, and NADP). GPCC Precipitation data is provided by the National Oceanic and Atmospheric Administration's Earth System Research Laboratory in the Physical Sciences Division (NOAA/OAR/ESRL PSD), Boulder, Colorado, USA, from their web site at http://www.esrl.noaa.gov/psd/. 2006 and 2010 SOA/OC data at RTP, NC, Bakersfield, CA and Pasadena, CA were provided by John Offenberg, U.S. EPA. Cloud variables were provided by MODIS. We thank Georg Grell, NOAA, Christian Hogrefe, U.S. EPA, Paul Makar, Environment Canada, Christoph Knote, NCAR, and Patrick Campbell, NCSU, for helpful discussions on inputs and outputs of AQMEII model intercomparison. We would also like to acknowledge high-performance computing support from Yellowstone by NCAR's Computational and Information Systems Laboratory, sponsored by the National Science Foundation. This work also used the Stampede Extreme Science and Engineering Discovery Environment (XSEDE) high-performance computing support which is supported by the National Science Foundation grant number ACI-1053575.

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References

Abdul-Razzak, H., Ghan, S.J., 2000. A parameterization of aerosol activation, 2. Multiple aerosol types, J. Geophys. Res., 105(5), 6837-6844.

663 Ahmadov, R., et al., 2012. A volatility basis set model for summertime secondary organic
664 aerosols over the eastern United States in 2006, J. Geophys. Res., 117, D06301,
665 doi:10.1029/2011JD016831.
666 Aitken et al., 2008. O/C and OM/OC ratios of primary, secondary and ambient organic aerosols
667 with high-resolution time-of-flight aerosol mass spectrometry, Environ. Sci. Technol., 42,
668 4478-4485.
669 Alapaty et al., 2012. New Directions: Understanding interactions of air quality and climate
670 change at regional scales, Atmos. Environ., 49(3), doi:10.1016/j.atmos.env.2011.12.016.
671 Baklanov et al., 2014. Online Coupled Regional Meteorology-Chemistry Models in Europe:
672 Current Status and Prospects, *Atmospheric Chemistry and Physics*, 14, 317-398,
673 doi:10.5194/acp-14-317-2014.
674 Byun, D., Schere, K.L., 2006. Review of the governing equations, computational algorithms, and
675 other components of the Models-3 Community Multiscale Air Quality (CMAQ) Modeling
676 system, Appl. Mech. Rev., 59, 51-77.
677 Campbell, P., Y. Zhang, K. Yahya, K. Wang, C. Hogrefe, G. Pouliot, C. Knote, A. Hodzic, R.
678 San Jose and J. L. Perez, P. J. Guerrero, R. Baro, and P. Makar, 2014, A Multi-Model
679 Assessment for the 2006 and 2010 Simulations under the Air Quality Model Evaluation
680 International Initiative (AQMEII) Phase 2 over North America, Part I. Indicators of the
681 Sensitivity of O_3 and $PM_{2.5}$ Formation to Precursor Gases, *Atmospheric Environment*, in
682 review.
683 Chen, F., 2007. The Noah Land Surface Model in WRF, A short tutorial, NCAR LSM group
684 meeting, 17 Apr, Boulder, CO.

685 Donahue, N.M., Robinson, A.L., Stanier, C.O., Pandis, S.N., 2006. Coupled partitioning, dilution
686 and chemical aging of semivolatile organics, Environ. Sci. Tech., 40, 2635-2643.
687 Dawson, J. P., Racherla, P. N., Lynn, B. H., Adams, P. J., Pandis, S. N., 2009. Impacts of climate
688 change on regional and urban air quality in the eastern United States: Role of meteorology.
689 Journal of Geophysical Research 114(D05308), doi:10.1029/2008JD009849.
690 Edwards, J.M., Beare, R.J., Lapworth, A.J., 2006. Simulation of the observed evening transition
691 and nocturnal boundary layers: single column modeling, Q.J.R. Meteorol. Soc., 132, 61 – 80.
692 EPA, 2004. National Emission Inventory – Ammonia emissions from animal husbandry
693 operations, Draft Report, January 30,
694 (http://www.epa.gov/ttnchie1/ap42/ch09/related/nh3inventorydraft_jan2004.pdf)
695 Gao, Y., Fu, J.S., Drake, J.B., Liu, Y., Lamarque, J.-F., 2012. Projected changes of extreme
696 weather events in the eastern United States based on a high resolution climate modeling
697 system, Environ. Res. Lett., 7, 044025.
698 Gao, Y., Fu, J. S., Drake, J. B., Lamarque, J. F., Liu, Y., 2013. The impact of emission
699 and climate change on ozone in the United States under representative concentration
700 pathways (RCPs). Atmospheric Chemistry and Physics 13, 9607–9621, doi:10.5194/acp-13-
701 9607-2013.
702 Grell, G.A., Peckham, S.E., Schmitz, R., McKeen, S.A., Frost, G., Skamarock, W.C., Eder, B.,
703 2005. Fully coupled “online” chemistry within the WRF model, Atmos. Environ., 39, 6957 –
704 6975.
705 Grundstein, A., Dowd, J., 2011. Trends in extreme apparent temperatures over the United States,
706 1949 – 2010. J. Appl. Meteor. Climatol., 50, 1650 – 1653.

Guenther, A., Kart, T., Harley, P., Wiedinmyer, C., Palmer, P.I., Geron, C., 2006. Emissions of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181-3210.

Hogrefe, C., Lynn, B., Civerolo, K., Ku, J.-Y., Rosenthal, J., Rosenzweig, C., Goldberg, R., Gaffin, S., Knowlton, K., Kinney, P.L., 2004. Simulating changes in regional air pollution over the eastern United States due to changes in global and regional climate and emissions, J. Geophys. Res., 109, doi: 10.1029/2004JD004690.

Hogrefe, C., Isukapalli, S.S., Tang, X., Georgopoulos, P.S., He, S., Zalewsky, E.E., Hao, W., Ku, J.-Y., Key, T., Sistla, G., 2012. Impact of biogenic emission uncertainties on the simulated response of ozone and fine particulate matter to anthropogenic emission reductions, J. Air. Waste. Manag. Assoc., 61(1), 92-108.

Hogrefe, C., Pouliot, G., Wong, D., Torian, A., Roselle, S., Pleim, J., Mathur, R., 2014. Annual application and evaluation of the online coupled WRF-CMAQ system over North America under AQMEII Phase 2, Atmos. Environ., in review.

Hong, S., Lakshmi, V., Small, E.E., Chen, F., Tewari, M., Manning, K.W., 2009. Effects of vegetation and soil moisture on the simulated land surface processes from the coupled WRF/Noah model. J. Geophys. Res., 114, D18118, doi:10.1029/2008JD011249.

Huber, G.D., Gulledge, J., 2011. Extreme weather and climate change: understanding the link, managing the risk., Pew Centre on Global Climate Change.

IPCC, 2007. Climate change 2007: the physical science basis. In: Solomon, S., Qin, D., Manning, M. (Eds.), Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.

IPCC, 2012. Managing the risks of extreme events and disasters to advance climate change adaptation. A special report of Working Groups I and II of the Intergovernmental on Climate Chang [Field, C.B., Barros, V., Stocker, T.F., Qin, D., Dokken, D.J., Ebi, K.L., Mastrandrea, M.J., Mach, K.J., Plattner, G.-K., Allen, S.K., Tignor, M., Migley, P.M. (Eds.)], Cambridge University Press, Cambridge, UK, and New York, NY, USA, pp 582.

Im et al., 2014. Evaluation of operational online-coupled regional air quality models over Europe and North America in the context of AQMEII phase 2. Part I: Ozone. Atmospheric Environment, in review.

Jimenez, P., Parra, R., Baldasano, J.M., 2007. Influence of initial and boundary conditions for ozone modeling in very complex terrains: A case study in the northeastern Iberian Peninsula, Environ. Modell. Softw., 22(9), 1294 – 1306.

Jimenez et al., 2009. Evolution of organic aerosols in the atmosphere, *Science.*, *326*, 1525-1529, doi:10.1126/science.1180353.

Jin, J., Miller, N.M., Schlegel, N., 2010. Sensitivity study of four land surface schemes in the WRF model, Adv. Met., 2010, doi: 10.1155/2010/167436.

Kleindienst, T.E., Jaoui, M., Lewandowski, M., Offenberg, J.H., Docherty, K.S., 2012. The formation of SOA and chemical tracer compounds from the photooxidation of naphthalene and its methyl analogs in the presence and absence of nitrogen oxides, Atmos. Chem. Phys., 12, 8711 – 8726.

Lee, L.A., Pringle, K.J., Reddington, C.L., Mann, G.W., Stier, P., Spracklen, D.V., Pierce, J.R., Carslaw, K.S., 2013. The magnitude and causes of uncertainty in global model simulations of cloud condensation nuclei, Atmos. Chem. Phys., 13, 8879 - 8914.

751 Leung, L., Gustafson, W., 2005. Potential regional climate change and implications to US air
752 quality. Geophysical Research Letters 32(16), L16711, doi:10.1029/2005GL022911.

753 Lewandowski, M., Piletic, I.R., Kleindienst, T.E., Offenberg, J.H., Beaver, M.R., Jaoui, M.,
754 Docherty, K.S., Edney, E.O., 2013. Secondary organic aerosol characterization at field sites
755 across the United States during the spring-summer period, Intern. J. Environ. Anal. Chem.,
756 2013.

757 Makar et al., 2014, Feedbacks between Air Pollution and Weather, Part 1: Effects on Chemistry,
758 Atmospheric Environment, in review.

759 Mass, C., Owens, D., 2010. WRF Model Physics: Progress, problems and perhaps some
760 solutions, Presented at the 11th WRF Users' Workshop, June 21 – 25, Boulder, CO.

761 Meir, T., Orton, P.M., Pullen, J., Holt, T., Thompson, W.T., Arend, M.F., 2013. Forecasting the
762 New York City Urban Heat Island and Sea Breeze during Extreme Heat Events, Wea.
763 Forecasting, 28, 1460 – 1477.

764 Murphy, B.N., Pandis, S.N., 2009. Simulating the Formation of Semivolatile Primary and
765 Secondary Organic Aerosol in a Regional Chemical Transport Model., Environ. Sci. Tech.,
766 43, 4722-4728.

767 Odum, J.R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R.C., Seinfeld, J.H., 1996.
768 Gas/Particle partitioning and secondary organic aerosol yields, Environ. Sci. Tech., 30, 2580-
769 2585.

770 Offenberg, J.H., Lewandowski, M., Jaoui, M., Kleindienst, T.E., 2011. Contributions of biogenic
771 and anthropogenic hydrocarbons to secondary organic aerosol during 2006 in Research
772 Triangle Park, NC, Aero. Air Qual. Res., 11, 99 - 108.

773 Oswald, E.M., Rood, R.B., 2014. A trend analysis of the 1930 – 2010 extreme heat events in the
774 continental United States, J. Appl. Meteor. Climatol., 53, 565 – 582.
775 Penrod, A., Y. Zhang, K. Wang, S.-Y. Wu, and R. L. Leung, 2014. Impacts of Future
776 Climate and Emission Changes on U.S. Air Quality, Atmospheric Environment, 89, 533-
777 547.
778 Pouliot, G., Hugo Denier can der Gon, J. Kuenen, P. Makar, J. Zhang, M. Moran (2014),
779 Analysis of the Emission Inventories and Model-Ready Emission Datasets of Europe and
780 North America for Phase 2 of the AQMEII Project, Atmospheric Environment, in review.
781 Pun B.K., Wu, S.-Y., Seigneur, C., Seinfeld, J.H., Griffin, R.J., Pandis, S.N., 2003. Uncertainties
782 in Modeling Secondary Organic Aerosols: Three-Dimensional Modeling Studies in
783 Nashville/Western Tennessee, Environ. Sci. Technol., 37, 3647-3661.
784 Rao, S., S. Galmarini, and D. G. Steyn (2012a), AQMEII: An International Initiative for the
785 Evaluation of Regional-Scale Air Quality Models-Phase 1, Atmospheric Environment,
786 Special Issue, 53, 1 – 224.
787 Rasmussen, D.J., Fiore, A.M., Naik, V., Horowitz, L.W., McGinnis, S.J., Schultz, M.G., 2012.
788 Surface ozone-temperature relationships in the eastern US: A monthly climatology for
789 evaluating chemistry-climate models, Atmos. Environ., 47, 142 – 153.
790 Reid, J.S., Koppmann, R., Eck, T.F., Eleuterio, D.P., 2005. A review of biomass burning
791 emissions part II: intensive physical properties of biomass burning particles, Atmos. Chem.
792 Phys., 5, 799 – 825.
793 Samaali, M., Moran, M.D., Bouchet, V.S., Pavlovic, R., Cousineau, S., Sassi, M., 2009. On the
794 influence of chemical initial and boundary conditions on annual regional air quality model
795 simulations for North America, Atmos. Environ., 43(32), 4873 – 4885.

796 Sarwar, G., Fahey, K., Napelenok, S., Roselle, S., Mathur, R., 2011. Examining the impact of
797 CMAQ model updates on aerosol sulfate predictions, the 10th Annual CMAS Models-3
798 User's Conference, October, Chapel Hill, NC.
799 Schell, B., Ackermann, I.J., Hass, H., Binkowski, F.S., Ebel, A., 2001. Modeling the formation
800 of secondary organic aerosol within a comprehensive air quality model system, J. Geophys.
801 Res., 106, 28275 – 28293.
802 Schere, K. et al., 2012. Trace gas/aerosol boundary concentrations and their impacts on
803 continental-scale AQMEII modeling domains, Atmos. Environ., 53, 38-50.
804 Stoeckenius, T., Chemel, C., Zagunis, J., Sakulyanontvittaya, T., 2014. A Comparison between
805 2010 and 2006 Air Quality and Meteorological Conditions, and Emissions and Boundary
806 Conditions for the AQMEII-2 North American Domain, Atmos. Environ., in review.
807 Van Lier-Walqui, M., Vukicevic, T., Posselt, D.J., 2014. Linearization of microphysical
808 parameterization uncertainty using multiplicative process perturbation parameters, Mon.
809 Wea. Rev., 142, 401 – 413.
810 Wang, K., K. Yahya, Y. Zhang, S.-Y. Wu, and G. Grell, 2014. Implementation and Initial
811 Application of A New Chemistry-Aerosol Option in WRF/Chem for Simulation of
812 Secondary Organic Aerosols and Aerosol Indirect Effects, Atmos. Environ., in review.
813 Wu, J., Zhang, M., 2005. Simulations of clouds and sensitivity study by Weather Research and
814 Forecast Model for Atmospheric Radiation Measurement case 4, Fifteenth Arm Science
815 Team Meeting Proceedings, Mar 14 – 18, Daytona Beach, FL.
816 Yahya, K., Wang, K., Gudoshava, M., Glotfelty, T., Zhang, Y., 2014. Application of WRF/Chem
817 over the continental U.S. under the AQMEII Phase II: Comprehensive Evaluation of 2006
818 Simulation, Atmos. Environ, in review.

819 Yang, B., Qian, Y., Lin, G., Leung, L.R., Rasch, P.J., Zhang, G.J., McFarlane, S.A., Zhao, C.,
820 Zhang, Y., Wang, H., Wang, M., Liu, X., 2013. Uncertainty quantification and parameter
821 running in the CAM5 Zhang-McFarlane convection scheme and impact of improved
822 convection on the global circulation and climate, J. Geophys. Res., 118, 395 – 415.
823 Yarwood, G., Rao., S., Yocke, M., Whitten, G.Z., 2005. Updates to the Carbon Bond
824 Mechanism: CB05, Report to the U.S. Environmental Protection Agency, RT-04-00675.
825 Zhang, Y., 2008. Online-coupled meteorology and chemistry models: history, current status, and
826 outlook, Atmos. Chem. Phys., 8, 2895-2932.
827 Zhang, Y., Hu, X., Leung, L. R., W. I. Gustafson Jr., 2008. Impacts of regional climate change
828 on biogenic emissions and air quality. Journal of Geophysical Research 113(D18), D18310,
829 doi:10.1029/2008JD009965.

830 Zhang, Y.**,** Chen, Y.-C., Sarwar, G., Schere, K., 2012. Impact of Gas-Phase Mechanisms on
831 Weather Research Forecasting Model with Chemistry (WRF/Chem) Predictions:
832 Mechanism Implementation and Comparative Evaluation, J. Geophys. Res., 117, D1,
833 doi:10.1029/2011JD015775.
834 Zhang, Y.**,** Wang, W., Wu, S.-Y., Wang, K., Minoura, H., Wang, Z.-F., 2014. Impacts of
835 Updated Emission Inventories on Source Apportionment of Fine Particle and Ozone over
836 the Southeastern U.S., Atmos. Environ., 588, 133-154.
837
838

Table 1. Annual performance statistics for Predictions of WRF/Chem and WRF only sensitivity simulation for 2010

		WRF					WRF/Chem				
Network or Site name	**Variable**	**Mean Obs**	**Mean Sim**	**Corr**	**NMB (%)**	**NME (%)**	**Mean Obs**	**Mean Sim**	**Corr**	**NMB (%)**	**NME (%)**
CASTNET	**T2**	15.9	15.0	0.93	-5.0	15.8	15.9	15.1	0.64	-4.9	32.9
SEARCH	**T2**	19.4	18.4	0.94	-4.3	12.3	19.4	18.4	0.65	-5.1	27.6
CASTNET	**SWDOWN**	176.1	214.7	0.91	21.8	36.2	176.1	189.2	0.80	7.4	50.4
SEARCH	**SWDOWN**	217.7	245.0	0.91	11.5	31.6	217.7	211.0	0.78	-3.0	47.2
CASTNET	**WS10**	2.3	3.0	0.44	28.1	66.4	2.3	2.4	0.14	3.5	84.3
SEARCH	**WS10**	2.2	2.4	0.47	9.6	50.9	2.2	2.4	0.23	8.0	62.3
NADP	**Precip**	18.9	20.7	0.54	10.2	71.2	18.9	19.4	0.10	2.5	112.7
GPCC	**Precip**	2.2	2.3	0.83	1.1	22.6	2.2	2.2	0.83	-1.3	22.0
MODIS	**CF**	57.6	60.4	0.82	6.2	12.7	57.6	57.8	0.87	0.3	8.9
MODIS	**AOD**	-	-	-	-	-	0.10	0.05	-0.09	-46.6	54.4
MODIS	**COT**	-	-	-	-	-	17.2	6.3	0.45	-63.5	63.6
MODIS	**CWP**	-	-	-	-	-	160.1	97.3	0.54	-39.2	54.9
MODIS	**QVAPOR**	-	-	-	-	-	1.04	1.13	0.96	9.0	27.7
MODIS	**CCN**	-	-	-	-	-	0.33	0.09	0.60	-73.2	73.2
TERRA	**CDNC**	-	-	-	-	-	155.0	123.5	0.10	-20.0	59.2
CASTNET	**Max 1-h O_3**	-	-	-	-	-	47.4	33.2	0.40	-30.0	34.8
CASTNET	**Max 8-h O_3**	-	-	-	-	-	43.8	32.7	0.40	-25.3	32.0
AQS	**Max 1-h O_3**	-	-	-	-	-	48.4	40.7	0.34	-15.8	28.0
AQS	**Max 8-h O_3**	-	-	-	-	-	42.3	35.3	0.20	-17.0	29.2
STN	**24-h $PM_{2.5}$**	-	-	-	-	-	11.0	9.7	0.17	-11.5	54.6
IMPROVE	**24-h $PM_{2.5}$**	-	-	-	-	-	4.5	4.0	0.44	-11.5	56.0
STN	**24-h SO_4**	-	-	-	-	-	11.0	9.7	0.17	19.0	68.5
IMPROVE	**24-h SO_4**	-	-	-	-	-	1.0	1.3	0.50	21.1	72.3
STN	**24-h NO_3**	-	-	-	-	-	1.4	0.7	0.10	-45.6	89.1
IMPROVE	**24-h NO_3**	-	-	-	-	-	0.4	0.2	0.30	-43.3	95.5
STN	**24-h NH_4**	-	-	-	-	-	1.0	1.0	0.21	1.5	72.5
STN	**24-h EC**	-	-	-	-	-	0.4	1.0	0.14	147.1	179.5
IMPROVE	**24-h EC**	-	-	-	-	-	0.2	0.3	0.29	78.5	123.8
STN	**24-h TC**	-	-	-	-	-	2.8	2.5	0.10	-11.9	62.0
IMPROVE	**24-h OC**	-	-	-	-	-	0.9	0.6	0.18	-29.6	74.2
IMPROVE	**24-h TC**	-	-	-	-	-	1.0	0.9	0.21	-11.8	72.8
Pasadena, CA[2]	**SOA**	-	-	-	-	-	0.63	0.16	0.1	-75.3	78.3
Bakersfield, CA[2]	**SOA**	-	-	-	-	-	0.51	0.23	0.3	-55.3	65.9

[1] Units are as follows: SWDOWN (W m^{-2}), GLW (W m^{-2}), OLR (W m^{-2}), T2 (ºC), RH2 (%), WS10 (m s^{-1}), WD10 (deg), Precip (mm), CWP (g m^{-2}), QVAPOR (cm), CCN (10^9 cm^{-2}), CDNC (cm^{-2}), O_3 (ppb), PM and PM species (μg m^{-3}). CASTNET - the Clean Air Status and Trends Network; AQS – the Aerometric Information Retrieval System Air Quality System; SEARCH - the Southeastern Aerosol Research and Characterization; GPCC - the Global Precipitation Climatology Centre; MODIS - the Moderate Resolution Imaging Spectroradiometer; IMPROVE – the Interagency Monitoring for Protected Visual Environmental; STN – the Speciated Trends Network. Note that IMPROVE did not contain NH4+ data for 2010. "-" indicates that the results of those variables not available from the WRF only simulation.

[2] The observed SOA data are taken from Klendienst et al. (2012) and Lewandowski et al. (2013).

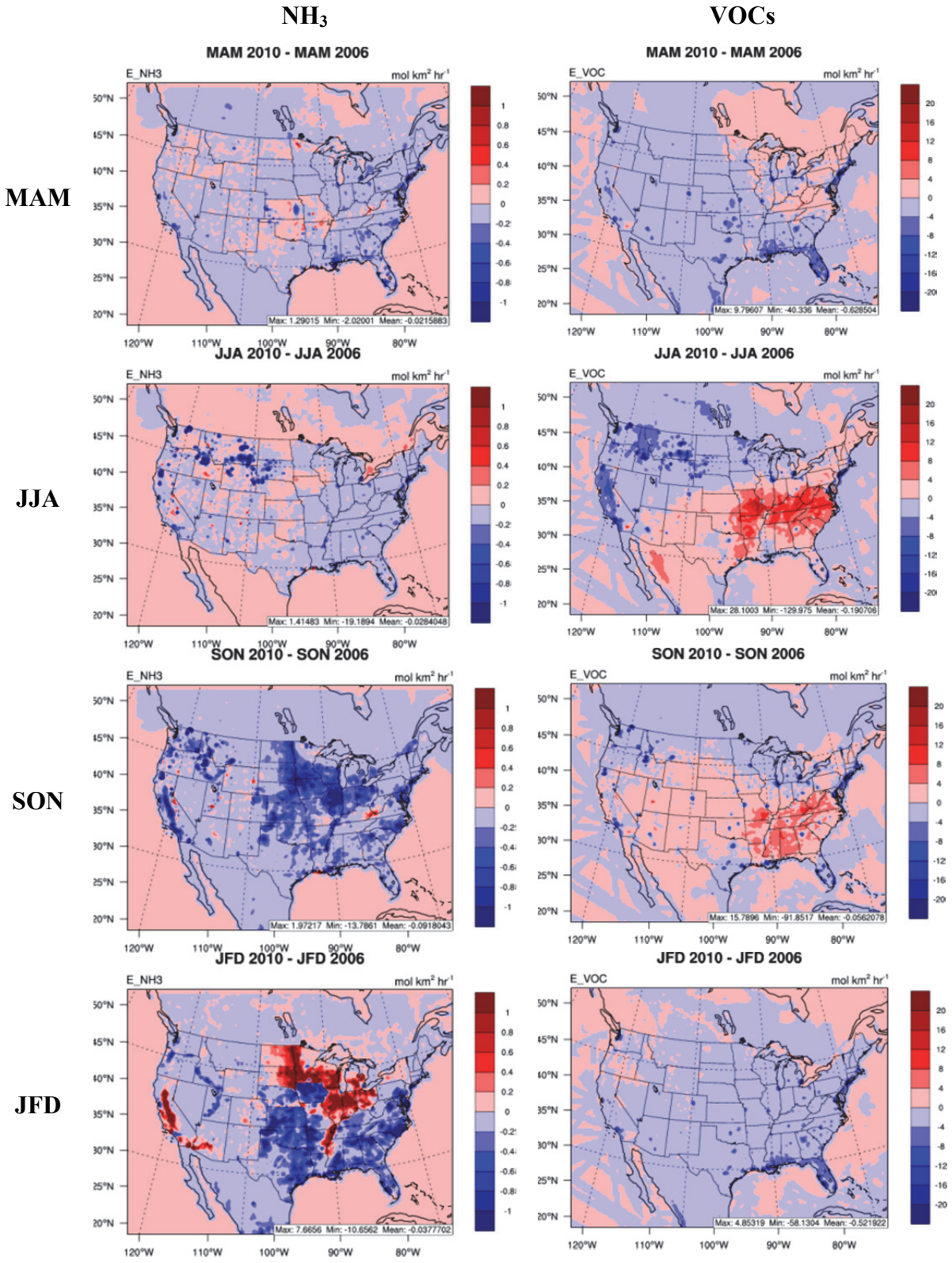


Figure 1. Hourly average emission changes for NH_3 and VOCs from 2010 to 2006 (2010 – 2006).

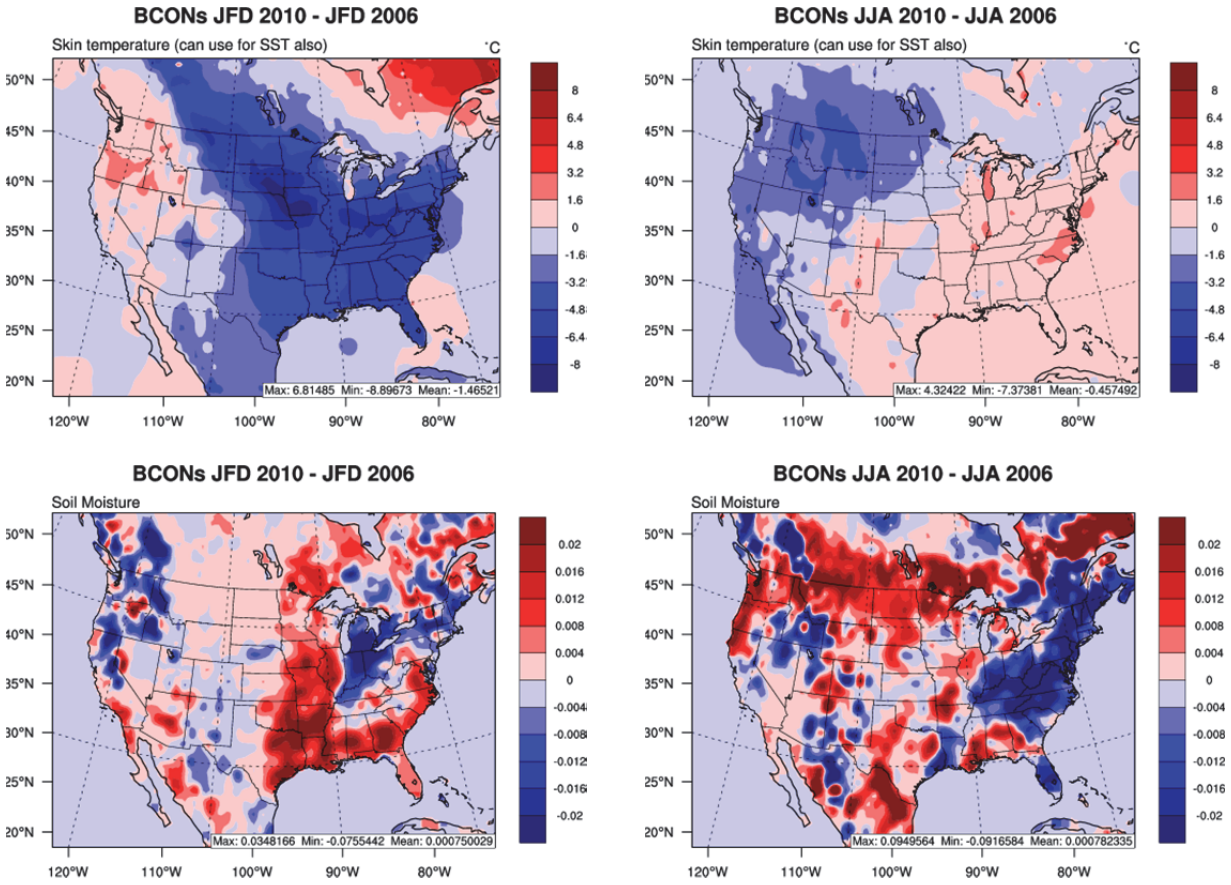


Figure 2. Skin temperature and soil moisture in winter (JFD) and summer (JJA) between 2010 and 2006 extracted from NCEP as boundary conditions for WRF and WRF/Chem simulations.

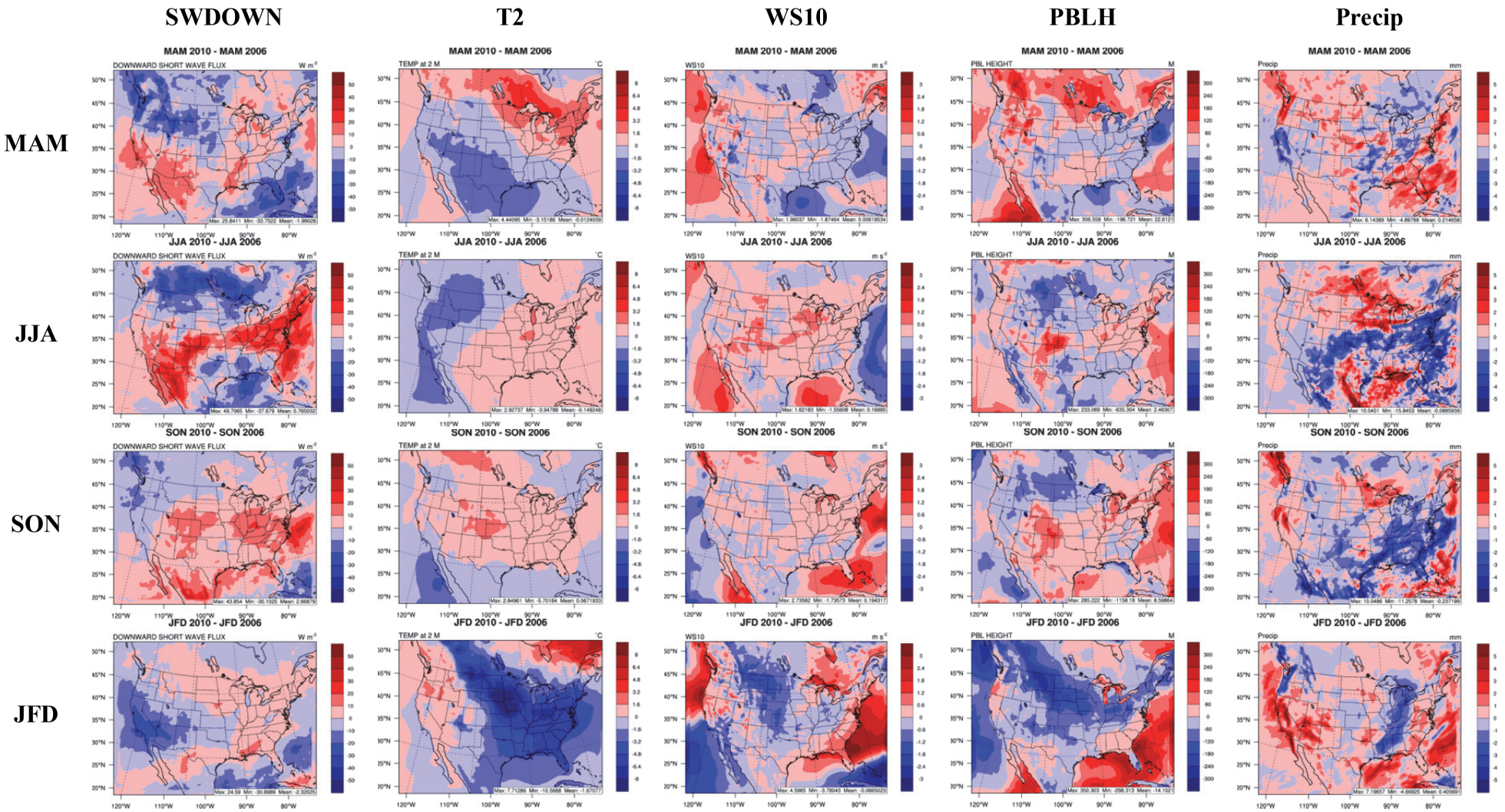


Figure 3. Hourly average changes for meteorological variables from WRF only simulations for 2010 to 2006 (2010 – 2006).

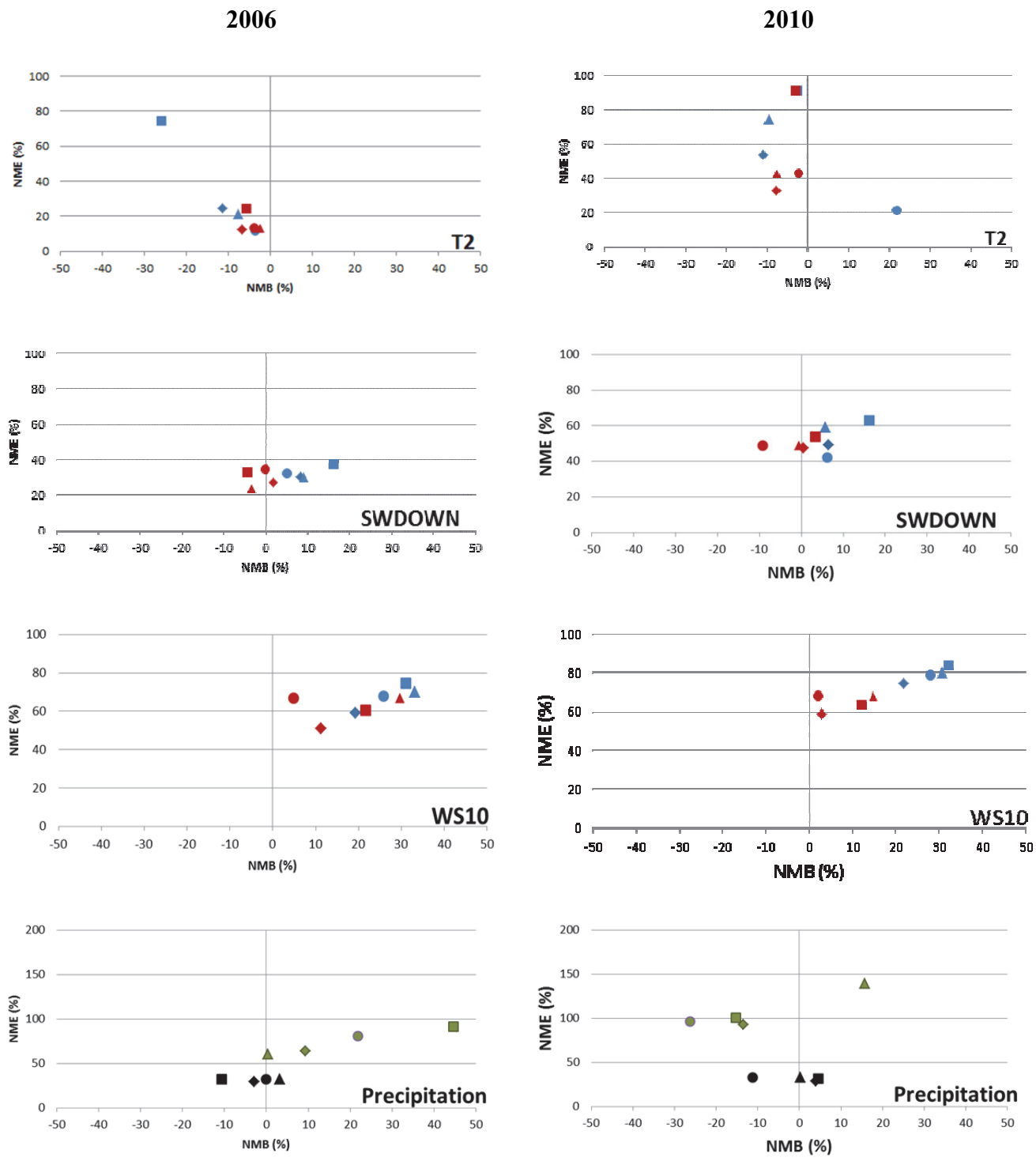


Figure 4. Comparison of seasonal plots of NMB vs NME of various meteorological variables for 2006 (left column) and 2010 (right column) – T2 (temperature at 2m), SWDOWN (downward shortwave radiation), WS10 (wind speed at 10m) and Precipitation where the shapes represent different seasons (diamond – MAM, circle – JJA, triangle – SON and square – JFD) and the different colors represent different observational data (red – SEARCH, blue – CASTNET, green – NADP, black – GPCC).

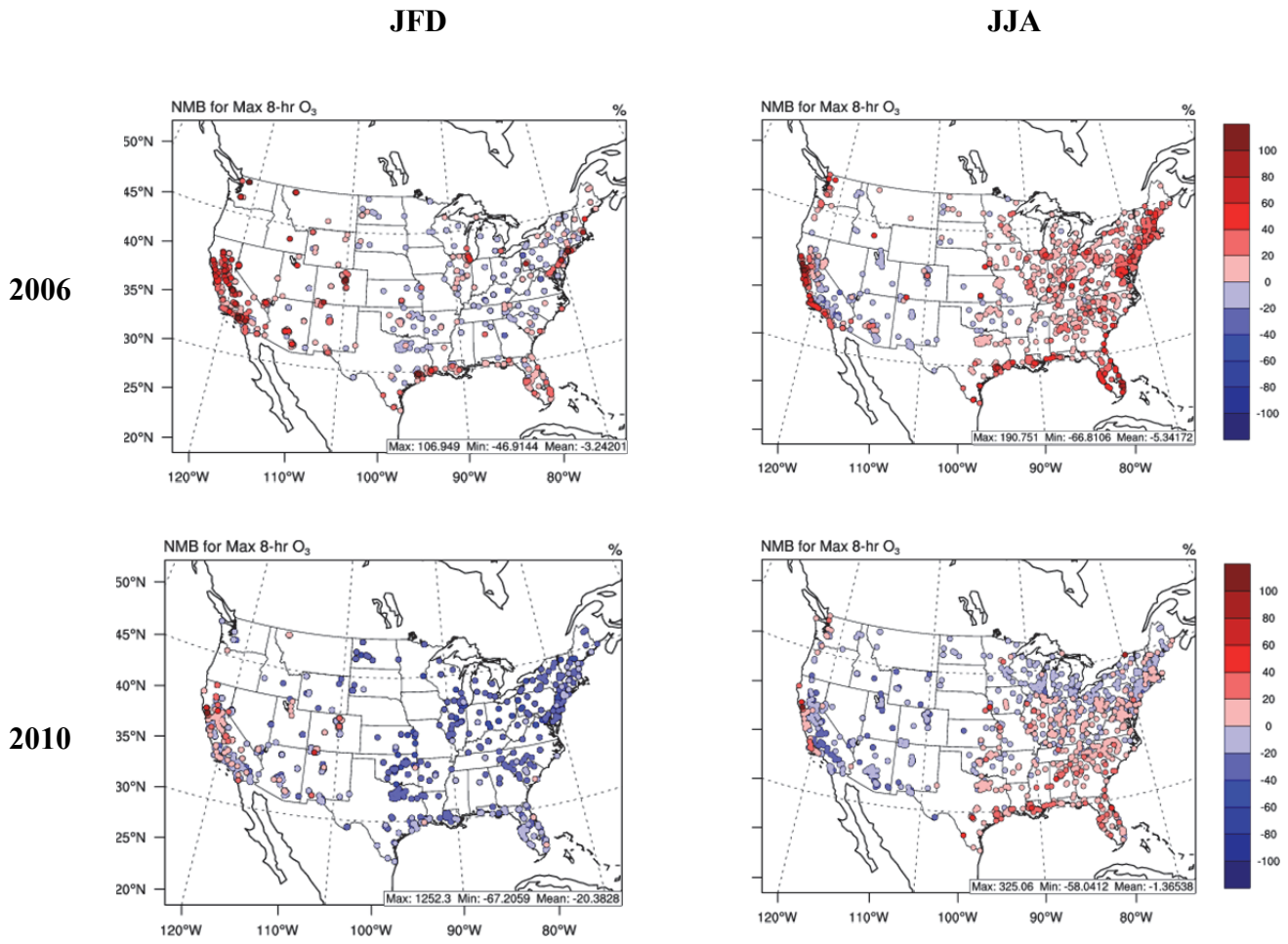


Figure 5. Spatial Distribution of NMB plots for JFD and JJA 2006 and 2010 for maximum 8-hr O_3 concentrations based on evaluation against CASTNET, AQS and SEARCH.

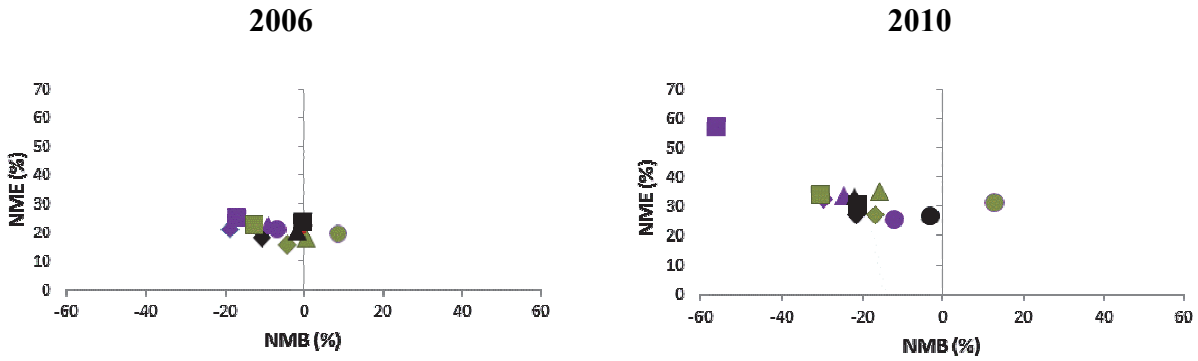


Figure 6. Comparison of seasonal plots of NMB vs NME for maximum 8-hr O_3 concentrations where the different shapes represent different seasons (diamond – MAM, circle – JJA, triangle – SON and square – JFD) and the different colors represent different observational data (purple – CASTNET, black – AQS and green - SEARCH).

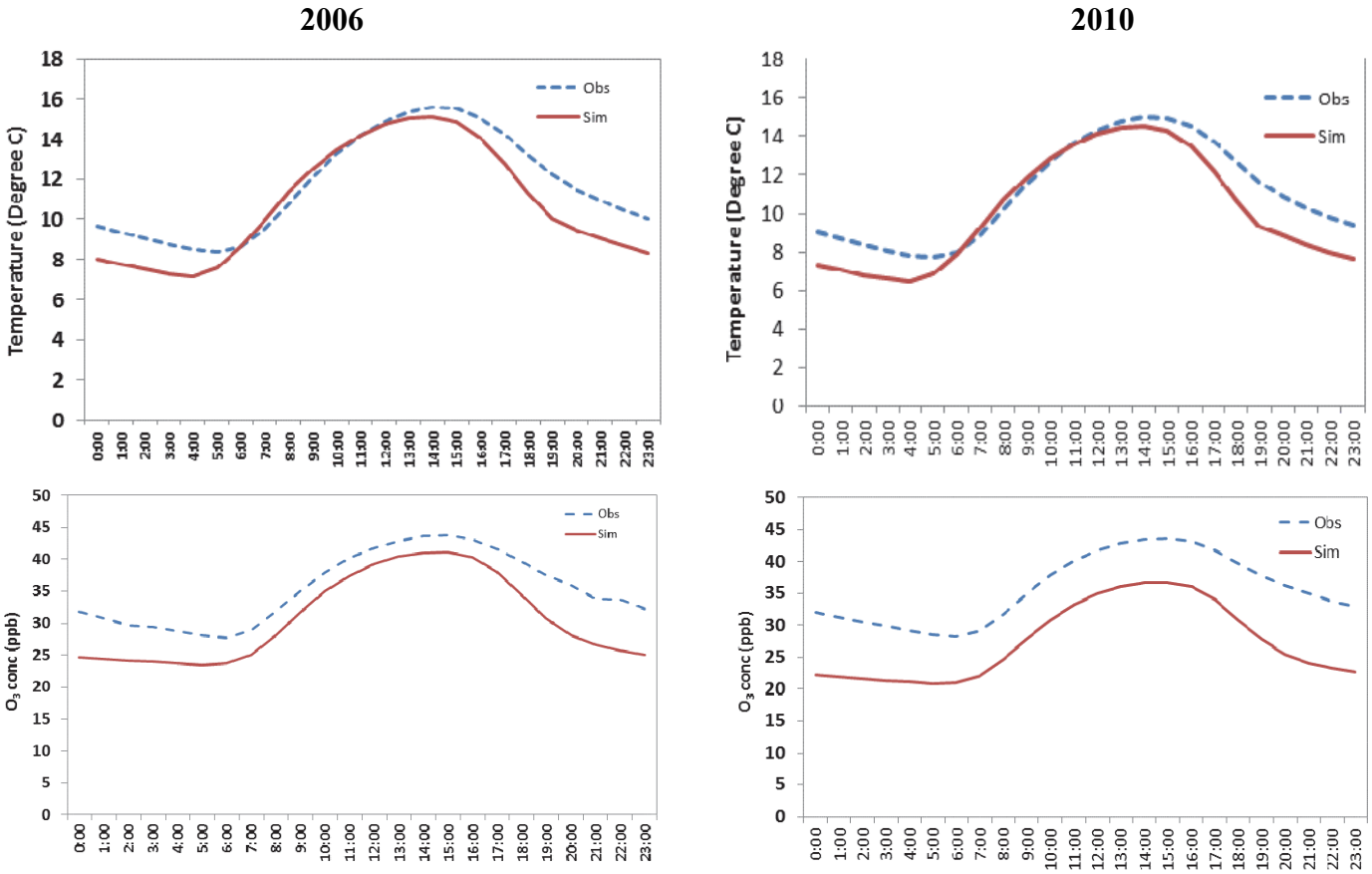


Figure 7. Diurnal variation of T2 (top row) and hourly O_3 concentrations (bottom row) against CASTNET for 2006 and 2010.

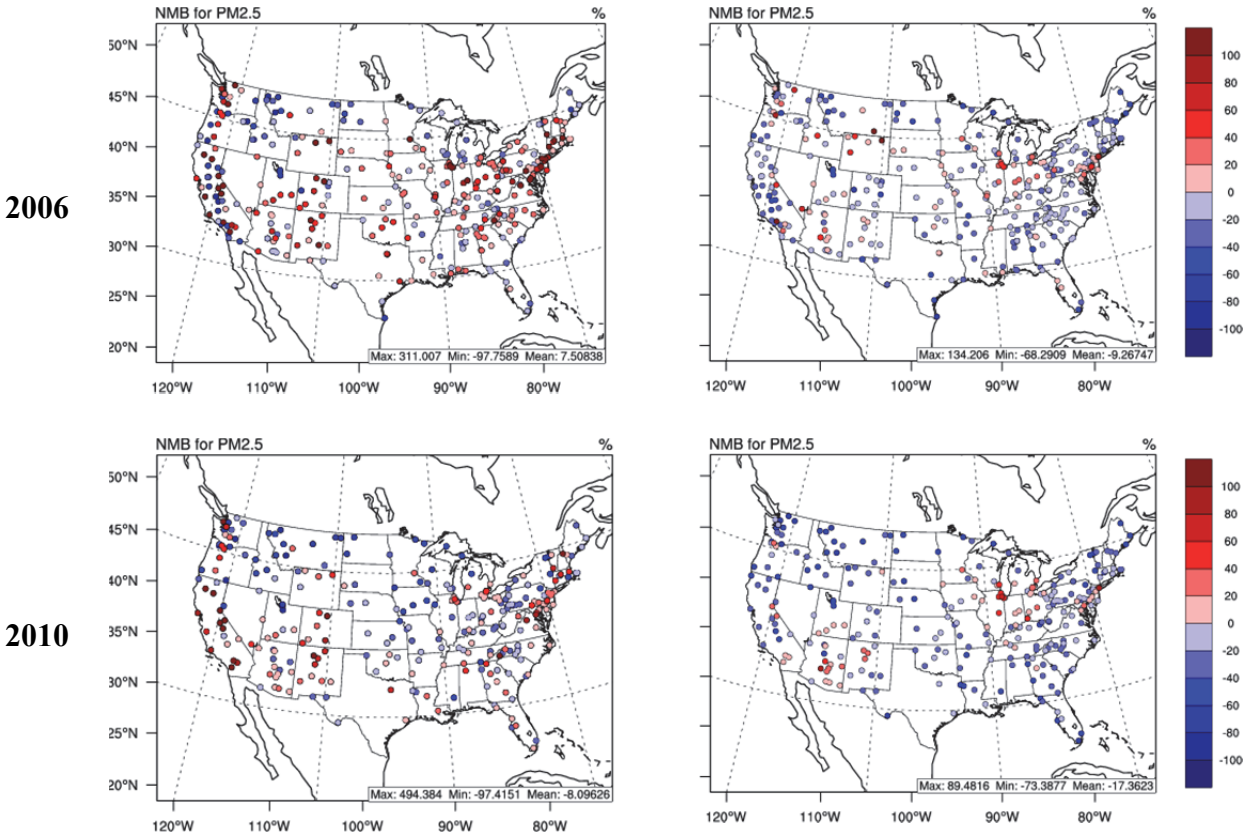


Figure 8. Spatial Distribution of NMB plots for JFD and JJA 2006 and 2010 for average 24-hr $PM_{2.5}$ concentrations based on evaluation against the IMPROVE, STN and SEARCH sites.

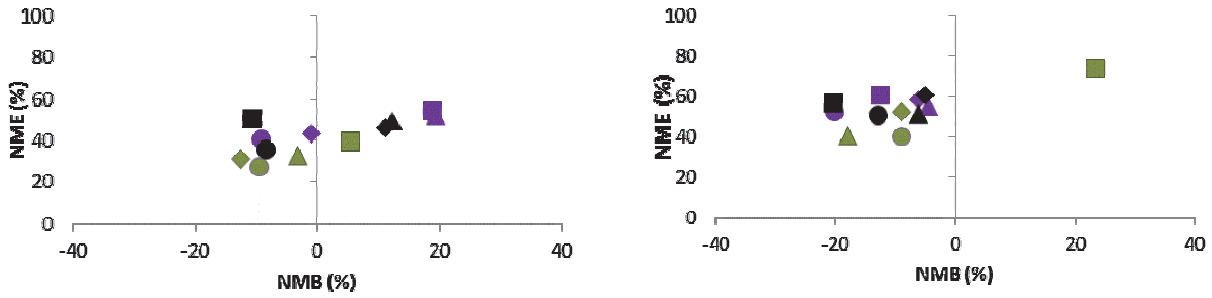


Figure 9. Comparison of seasonal plots of NMB vs NME for average 24-hr $PM_{2.5}$ concentrations where the different shapes represent different seasons (diamond – MAM, circle – JJA, triangle – SON and square – JFD) and the different colors represent different observational data (purple – IMPROVE, black – STN and green - SEARCH).

2006 **2010**

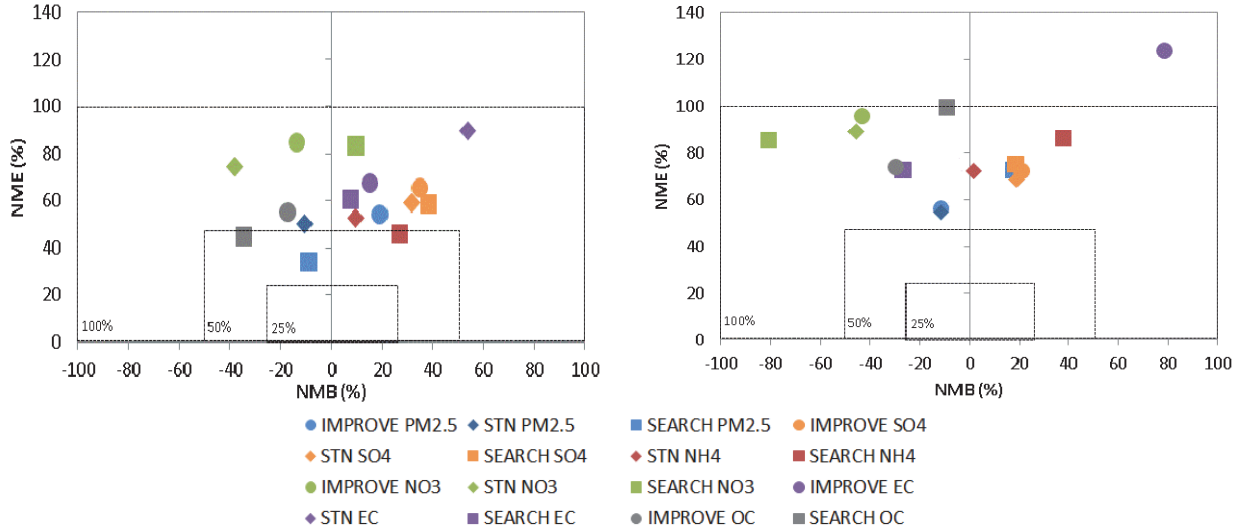


Figure 10. Plots of annual statistics (NMB vs NME) for average 24-hr $PM_{2.5}$ concentrations and $PM_{2.5}$ species against different observational networks.

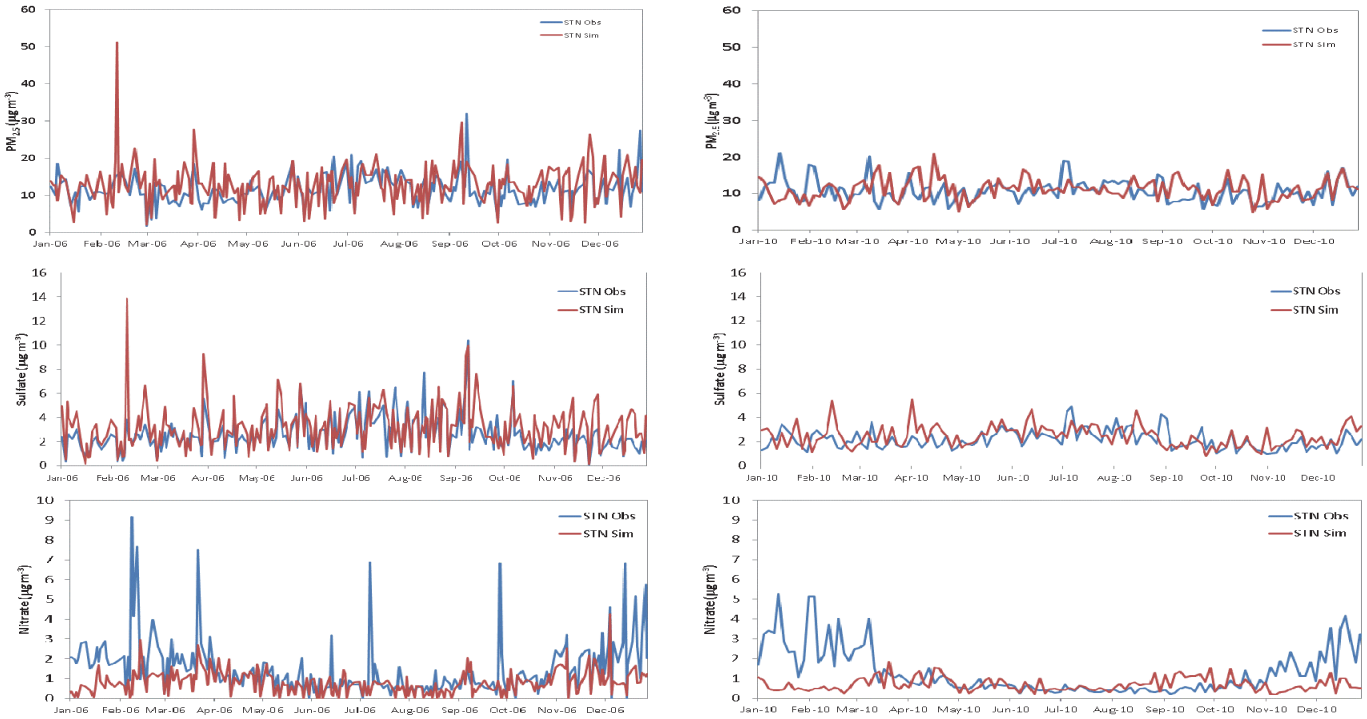


Figure 11. Time series of Obs vs. Sim $PM_{2.5}$, SO_4 and NO_3 concentrations against STN for 2006 and 2010.

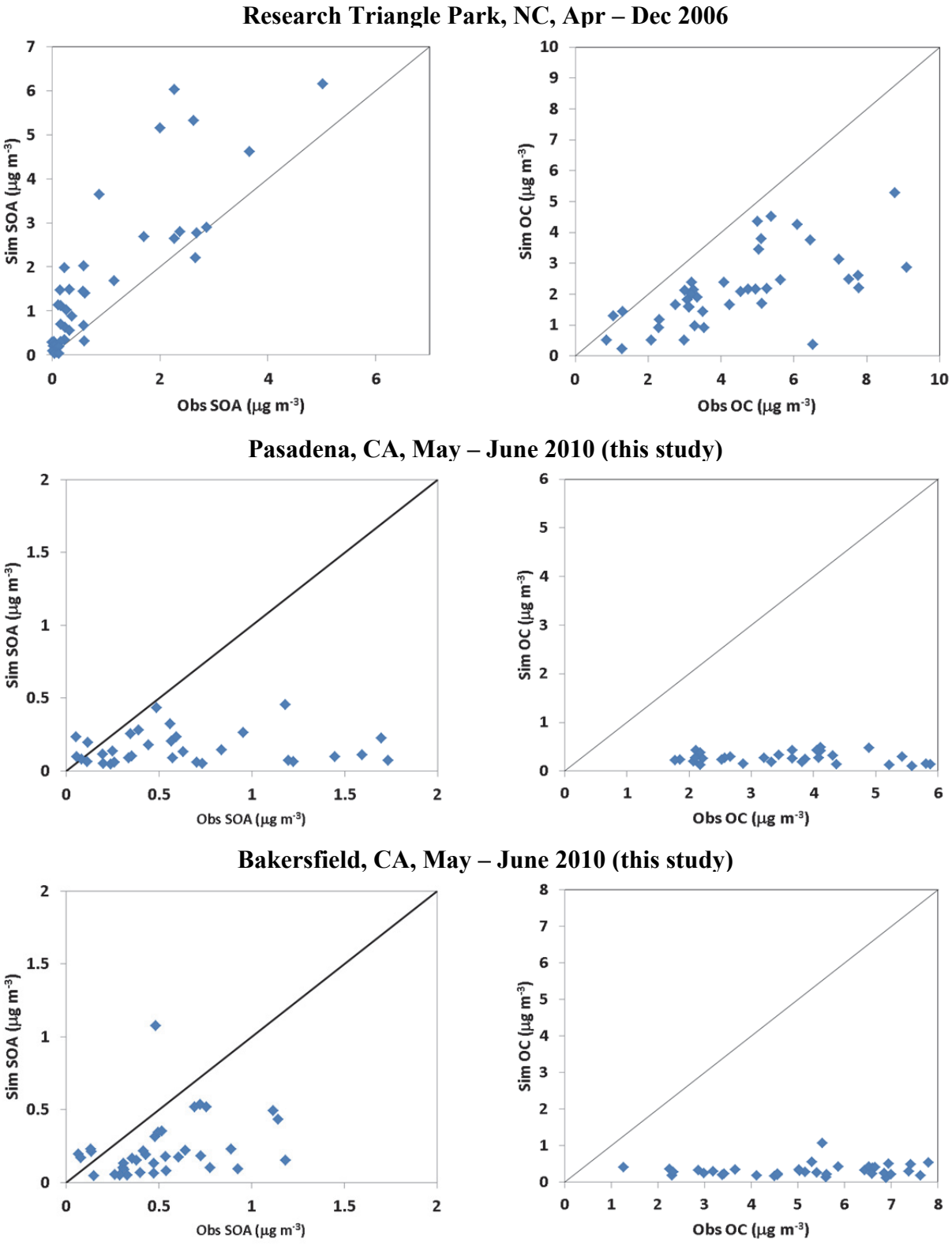
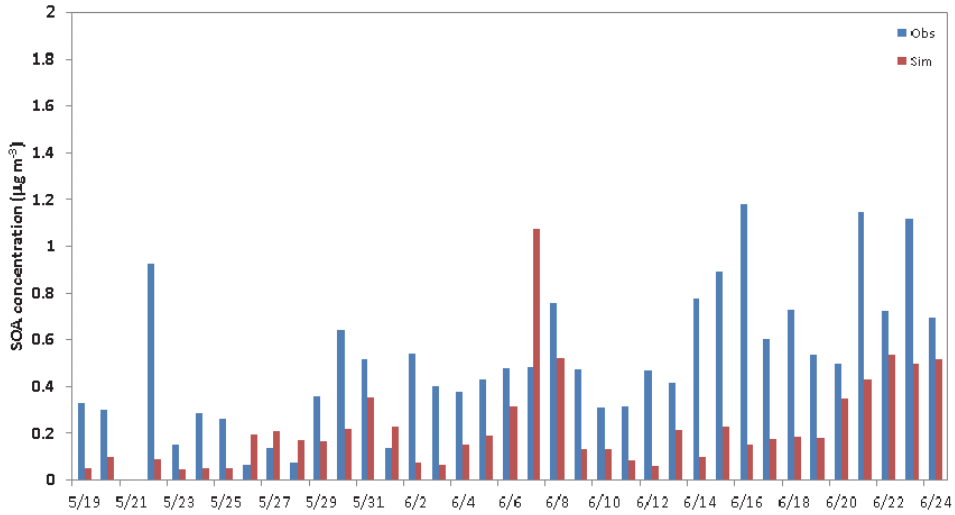
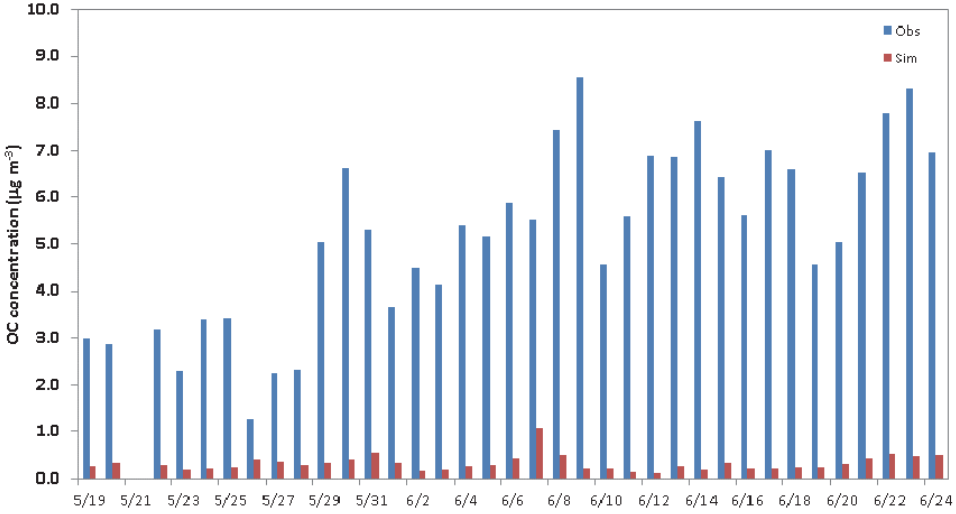


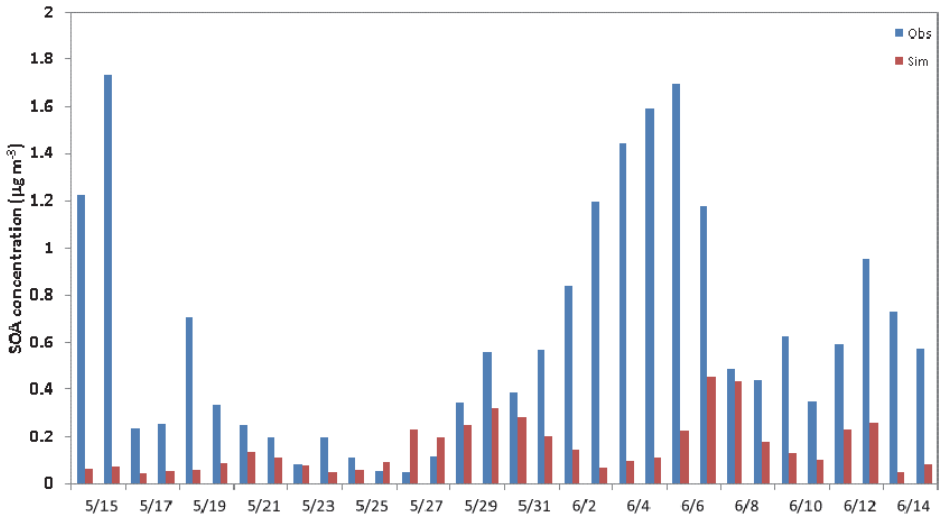
Figure 12. Scatter plots of SOA (left column) and OC (right column) concentrations at various sites.

May – June 2010, Bakersfield, CA





May – June 2010, Pasadena, CA



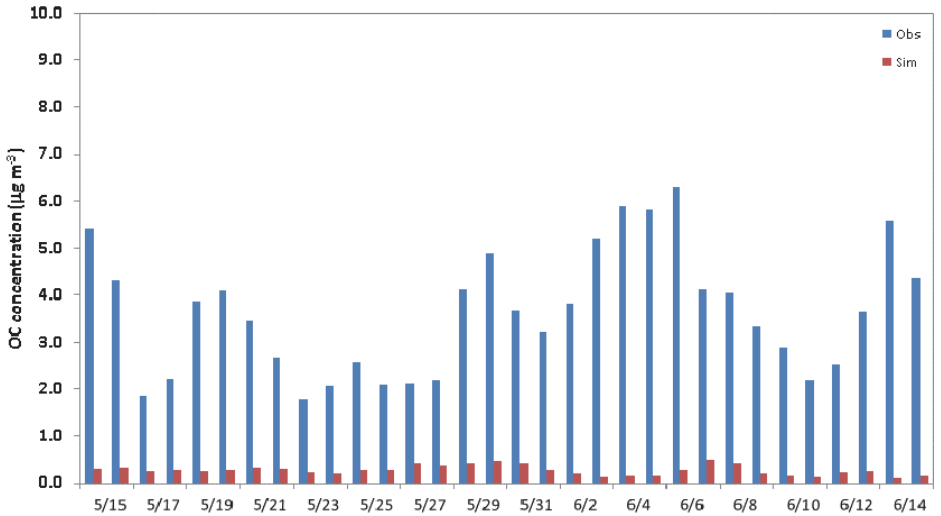


Figure 13. Column Plots of SOA and OC concentrations at Bakersfield, CA and Pasadena, CA from May – June 2010.

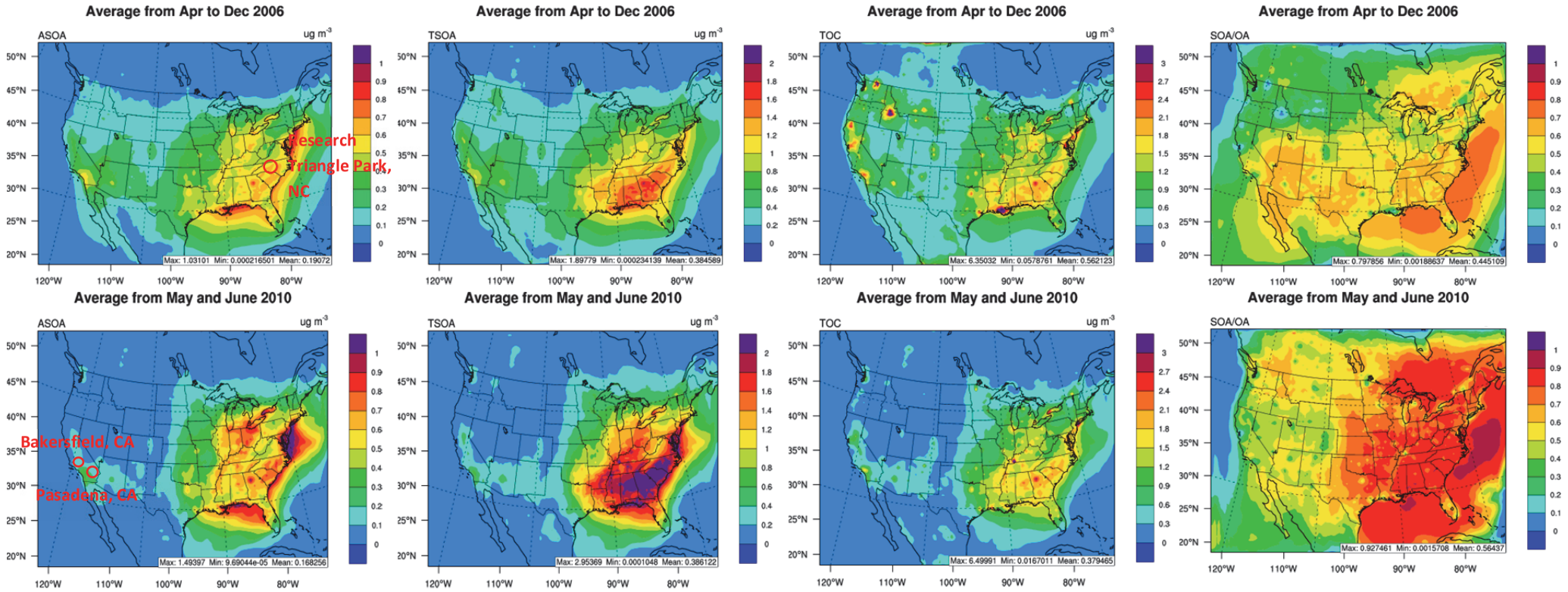


Figure 14. Spatial Distribution plots of average anthropogenic SOA (ASOA), total SOA (TSOA), total OC (TOC) and ratio of SOA/TSOA across months in 2006 and 2010 based on Figure 12.

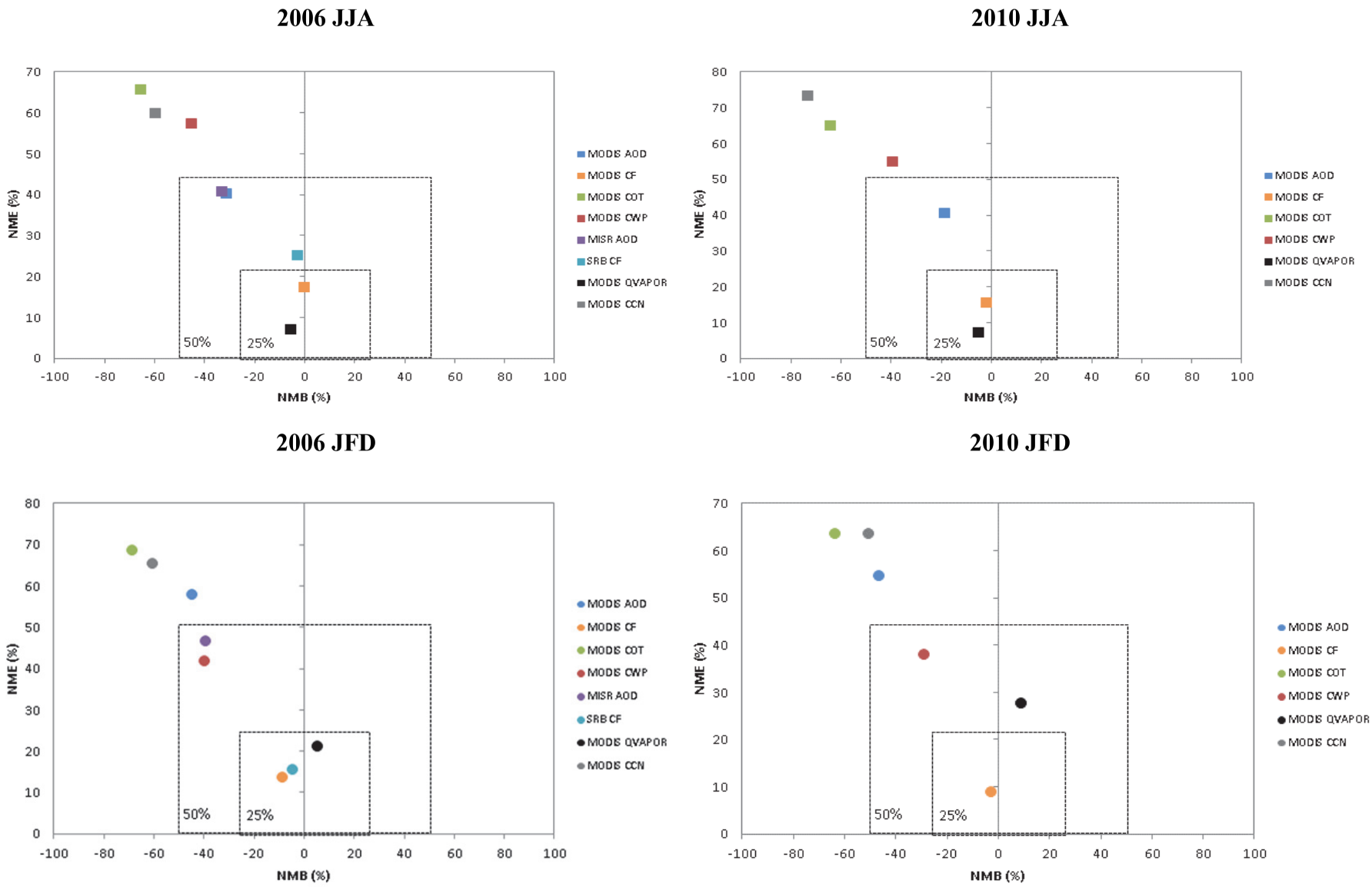


Figure 15. Comparison of soccer plots for JFD and JJA 2006 and 2010 evaluation of aerosol and cloud variables. MISR AOD, and SRB CF obs data was not available for 2010.

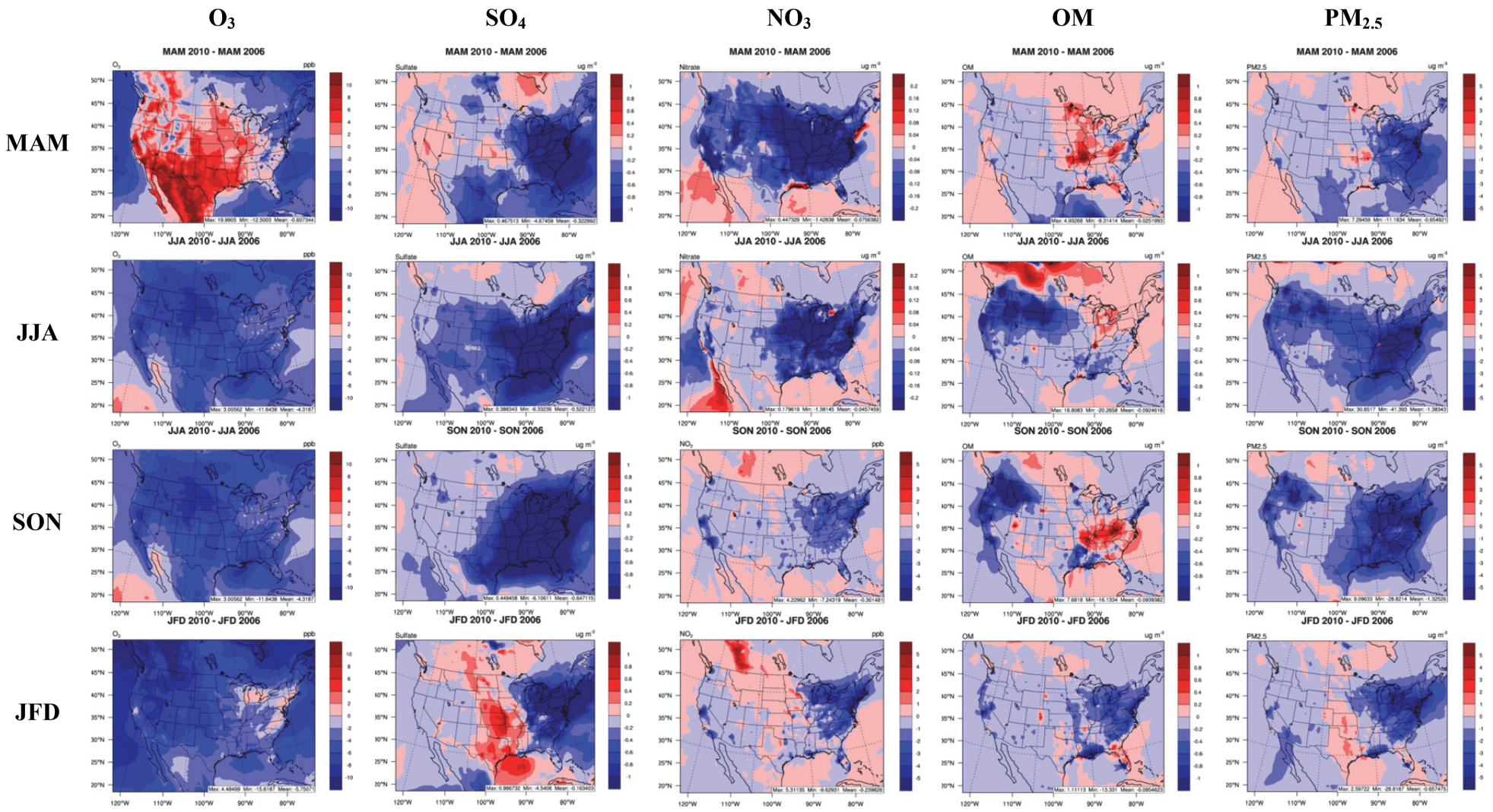


Figure 16. Chanegs in hourly average surface concentrations of O_3 and PM species from 2010 to 2006 (2010 – 2006).

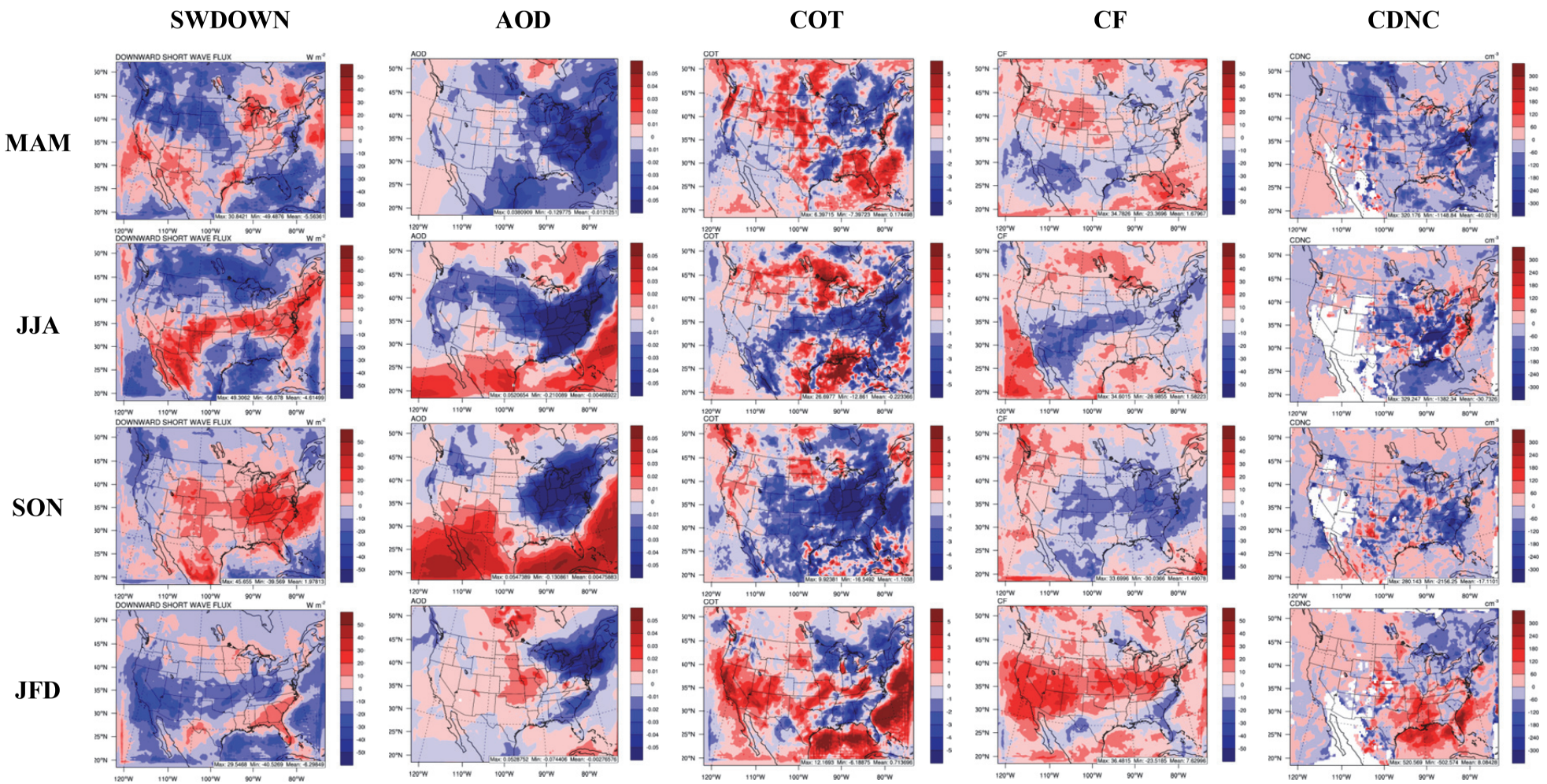


Figure 17. Changes in hourly average predictions of aerosol-cloud variables at surface from WRF/Chem simulations from 2010 to 2006 (2010 – 2006).

Supplementary Material

Application of WRF/Chem over the Continental U.S. under the AQMEII Phase II: Part 2. Evaluation of 2010 Application and Responses of Air Quality and Meteorology-Chemistry Interactions to Changes in Emissions and Meteorology from 2006 to 2010

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1. Emission Trends

Figure A1 shows annual mean hourly average emission changes for SO_2, NO_x, VOCs, NH_3, EC, and POA from 2010 to 2006.

2. Model Evaluation

Figure A2 shows the spatial Distribution of NMB plots for JFD and JJA 2006 and 2010 for T2 based on evaluation against CASTNET and SEARCH.

3. Changes in the concentrations of gas and PM species, the wind vector, and T2 from 2010 to 2006

As shown in Figure A3, SO_2 concentrations tend to decrease for all seasons at most locations (except for several locations in western U.S. in JJA, SON and JFD) over CONUS due to the decrease in SO_2 emissions. The slight increase in SO_2 concentrations over northwestern U.S. in JFD could be due to lower T2, reduced WS10 for dispersion, and decreased PBLH as shown in

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Figure 3. The slight increase in SO_2 concentrations over several locations in SON corresponds to the spatial pattern of reduced precipitation as shown in Figure 3. NO_2 concentrations in general decrease over most parts of CONUS except in parts of Canada in SON and JFD, and in largely populated areas in eastern U.S. in MAM. The large increases in NO_2 concentrations over Canada are a result of increases in NO_2 concentrations from the MACC BCONs, and not likely due to MACC ICONs. Jimenez et al. (2006) reported that a 48-hr spin-up time is sufficient to reduce the impact of ICONs to $\leq 10\%$ for O_3, but the impact of BCONs is more significant and persistent near domain boundaries, consistent with findings from Samaali et al. (2009) and Schere et al. (2012). The 2010 – 2006 increase in NO_2 concentrations over urban areas in eastern U.S. in MAM could be due to a few reasons. Figure A1 shows a decrease in NO_x emissions; however, the decrease in NO_2 emissions over eastern U.S. is very small compared to the decrease in nitrogen oxide (NO) emissions (figure not shown), which had a maximum decrease of ~15 mol km^2 hr^{-1} over eastern U.S. In addition to the decrease in NO emissions, it could also signify decreased photolytic conversion from NO_2 to NO due to a decrease in SWDOWN. Less NO_2 could also have been converted into nitrate radical (NO_3) due to decreased OH concentrations, as Table 1 also shows an overall decrease in NO_3 concentrations. The NO_2 hotspots also correlate to the decrease in O_3 concentrations in urban areas. This could indicate an increased titration of O_3 by NO. This is an important result for policy implications, as reducing NO_x emissions may reduce NO_2 concentrations overall for CONUS, but may not reduce NO_2 concentrations in several areas, especially in urban areas due to a combination of titration and complex interplay with local meteorology. NH_3 mixing ratios generally decrease in the U.S., except over the eastern U.S. in MAM and SON, where there are increases. NH_3 emissions decrease however, over eastern U.S. for all seasons. The increase in

NH_3 concentrations in MAM and SON could be attributed to a number of reasons. Concentrations of NH_4^+ decrease for all seasons over eastern U.S. with the largest decreases in MAM and JJA. This could mean that less NH_3 is converted to NH_4^+, especially for MAM and SON over eastern U.S. due to increases in T2 (as shown in Figure 3), which shifts the partitioning towards the gas-phase rather than the particulate phase. Second, as shown in Figures 16 and A4, SO_4^{2-} concentrations decrease the most over eastern U.S. in SON, which means that less NH_4^+ is needed to neutralize SO_4^{2-}. As shown in Figures A5 and A6, nitric acid (HNO_3) concentrations decrease over eastern U.S. in MAM and SON. The decrease in HNO_3 concentrations results in decreases in NO_3^- concentrations over eastern U.S., which means that less NH_4^+ is used up in neutralizing NO_3^-. Less NH_4^+ required for neutralization would mean that more NH_3 remained in the gas phase. Third, as shown in Figure A7, wind speeds decrease over eastern and southeastern U.S. for MAM and SON, respectively, in 2010 compared to 2006, which could result in less dispersion of NH_3 concentrations over eastern U.S. In JJA and SON, high OM concentrations in Canada are attributed to the enhanced impacts of BCONs in JJA by increasingly convergent flow in this region. OM is made up of both POA and SOA. An increase in VOC emissions in eastern U.S. in MAM and SON leads to increases in OM concentrations. Decreases in VOC emissions in western U.S. for all seasons lead to decreases in OM concentrations. The OM concentrations in some areas do not follow a linear relationship with VOC emissions, however, such as southeastern U.S. in JJA, where VOC emissions increase from 2006 to 2010 but OM concentrations decrease. A decrease in POA concentrations must dominate the overall decrease in OM concentrations, even under increased temperatures and biogenic VOC emissions in this area. $PM_{2.5}$ concentrations decrease for all seasons and most regions of the CONUS, which is attributed mainly to decreases in precursor

gases, especially the inorganic precursors SO_2 and NO_x in eastern U.S. Increased $PM_{2.5}$ concentrations in JFD and MAM in the Midwest are due to surface temperature decreases, dominating in this region (Stoeckenius et al., 2014). This in turn leads to increased particle nitrate concentrations (Campbell et al., 2014).

4. Differences between predictions of meteorological variables by WRF/Chem and WRF

Figure A8 shows absolute Differences between predictions of meteorological variables by WRF/Chem and WRF (WRF/Chem – WRF) simulations for 2010.

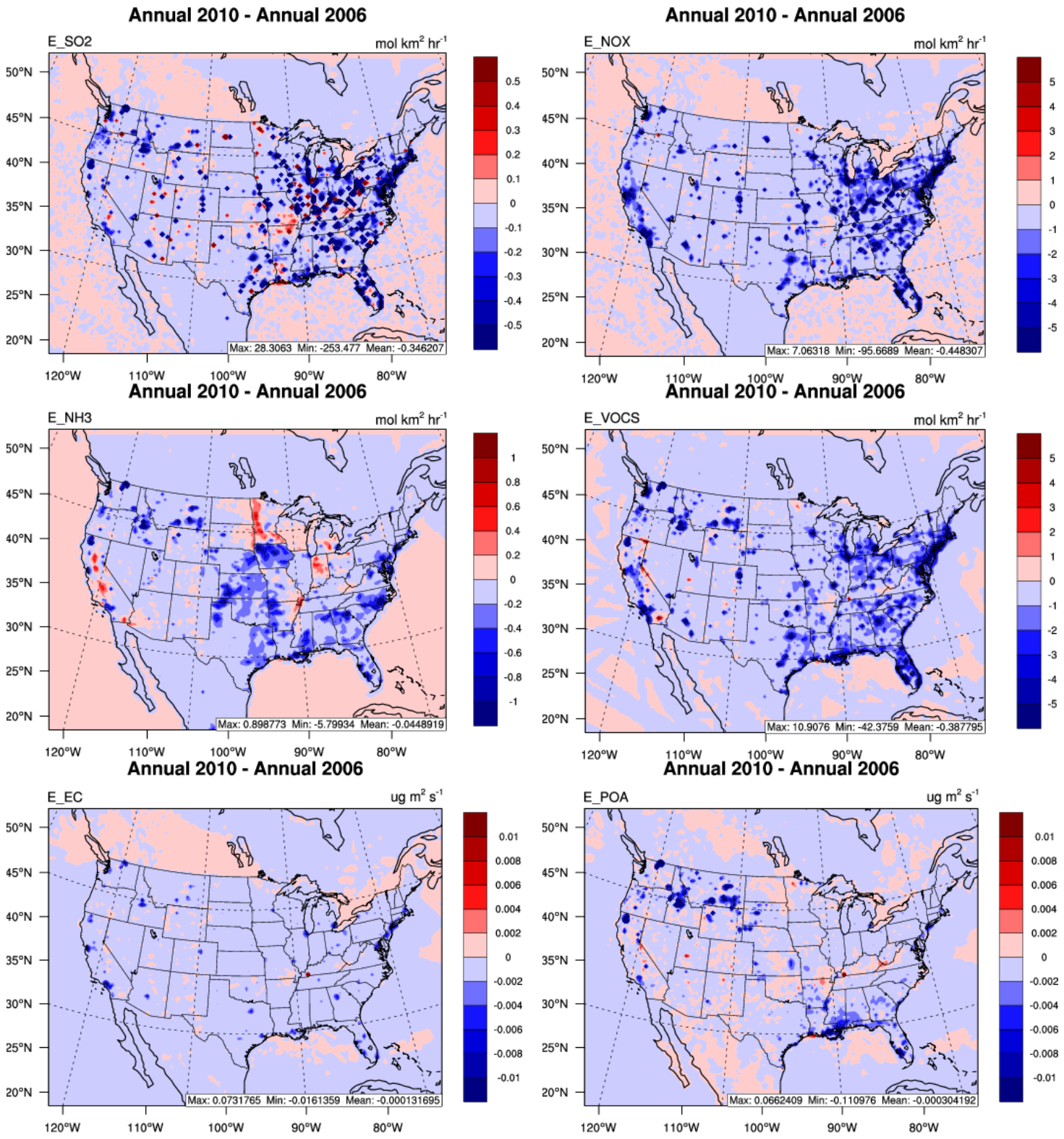

Figure A1. Annual mean changes in the hourly average emission for SO_2, NO_x, VOCs, NH3, EC, and POA from 2010 to 2006 (2010 – 2006).

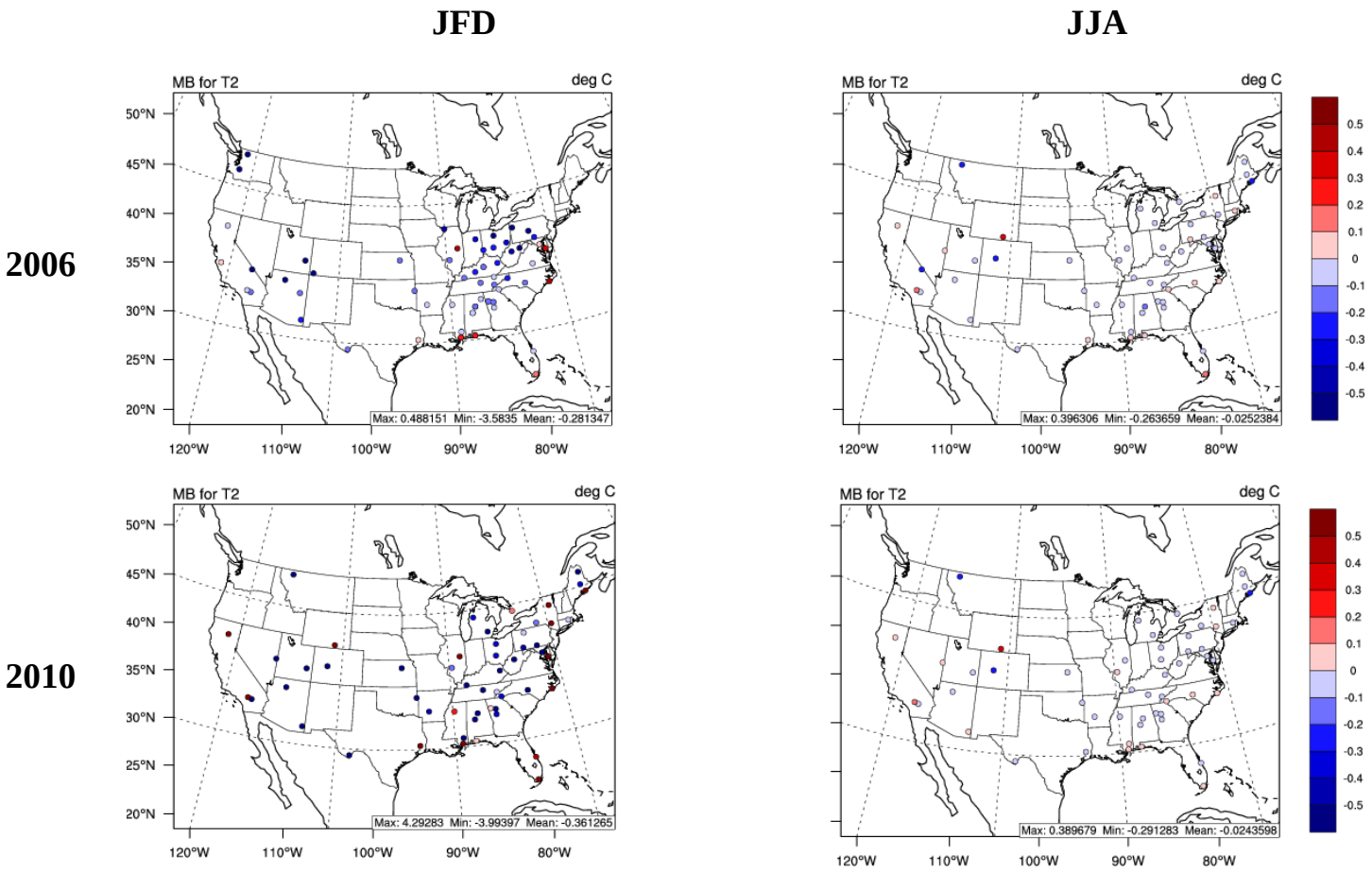

Figure A2. Spatial Distribution of NMB plots for JFD and JJA 2006 and 2010 for T2 based on evaluation against CASTNET and SEARCH.

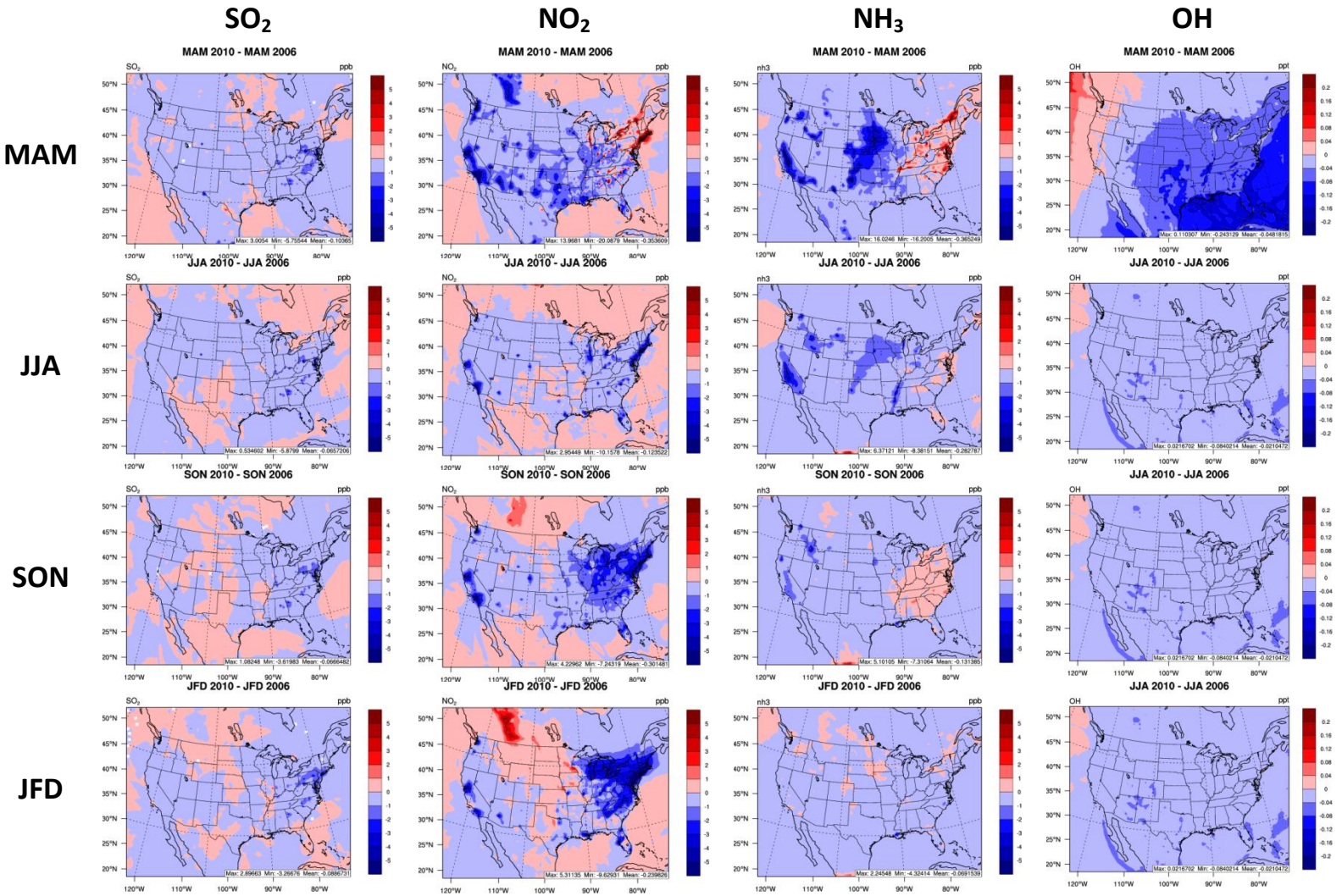

Figure A3. Changes in hourly average surface concentrations of selected gaseous species from 2010 to 2006 (2010 – 2006).

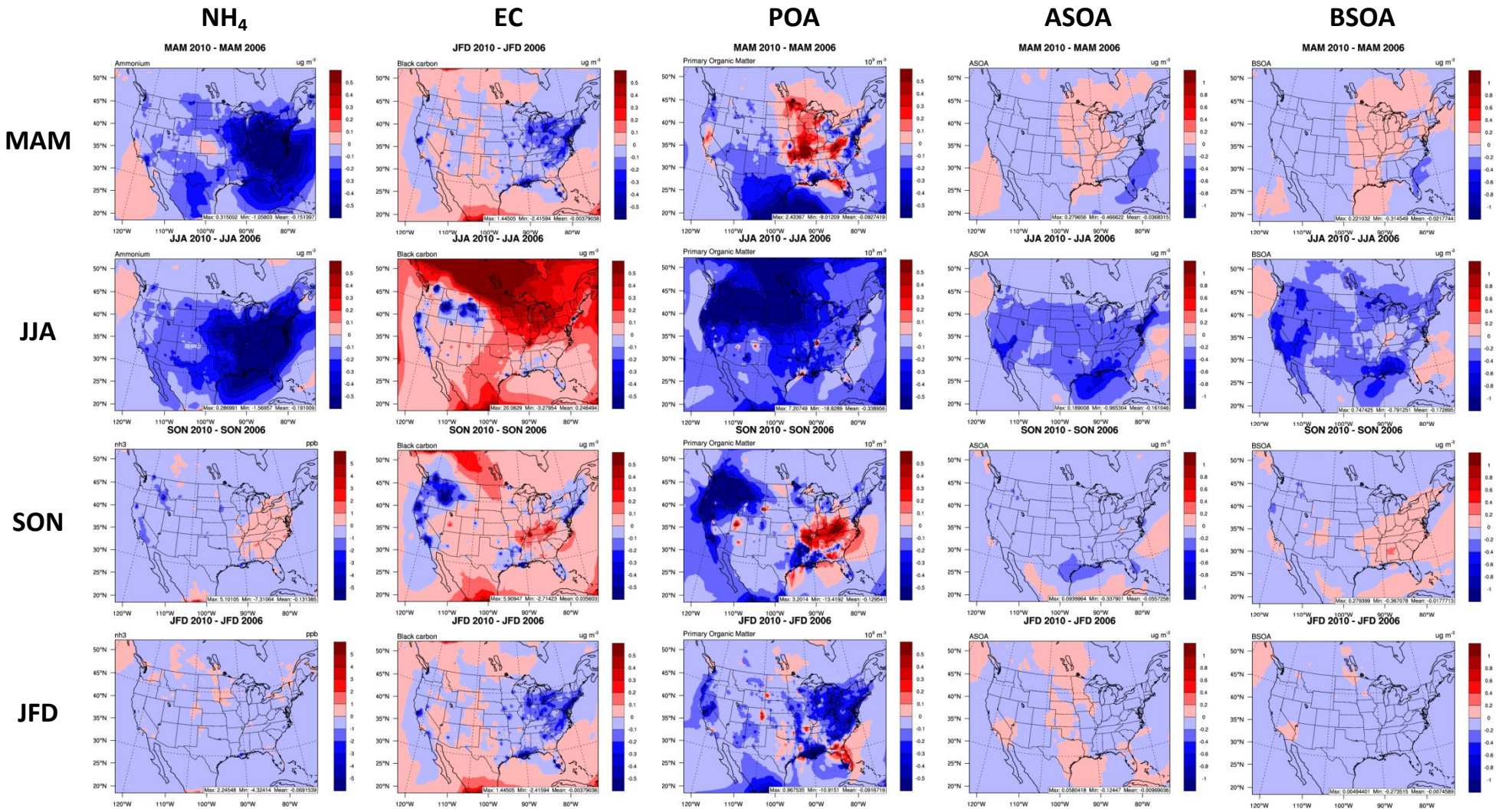

Figure A4. Changes in the hourly average surface concentration of selected PM species from 2010 to 2006 (2010 – 2006).

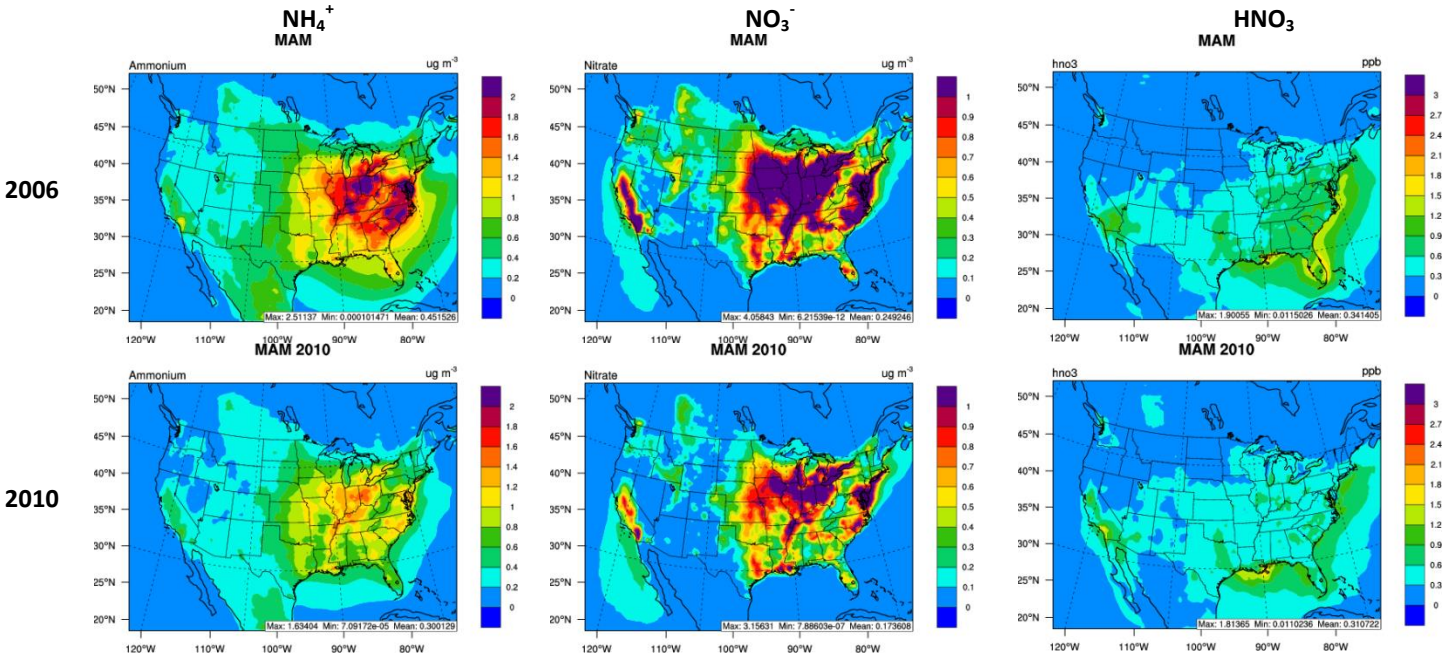

Figure A5. Ammonium, nitrate and nitric acid concentrations for MAM 2006 and 2010.

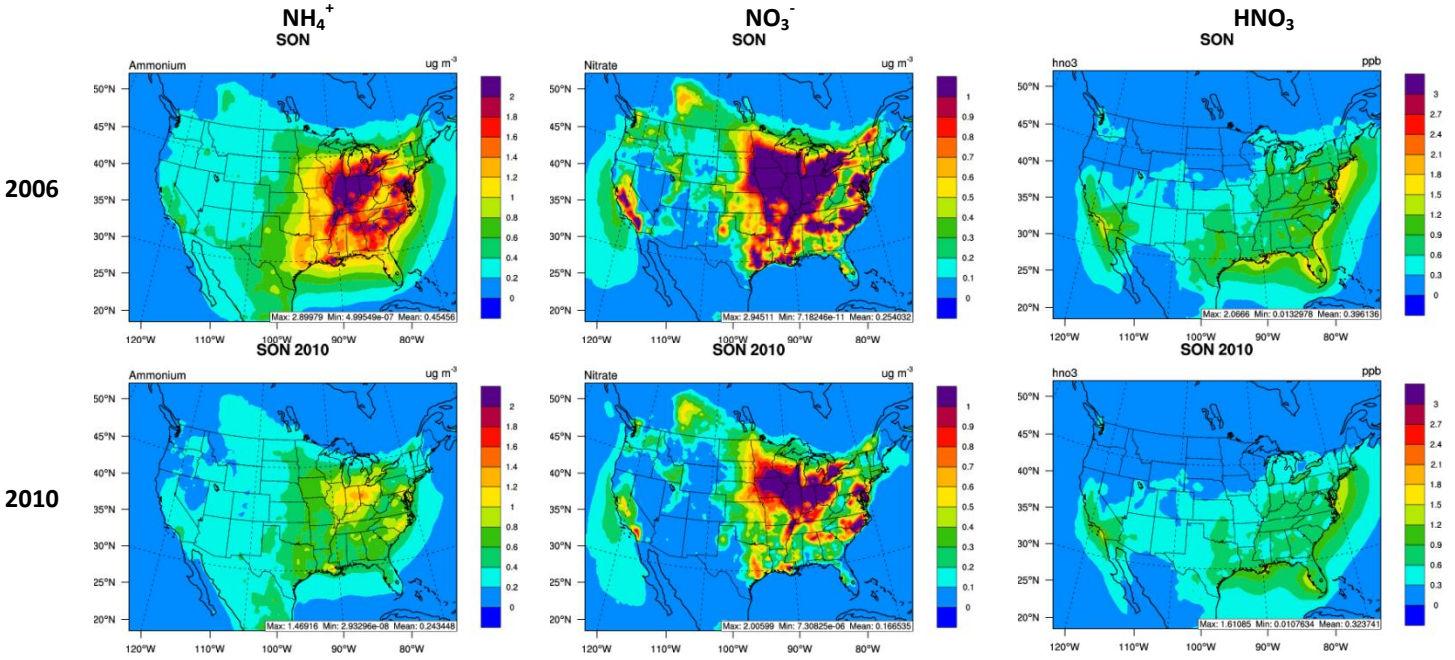

Figure A6. Ammonium, nitrate and nitric acid concentrations for SON 2006 and 2010.

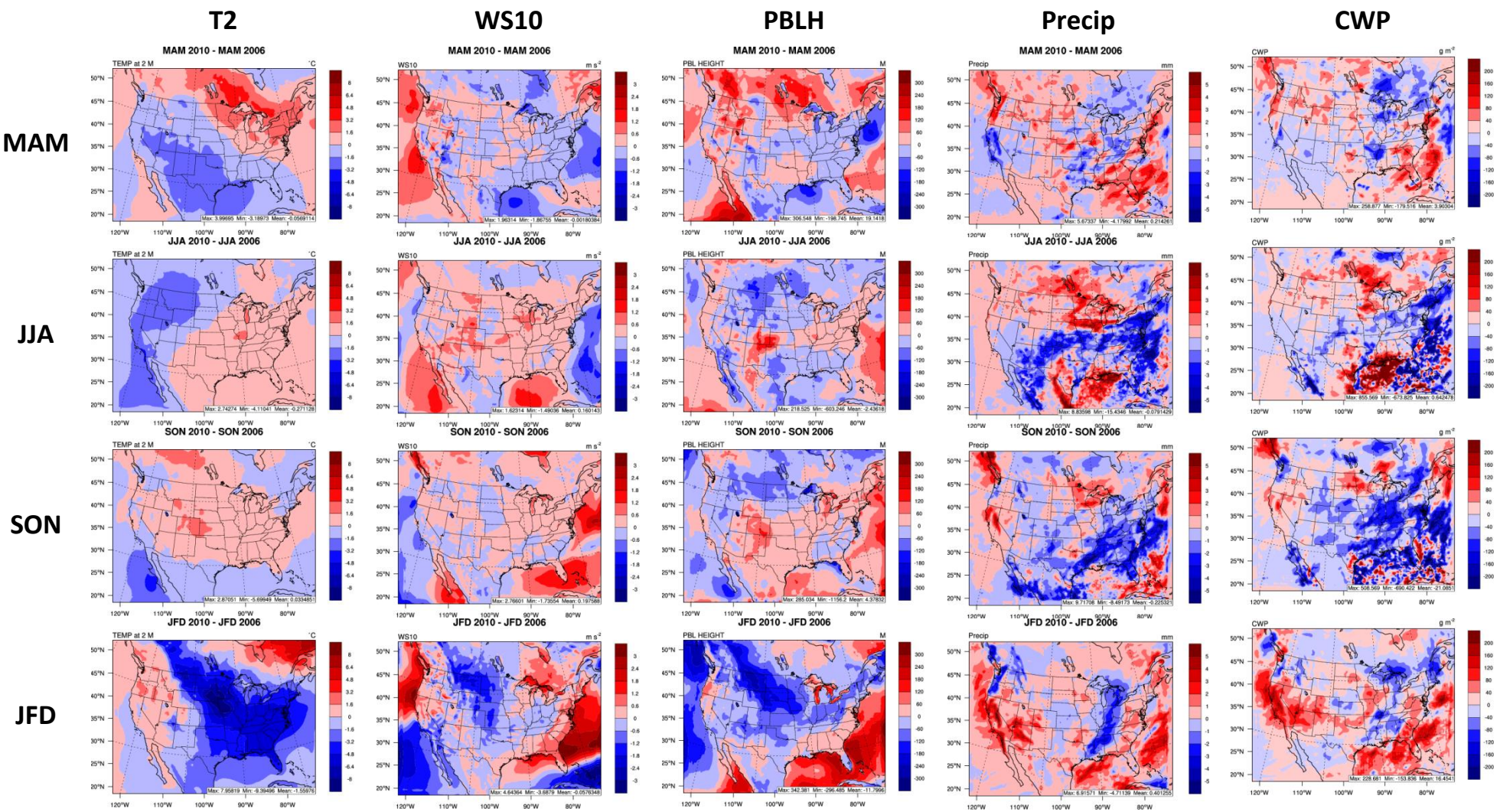

Figure A7. Changes in the hourly average surface predictions of meteorological variables from WRF/Chem simulations from 2010 to 2006 (2010 – 2006).

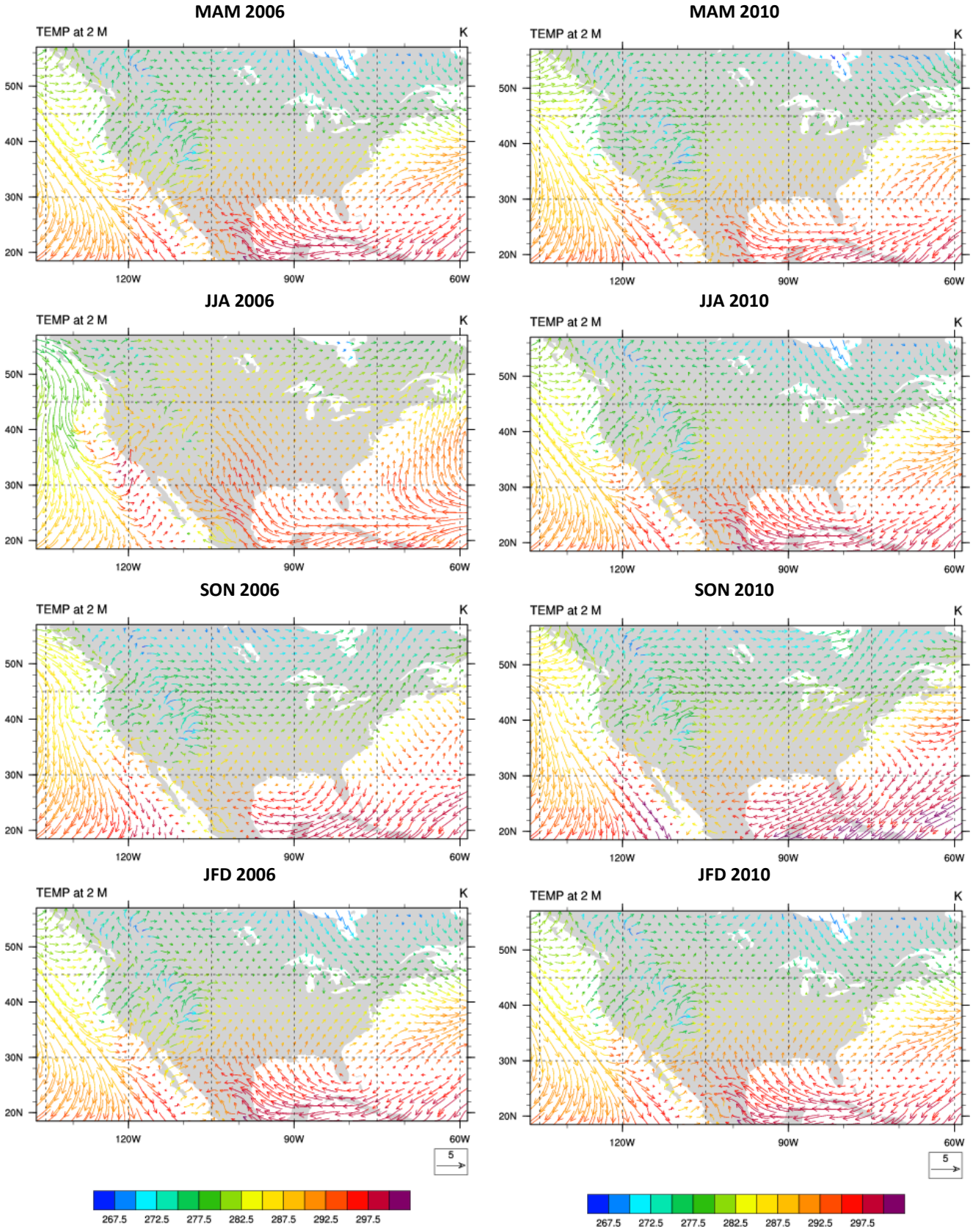

Figure A8. Wind vectors at 10-m and T2 by for all seasons for 2006 and 2010.

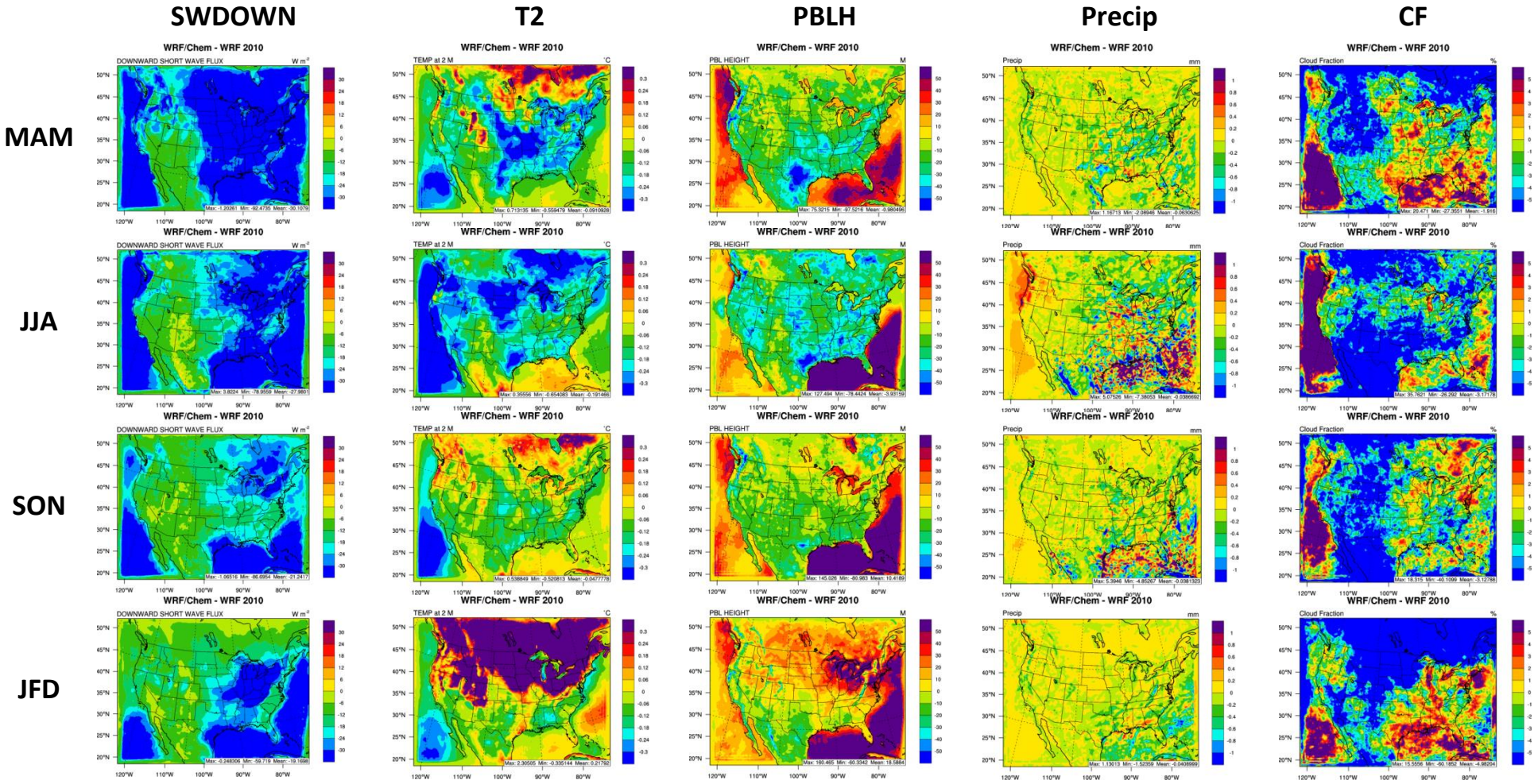

Figure A8. Absolute Differences between predictions of meteorological variables by WRF/Chem and WRF (WRF/Chem – WRF) simulations for 2010.