A Multi-Model Assessment for the 2006 and 2010 Simulations under the Air Quality Model Evaluation International Initiative (AQMEII) Phase 2 over North America: Part I. Indicators of the Sensitivity of O₃ and PM_{2.5} Formation Regimes

Patrick Campbell^{*}, Yang Zhang^{*}, Khairunnisa Yahya, and Kai Wang, Department of Marine, Earth, and Atmospheric Sciences, NCSU, Raleigh, NC 27695

Christian Hogrefe, George Pouliot, ORD, U.S. EPA, Research Triangle Park, NC 27711

Christoph Knote and Alma Hodzic, Atmospheric Chemistry Division, NCAR Earth System Laboratory, NCAR, Boulder, CO 80301

Roberto San Jose and Juan L. Perez, Computer Science School, Technical University of Madrid, Campus de Montegancedo - Boadilla del Monte-28660 Madrid, Spain

Pedro Jimenez Guerrero, Rocio Baro, Department of Physics, University of Murcia, Ed. CIOyN, Campus de Espinardo, Regional Campus of International Excellence "Campus Mare Nostrum", University of Murcia, 30100 Murcia, Spain.

Paul Makar, Air Quality Research Division, Environment Canada, Toronto, Ontario, Canada M3H 5T4

*Corresponding Authors. Email Addresses: <u>pccampb2@ncsu.edu</u> (P. Campbell), <u>yzhang9@ncsu.edu</u> (Y. Zhang)

Highlights

- A multi-model evaluation of O₃ and PM_{2.5} indicators is presented for North America
- Widespread NO_x-limited regimes during May September, and localized VOC-limited
- Overprediction in the extent of VOC-limited chemistry in southeast U.S.
- NO_y and O_3/NO_y are the most robust O_3 indicators
- PM_{2.5} indicators are less robust than O₃ indicators

1 Abstract

2 Under the Air Quality Model Evaluation International Initiative, Phase 2 (AQMEII-2), 3 three online-coupled air quality model simulations, with six different configurations, are 4 analyzed for their performance, inter-model agreement, and responses to emission and 5 meteorological changes between 2006 and 2010. In this Part I paper, we focus on evaluating O₃ 6 and $PM_{2.5}$ indicator-based analyses, which are important in the development of applicable 7 control strategies of O₃ and PM_{2.5} pollution in different regions worldwide. The O₃ indicators 8 agree on widespread NO_x-limited and localized VOC-limited conditions in the U.S. The NO_y 9 and O₃/NO_y indicators overpredict the extent of the VOC-limited chemistry in southeast U.S., 10 but are more robust than the H₂O₂/HNO₃, HCHO/NO_y, and HCHO/NO₂ indicators at the surface, 11 which exhibit relatively more inter-model variability. The column HCHO/NO₂ indicator is 12 underpredicted in the O_3 and non- O_3 seasons, but there is regional variability. For surface $PM_{2.5}$ 13 indicators, there is good inter-model agreement for the degree of sulfate neutralization; however there are systematic underpredictions in the southeast U.S. There is relatively poor inter-model 14 15 agreement for the less robust adjusted gas ratio indicator, which is largely overpredicted in the 16 summer and both under- and overpredicted in winter in the southeast U.S. There is good inter-17 model agreement for the O_3 indicator sensitivities, indicating a predominant shift to more NO_{x-1} 18 limited conditions in 2010 relative to 2006. There is less agreement for $PM_{2.5}$ indicator 19 sensitivities, which are less robust, while indicating shifts to either regime due to different 20 responses of aerosol treatments to changes in emissions and meteorology.

1. Introduction

23 Significant advancements over the last decade have been made in modeling the tropospheric 24 pollutants ozone (O₃) and particulate matter with an aerodynamic diameter $\leq 2.5 \ \mu m \ (PM_{2.5})$, 25 including rapid development and application of 3-D online-coupled meteorology and air quality 26 models (AQMs) [Y. Zhang, 2008; Baklanov et al., 2014]. Online-coupled AQMs allow for more 27 detailed studies of the feedbacks between air quality and the climate/meteorology system [Y. 28 Zhang et al., 2010, 2012a]. AQMs such as the Community Multiscale Air Quality (CMAQ) [Byun 29 and Schere, 2006] model, the Weather Research and Forecasting model with Chemistry 30 (WRF/Chem) [Grell et al., 2005; Skamarock et al., 2008], and the Global Environmental Multi-31 scale Modelling Air Quality and Chemistry (GEM/MACH) [Moran et al., 2010] are used to model 32 indicators of formation regimes, transport, and fate of O₃ and PM_{2.5}, thus providing regulatory 33 decision-making value for the overall control of O_3 and $PM_{2.5}$ concentrations across the continental 34 United States (U.S.) [Y. Zhang et al., 2009a, b; Liu et al., 2010].

35 AQMs need to be systematically evaluated using a common testbed/episode; however, unlike 36 the global-scale climate modeling community, the regional-scale modeling communities in different continents, e.g. North America (NA) and Europe (EU), have begun such investigations 37 38 only recently. Whereas Phase 1 of the Air Quality Modeling Evaluation International Initiative 39 (AQMEII) focused on evaluation of regional scale, offline-coupled AQMs [Rao et al., 2011; 40 Galmarini et al., 2012a], AQMEII Phase 2 (AQMEII-2) placed its emphasis on evaluation of 41 online-coupled AQMs utilizing common sets of time-dependent emissions and meteorological and 42 chemical initial and boundary conditions, thus allowing for a diagnostic evaluation of inter-model 43 discrepancies caused by specific model processes [Dennis et al., 2010]. Such independent 44 evaluations of regional-scale AQMs help place AQM results in context for the modeling

community [e.g., *Huijnen et al.*, 2010], while aiding their interpretation for future policy,
regulation, and control decisions, with an overarching goal to improve our understanding of the
connections between air quality and climate change [*Alapaty et al.*, 2012].

48 Motivation to develop methods to diagnose the NO_x-VOC sensitivity, has led to significant 49 development of "indicator-based" analyses, which are theoretically formulated from chemical 50 reaction mechanisms and measurements of key gaseous species that lead to O_3 concentration 51 changes in certain regions, and then applied to other regions where similar measurements are 52 available by calculating the observation-based indicators, or to the regions where measurements 53 are sparse through AQM simulations. These analysis methods use specific indicator quantities to 54 determine the NO_x-VOC sensitivity of O_3 concentrations to precursor emission reductions [e.g., Milford et al., 1994; Sillman, 1995, 1999; Sillman et al., 1997, 1998; Lu and Chang, 1998; 55 56 Tonnesen and Dennis, 2000; Hammer et al., 2002; Sillman and He, 2002; Martin et al., 2004; 57 Previous modeling studies indicate that the ratio of production rates of Liang et al., 2006]. 58 hydrogen peroxide to nitric acid ($PH_2O_2/PHNO_3$), the concentration ratios of formal dehyde to total 59 reactive nitrogen (HCHO/NO_v), and the ratios of the column abundances of HCHO to nitrogen 60 dioxide (HCHO/NO₂) [Martin et al., 2004], are currently the most robust indicators [Y. Zhang et 61 al., 2009b; Liu et al., 2010]. Here we adopt 5 indicators from a compilation of studies along with 62 their associated NO_x-VOC transition values summarized in Table 2 of Y. Zhang et al. [2009b]. 63 Specifically, the indicators (NO_x-limited transition values recommended by Y. Zhang et al. 64 [2009b]) include H₂O₂/HNO₃ (\geq 2.4), HCHO/NO_y (\geq 0.28), HCHO/NO₂ (\geq 1), NO_y (\leq 5), and O_3/NO_y (\geq 15). The simulations analyzed here did not include process analysis that calculates 65 hourly values of PH₂O₂ and PHNO₃, and those productions rates are not included in the model 66

67 output. The concentration ratio of H_2O_2/HNO_3 is thus used as a proxy for $PH_2O_2/PHNO_3$, although 68 H_2O_2/HNO_3 is not as robust as $PH_2O_2/PHNO_3$.

A large fraction of secondary inorganic PM_{2.5} in the troposphere is composed of sulfate (SO₄²⁻ 69 70), nitrate (NO₃⁻), and ammonium (NH₄⁺). Indicators for the complex interactions between the 71 sensitivity of PM_{2.5} concentrations to relations among total nitrate (TN \equiv HNO₃ + NO₃⁻), total sulfate (TS = SO₄²⁻), and total ammonia (TA = NH₃ + NH₄⁺) have also been derived, tested, and 72 73 implemented. From the work of Ansari and Pandis [1998], Pinder et al. [2008] derived a molar ratio known as the degree of sulfate neutralization (DSN $\equiv ([NH_4^+] - [NO_3^-])/[SO_4^{2-}])$, and used 74 the DSN to express a refined gaseous free ammonia, $NH_3^F(NH_3^F \equiv TA - DSN \times TS)$ and adjusted 75 76 gas ratio, GR (AdjGR \equiv NH₃^F/TN), which are used as indicators of ammonia- and nitrate-limited 77 regimes. Generally, in regions where the AdjGR is relatively large, sufficient gaseous NH₃ exists to neutralize SO_4^{2-} , and $PM_{2.5}NO_3^{-}$ concentrations are most sensitive to changes in TN. In regions 78 79 of relatively smaller AdjGR, PM_{2.5}NO₃⁻ concentrations are most sensitive to changes in NH₃. Here 80 we adopt recommended transition values of DSN and AdjGR from Y. Zhang et al. [2009b], indicating the degree in which SO_4^{2-} has been neutralized by ammonium (DSN ≥ 1.5 ; fully 81 82 neutralized or DSN < 1.5; insufficiently neutralized), while determining NH₃ rich (AdjGR > 1) 83 from NH₃ neutral/poor (AdjGR \leq 1) conditions. We also adopt two other molar ratios, TN/TS and 84 TA/TS, which provide insight into NO_3^- poor (TN/TS < 1), medium (TN/TS = 1 - 2), or rich conditions (TN/TS > 2), and SO_4^{2-} rich (TA/TS < 2), neutral (TA/TS = 2), or poor (TA/TS > 2) 85 86 conditions respectively [Y. Zhang et al., 2000; 2009b].

Extending the operational evaluation of O₃ and PM predictions against observations from
surface monitoring stations for individual [e.g., *Yahya et al.*, 2014a, b] and multiple models [e.g., *Im et al.*, 2014a, b; *Makar et al.*, 2014a, b] included in the AQMEII-2, this work further evaluates

90 the models' performance in reproducing the selected indicators for O₃ and PM formation regimes 91 and column predictions of gaseous mass abundance and aerosol and cloud properties for six 92 AOMEII-2 participating groups. Such model evaluations complement traditional model 93 evaluation that primarily focuses on surface O₃ and PM predictions, provide insights into the 94 models' capability of probing into the underlying O₃ and PM formation mechanisms for emission 95 control policy-making, and examine the interplay among chemistry, aerosol, and cloud through 96 several feedback mechanisms, as well as the importance of upper boundary conditions in accurate 97 predictions of column variables. These results are presented as a sequence of two parts. Part I 98 describes the evaluation and inter-comparison of indicators of the sensitivity of O_3 and $PM_{2.5}$ formation regimes predicted by multiple model simulations against available surface and satellite 99 100 observations, and the resulting policy implications. Part II describes the evaluation and inter-101 comparison of column mass abundance of gases and aerosol/cloud properties against satellite 102 observations as well as potential model improvement in simulating chemistry-aerosol-cloud-103 climate feedbacks [Wang et al., 2014a]. Main objectives of this Part I paper are to perform an 104 operational evaluation, investigatory/diagnostic, and dynamic analysis [Y. Zhang et al., 2006; 105 Dennis et al., 2010] of four 2006 and five 2010 simulations with three online-coupled AQMs 106 (WRF/Chem, WRF/CMAQ and GEM/MACH) for a NA domain, with a focus on the selected 107 indicators that probe into the sensitivity of O₃ and PM_{2.5} formation regimes in NA, specifically for 108 U.S. sub-regions. Specifically, we will 1) assess the models' accuracy against surface and satellite 109 observations, 2) compare seasonal inter-model differences in spatial and temporal (2006 - 2010)110 variability, 3) discuss potential reasoning for any model biases and differences, and 4) use the 111 results from 1) - 3) to assess the robustness of the different indicators used in policy-making

112	decisions, while demonstrating a need for increasing measurements and modeling of O_3 and $PM_{2.5}$
113	indicators, which would further serve to impact future policy-making.
114	2. AQMEII-2 Model Configurations, Observations, and Evaluation Protocols
115 116	2.1 AQMEII-2 Configurations and Input
117	Table 1 summarizes the six AQMEII-2 participating models over NA in this study (four from
119	NA and two from EU), and their model configurations. Those models include US8, US7, ES3,
120	CA2f, and US6. US8, US7, ES1, and ES3 are based on WRF/Chem version 3.4.1 or its variant
121	[Wang et al., 2014b], CA2f is the GEM/MACH version 1.51 [Moran et al., 2010], and US6 is the
122	two-way coupled WRF/CMAQ version 5.0.1 with aerosol direct effect only [Wong et al., 2012].
123	Each model uses the same time-resolved emissions and chemical initial and boundary
124	conditions (ICs and BCs respectively). Emissions are comprised of data from the U.S., Canada,
125	and Mexico. For the U.S. emissions, the 2008 National Emission Inventory (NEI) (version 2,
126	released April 10, 2012) was used as the basis for both the 2006 and 2010 model ready emission
127	datasets (http://www.epa.gov/ttn/chief/net/2008inventory.html) [Pouliot et al., 2014]. The 2008-
128	based modeling platform (2007v5 in final form dated 12/14/2012;
129	http://www.epa.gov/ttn/chief/emch/index.html#2008) provided all necessary inputs and datasets
130	for emission processing [Pouliot et al., 2014]. These files contain the chemical speciation files,
131	the temporal allocation, and spatial allocation data. A technical support document (2007v5
132	Emissions Platform Technical Support Document-12/14/2012) is available for this modeling
133	platform, and contains the full details of the inventory preparation and processing. Year specific
134	(2006 and 2010) updates for these sectors were used for on/off road transport, wildfires and
135	prescribed fires, and Continuous Emission Monitoring (CEM)-equipped point sources. There are
136	widespread decreases in SO ₂ , NO _x , and NH ₃ emissions between 2006 and 2010 across the NA

137 domain, with the exception of some large NH_3 emission increases in the Midwestern U.S. and 138 California in winter [Pouliot et al., 2014; Yahya et al., 2014b]. Dependent on the region of the 139 NA domain and season considered, there were both increases (summer and fall in southeast U.S.) 140 and decreases (winter and spring across most of U.S.) in VOC emissions between 2006 and 2010 141 [Pouliot et al., 2014; Yahya et al., 2014b]. The chemical 2006 and 2010 ICs and BCs are from 142 global 3-hr Monitoring Atmospheric Composition and Climate - Interim Implementation (MACC-143 II; http://www.gmes-atmosphere.eu/) fields [Inness et al., 2013]. Further details regarding both 144 the 2006 - 2010 emission and IC and BC changes for the AQMEII-2 NA domain are found in this 145 issue [Pouliot et al., 2014; Stoeckenius et al., 2014; Yahva et al., 2014b].

146 There are many similarities and differences in model configurations across the participating 147 groups (Table 1). US8, US7, ES1, and ES3 share the most similar configurations available in 148 WRF/Chem, and employ the same horizontal resolution of 36×36 km; although there is at least 149 one configuration difference between each model. There are more differences than similarities 150 among those WRF/Chem-based models, compared to the CA2f and US6 configurations. CA2f and 151 US6 also utilize finer horizontal resolutions of 15×15 km and 12×12 km, respectively. Important for diagnosing model differences in O₃ and inorganic PM_{2.5} indicators, all groups employ different 152 153 gas-phase mechanisms, as well as different combinations of gas-phase and aerosol mechanisms. 154 Inter-model comparisons in Section 4 use such similarities and differences as a basis for 155 investigatory/diagnostic analyses.

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159 2.2 Observations from Surface Networks and Satellites

161	Observations from both surface and satellite platforms are used for the evaluation. For a
162	detailed site-specific comparison, surface observations from the SouthEastern Aerosol Research
163	and Characterization (SEARCH) network [Hansen et al., 2003] are used. This is an ideal
164	network for comparison, as it readily provides coincident measurements of trace gas and
165	particulate species necessary to calculate the surface O_3/NO_y indicator, and $PM_{2.5}$ indicators such
166	as DSN, AdjGR, and NH3 ^F . With the exception of specific field campaigns, such routine
167	measurement combinations are sparse for other regions of the U.S., especially for gas-phase NH ₃
168	and HNO ₃ , which is needed for calculating $PM_{2.5}$ indicators AdjGR and NH_3^F . From the
169	SEARCH network, four sites are selected from urban/suburban locations, Birmingham, Alabama
170	(BHM), Jefferson Street, Atlanta (JST), Gulfport, Mississippi (GFP), and the Outlying Landing
171	Field #8, Florida (OLF). Three sites are also selected from rural areas, Centreville, Alabama
172	(CTR), Yorkville, Georgia (YRK), and Oak Grove, Mississippi (OAK). Full descriptive
173	information regarding the SEARCH network, including each site's location, descriptive
174	information, and relevant measurements necessary for calculations of O_3 and $PM_{2.5}$ indicators in
175	2006 and 2010, may be found at http://www.atmospheric-research.com/. Tropospheric column
176	observations of level-3 monthly averaged NO_2 and HCHO data are also obtained from the
177	Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY)
178	[Boersma et al., 2004; De Smedt et al., 2008], and are used for a domain-wide evaluation of the
179	column HCHO/NO2 indicator [Martin et al., 2004]. SCIAMACHY column NO2 and HCHO
180	data have been validated and applied in previous investigations [e.g., van der A et al., 2006,
181	2008; Barkley et al., 2013].

183 2.3 Evaluation Protocols

184 Following Y. Zhang et al. [2009a], our protocol includes an evaluation between model and 185 observations using different statistical measures, and a diagnostic/dynamic evaluation of model 186 inter-comparisons for the investigation of process-based differences and systematic biases on a 187 seasonal and regional basis. Simulated O_3 and $PM_{2.5}$ indicators are compared against 188 observations from the SEARCH locations in southeast U.S., using the closest horizontal grid 189 values, at the vertical layer closest to the surface for each model (Table 1). We note that this is 190 similar to a case study based evaluation limited to southeast U.S. In light of this, Section 5 of 191 this paper provides additional discussion on the benefits, limitations, and recommendations 192 regarding this evaluation. Statistical measures typically used to evaluate AQMs are implemented 193 here. These include the normalized mean bias (NMB), normalized mean error (NME), and 194 Pearson's correlation coefficient, R [Y. Zhang et al., 2006]. Statistical measures R, NMB, and 195 NME provide measures of the associativity (i.e., correlation), bias, and accuracy, respectively, of 196 specific modeled surface O₃ and PM_{2.5} indicators. A model spatial and statistical (NME vs. 197 NMB) comparison of the tropospheric column HCHO/NO₂ [Martin et al., 2004] indicator is also 198 made against SCIAMACHY satellite observations for the O_3 (May – September) and non- O_3 199 (January – April and October – December) seasons. The hour during the orbit crossing-time of 200 SCIAMACHY is ~ 10:00 a.m. local time. The model results from 1500 to 2000 UTC are 201 averaged to approximately match the 10:00 local time of the SCIAMACHY observations [Wang 202 et al., 2014a]. Modeled HCHO and NO₂ column abundances are determined by vertically 203 integrating up to the tropopause, which is assumed to be 100 hPa following Y. Zhang et al. 204 [2009a], while also cloud screening the model output using a 40% cloud fraction threshold that is 205 consistent with the SCIAMACHY retrieval [De Smedt et al., 2008]. Considering that an 206 averaging kernel is not available for the level-3 SCIAMACHY data used in this comparison, an

averaging kernel is not applied to the model data. Our calculation of the model column HCHO
and NO₂ abundances represents an approximate comparison of the tropospheric amounts to
match the satellite data. Thus the model-satellite matching, as well as the model and
SCIAMACHY column data, is subject to uncertainties. More details in regards to the
uncertainties and limitations associated with SCIAMACHY column HCHO and NO₂ ratios data
are found in *Wang et al.* [2014a].

213 Diagnostic/dynamic inter-model comparisons are performed by analyzing the seasonal 214 variation of the spatial distribution of indicators and investigating process-based reasoning due to 215 model configuration differences (Table 1), as well as different model responses to changes in 216 emissions and meteorology between the 2006 and 2010 simulations. Analyses and comparisons 217 are based on a geographical separation into 4 sub-regions across NA, which have been defined in 218 Solazzo et al. [2012a, b]. Adapting a similar definition, henceforth we refer to NA1, NA2, NA3, 219 and NA4 as the west (120 - 105°W/30 - 50°N), Midwest (105 - 90°W/30°N - 50°N), southeast 220 (90 - 75 °W/25 - 40 °N), and northeast (90 - 65 °W/40 - 50 °N) regions of the NA domain 221 respectively. The entire continental U.S. region of the NA domain, i.e., NA/U.S. is 222 approximated using the areas encompassed by sub-regions NA1-NA4.

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3. Evaluation of Simulated Indicators Against Observations

225 3.1 O₃/NO_y Statistical Comparison

Figure 1 provides statistical plots (NMB vs. NME) for simulated O₃/NO_y indicator ratios

against those calculated based on the averaged SEARCH observations of O_3 and NO_y in 2006

229 (ES3), 2010 (US7 and ES1), or the average of 2006 and 2010 (US8, CA2f, and US6), for

afternoon hours (1 p.m. - 6 p.m. LST) during the O₃ and non-O₃ seasons in the southeast U.S.,

NA3. There is predominantly a negative O_3/NO_y bias for the models, especially at the rural sites

232	(Figure 1b). The negative O_3/NO_y bias for the models is dominated by an overprediction in
233	NO_y , except for CA2f which has an underprediction in NO_y (Figure S1), and a positive O_3/NO_y
234	bias at the urban sites during both seasons (Figure 1a). More details regarding the model
235	predictions of O_3 and NO_y individually, and their underlying causes, are found in comparisons
236	against four SEARCH sites in Supplementary Section 1 and Figure S1. US6 and US8 have the
237	highest correlation coefficient, R (not shown), while ES3 and US7 have the smallest bias and
238	error in NO _x -VOC sensitivity for the urban sites (Figure 1a), i.e., they have the most similar
239	distance to the linear transition line compared to observations in Figure S1. At the rural sites,
240	there is generally less error (Figure 1b), while US7 and CA2f have the smallest bias and error
241	during the O ₃ and non-O ₃ seasons respectively. On average across both seasons, the most finely
242	resolved US6 model (12×12 km) has the highest correlation (not shown), and best represents
243	local changes in the O ₃ /NO _y ratio in NA3.
244	For the models at the urban sites, the NMB for O_3/NO_y ranges from -62% to +6.9% in the
245	O_3 season, and from -58% to +36% in the non- O_3 season. At the rural sites, the models' NMB
246	range is -62% to +5.7%, and -46% to +8% in the O_3 and non- O_3 season, respectively.
247	Future improvement in the models' predominant overprediction of NO _y is needed to reduce the
248	predominant negative O_3/NO_y bias, and the overprediction in VOC-limited extent of O_3
249	chemistry in NA3.
250 251	3.2 DSN, AdjGR, and NH ₃ ^F Statistical Comparison
252	Figure 2 provides NMB vs. NME plots for DSN, AdjGR, and NH ₃ ^F indicators against
253	SEARCH observations in NA3 for the 2010 (US8, US7, CA2f, and US6) winter and summer
254	seasons. Supplementary Section 2 and Figure S2 provide additional details for each model's
255	average PM _{2.5} regime indicators TA/TS, TN/TS, DSN, AdjGR, and NH ₃ ^F , compared to four

256 SEARCH sites during all seasons in 2010. Although ES1's simulation is included in the analyses 257 in Section 3.1 (see additional discussion in Supplementary Section 1), exclusion of SO_2 and NO_x 258 point sources for ES1 led to unrealistic concentrations of inorganic $PM_{2.5}$ species. Thus ES1's 259 results are not included in Figure 2 and subsequent figures comparing PM_{2.5} indicators. For all 260 models, seasons, and sites the correlation coefficient, R (not shown), is very low for all 261 indicators, and at times negative. This illustrates the difficulty for models to capture observed 262 trends in PM_{2.5} regime indicators at individual sites; although higher statistical scores may be 263 found for individual particle species when larger numbers of stations are included in the analysis 264 [Table 4 in *Makar et al.*, 2014a]. All models predict a negatively biased DSN at both urban and rural sites, thus underestimating SO_4^{2-} neutralization by ammonium in both seasons (Figures 2a 265 266 and 2b). The US8 model has the smallest DSN bias and error, on average, during the winter and 267 summer at the urban sites. At the rural sites, US6 and US8 have the smallest bias and error in the 268 winter and summer, respectively. Given model overpredictions of NH₃ and TA (not shown), a 269 negatively biased DSN, and impacts from uncertainties in NO_x emissions leading to 270 underpredictions in TN, the result is a majority of very large positive biases and error for AdjGR and NH_3^F at both urban and rural sites, especially in the summer (Figures 2c - 2f). There is also 271 272 significantly more spread across the models for the positive biases in the summer. CA2f has consistently the lowest bias and error for AdjGR and NH₃^F during the summer at both urban and 273 274 rural sites, which is due to partial compensation from large underpredictions in NO_2 275 concentrations [Table S1 in Makar et al., 2014a]. For the winter, US6 and US8 have the 276 smallest magnitudes in bias and error. For the models at the urban sites, the NMB for DSN, AdjGR, and NH₃^F have ranges of -58% 277

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to -32%, -86% to +48%, and -60% to +95% in the winter season, and -28% to -2.5%, +112% to

279	+970%, and -8% to +782%, during the summer season, respectively. There is a large NMB
280	range for AdjGR and NH ₃ ^F , and largely positive NMB during the summer season. In both the
281	winter and summer seasons at urban sites, there is an overprediction in the extent of NH_3 rich
282	conditions, and associated PM _{2.5} sensitivity to TN changes. There are similar large ranges at the
283	rural sites, where the model range NMB for DSN, AdjGR, and NH_3^F are -61% to -27%, -56% to
284	+300%, and -37% to +112% during the winter season, and -46% to -26%, +226% to +978%, and
285	-37% to +471% during the summer season respectively. There is clearly more error and bias
286	when simulating $PM_{2.5}$ indicators, relative to the O_3 indicators in Section 3.1. Much of the
287	additional model uncertainty for PM2.5 indicators, especially for AdjGR, stems from additional
288	complexities of accurately predicting thermodynamic partitioning for different species,
289	uncertainties in gas emissions and meteorological conditions, as well as approximations
290	contained within each model's gas-phase and aerosol module combinations.
291	3.3 Satellite HCHO/NO ₂ Statistical Comparison
292 293	Figure 3 provides NMB vs. NME plots for tropospheric HCHO/NO ₂ column abundance ratio
294	[Martin et al., 2004] against SCIAMACHY observations, averaged across the approximated
295	continental U.S. (NA/U.S.), and over sub-regions in northwest (NA1), Midwest (NA2), southeast
296	(NA3), and northeast U.S. (NA4), in 2006 (ES3), 2010 (US7 and ES1), or the average of 2006
297	and 2010 (US8, CA2f, and US6) O_3 and non- O_3 seasons. More details regarding the spatial
298	agreement for each model against SCIAMACHY observations can be found in Supplementary
299	Section 3 and Figure S3. For NA/U.S. (Figure 3a), there is a negative HCHO/NO ₂ bias for both
300	seasons, with the exception of positive biases for ES1 and CA2f during the O_3 season. The
301	underprediction in the NO _x -limited chemistry is mainly due to lower HCHO in rural regions, and
302	larger NO ₂ in urban regions. The NO _x -limited underprediction is apparent for all models and

303	seasons in sub-region NA1 (Figure 3b), except ES1 and CA2f in the O3 season, covering the
304	western U.S domain. In fact, during the non- O_3 season, there is a clear NO_x -limited
305	underprediction in all NA/U.S. sub-regions (Figures $3b - 3e$) for the models, with the exception
306	of ES1 and CA2f in NA2 and NA3. In NA2 (Figure 3c) and NA3 (Figure 3d) during the O_3
307	season, however, most models actually have a relatively slight overprediction of the NO _x -limited
308	chemistry, due to overpredictions in HCHO concentration. There are significant contributions
309	from underpredictions in NO ₂ , and hence NO _x concentrations for CA2f [Makar et al., 2014a], as
310	well as known impacts from exclusion of NO_x point sources for ES1 during the O_3 season. Such
311	NO_x underpredictions for ES1 and CA2f cause these models to be outliers for NA/U.S. and all
312	sub-regions. When ES1 and CA2f are not considered, the models' NMBs for the O_3 season in
313	NA1, NA2, NA3, NA4, and NA/U.S. range from -49% to -34%, +12% to +21%, -20% to +36%,
314	-36% to -26%, and -32% to -15%, respectively. In the non-O ₃ season, NMBs range from -93%
315	to -90%, -82% to -31%, -55% to -7%, -99% to -92%, and -96% to -78% respectively. With
316	exception of ES1 and CA2f, the models predominantly underpredict the extent of NO _x -limited
317	chemistry for the column HCHO/NO2 indicator, except in parts of NA2 and NA3, Canada,
318	Mexico and the Atlantic Ocean (Figure S3), where there is a tendency to overpredict NO _x -
319	limited chemistry in the O ₃ season.

320 **4** Spatial Distribution of Seasonally Averaged Indicators

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This section performs an inter-model comparison using ensemble model averages, standard deviations (SD), and normalized standard deviations (NSD = standard deviation/average) of the different NO_x-VOC-limited indicators during the O₃ season (Section 4.1), regime indicators for the formation of PM_{2.5} in the winter (Section 4.2), and the inter-model changes between 2006 and 2010 (Section 4.3). Supplementary Section 4 provides additional details of the inter-model

327 spatial comparisons, and further supplements the analyses in the following sections. The CA2f 328 model did not contain H_2O_2 in its output, and thus the H_2O_2/HNO_3 indicator for CA2f is not 329 included in these analyses.

330 4.1 NO_x-VOC Sensitivity in the O₃ Season 331 332 Figure 4 shows the ensemble model average and NSD of the five surface photochemical 333 indicators (H₂O₂/HNO₃, NO_y, O₃/NO_y, HCHO/NO_y, and HCHO/NO₂), averaged over afternoon 334 hours (1 p.m. – 6 p.m. LST) during the O₃ season. For the H₂O₂/HNO₃ indicator (Figure 4a), on 335 average the models predict NO_x-limited chemistry in NA1, NA2, and NA4, with local areas of 336 VOC-limited chemistry near urban centers. Models best agree in the relatively low biogenic 337 emission region of NA2, which has the lowest NSD for H_2O_2/HNO_3 ; however, there are larger 338 NSDs in the relatively high biogenic emission region of NA3 (Figure 4f). Table 2 indicates 339 average SDs of 1.18 and 3.13 and NSDs of 0.29 and 0.62 for H_2O_2/HNO_3 in NA2 and NA3, 340 respectively. The higher inter-model variability in NA3 are due to differences in regional 341 background H_2O_2 mixing ratios (~ factor of 2; not shown), stemming from application of 342 different gas-phase chemistry mechanisms between the models (Table 1). ES3 incorporates a 343 different version of the Carbon Bond Mechanism (CBM), CBM-Z, compared to both US8 and 344 US6 that use an updated CBM, i.e., CB05, while US7 uses a non-CBM (Table 1). Compared to 345 CBM-Z, CB05 includes additional species such as higher aldehyde and internal olefin species, 346 which increase radical production; it also explicitly defines methylperoxy radicals [Yarwood et 347 al., 2005]. Thus larger H_2O_2 may be attributed to gas-phase chemistry updates in CB05, and also 348 differences between CBM and non-CBM (US7 and ES1) treatments (Table 1). Knote et al. 349 [2014] conducted a diagnostic evaluation of the different chemical mechanisms used here in a 350 box modeling approach, and their results support this suggestion.

351	For NO _y (Figure 4b) and O ₃ /NO _y (Figure 4c), there is also dominant NO _x -limited chemistry
352	across NA/U.S., and local areas of VOC-limited chemistry near major urban centers. There are
353	lower NSDs and better agreement across the models for the NO_y (Figure 4g) and O_3/NO_y (Figure
354	4h) indicators compared to H_2O_2/HNO_3 . In NA3 the average SDs are 0.88 ppb and 4.33 and
355	NSDs are 0.23 and 0.31 for NO _y and O_3/NO_y , respectively. These NSDs are about a factor of two
356	lower than those for H_2O_2/HNO_3 in this region (Table 2). There is disparity across different
357	model resolutions, however, when comparing the magnitude of NO _y for the different models at
358	local areas (supplementary Figure S4g - S4l), consistent with the comparison at local SEARCH
359	sites, and the apparent spread in NO _y mixing ratios among models (Figure S1). ES1 agrees well
360	for NO_y , but is biased low compared to other models for O_3/NO_y (Figure S4o). This is due to the
361	impacts from exclusion of NOx point sources important to O3 formation. A negative O3 bias for
362	ES1 is apparent in other AQMEII-2 evaluations as well [Im et al., 2014a].
363	For HCHO/NO _y (Figure 4d) and HCHO/NO ₂ (Figure 4e) indicators, the model average also
364	indicates strongly NOx- limited conditions in NA/U.S. (dominated by the non-CBM model
365	values; Figure S4). There is significant inter-model variability for these indicators, and relatively
366	larger average NSDs across NA/U.S. (Figures 4i – 4j), especially for HCHO/NO ₂ . The NSDs are
367	the largest, 0.58, for HCHO/NO _y in NA3, and 0.66, for HCHO/NO ₂ in NA4 (Table 2). This is
368	attributed to different biogenic emission models and versions employed for different models
369	(Table 1; MEGAN2 vs. BEIS3.09 vs. BEIS3.14), combined with different gas-phase chemistry
370	mechanisms, especially for the CBM versus non-CBM treatments. Better inter-model and
371	observational agreement for US6 compared to CA2f (Figures 3 and S4y-S4dd), may also be
372	impacted by updated biogenic emission factors and treatment of light correction factors for
373	isoprene [Schwede et al., 2005] used in conjunction with recent organic chemistry updates in

374 CB05-TU for US6. Both CA2f and ES1, however, are also impacted by low NO_x concentrations 375 (discussed above), and this contributes to their inter-model differences in HCHO/NO_v and 376 HCHO/NO₂. Significant differences near urban centers may also similarly be attributed to 377 differences in organic chemistry treatment in the non-CBM gas-phase chemistry for US7, ES1, 378 and CA2f (Table 1). Box model simulations for Detroit metro emissions indicate that the non-379 CBM mechanism for CA2f (ADOMII; Table 1) is ~ 100 % larger than the CBM for US8 and 380 US6 (CB05; Table 1) for HCHO, and ~ 50 % lower for NO_x [*Knote et al.*, 2014]. This agrees 381 with the HCHO/NO_v differences near urban centers shown here. Comparison of the tropospheric 382 column HCHO/NO₂ (Figures S3a – S3g) to surface HCHO/NO₂ (Figures S4y – S4dd) in the O₃ 383 season indicates a similar spatial distribution in formation regimes; however, there are less VOC-384 limited regions near the urban centers for the column HCHO/NO₂ indicator, as well as more 385 widespread NO_x -limited regimes. The impact of local NO_x sources is dampened when using the 386 column HCHO/NO₂ indicator, as the NO₂ concentration is dominated by surface emissions, 387 while the HCHO in the free troposphere is controlled by methane oxidation [Lowe and Schmidt, 388 1983; Wuebbles and Hayhoe, 2002; Palmer et al., 2003]. Given the long lifetime of methane, 389 the HCHO column is relatively well mixed [Figure 1 in *Li et al.*, 2012] compared to the NO₂ 390 column. This impact is especially apparent where there is already known deficiencies in NO_x 391 concentrations for ES1 and CA2f. Thus the predicted NO_x-VOC limited regimes are dependent 392 upon either using a modeled surface or column HCHO/NO₂ indicator to predict NO_x- versus 393 VOC-limited regimes in NA/U.S. The NSDs for NA/U.S. in Table 2 indicate relatively small 394 inter-model variability for NO_v (0.28) and O₃/NO_v (0.33) indicators, but larger inter-model 395 variability for HCHO/NO_v (0.50) and HCHO/NO₂ (0.62). The lowest inter-model variability is

for NO_y in NA3 (0.23), while the largest is for HCHO/NO₂ in NA4 (0.66). Based on these results, the NO_y and O_3/NO_y indicators are the most robust.

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4.2 PM_{2.5} Sensitivity in Winter

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400	Figure 5 shows the ensemble model average and NSD of TN/TS, DSN, AdjGR, NH_3^F , and
401	NO_3^- in winter (DJF), as this season is when $PM_{2.5}NO_3^-$ formation is thermodynamically
402	favored. On average, models predict NO_3^- medium (TN/TS = 1 - 2) to rich (TN/TS > 2)
403	conditions across the U.S (Figure 5a). Individual models agree that where SO_4^{2-} is fully
404	neutralized, there is excess NH_3^F for $PM_{2.5} NO_3^-$ formation under cold temperatures (Figure S5)
405	[Ansari and Pandis, 1998; Pinder et al., 2008]. Average model results indicate that there is
406	mainly sufficiently neutralized conditions, NH_3 rich conditions, and $PM_{2.5}$ sensitivity to TN
407	changes in NA2 and NA3, while more NH3 poor conditions (embedded with localized NH3 rich),
408	and $PM_{2.5}$ sensitivity to NH_3 changes in NA1 and NA4 (Figure 5b – 5d). There is good inter-
409	model agreement in DSN, with the lowest NSDs across NA/U.S. (Figure 5g, Table 2); however,
410	there is larger inter-model variability for the other indicators, especially for TN/TS in parts of
411	NA1 and NA4, and AdjGR in NA2 – NA4 (Figures 5f and 5h). The NA/U.S. average NSD is
412	over twice as large as that for DSN. The relatively larger inter-model variability in TN/TS in
413	NA1 stems from inter-model differences in predicted SO_4^{2-} concentrations, as there is relatively
414	smaller variability in NO_3^- concentrations in this region (Figure 5j). In NA2 – NA4, the TN/TS
415	and AdjGR variability stems from relatively different amounts of NO3 ⁻ formation for some
416	models under cold winter temperatures (Figures 5e, 5j, and S5u - S5y). The models employ four
417	different combinations for their inorganic aerosol, gas-, and aqueous-phase chemistry
418	mechanisms (Table 1). Kim et al. [2011] and Y. Zhang et al. [2012b] indicated less than a 1 %
419	PM _{2.5} concentration difference, but up to a 26 % PM _{2.5} composition difference from a

420	comparison of models that used the same aerosol mechanism, but different gas-phase
421	mechanisms. Furthermore, the reaction rate constant of $SO_2 + OH$ is the same across all models,
422	such that the larger inter-model variability in TN/TS in NA1, and TN/TS and AdjGR in NA2 -
423	NA4, are also likely impacted by different SO ₂ (e.g., different plume rise calculations) or OH
424	concentrations. Other impacts may also derive from different spatial resolutions. These lead to
425	significant impacts on PM _{2.5} sensitivity, e.g., the calculated average values of AdjGR over NA2-
426	NA4 range from about 0.3 (NH $_3$ poor) - 1.4 (NH $_3$ rich) for the different models (Figure S5k –
427	S5t). Overall, NA/U.Swide NSD averages in Table 2 indicate that there is relatively low inter-
428	model variability for DSN (0.30), but larger variability for AdjGR (0.80). The lowest inter-
429	model variability is for DSN in NA3 (0.23), while the largest is for AdjGR in NA4 (1.04). The
430	larger inter-model variability for the surface $PM_{2.5}$ indicators, especially AdjGR, indicates that
431	they are less robust than the surface O ₃ indicators.
432	4.3 Changes in O_3 and $PM_{2.5}$ Sensitivity from 2006 to 2010
433 434	Figure 6 presents difference $(2010 - 2006)$ plots for the five O ₃ indicators to provide
435	additional insight into changes in NO _x -VOC-O ₃ sensitivity to emission and meteorological
436	changes between the 2006 and 2010 O_3 season. The models indicate increases in all indicator
437	ratios (Figures 6a – 6c, 6g – 6i, and 6j – 6o) for southern NA1-NA2, and nearly all of NA3 –
438	NA4, along with NA/U.Swide decreases in NO_y (Figures 6d – 6f). Analyses of the emissions
439	support this finding, indicating NA/U.Swide decreases in summertime average NO _x daily
440	emissions between 2006 and 2010, especially near point sources and urban centers [Pouliot et
441	al., 2014; Stoeckenius et al., 2014; Yahya et al., 2014b]. There is however a dipole in the sign
442	of NO _x - and VOC-limited changes between northern NA1- NA2 and NA3. For NA1-NA2,
443	further analysis of the meteorological IC-BCs show a decrease in mean summer surface

444	temperatures, coincident with decreases in emissions of NO_x and anthropogenic VOCs of about -
445	1000 and -4500 Mg day ⁻¹ respectively [Stoeckenius et al., 2014]. Decreased temperature and
446	resultant biogenic VOC emissions, occurring in tandem with relatively large anthropogenic VOC
447	emission reductions compared to NO _x between 2006 and 2010, is conducive for increased VOC-
448	limited conditions in NA1-NA2. Increased temperature, biogenic VOC emissions, and relatively
449	large NO _x emission reductions of about -2000 Mg day ⁻¹ compared to VOC emissions of about -
450	500 Mg day ⁻¹ , further increased the NO _x -limited conditions in NA3. Figure 1 in Yahya et al.
451	[2014b] supports our hypothesis, while indicating a similar dipole in 2006 – 2010 summertime
452	VOC emission (anthropogenic + biogenic) changes, which was largely driven by temperature
453	changes in NA1-NA2 and NA3. All three models shown in Figure 6 indicate similar spatial
454	patterns in the change in O ₃ sensitivity in 2010 relative to 2006; however, there are differences in
455	magnitude, especially for HCHO/NO _{y} and HCHO/NO _{2} in NA1 and NA3. The larger in
456	magnitude shift towards more NO _x -limited conditions for CA2f and US6 in NA3, compared to
457	US8, is due to a combination of different responses from different biogenic emission models and
458	versions (MEGAN vs. BEIS; Table 1) impacting isoprene emissions and resulting HCHO
459	concentrations, different gas-phase chemistry mechanisms (CB05 vs. ADOMII; Table 1) that
460	implement different VOC chemistry, and lower NOx concentrations for the CA2f model
461	specifically [Table S1 in Makar et al., 2014a]. The policy implications from results in Figure 6
462	are that 1) inter-model variability demonstrates a need for continued multi-model dynamic
463	assessments of indicator sensitivities, which should be based on the most detailed current
464	emission inventories as they become available every three years from NEI, while 2) enactment of
465	individual state implementation plans following multi-model dynamic assessments are important
466	to deriving state-specific NO _x -VOC policy for the appropriate control strategies of O ₃ pollution.

467	Figure 7 shows the changes in sensitivity for the PM _{2.5} indicators TN/TS, DSN, AdjGR, and
468	$\rm NH_3^F$, as well as for $\rm NO_3^-$ concentration between 2006 and 2010. Supplementary Section 4.3 and
469	Figure S6, provide additional details on the changes in sensitivity for the $PM_{2.5}$ indicator TA/TS,
470	and for $PM_{2.5}$ species NH_4^+ , SO_4^{2-} , and NO_3^- between 2006 and 2010. There is considerable
471	spatial and inter-model variability in the changes in PM _{2.5} sensitivity, such as in NA1, where
472	there are large differences in the spatial distribution of increasing NO ₃ ⁻ rich versus poor
473	conditions (Figures 7a - 7c), with less variability for changes in NO_3^- concentrations (Figures 7m
474	-70). The impact of TS is larger than TN on changes on TN/TS in NA1, where the regions of
475	SO_4^{2-} decreases in NA1 correlate well with the TN/TS increases for winter 2006 - 2010 (Figure
476	S6g – S6i). There are widespread increases in DSN across NA/U.S. for US6, due to more
477	predominant increases in NH_4^+ , in conjunction with less SO_4^{2-} increases compared to the other
478	models, in spite of larger NO_3^- increases for US6. In NA1 – NA3, there are differences in
479	response of AdjGR and NH_3^F for US8 (Figures 7g and 7j), while indicating widespread
480	decreases, as compared to increases for CA2f (Figures 7h and 7k) and US6 (Figures 7i and 7l).
481	An interesting response is in central California, where all models have increased AdjGR under
482	decreased NH ₃ ^F , indicating that the increases in AdjGR are driven by local NO ₃ ⁻ decreases, likely
483	due to relatively large local wintertime NO _x emission decreases of about -1000 Mg day ⁻¹ ,
484	compared to minimal surface temperature changes and NH ₃ and SO ₂ emission decreases of about
485	-100 Mg day ⁻¹ [<i>Stoeckenius et al.</i> , 2014].
486	In NA2, the models agree for decreases in AdjGR due to increases in $PM_{2.5} NO_3^-$
487	concentrations, with CA2f and US6 indicating the largest $PM_{2.5} NO_3^-$ increase. In spite of
488	decreases in NO _x emissions in NA2 of about -3000 Mg/day, significant surface temperature
489	decreases in the region (exhibited in both the initial and modeled conditions) lead to increased

490	$PM_{2.5} NO_3^-$ formation in the models, in agreement with analysis of $PM_{2.5}$ composition
491	observations at the surface [Stoeckenius et al., 2014]. In NA3, average surface temperature and
492	NO _x emissions decrease in 2010 relative to their values in 2006. US6 predicts large increases in
493	$PM_{2.5} NO_3^-$, but CA2f and US8 predict smaller $PM_{2.5} NO_3^-$ increases or even decreases. Other
494	instances of opposite PM _{2.5} sensitivity changes include US8 predicting decreases in AdjGR and
495	$\mathrm{NH_3}^\mathrm{F}$ (shift towards more $\mathrm{PM}_{2.5}$ sensitivity to $\mathrm{NH_3}$) across many areas of $\mathrm{NA}/\mathrm{U.S.}$, while $\mathrm{CA2f}$
496	and US6 oppositely predicting increases (shift towards more $PM_{2.5}$ sensitivity to TN) for these
497	indicators. This is a result of the use of the gas-phase mechanism/aerosol module combination
498	(CB05/MADE) used in US8, which is different than both CA2f (ADOMII/CAM) and US6
499	(CB05-TU/AERO6) responding differently to the predominant gas (SO ₂ , NO _x , and NH ₃)
500	emission decreases and temperature changes across NA/U.S. between winter 2006 and 2010
501	[Yahya et al., 2014a]. In contrast to the other models, US8 predicts overall less increase (or more
502	decrease) in NH_4^+ for all regions, however, with similar SO_4^{2-} increases, thus leading to
503	predominantly decreasing TA/TS (Figure S6a – S6i), and corresponding decreases in NH_3^F and
504	AdjGR. US8, CA2f, and US6 indicate progressively increased AdjGR in northeast NA4, due to
505	progressively increasing TA/TS, and enhanced TA and NH_3^F in this region. There are clearly
506	large ranges for different model responses of TN/TS, DSN, and AdjGR, which depend on
507	specific gas-phase mechanism, aerosol module, spatial resolution, and region of NA/U.S.
508	considered. Considering the large inter-model variability in PM _{2.5} indicator sensitivity, caution
509	must be used when using a single model prediction of changes in AdjGR to address the
510	appropriate policy and control strategies for PM2.5 pollution, i.e., the choice in implementing
511	future measures to reduce either NH_3 or TN for different regions of the U.S in the winter.
512	5 Summary and Conclusions

514 In the O₃ season, the six simulations that participated in this model inter-comparison predict 515 similar values for H₂O₂/HNO₃, NO_y, and O₃/NO_y, while indicating dominant NO_x-limited 516 chemistry for NA/U.S., except near urban centers that are predicted to be VOC-limited, 517 especially by the higher resolution models. NOy and O_3/NO_v overpredict the extent of VOC-518 limited chemistry in the southeast U.S. (Figures 1 and S1), but are more robust (smaller standard 519 deviations and inter-model variability) compared to the H₂O₂/HNO₃, HCHO/NO_y, and 520 HCHO/NO₂ (larger standard deviations and inter-model variability) indicators (Figure 4). Larger 521 differences arise for HCHO/NO_v and HCHO/NO₂ due to dependencies on the model gas-phase 522 mechanism (CBM vs. non-CBM), spatial resolution, and other differences such as the biogenic 523 emissions model (Table 1). Additional work, however, comparing model response of these (and 524 other) indicators to focused NO_x and VOC emission reductions, are needed before definite 525 recommendations on can be made. Additional measurements compared to further short-term 526 diagnostic modeling, would provide even more vigorous evaluations outside of the southeast 527 U.S. region, as well as lead to significant O_3 and $PM_{2.5}$ policy implications across the NA 528 domain. 529 The SCIAMACHY comparison indicates that models tend to underpredict the HCHO/NO₂

column indicator in both the O_3 and non- O_3 season, with the exception of those models that had large underpredictions in NO_x concentrations (Figure 3). Inter-model and SCIAMACHY observation comparisons also help put these models in context when they are used to develop effective O_3 control strategies across NA domain, while unveiling differences in using either a tropospheric column or surface HCHO/NO₂ indicator to diagnose the O_3 formation regime. Our results show that use of a column HCHO/NO₂ indicator leads to less VOC-limited regions near the urban centers, as well as more widespread NO_x-limited regimes compared to the surface

HCHO/NO2 indicator (Figures 4 and S3). Furthermore, when models employ a combined 537 538 Carbon Bond Mechanism, with the latest biogenic emission model, there are more consistent 539 NO_x-limited predictions in surface HCHO/NO_y and HCHO/NO₂ in the southeast U.S., but less 540 consistent than other models in northwestern U.S., surrounding urban centers in northeast U.S., 541 and in parts of Canada and Mexico, where emissions data are sparser (Figure S4). 542 In addition, we analyzed modeled $PM_{2.5}$ indicators over NA/U.S. in winter. Although there is 543 a systematic underprediction in the degree of sulfate neutralization (DSN) (Figure 2), it is 544 currently a more robust (smaller standard deviations and inter-model variability) PM_{2.5} indicator 545 than the adjusted gas ratio (AdjGR) (larger standard deviations and inter-model variability), 546 which exhibits a large range in predicted NH₃ poor (AdjGR \leq 1) versus NH₃ rich (AdjGR > 1) in 547 the Midwest to northeast U.S. Such a model disparity in AdjGR, leads to a prediction of 548 different NH₃ or TN sensitivities for the control of PM_{2.5} concentrations in the winter. 549 Furthermore in summer, all models perform poorly for AdjGR, indicating very large 550 overpredictions in AdjGR and the extent of the NH₃ rich conditions here. This suggests that 551 there is low confidence in modeled AdjGR for application to PM_{2.5} control and policy strategies, 552 and that more detailed diagnostic work is needed to determine the underlying mechanistic causes 553 of these differences in model sensitivity. 554 Analyzing the inter-model comparison changes in O₃ and PM_{2.5} sensitivity from 2006 to 2010 555 allows us to diagnose the responses of different models to changes in chemical emissions and

556 meteorology. Increases in NO_x-limited conditions dominated across the U.S., especially near

557 point sources, and are predicted by all models. The change is attributed to NO_x emission

decreases in 2010 relative to the level in 2006. The three models also agree on the spatial

559 distribution of change for O₃ indicator sensitivity, due to the relative surface temperature and

560 emission changes between 2006 and 2010, while differences in the magnitude are attributed to 561 different biogenic emission models and gas-phase chemistry impacts. This leads to policy 562 implications regarding the need for continued multi-model assessments at the highest possible 563 resolution, while using the most detailed emission inventories currently available. There is 564 larger variability in the modeled change in $PM_{2.5}$ indicators, DSN and AdjGR, between 2006 and 565 2010, in part due to inter-model variability in the biogenic emissions, oxidation chemistry, and 566 secondary organic aerosol abundance predicted by different model treatments (Table 1), which can in turn impact the response for the inorganic species. Thus compared to the O₃ indicators, 567 568 the $PM_{2.5}$ indicators are currently less robust, while suggesting that further model development is 569 needed in this area.

570

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	US8	US7	ES1	ES3	CA2f	US6
AO Motoo	Modified WPF	WRE Chem/3 / 1	WRE Chem/3/11	WRE-Chem/3 / 1	GEM-	WPE-CMAO/5.0.1
Model/	Chem/3 4 1	C05 Sk08	C05 Sk08	C05 Sk08	MACH/1.5.1	RS06 Fo10 W12
Vargion		005, 5600	005, 5000	005, 5600	MIQ	b300, 1010, W12
version	G05, 5k06, W14	2010	2010	2007	M10	2006 8 2010
Years	2006 & 2010	2010	2010	2006	2006 & 2010	2006 & 2010
Dx-Dy	36 km	36 km	36 km	36 km	15 km	12 km
Vertical	35 eta levels	33 eta levels	33 eta levels	33 eta levels	58 eta levels	35 eta levels
Resolution						
1 st Layer	38 m	60 m	29 m	18 m	21 m	19 m
Height						
Model Top	100 hPa	10 hPa	50 hPa	100 hPa	10 mb (2006), 0,1	100 hPa
Pressure					hPa (2010)	
Projection	Lambert	Lambert	Lambert	Lambert	Rotated Lat-Lon	Lambert
Domain	30 3°N·07 6°W	30 0°N:07 5°W	30 0°N 07 5°W	40.0°N:97.0°W	n/a	40.0°N·97.0°W
Conton	39.3 IN,97.0 W	39.0 IN,97.5 W	39.0 IN,97.5 W	40.0 IN,97.0 W	ii/ a	40.0 N,97.0 W
Center	NOED ENIL (1.00)	NCED ENIL (1.00)	NOED OF (1.00)	NOED OPS (1.00)		
Meteo.	NCEP FNL (1.0°)	NCEP FNL (1.0°)	NCEP GFS (1.0°)	NCEP GFS (1.0°)	GEM (15km) -	NCEP NAM (12-km)
ICs/BCs					CMC M06,Fi10	
Chemical	MACC-II	MACC-II	MACC-II	MACC-II	MACC-II	MACC-II
ICs/BCs	H08, S12	H08, S12	H08, S12	H08, S12	H08, S12	H08, S12
Land	NOAH	NOAH	NOAH	NOAH	ISBA2	Pleim-Xiu
Surface	CD01, Ek03	CD01, Ek03	CD01, Ek03	CD01, Ek03	B03	XP01
Model						
Surface Laver	Monin-Obukhoy	Monin-Obukhov	Monin-Obukhov	Monin-Obukhov	ISBA2	Monin-Obukhov
~,,,	MO54_102	M054_102	M054_102	MO54_102	B03	MO54_102
DDI	VII	MVNN	VSU	VSU	MOISTKEA	ACM2
Fahama	150	N/N/0.4	130	150	MD92 D05	DO7
Scheme	HOO	101004	H00	H00	MB02, B03	<i>P07</i>
D 11 11	5550 (G		DDM (G	555 (G	1005	DD (7)
Radiative	RRIMG	RRIM	RRIMG	RRIMG	LB05	RRIMG
Transfer	C05	M97	C05	C05		C05
Mech.						
Photolysis	FTUV	FTUV	Fast-J	Fast-J	ADOM-II	In-Line
	T03	T03	WOO	WOO	D72, P76, D88	B07
Microphysics	Morrison	Morrison	Lin (Purdue)	Morrison	Milbrandt-Yao	Morrison
	M09	M09	L83	M09	MY05	M09
Cloud	Grell 3D	Grell 3D	Grell 3D	Grell 3D	KF	KF2
Paramet	GF13	GF13	GF13	GF13	KF90	K04
Biogenic	MEGAN	MEGAN	MEGAN	MEGAN	BEIS309	BEIS3 14
Emissions	Gu06	Cy06	Cu06	Cu06	DE135.0.7	V02 S05
Car Discor	Madified CD05 Cl	MOZADT 4	DADM2	CDMZ	ADOMII	CD05 TU
Gas Phase	Not coc cpo7	MOZARI-4	KADWIZ	CBMZ	ADOMII	CB05-10
Mech.	Y05, S06, SB07	Em10, K13	590	299	SL89	W10
Aerosol	MADE/3 modes	MOSAIC/ 4 bins	MADE/3 modes	MOSAIC/ 4 bins	CAM/12 bins	AERO6/3 modes
Mechanism/	A98, G05	Z08	A98, G05	Z08	G03	A13
Size						
SOA	VBS	Hodzic and Jimenez	SORGAM	None	096	CMAQ SOA
Mechanism	A12	HJ11	S01			C10, S12
Aqueous	CMAQ AQCHem	Grid and Sub-Grid	Grid/Sub Grid	Grid/Sub Grid	ADOM	Grid/Sub Grid
Chemistry	<i>S</i> 11	WT86. FP01	WT86. FP01	WT86. FP01	V88. F91	
Dust & Sea-	Dust: AER/AFWA IC11	Dust: MOSIAC	Dust: MOSIAC Sh08	Dust: MOSIAC Sh08	Dust: None	Dust In-Line A13
Salt Scheme	Sea-calt: G07	Sh08 Sea-salt: C07	Sea-salt: C07	Sea-salt: C07	See selt: CO3	Sea-salt : In-Line K10
San Scheme	beu suit. 697	Shoo Bea sait. 077	Bed Sait. 697	beu suit. 677	Bea sait. 005	beu suit : In Enice Mite
Aerosol	Fast-Chapman	Fast-Chapman	Fast-Chapman	Fast-Chapman	GEM-MACH	CMAQ Feedback
Direct	F06, C09	F06, C09	F06,C09	F06,C09	Feedback BH83	BH98, W12
Effect						
Aerosol	AR-G00	AR-G00	AR-G00	AR-G00	AR-G00	None
Indirect	ARG00	ARG00	ARG00	ARG00	ARG00	
Effect						
Linker	UCM	LICM	News	N	Mana	News
Urban	UCM	UCM	None	None	None	None
Canopy	K01	K01	0.11/0.1.0.11		1775 1370	21 (1) 0
Wet	Grid/Sub-Grid	Grid/Sub-Grid	Grid/Sub-Grid	Grid/Sub-Grid	AURAMS	CMAQ
Deposition	E04	E04	E04	E04	Go06	WT86, BS06
Dry	Gases: Wesely	Gases: Wesely	Gases: Wesely	Gases: Wesely	Gases: Wesley	Gases & Particles:
Deposition	W89, WH00, Z02	W89, WH00, Z02	W89, WH00, Z02	W89, WH00, Z02	Particles: G03[a],	CMAQ In-Line
-	Particles: CMAQ - BS95	Particles: MOSAIC	Particles: MADE Driven	Particles: MOSAIC Driven	Z01	P01, PR11

 Table 1. AQMEII-2 participating models and configurations for the North American domain simulations.

 The full citations for their italicized short-names are provided in the footnote (alphabetically) below the table.

References: ARG00 – Abdul-Razzak and Ghan [2000]; A98 - Ackerman et al. [1998]; A12 - Ahmadov et al. [2012]; A13 - Appel et al. [2013]; B03 - Belair et al. [2003a,b]; B05 - Bélair et al. [2005]; BS95 – Binkowski and Shankar [1995]; B07 - Binkowski et al. [2007]; BH38 - Bohren and Huffmann [1983]; BH98 - Bohren and Huffman [1998]; BS06 - Byun and Schere [2006]; C10 - Carlton et al. [2010]; C09 - Chapman et al. [2009]; CD01 - Chen and Dudhia [2001]; C05 - Clough et al. [2005]; D72 - Dave [1972]; D88 - DeMore et al. [1908]; E04 - Easter et al. [2004]; Ek03 - Ek et al. [2003]; En10 - Emmons et al. [2010]; F91 - Schey and Pandis [2001]; F06 - Fast et al. [2005]; T10 - Filion et al. [2010]; F01 - Foley et al [2010]; F91 - Fung et al. [1991]; G97 - Gong et al. [1997]; G03 - Gong et al. [2006]; G06 - Gong et al. [2006]; G02 - Gangit et al. [2005]; GF13 - Grell and Freitas [2013]; Gu06 - Guenther et al. [2006]; H11 - Hodzic and Jimenz [2011]; H08 - Hollingsworth et al. [2008]; H06 - Hong et al. [2006]; J02 - Janijc [2002]; JC11 - Jones and Creighton [2011]; KF90 - Kain and Fritsch [1990]; K04 - Kain [2004]; L80 - Kain (2004]; M95 - Milhort et al. [2010]; K13 - Knote et al. [2003]; M07 - Miaswa et al. [2001]; L805 - Li and Barker [2005]; L83 - Lin et al. [1983]; MB82 - Mailhort and Benoit [1982]; M06 - Maini and Obukhov [1954]; M10 - Moran et al. [2010]; M09 - Morrison et al. [2009]; NN04 - Nakanishi and Niino [2004]; O96 - Odum et al. [1976]; P76 - Peterson [1976]; P78 - Pierce et al. [1001]; K17 - Schere et al. [2001]; K17 - Schere et al. [2001]; K17 - Schere et al. [2001]; S12 - Schwede et al. [2001]; S12 - Schwede et al. [2001]; S12 - Schere et al. [2001]; S12 - Schere et al. [2001]; K10 - Moran et al. [2001]; M08 - Marrison et al. [2009]; NN04 - Nakanishi and Niino [2004]; O96 - Odum et al. [1996]; P76 - Peterson [1976]; P78 - Pierce et al. [2001]; S12 - Schere et al. [2011]; S05 - Schwede et al. [2001]; S05 - Schwede et al. [2005]; S12 - Simon and Bhave [2012]; S08 - Skamarock et al. [2008]; SL89 - Stockwell and Lu

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	Average												
Indicator	H ₂ O ₂ /HNO ₃	NOy	O ₃ /NO _y	HCHO/NO _y	HCHO/NO ₂	TN/TS	DSN	AdjGR	NH ₃ ^F	NO ₃ -			
Region	ratio	ppb	ratio	ratio	ratio	ratio	ratio	ratio	ppb	μg m ⁻³			
NA1	4.15	1.36	39.22	0.93	5.33	2.27	1.33	1.12	0.45	0.29			
NA2	4.10	2.06	24.32	0.97	3.24	2.61	1.53	1.92	1.04	1.02			
NA3	5.09	3.83	13.94	1.01	2.85	2.35	1.38	1.05	0.83	1.16			
NA4	4.91	3.04	23.78	0.81	3.19	2.29	1.05	1.10	0.53	0.93			
NA/U.S.	4.57	2.57	25.31	0.93	3.66	2.38	1.32	1.30	0.71	0.85			
Standard Deviation (SD)													
NA1	1.49	0.42	12.99	0.41	3.34	1.29	0.38	0.69	0.18	0.14			
NA2	1.18	0.64	8.13	0.47	1.88	1.21	0.37	1.39	0.40	0.61			
NA3	3.13	0.88	4.33	0.58	1.79	1.22	0.31	0.85	0.37	0.65			
NA4	2.14	0.84	8.19	0.41	2.11	1.42	0.45	1.14	0.31	0.66			
NA/U.S.	1.94	0.72	8.36	0.47	2.28	1.29	0.39	1.03	0.33	0.50			
	Normalized Standard Deviation (NSD)												
NA1	0.36	0.31	0.33	0.44	0.63	0.57	0.28	0.62	0.40	0.48			
NA2	0.29	0.31	0.33	0.48	0.58	0.46	0.24	0.72	0.38	0.60			
NA3	0.62	0.23	0.31	0.57	0.63	0.52	0.23	0.81	0.45	0.56			
NA4	0.44	0.28	0.34	0.51	0.66	0.62	0.43	1.04	0.59	0.70			
NA/U.S.	0.42	0.28	0.33	0.50	0.62	0.54	0.30	0.80	0.46	0.59			

Table2. Statistical summary of the NA1, NA2, NA3, NA4, and NA/U.S.-wide ensemble model average, standard deviation, and normalized standard deviation (standard deviation/average) for each O₃ and PM_{2.5} indicator in the O₃ and winter (DJF) seasons respectively.



Figure 1. Averaged NMB and NME for modeled O₃/NO_y against SEARCH observations averaged over the urban (a) and a rural sites (b) in NA3. Colored circles and triangles pertain to the model's average values over O₃ and non-O₃ seasons, respectively.



Figure 2. Averaged NMB and NME for the comparison of the modeled DSN (a, b), AdjGR (c, d), and NH₃^F (e, f) against SEARCH observations avearaged over the urban (top) and a rural sites (bottom) in NA3. Colored circles and triangles pertain to the model's average values over O₃ and non-O₃ seasons, respectively.



Figure 3. Averaged NMB and NME for the comparison of modeled HCHO/NO₂ against SCIAMACHY observations averaged over the (a) NA/U.S., and sub-regions (b) NA1, (c) NA2, (d) NA3, and (e) NA4. Colored circles and triangles pertain to the model's average values over O₃ and non-O₃ seasons, respectively.



Figure 4. Ensemble model average and normalized standard deviation of surface H_2O_2/HNO_3 , NO_y , O_3/NO_y , $HCHO/NO_y$, and $HCHO/NO_2$, for average afternoon hours, during the O_3 season (May – September). Average NO_x -VOC-limited chemistry indicator value (a - e) is color shaded according to the legends on the left, while the normalized standard deviation's (f - j) color shading corresponds to the legend on the right . The panel in the top right shows the geographical sub-regions of NA used for discussion in the text.



Figure 5. Same as in Figure 4, but for TN/TS, DSN, AdjGR, NH₃^F, and NO₃⁻ for the winter (DJF) season.



Figure 6. Difference (2010 – 2006) plots representing changes in H_2O_2/HNO_3 (a – c), NO_y (d – f), O_3/NO_y (g – i), HCHO/NO_y (j – l), and HCHO/NO₂ (m – o) for averaged afternoon hours during the O₃ season. NO_x-VOC-limited chemistry indicator changes are color shaded according to the legends on the left.



- t) changes for the winter (DJF) season.

Supplementary Material

A Multi-Model Assessment for the 2006 and 2010 Simulations under the Air Quality Model Evaluation International Initiative (AQMEII) Phase 2 over North America: Part I. Indicators of the Sensitivity of O₃ and PM_{2.5} Formation Regimes

Patrick Campbell^{a,*}, Yang Zhang^{a,*}, Khairunnisa Yahya^a, Kai Wang^a, Christian Hogrefe^b, George

Pouliot^b, Christoph Knote^c, Alma Hodzic^c, Roberto San Jose^d, Juan L. Perez^d, Pedro Jimenez

Guerrero^e, Rocio Baro^e, and Paul Makar^f

^aDepartment of Marine, Earth, and Atmospheric Sciences, NCSU, Raleigh, NC 27695.
^bORD, ORD, U.S. EPA, Research Triangle Park, NC 27711.
^cAtmospheric Chemistry Division, NCAR Earth System Laboratory, NCAR, Boulder, CO 80301.
^dComputer Science School, Technical University of Madrid, Campus de Montegancedo - Boadilla del Monte-28660 Madrid, Spain
^eDepartment of Physics, University of Murcia, Ed. CIOyN, Campus de Espinardo, Regional Campus of International Excellence "Campus Mare Nostrum", University of Murcia, 30100 Murcia, Spain.
^fAir Quality Research Division, Environment Canada, Toronto, Ontario, Canada M3H 5T4

1. Surface O₃/NO_y Indicator Comparison

Figure S1 shows a scatter plot comparison of the observed SEARCH (BHM, CTR, JST, and

YRK) hourly maximum O₃ mixing ratio in the afternoon (1 p.m. – 6 p.m. LST), versus

concurrent NO_y mixing ratio, for the 2006 and 2010 O₃ and non-O₃ seasons in the southeast U.S.,

NA3 (see description in main text), and a comparison between the SEARCH observed and

simulated seasonally-averaged values. The dividing line in Figure S1 pertains to the transition

between the NO_x- and VOC-limited regimes ($O_3/NO_y = 15$), based on Sillman et al. [1997], and

updated in Zhang et al. [2009]. There was problem in ES1's point source emissions processing

for their simulations, which led to inadvertent exclusion of point sources such as SO₂ and NO_x.

^{*}Corresponding authors: Patrick Campbell and Yang Zhang, Department of MEAS, US8, Campus Box 8208, Raleigh, NC 27695-8208, USA. Tel: 919 515 9688; fax: 919 515 7802. Email addresses: <u>pccampb2@ncsu.edu</u> <u>yang zhang@ncsu.edu</u>

This impacts O_3 and its associated indicators in parts of the domain where point sources are major contributors to their concentrations, while having less impact over regions where area and biogenic sources are dominant. Despite this limitation, analysis of the ES1 simulation is still valuable, as its differences provide an outlook on the influence of point sources on ES1's O_3 concentrations and indicators. At the urban BHM and JST sites in 2006 and 2010 (Figures S1a, S1c, S1e, S1g), both observations and the models indicate VOC-limited conditions, with a less or more pronounced VOC-limited regime during the O₃ or non-O₃ seasons, respectively. VOClimited chemistry and high O_3 levels are frequently observed and modeled near high NO_x emissions emanating from metropolitan areas in NA/U.S. [Milford et al., 1989; Sillman et al., 1998; Kleinman et al., 2005; Zhang et al., 2009]. A high rate of biogenic VOC emissions, typical of the NA3 O₃ season, will result in shift towards NO_x-limited chemistry [*Chameides et* al., 1988; 1992; Pierce et al., 1998; Kang et al., 2004]. ES1 and US6 in 2010, however, do not exhibit such a shift towards NO_x-limited conditions during the O₃ season at BHM (Figure S1e). The larger range in model predicted NO_y mixing ratios, compared to that of O_3 , has the largest impact on model predicted O₃/NO_y in 2006 (Figures S1a and S1c). The majority of models also agree more favorably for O₃ mixing ratios in 2010 (Figures S1e and S1g). US7 and ES1 predict the largest over- and underpredictions for O_3 mixing ratios in the O_3 season, and US8 and ES1 have the largest underpredictions in the non- O_3 season. There is also considerable spread for predicted NO_y in 2010. An average of both years and seasons, and over all four SEARCH locations, indicates that US8, US7, ES1, and US6 overpredict NO_v by 30, 40, 50, and 140 %, and that ES3 and CA2f underpredict NO_y by 11 and 30 %. Thus AQMs may predict accurate O₃ coincident with inaccurate NO_v mixing ratios, thus leading to moderately under- to largely overpredicting the extent of urban VOC-limited chemistry. We note that US6 has a positive NO_{v} bias (~ 140 %) that is much larger than other models at BHM and JST, and is the only model to utilize a gas-phase chemistry mechanism (CB05-TU; Table 1) that includes nitro-cresols and particulate NO_3^- in calculation of NO_y . *Sawar et al.* [2013] indicated that particulate NO_3^- is the most dominant chemical species in calculation of mean NO_z ($NO_z = NO_y - NO_x$), accounting for 34 % of NO_z in CB05-TU, and that the CB05-TU mechanism over-predicts NO_z compared to observations. Thus assuming similar NO_x across all models, the inclusion of particulate NO_3^- by US6 may contribute to its large positive bias. Interestingly, however, is that all other models have better agreement with the observed NO_y , which leads to a proposal of two different situations: 1) particulate NO_3^- is present in quantities that have a large impact on NO_y mixing ratios, but are not accounted for by SEARCH NO_y instrumentation at BHM or JST, or, 2) particulate NO_3^- is not present in measurable quantities to have a large impact on NO_y mixing ratios, and its inclusion in the NO_x calculation by US6 is largely overpredicted.

Observations indicate a clear shift towards NO_x -limited chemistry at the rural CTR and YRK sites in 2006 and 2010 (Figures S1b, S1d, S1f, S1h), most pronounced in the O₃ season. A shift in VOC- to NO_x-limited O₃ chemistry away from emission sources has been readily observed and modeled [*Kleinman*, 1994; *Buhr et al.*, 1995; *Zhang et al.*, 2009], with more pronounced NO_x-limited chemistry in the O₃ season partly impacted by the increased biogenic VOC emissions associated with warmer temperatures. Indeed the more remote forest location of CTR is more NO_x-limited than YRK, which has closer proximity to large urban plumes. The majority of models agree well for O₃ concentrations, and there is less spread in NO_y at the rural locations; however, there is also less room for model error given that conditions are closer to the NO_x-VOC transition line, such that underpredictions in O₃ by ES1 in 2010 lead to erroneous predictions of the NO_x-VOC-limited chemical regimes (Figures S1f and S1h). Furthermore,

slight overpredictions in NO_y by US8, CA2f, and US6 occurring in both seasons, also lead to a small deviation of the simulated (slightly VOC-limited) from the observed O₃ chemical regime (slightly NO_x-limited) (Figure S1b, S1d, S1h). Overall for the two rural locations, CTR and YRK, there is a relatively closer agreement in NO_y mixing ratios, and less systematic bias for the different models compared to the urban locations, BHM and JST. This may be caused by increased distance from local emission sources for the rural locations, lower NO_y mixing ratios, and the additional influences of transport relative to the urban locations. There may also be relatively less pronounced impacts from differences in model NO_y calculations (discussed above) at the rural sites.

2. Detailed PM_{2.5} Regime Indicator Comparison

Figure S2 presents a 2010 bar chart comparison between SEARCH observations (BHM, CTR, JST, and YRK) and models, for seasonal (winter – DJF, spring – MAM, summer – JJA, fall – SON) average PM_{2.5} regime indicators TA/TS, TN/TS, DSN, AdjGR, and NH₃^F. As discussed in the main text, ES1 was removed from analyses due to emission processing errors for their simulation. For TA/TS (Figure S2a – S2d), the observations indicate approximately SO_4^{2-} neutral (TA/TS ~ 2) or poor (TA/TS > 2) conditions for all seasons and locations. The ratio of TA/TS is smaller, i.e. less SO_4^{2-} poor at BHM (urban) and CTR (rural) compared to JST (urban) and YRK (rural). BHM and CTR are similarly located closer to significant SO₂ emission sources in Alabama (resulting in larger TS), but are relatively farther from significant NH₃ emissions (resulting in smaller TA) compared to similarly located JST and YRK in Georgia. All models generally agree with this pattern of observations, except CA2f, which has a relatively larger values of TS and smaller values of TA compared to other models (not shown), has the smallest TA/TS, and predicts SO_4^{2-} rich conditions at BHM and CTR for all seasons. US7 and US6

models have the largest TA/TS ratios in winter at all sites, especially at JST where they are more than a factor of 2 larger than other models. Compared to the other models and observations, for a wintertime average the dominant factor controlling the bias in TA/TS for US7 and US6 is a lower TS and larger TA respectively. Thus differences for US7 are attributed to different gasand aqueous-phase chemistry, thus impacting TS, while differences for US6 are more impacted by its different aerosol module's thermodynamic partitioning of TA (Table 1). Further insights into these differences are provided in the main text, Sections 4 and 5.

TN/TS observations indicate NO₃⁻ poor conditions in the summer, and NO₃⁻ medium conditions in the winter, spring, and fall, except at BHM in spring - fall, which is NO₃⁻ poor (Figures S2e – S2h). The CA2f model has the lowest TN/TS and predicts NO₃⁻ poor conditions throughout, likely due to relatively large underpredictions in NO_x concentrations [Table S1 in *Makar et al.*, 2014]. In winter, US8 and US7 agree with observations and predict NO₃⁻ medium, while US6 has the largest TN/TS indicating NO₃⁻ rich conditions, due to overprediction in NO₃⁻ in the winter. Other AQMEII-2 analyses for NA show that the US6 overpredicts PM_{2.5} mass concentration for urban areas in the winter [*Hogrefe et al.*, 2014; *Im et al.*, 2014]. In summer all models accordingly predict NO₃⁻ poor conditions at the rural sites, while US8 and US7 indicate slightly higher TN/TS and NO₃⁻ medium conditions at the urban sites. There is good agreement in spring except for CA2f, which is consistently lower. In the fall, US8 consistently overpredicts TN/TS and NO₃⁻ rich conditions at JST and YRK. This is a result of a larger TN and smaller TS for US8, due to a combination of impacts from different thermodynamic partitioning of TN and gas-phase chemistry impacts on TS.

DSN observations indicate sufficiently SO_4^{2-} neutralized conditions (DSN ≥ 1.5) for all sites and seasons (Figures S2i – S2l). This is somewhat consistent with the SO_4^{2-} poor/neutral

conditions based on the observed TA/TS indicator (i.e., there was sufficient ammonium to fully neutralize the relatively low SO_4^{2-} conditions). The models tend to underpredict the DSN, and at times predict insufficiently neutralized conditions. In fact, Figure 2 in the main text indicates a systematic underprediction in DSN across all models, seasons, and sites. This is due to an overprediction in NO_3^- and TN for the models, stemming from inaccuracies in thermodynamic partitioning within their aerosol modules, and inaccurate NO_x emission estimates here. An underprediction of DSN by the models contributes to an overprediction in AdjGR. The models exhibit better agreement in warmer seasons (JJA and SON), e.g., US8 has DSN values consistently in the same regime, with < 10 % mean difference across all sites. Other models, however, have consistently low DSN during the warmer seasons.

AdjGR and NH_3^F observations indicate mainly NH_3 poor conditions at BHM and CTR ($PM_{2.5}$ more sensitive to NH_3 changes), except at BHM in DJF, and NH_3 rich conditions at JST and YRK ($PM_{2.5}$ more sensitive to TN changes) (Figures S2m - S2t). There is a different $PM_{2.5}$ sensitivity for these sites in part impacted by the relatively farther distance of BHM and CTR, and closer distance of JST and YRK to specific NH_3 emission sources. The models indicate increasingly more NH_3 rich conditions for JST and YRK, but at times inaccurately predict the AdjGR regime. The seasonal pattern and agreement between observed and modeled NH_3^F are similar to AdjGR for lower NH_3^F at BHM and CTR, and generally larger NH_3^F at JST and YRK (Figures S2s - S2t). There are large overpredictions in AdjGR and NH_3^F at many sites and seasons for the models, e.g., US7 and US6 in the summer season. Such overpredictions are a result of impacts from previously described gas-phase chemistry impacts on underpredictions in TS and thermodynamic partitioning of TA and TN, as well as underpredictions on dry deposition

of NH₃ across the models. There may also be impacts stemming from common over- or underpredictions in NH₃ or NO_x gas emissions, respectively.

3. Spatial Plots for the Satellite HCHO/NO₂ Comparison

Figure S3 shows a comparison of the modeled tropospheric column HCHO/NO₂ ratio [Martin et al., 2004] against SCIAMACHY observations, for O_3 and non- O_3 seasonal averages in subdomains NA1 - NA4 (see description in main text), while extending to parts of Canada and Mexico. In the O₃ season, SCIAMACHY indicates generally NO_x-limited conditions (HCHO/NO₂ \geq 1) across NA/U.S., except for local VOC-limited conditions (HCHO/NO₂ < 1) near large urban (i.e., highest population density) centers (Figure S3a). Transitional-weak NO_xlimited areas (HCHO/NO₂ = 1 - 2) correlate with smaller urban centers. There are moderate (HCHO/NO₂ = 2 - 6) NO_x-limited areas in NA4 and NA1, and strong (HCHO/NO₂ > 6 - 10) NO_x-limited areas in NA3. US8, US7, ES3, and US6 accurately predict VOC-limited chemistry in the large urban centers; however, these models underpredict the NO_x-limited conditions in some northern NA1 regions. In Canada, with the exception of ES1 and CA2f, the models underpredict the NO_x-limited chemistry. These differences are due to a factor of 2 lower HCHO in rural background regions, and up to an order of magnitude higher NO₂ predicted near urban centers (not shown). ES1 and CA2f are clear outliers in Figure S3, as they both largely overpredict the NO_x-limited conditions in NA1-NA4, and near major urban centers (Figures S3e and S3f); in part due to enhanced HCHO, but with larger impacts from underprediction of NO₂. This is an impact of the exclusion of NO_x point sources by ES1, and CA2f underpredictions in NO_x concentrations contributing to its overpredictions of the NO_x-limited extent. US7 and US6 overpredict NO_x-limited chemistry in parts of NA3, associated with approximately a factor of 10 larger HCHO column concentrations. In parts of Mexico, all models overpredict NO_x-limited

chemistry, with the exception of CA2f (outside of its domain). This is due to an over- and underprediction of about a factor of 2 and 10 in column HCHO and NO₂ mixing ratio respectively, likely attributed to the sparse emission data available in Mexico.

In the non-O₃ season, SCIAMACHY indicates a general transition from NO_x-to-VOClimited conditions, especially in NA2 – NA4 (Figure S3h). All models (Figures S3i – 3n) qualitatively agree with such a transition; however, with the exception of ES1 and CA2f, the area of VOC-limited conditions is overpredicted. These models indicate larger areas of moderately (HCHO/NO₂ = 0.8 - 0.4) to strongly VOC-limited (HCHO/NO₂ < 0.4) chemistry in NA2-NA4. US7 has the largest overprediction in VOC-limited chemistry across NA/U.S. (Figure S3j). Observations indicate a larger area of transitional to weak VOC-limited (HCHO/NO₂ = 1 - 0.8), or even a NO_x-limited (HCHO/NO₂ > 1) environment. Much larger HCHO/NO₂ values for ES1 and CA2f, due to underprediction of NO₂, again lead to overpredictions in NO_x-limited conditions across NA/U.S.

4. Inter-Model Comparison Plots of Seasonally Averaged Indicators

This section provides additional inter-model comparison plots of different NO_x -VOC-limited indicators during the O_3 season (Section 4.1), regime indicators for the formation of $PM_{2.5}$ in winter (Section 4.2), and changes in $PM_{2.5}$ sensitivity for winter 2010 relative to 2006 (Section 4.3). The additional diagnostic/dynamic comparison details are meant to supplement Section 4 of the main text.

5.1 Spatial Comparison Plots of NO_x-VOC Sensitivity in the O₃ Season

Figure S4 shows an inter-model comparison of five surface photochemical indicators $(H_2O_2/HNO_3, NO_y, O_3/NO_y, HCHO/NO_y, and HCHO/NO_2)$ averaged over afternoon hours during the 2006, 2010, or average 2006 and 2010 O₃ season. For the H_2O_2/HNO_3 indicator

(Figures S4a – S4f), there is good agreement in spatial variability across NA1-NA4 for the different models. All models predict NO_x -limited chemistry in northern NA1, with the largest values of H_2O_2/HNO_3 for US6 that has a higher spatial resolution of 12 km compared to the other models, while predicting NO_x -limited to transitional VOC-limited O₃ chemistry over NA2 and NA4. There are also locations with VOC-limited chemistry near urban centers. There is a discrepancy in NA3, where the majority of the models predict higher regional background H_2O_2 mixing ratios (~ factor of 2; not shown), which leads to more enhanced NO_x -limited chemistry compared to ES3. For gas-phase chemistry, ES3 incorporates a different version of the Carbon Bond Mechanism (CBM), CBM-Z, compared to both US8 and US6 that use an updated CBM, CB05 (Table 1). US7 indicates the most enhanced NO_x -limited chemistry for NA/U.S., especially in NA3, and less apparent VOC-limited conditions near the major urban centers. This is due to larger H_2O_2 mixing ratios for US7 (not shown). US7 and ES1 use non-CBM gas phase mechanisms MOZART-4 and RADM2 respectively (Table 1). MOZART-4 is more updated than mechanisms in RADM2.

There is generally good agreement for modeled NO_y (Figures S4g – S4l) and O₃/NO_y (Figures S4m – S4r), with dominant NO_x-limited chemistry, and local areas of VOC-limited chemistry near major urban centers. There is disparity, however, when comparing the magnitude of NO_y for the different models at local areas. This is consistent with the previous comparison at local SEARCH sites, and the apparent spread in NO_y mixing ratios between models (Figure S1). US8 and US6 have a larger number and area of VOC-limited "hotspots", defined as enhanced VOC-limited chemistry, with even larger NO_y mixing ratios for the higher resolution US6. This is in contrast to the H₂O₂/HNO₃ indicator, which indicates broader regions of weakly VOC-limited chemistry, and less VOC-limited hotspots. Out of the models implementing a CBM, ES3

has a lower NO_y, e.g., in NA3-NA4, but also had some of the least model bias and error for O_3/NO_y in NA3 (Figure 1). US6 overpredicts NO_y and underpredicts O_3/NO_y compared to SEARCH observations at the urban sites in NA3 (Figures 1 and S1). ES1 has the lowest O_3/NO_y (Figure S4o), with regions of significantly less NO_x-limited conditions or more VOC-limited conditions, due to lower O_3 mixing ratios (also predicted for NA3 in Figures S1e – S1h).

For HCHO/NO_y (Figures S4s – S4x) and HCHO/NO₂ (Figures S4y – S4dd) indicators, all models predict dominant NO_x- limited conditions in NA1, NA2, and NA3; however, by comparison US7, ES1, and CA2f, all of which implement non-CBM gas-phase chemistry, have the most enhanced NO_x-limited chemistry; thus dominating the ensemble model average in Figure 4. US6 agrees with US8 and ES3 more favorably, but also exhibits more enhanced NO_x-limited conditions in NA3. The increased HCHO in NA3 may in part be attributed to different biogenic emission models employed for US8 and ES3 compared to CA2f and US6, MEGAN2 vs. BEIS respectively, where CA2f also uses an older version of BEIS than US6 (Table 1). Out of these 4 simulations for 2006 (US8, ES3, CA2f, and US6), CA2f is also the only model that does not employ a CBM for the gas-phase chemistry (Table 1). ES3 also uses an older version of CBM, CBM-Z, which helps explain in part some discrepancies compared to US8 and US6. Comparison against observations and other models (Figures 3 and S3), indicate that US8, US7, and ES3 predict less enhanced NO_x-limited chemistry in northwestern NA1.

5.2 Spatial Comparison Plots of PM_{2.5} Sensitivity in Winter

Figure S5 shows an evaluation of indicators for PM_{2.5} sensitivity (TN/TS, DSN, AdjGR, NH₃^F) and NO₃⁻ concentrations in winter (DJF). Individual models predict similar association of regions of NO₃⁻ rich conditions (TN/TS > 2; Figures S5a – Se) and full SO₄²⁻neutralization (DSN ≥ 1.5 ; Figures S5f – S5j), with NH₃ rich (AdjGR > 1; Figures S5k – S5o), excess NH₃^F (NH₃^F > 1

ppb; Figures S5p – S5t) and enhanced PM_{2.5}NO₃⁻ formation (Figures S5u – S5y). There are, however, inter-model differences. US8 and ES3 predict rather uniform NO₃⁻ medium-to-rich conditions across NA1 (Figures S5a – S5c), while the higher resolution CA2f (15×15 km) and US6 (12×12 km) models predict a progressively larger NO₃⁻ poor area, embedded with more localized NO₃⁻ medium-to-rich regions (Figures S5d – S5e), NH₃ rich (Figures S5n– S5o), excess NH₃^F (Figures S5s– S5t), and enhanced NO₃⁻ concentrations in NA1 (Figures S5x – S5y). US6 also indicates local areas of insufficiently neutralized SO₄²⁻ in NA1, e.g., near the Front Range in Colorado for US6 (Figure 9j), while remaining NH₃ rich (Figure 9o), with excess NH₃^F (NH₃^F > 1 ppb) and enhanced PM_{2.5} NO₃⁻ concentrations. This is largely opposite the other models. Thus US6 may more finely represent the interactions between high NO_x emissions near Denver, topographical effects, and local meteorology, thus enhancing PM_{2.5} NO₃⁻ under insufficiently neutralized SO₄²⁻.

In NA2-NA4 there is a notable bias for the ES3 and US6, which predict relatively larger NO_3^- rich and sufficiently neutralized SO_4^{2-} conditions, in conjunction with more enhanced $PM_{2.5}$ NO_3^- concentrations compared to the other models. The differences in TN/TS and DSN are due to relatively larger TN for ES3 and US6.

US7 is rather different from other models and indicates larger regions of NO₃⁻ medium-topoor conditions (TN/TS ≤ 2 ; Figure S5b) and insufficiently neutralized SO₄²⁻ (DSN < 1.5; Figure S5g) in the winter. This occurs in conjunction with the most enhanced NH₃^F and NH₃ rich conditions (AdjGR >> 1; Figure S5l), however, counterintuitively with the lowest associated NO₃⁻ concentrations. Compared against SEARCH observations in NA3, the US7 model has the largest DSN and AdjGR bias and error at both urban and rural sites in the winter (Figure S2). On average, US7 also predicts a total PM_{2.5} concentration about 2 – 3 times larger (~ 8.4 µg m⁻³) than other models (~ $2.9 - 4.2 \ \mu g \ m^{-3}$) in NA2-NA4, while concurrently predicting lower concentrations for all inorganic species (not shown), likely a result of different combinations of gas-phase (non-CBM), aqueous chemistry, and aerosol mechanisms (Table 1), thus impacting their individual treatments of gas-aerosol partitioning. This indicates that a larger fraction of other species such as organics contributing to the PM_{2.5} mass speciation, may lead to an impact on predicted AdjGR and inorganic PM_{2.5} sensitivity. In fact, US7 predicts a factor of 3 larger primary organic PM_{2.5} concentration compared to US8 in NA2-NA4 for winter 2010 (not shown).

5.3 Changes in PM_{2.5} Sensitivity from 2006 to 2010

Figure S6 shows the changes in sensitivity for the PM_{2.5} indicator TA/TS, and for PM_{2.5} species NH₄⁺, SO₄²⁻, and NO₃⁻ between 2006 and 2010. For TA/TS (Figure S6a – S6c), US8 indicates predominantly decreases in TA/TS, while the higher resolution models of CA2f and US6 show progressively more increases in TA/TS for 2010 relative to 2006. Thus US8 indicates a shift towards more SO₄²⁻ poor conditions across NA/U.S., while US6 indicates a shift to more SO₄²⁻ rich conditions. These differences are a result of differences in the relative change in PM_{2.5} species, such as smaller increases in NH₄⁺ for US8 (Figure S6d – S6f), in conjunction with relatively larger increases in SO₄²⁻ (Figure 6g – 6i). In contrast, US6 has larger increases in NH₄⁺ compared to SO₄²⁻. Although there were NA/U.S.-wide decreases in gas emissions (SO₂, NO_x, and NH₃), there are increases in all particulate species in NA2 due to large temperature decreases in this region. The differences in the relative amounts for each inorganic PM_{2.5} species is due to mechanistic differences within the different model combinations of gas-phase chemistry and

aerosol module's (Table 1) thermodynamic partitioning response to meteorological and emission changes (see discussions in the main text, Section 4).

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Figure S1. Scatter plot comparisons of the hourly maximum, afternoon, O3 mixing ratio (ppb), versus the concurrent NO_y mixing ratio (ppb), for the four SE ARCH sites in NA3 (top-to-bottom), for 2006 (left) and 2010 (right). Small grey circles (triangles) pertain to the daily maximum hourly SE ARCH values for the O3 (non-O3) seasons. Large colored circles (triangles) pertain to the SE ARCH observation's, model's, and ensemble model's seasonally averaged O3 (non-O3) values, according to the legends in a) and e). The black line pertains to the transition (O3/NO_y = 15) between NO_x-limited and VOC-limited O3 chemistry, recommended by *Zhang et al.* [2009].



Figure S2. 2010 Bar chart comparisons of seasonally (winter-DJF, spring-MAM, summer-JJA, fall-SON) averaged $PM_{2.5}$ regime indicators, TA/TS (a-d), TN/TS (e - h), DSN (f - l), AdjGR (m - p), and NH_3^F (q - t), for each model, and ensemble model average against SEARCH observations according to the color bar at the top, for the four SEARCH sites in NA3 (left-to-right). The horizontal black lines mark the transitions of relevant indicator species that impact $PM_{2.5}$ formation sensitivity regimes, as discussed in the text.



Figure S3. Column HCHO/NO₂ spatial comparison of SCIAMACHY (ave of 2006 and 2010) observations to the US8 (ave. of 2006 and 2010), US7 (2010), ES3 (2006), ES1 (2010), CA2f (ave. of 2006 and 2010), and US6 (ave. of 2006 and 2010) models (top-to-bottom), for the O₃ (left) and non-O₃ season (right). NO_x-VOC-limited chemistry indicator value is color shaded according to the legend on the right. The panel in the top right shows the geographical sub-regions of NA used for discussion in the text.



Figure S4. Inter-model comparison of surface H_2O_2/HNO_3 (a – f), NO_y (g – l), O_3/NO_y (q – r), $HCHO/NO_y$ (s – x), and $HCHO/NO_2$ (y – dd), for average afternoon hours, during the 2006, 2010, or average 2006 and 2010 O₃ season (May – September). NO_x -VOC-limited chemistry indicator value is color shaded according to the legends on the left. The panel in the top right shows the geographical sub-regions of NA used for discussion in the text.



Figure S5. Same as in Figure S4, but for TN/TS (a - e), DSN(f - j), AdjGR (k - o), NH₃^F (p - t), and NO₃⁻ (u - y).



Figure S6. Difference (2010 – 2006) plots representing changes in surface TA/TS (a – c), NH4⁺ (d – f), SO4²⁻ (g – i), and NO₃⁻ (j – l) for the winter season. PM_{2.5} indicator sensitivity and concentration changes are color shaded according to the legends on the left.