Supporting information:

Understanding nitrate formation in a world with less sulfate.

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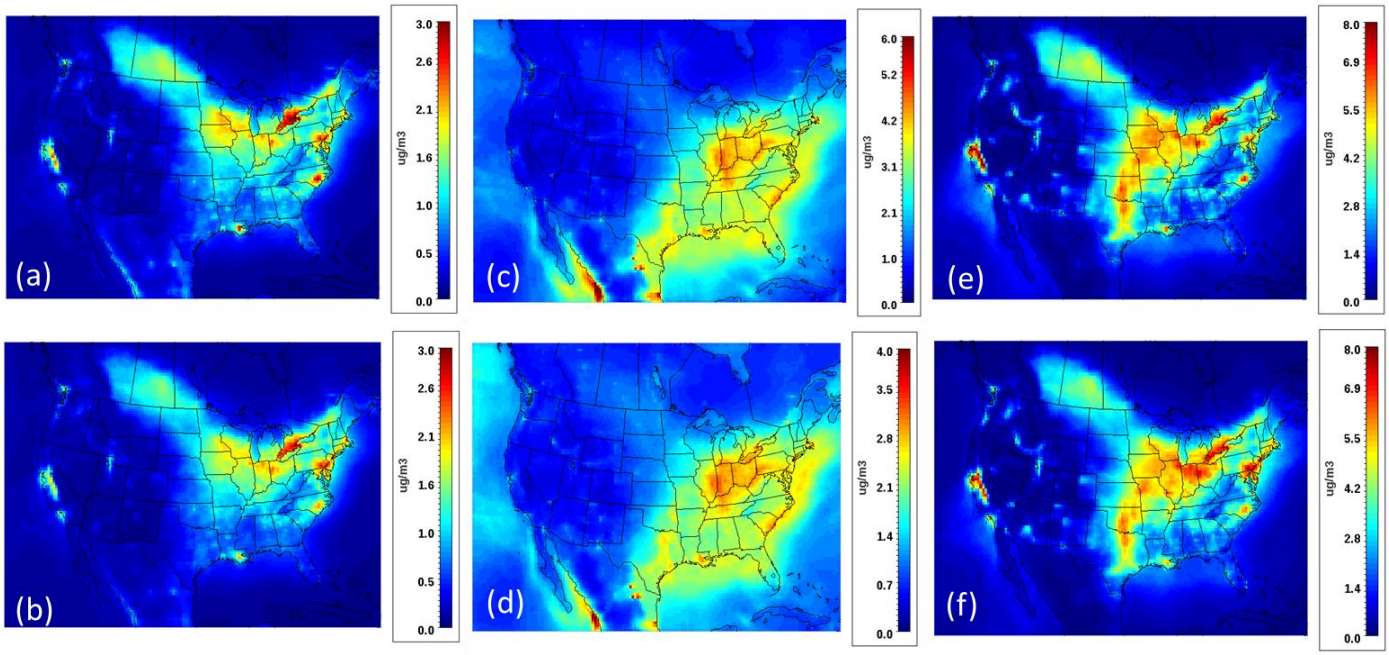


Figure S1 - Yearly averaged predicted concentration fields of (a) 2001 NH_4, (b) 2011 NH_4, (c) 2001 SO_4 (d) 2011 SO_4, (e) 2001 NO_3, (f) 2011 NO_3. Color scales between years are kept the same for parity, except for sulfate, due to its drastic reduction during the decade

Table S1 – Yearly domain averages and standard deviations for ammonium, sulfate and nitrate in μg m^{-3} for 2001 & 2011

2001	*NH_4*	*SO_4*	*NO_3*	**2011**	*NH_4*	*SO_4*	*NO_3*
Domain average	0.42	1.67	1.28	**Domain average**	0.40	1.20	1.27
St.dev	0.47	1.02	1.43	**St.dev**	0.45	0.63	1.48

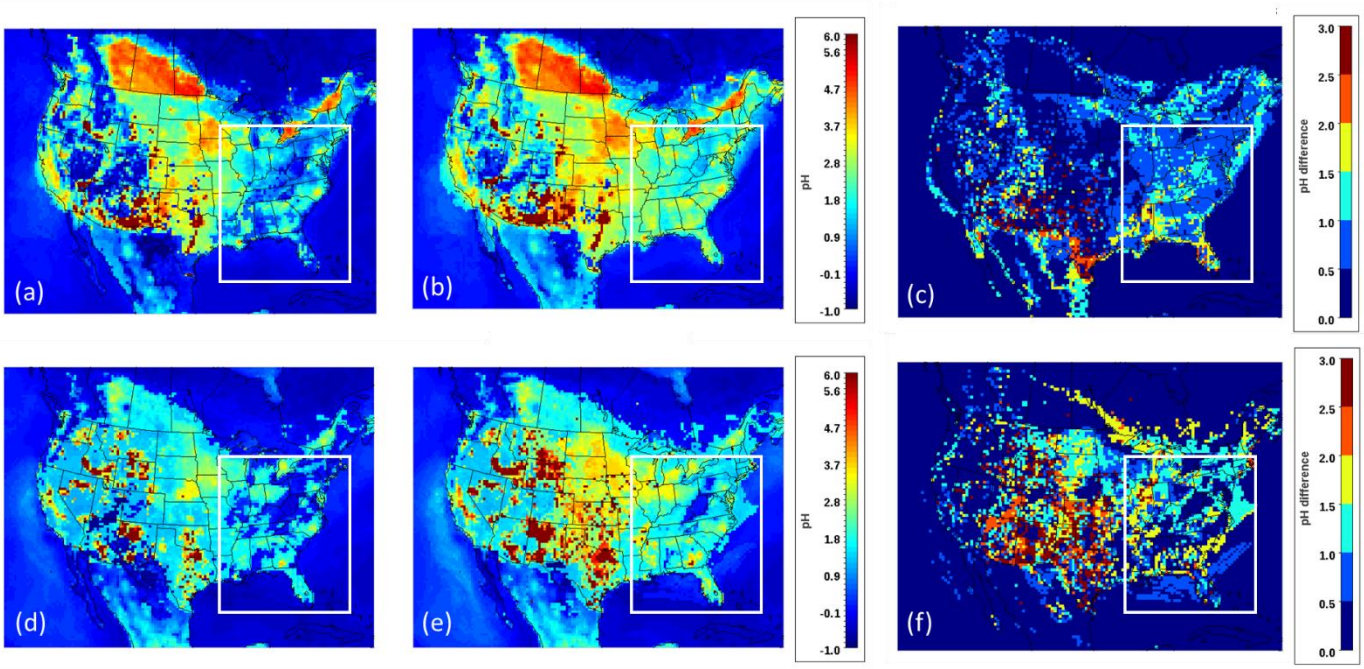


Figure S2 - Seasonally averaged pH over CONUS for the winter (January) of (a) 2001, (b) 2011, the summer (July) of (d) 2001, (e) 2011. Panel (c) is difference between the simulation years for the winter, and (f) is the difference for the summer. As in Figure 3, the study domain is highlighted.

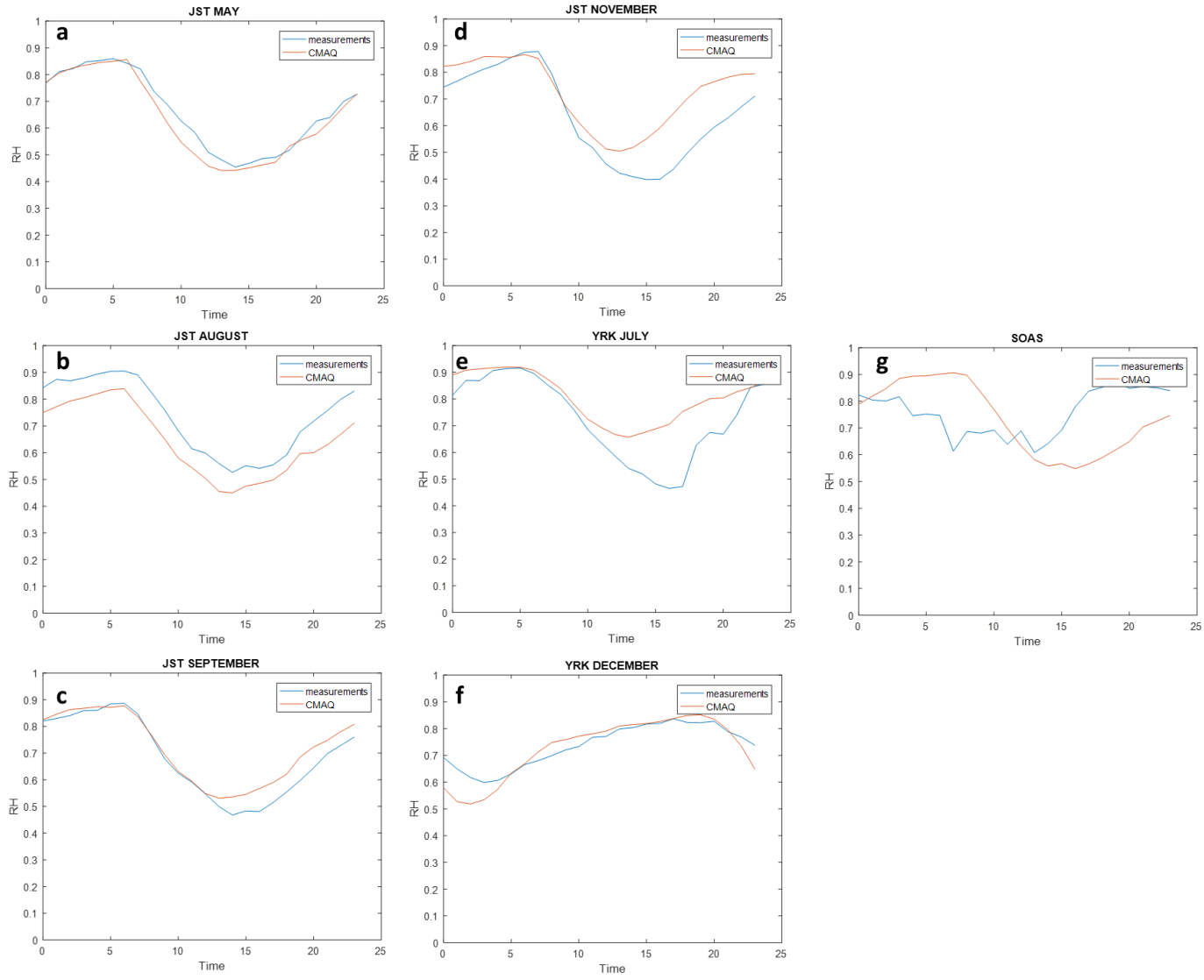


Figure S3 – RH diurnal profiles for May (a), August (b), September (c) and November (d) at JST/RS/GT, July (e) and December (f) at YRK and for the SOAS campaign period (g). Blue line is the CMAQ predicted RH for 2001 and 2011, while the red line represents the measurements

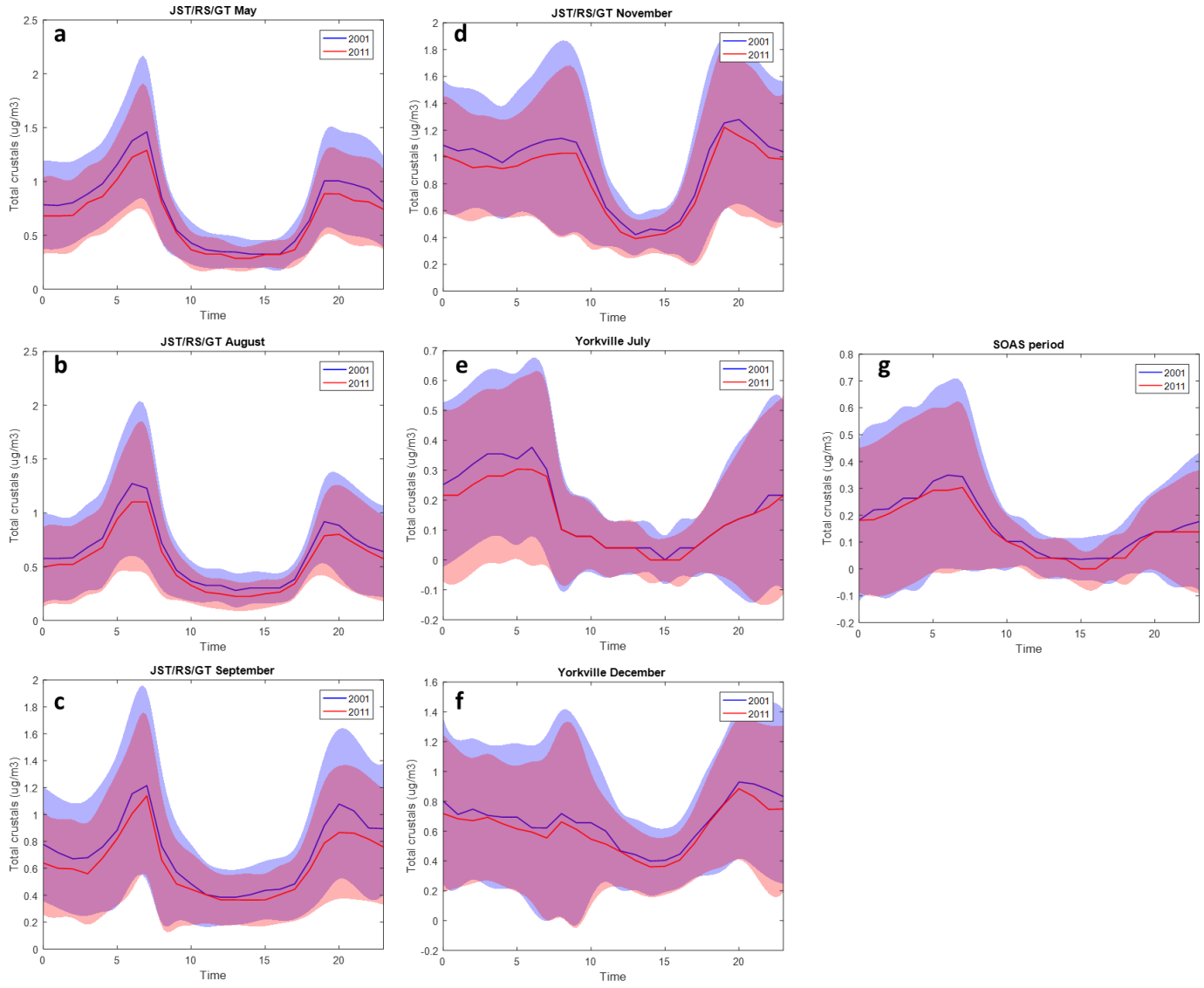


Figure S4 – Total NVC diurnal profiles (Na^{+}, Ca^{+2}, K^{+} and Mg^{+2}) for May (a), August (b), September (c) and November (d) at JST/RS/GT, July (e) and December (f) at YRK and for the SOAS campaign period (g). Blue and red lines are the CMAQ predicted NVCs for 2001 and 2011 respectively, while the shaded areas are one model standard deviation.

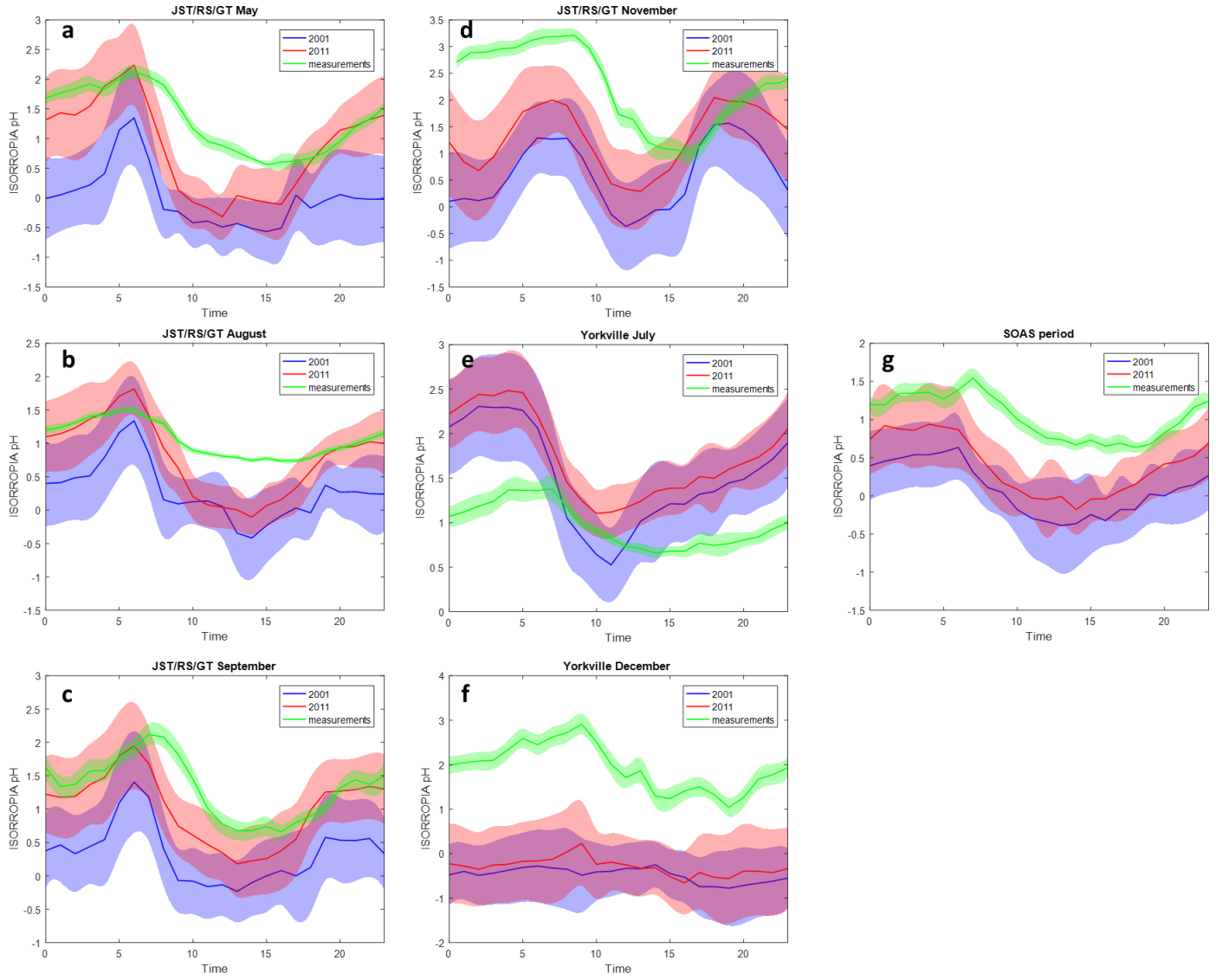


Figure S5 – pH diurnal profiles when not accounting for NVCs, for May (a), August (b), September (c) and November (d) at JST/RS/GT, July (e) and December (f) at YRK and for the SOAS campaign period (g). Blue and red lines are the CMAQ predicted pH for 2001 and 2011 respectively, while the shaded areas are one model standard deviation. Green line represents the measurements and the shades area is standard error.

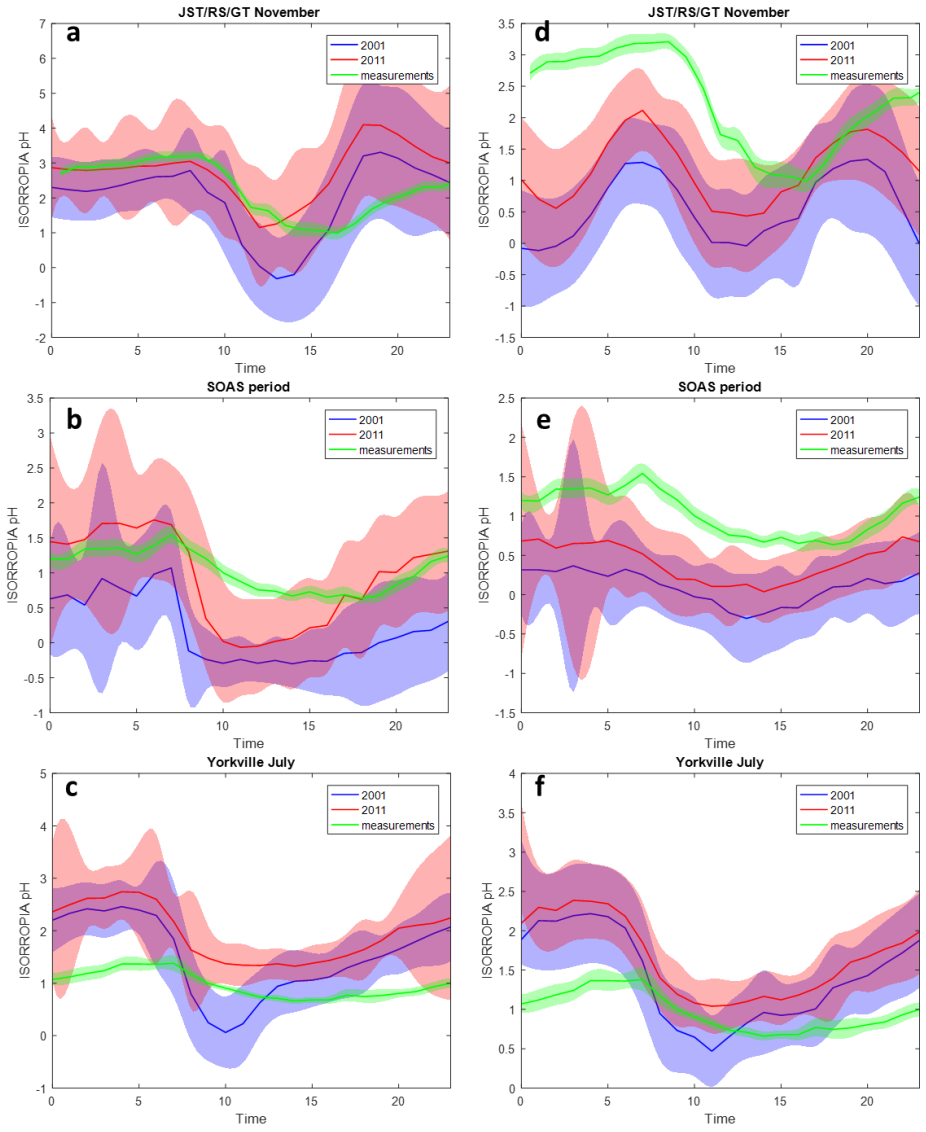


Figure S6 – pH diurnal profiles with assimilated RH when NVCs are included in the calculations, for November at JST/RS/GT (a), the SOAS period (b) and July at YRK (c), and when NVCs are not included for November at JST/RS/GT (d), the SOAS period (e) and July at YRK (f). Blue and red lines are the CMAQ predicted pH for 2001 and 2011 respectively, while the shaded areas are one model standard deviation. Green line represents the measurements and the shades area is standard error.

Organic acids and pH

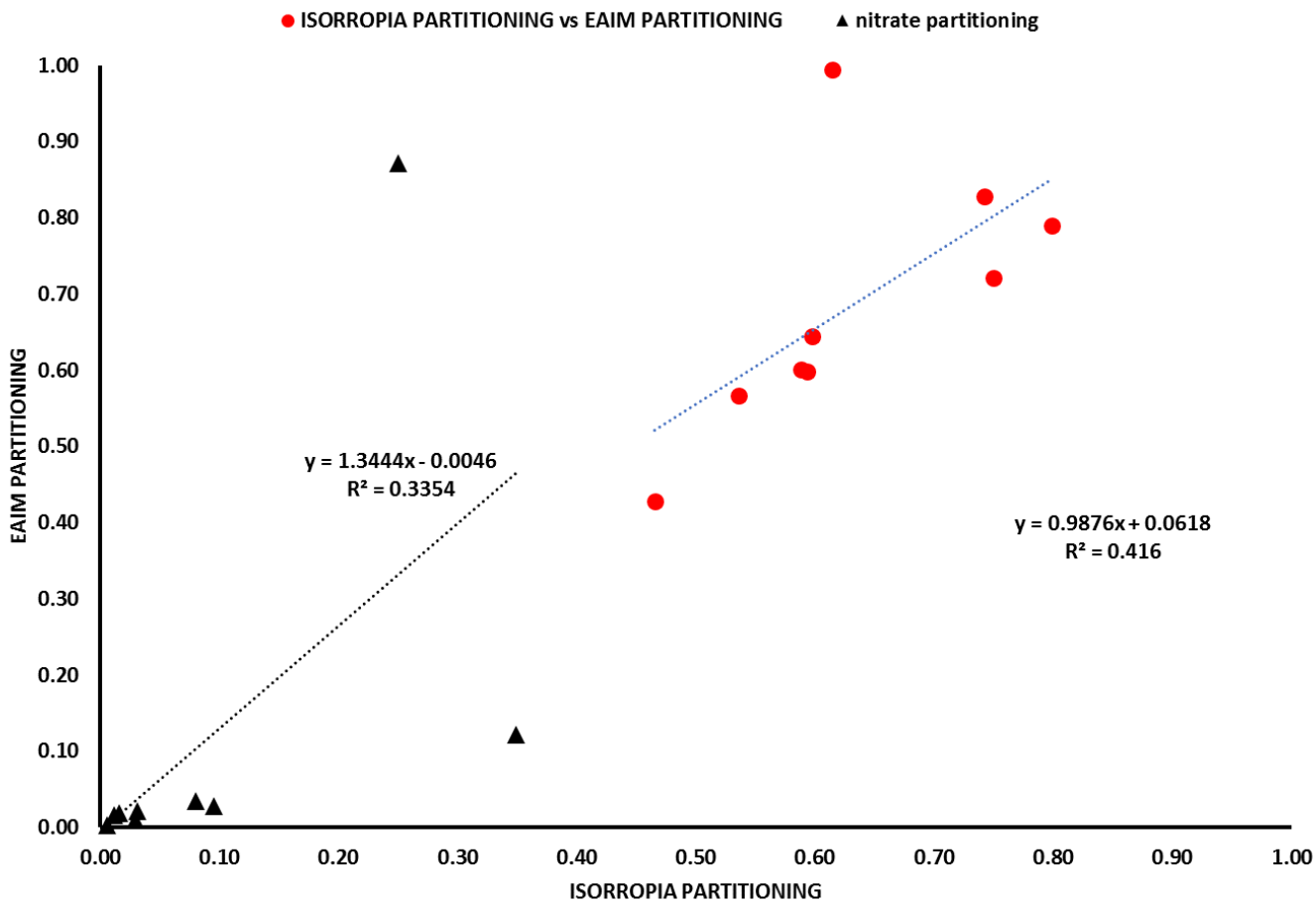
To determine the impact of organic compounds on acidity we tested a variety of scenarios for our CMAQ results at the SEARCH sites, using the web-version of the Extended Aerosol Inorganics Model (E-AIM) model (Wexler & Clegg 2002, Friese & Ebel 2010, Clegg et al. 1992) (http://www.aim.env.uea.ac.uk/aim/aim.php). More specifically, we assumed that a set amount (25 or 50% on a mole basis) of either oxalic, maleic, succinic or malonic acid already exists in the aerosol phase but is not accounted for. Given the constant reductions in sulfate, we also tested the potential of sulfate to be substituted by the same organics. To avoid the potential biases that NVCs can incur on simulations, all runs were conducted without them. E-AIM was run using the comprehensive Model IV configuration, in metastable mode. The baseline case that we used, was the average composition, temperature and RH across all sites.

When comparing the total aerosol partitioning (particle to gas) for each SEARCH site between ISORROPIA and E-AIM, they compare favorably, displaying an almost linear correlation between the two (Fig. S7). For the low temperatures of December in Yorkville ($\overline{\overline{T}} \leq 10^{o}C$) E-AIM predicts a near complete absence of gas phase, in contrast to ISORROPIA, which is attributed to the difference of how the activity coefficients are calculated between the two models (Wexler & Clegg 2002, Friese & Ebel 2010, Clegg et al. 1992). Acidity between the two models differs, but both predict sufficiently low values for pH for all sites (Table S2).

Initially, an amount of 25 or 50% of additional oxalic acid on a mole basis was added to the baseline case, and then the pH was compared (Table S2). We find that for the cases presented in this study, addition of organic compounds to the model did not have a significant impact on acidity when compared to the baseline run, apart from the cases where RH was higher than 80% and the mole fraction of organic acids in the aqueous phase is greater than 25%. pH remains rather insensitive to the addition of oxalic acid for most cases, apart from the case that has the highest RH=0.8, and subsequently the highest amount of liquid water. For all other cases, most of oxalic acid partitions to the gas phase and its impact is negligible. Similarly, when other organic acids are tested against the baseline, under the same conditions (maleic, succinic, malonic), they incur a maximum 4% change on pH (Table S3).

For the substitution tests with oxalic acid, removal of sulfate from the system rapidly decreases the amount of total water in the particulate phase (Fig. S8). This leads to the partitioning of organics to the gas phase (Fig. S8), abating their impact on pH, since the relative composition on a mole fraction basis remains largely the same.

The above analysis demonstrates that, for the cases presented in this paper, organics do not have an appreciable impact on pH when only one liquid phase exists. Allowing more than one liquid phase of different compositions to form, can still potentially impact pH (Pye et al. 2018).



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81 **Figure S7** –Nitrate (black) and total (red) particle-to-gas partitioning predicted between E-AIM
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Table S2 – ISORROPIA, E-AIM and E-AIM with an additional 25 and 50% oxalic acid predicted pH for all sites.

ISORROPIA PH	pH EAIM	pH 25% OXALIC	pH 50% OXALIC
-0.22	0.81	0.82	0.83
-0.30	0.92	0.92	0.91
0.55	1.31	1.32	1.25
-0.04	0.91	0.90	0.83
-0.01	0.55	0.55	0.55
0.07	0.34	0.34	0.34
0.14	0.53	0.53	0.52
-0.46	0.91	0.71	0.57
1.49	1.00	1.10	1.18

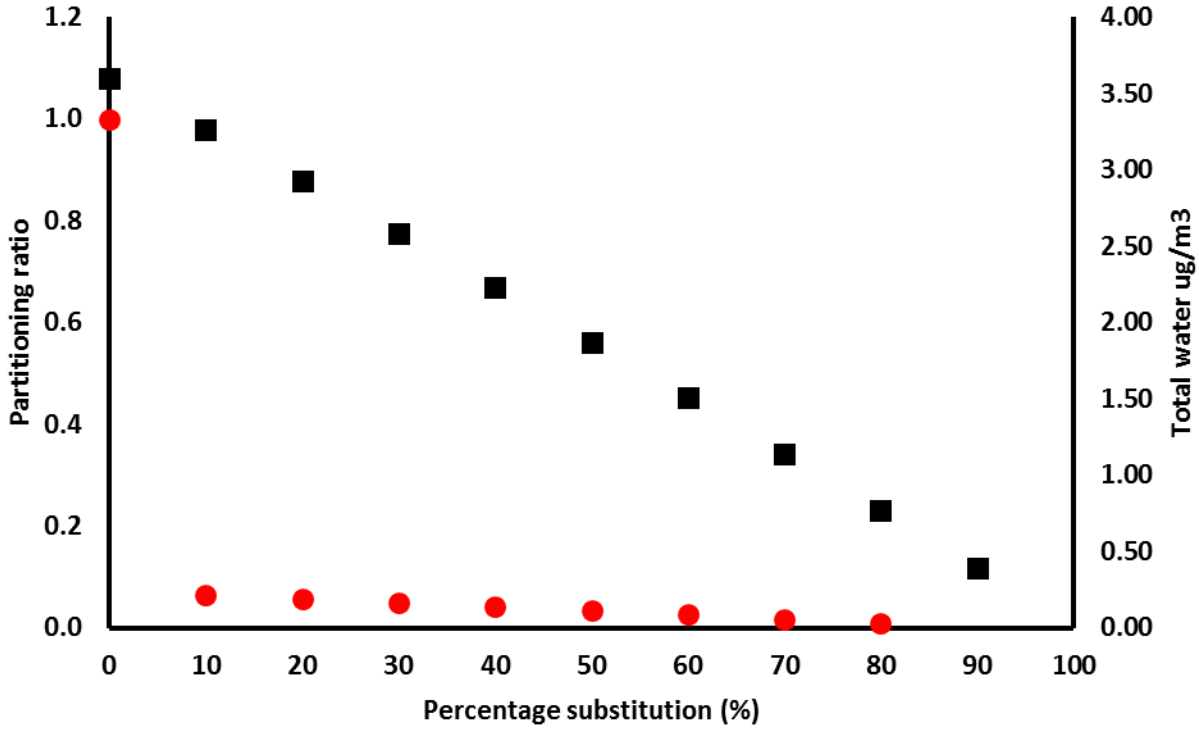

Figure S8 –Comparison of predicted particle-to-gas partitioning of oxalic acid (red) and total water (black) between E-AIM and ISORROPIA as a function of sulfate substitution to oxalic acid.

Table S3 – E-AIM predicted pH for the baseline case and for the cases with 25 and 50% addition of maleic, succinic or malonic acid.

Default pH EAIM	
0.809500489	
pH 25% MALEIC	**pH 50% MALEIC**
0.827689031	0.832387327
pH 25% SUCCINIC	**pH 50% SUCCINIC**
0.821886748	0.821886748
pH 25% MALONIC	**pH 50% MALONIC**
0.81276138	0.808548986

The role of non-volatile cations in PM 2.5 pH

To test whether the PM 2.5 pH bias can be attributed to the internally-mixed NVCs, we omit their presence and repeat the aerosol thermodynamic calculations (offline) for 2001 and 2011. The pH values of 2011 plotted against 2001 for each grid cell in the Eastern US study domain, for the winter (a) and summer (b) seasons are shown in Figure S10. On a seasonal basis, when NVCs are included in the thermodynamic calculations, for the winter the strongest biases are observed for gridcells that in 2001 had pH between -1 and 3, with differences becoming smaller with increasing pH. The largest differences during summer are localized for the gridcells that had pH values between -1 and 0.5 in 2001, while some gridcells from the Southern Lake Michigan and the coastal area of Massachusetts, New Hampshire, Maine and South Carolina exhibit very strong biases of 5 to 3 units. The proximity to marine aerosol and non-volatile Na is the underlying reason for this large change in aerosol pH.

With the removal of these NVCs and sea salt, there is remarkable agreement between the 2001 and 2011 predicted $PM_{2.5}$ pH, with only a small positive bias for the grid cells that in 2001 had a pH of less than unity (Fig. S9). Although NVCs can sometimes comprise a significant

119 portion of PM2.5, as it was the case for the SOAS campaign (Allen et al. 2015, Bondy et al. 2017),
120 on average they should not be a major constituent of PM2.5 (Guo et al. 2015) over the Eastern
121 US, which is indicative of a portion of coarse mode dust being distributed to the smaller sized
122 aerosol in CMAQ , contrary to what has thus far been observed (Foroutan et al. 2017). While the
123 dust emissions were the same between the 2001 and 2011 simulations, given the same meteorology
124 for these years, and the fact that they were not scaled up/down in our model emissions, their impact
125 became much larger in 2011 due to the reductions in sulfate. NVCs on average account for 0.39
126 μg m^{-3} of CMAQ $PM_{2.5}$ both in 2011 and 2001 over the Eastern US, which a factor of 4 higher
127 than the measured PM_1 NVCs during the WINTER campaign (Guo et al. 2016). There is no bias
128 for the gridcells near coastal areas for this case, indicating that these areas were strongly affected
129 by the abundance of sea salt aerosol in fine PM.
130 To verify this finding, we compared observations of NVCs from the Metrohm Monitor for
131 AeRosol and Gases (MARGA) for the SOAS campaign, as well as the SEARCH and CSN sites,
132 to CMAQ results. The average mass of modelled NVCs for these sites is 0. 56 μg m^{-3}, when
133 compared to 0.14 μg m^{-3} for the SEARCH/CSN average, indicating a factor of 4 overestimation,
134 mainly from crustal elements (K^+, Ca^{+2} and Mg^{+2}), further corroborated by the findings of Pye et
135 al. 2018, where the same comparison was carried out.
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138 **Table S4** – Comparison of NVCs (μg m^{-3}) between simulation results for the 3 SEARCH
139 sites, and the measurements provided in Allen et al. 2015 and Pye et al. 2018
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	Na	Mg	K	Ca	Total NVCs
JST AUG	0.024	0.033	0.135	0.462	**0.653**
JST MAY	0.039	0.040	0.146	0.473	**0.697**
JST NOV	0.053	0.049	0.192	0.533	**0.826**
JST SEP	0.029	0.038	0.155	0.450	**0.671**
YRK DEC	0.052	0.044	0.184	0.412	**0.692**
YRK JUL	0.014	0.010	0.063	0.098	**0.185**
CSN	0.050	0.000	0.060	0.030	**0.140**
SEARCH	0.050	-	0.060	0.030	**0.140**
SOAS	0.032	0.007	0.071	0.083	**0.193**
MARGA	0.074	0.010	0.045	0.047	**0.175**

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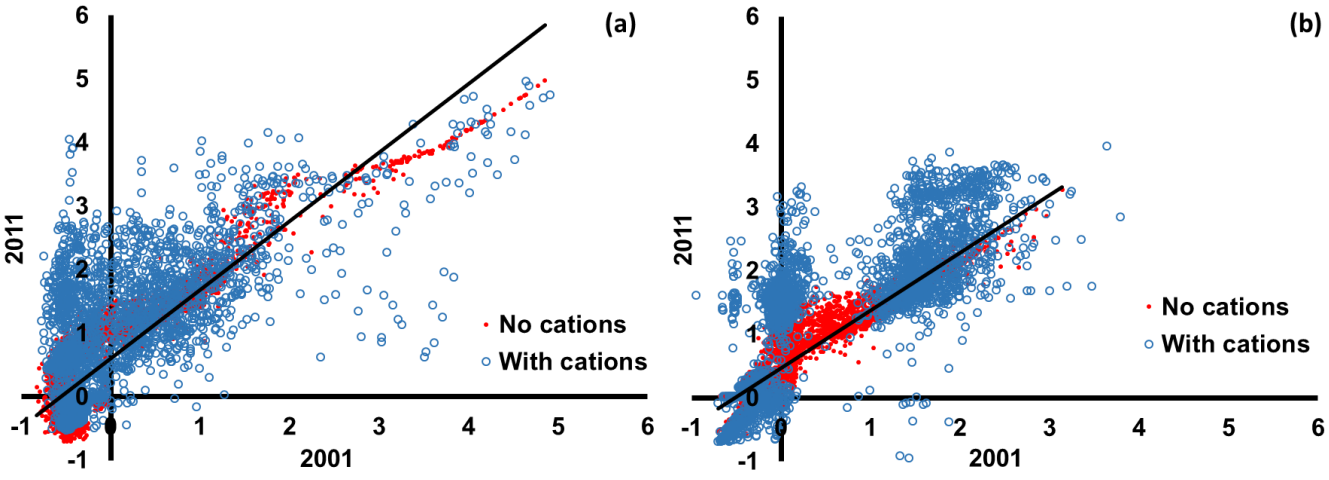

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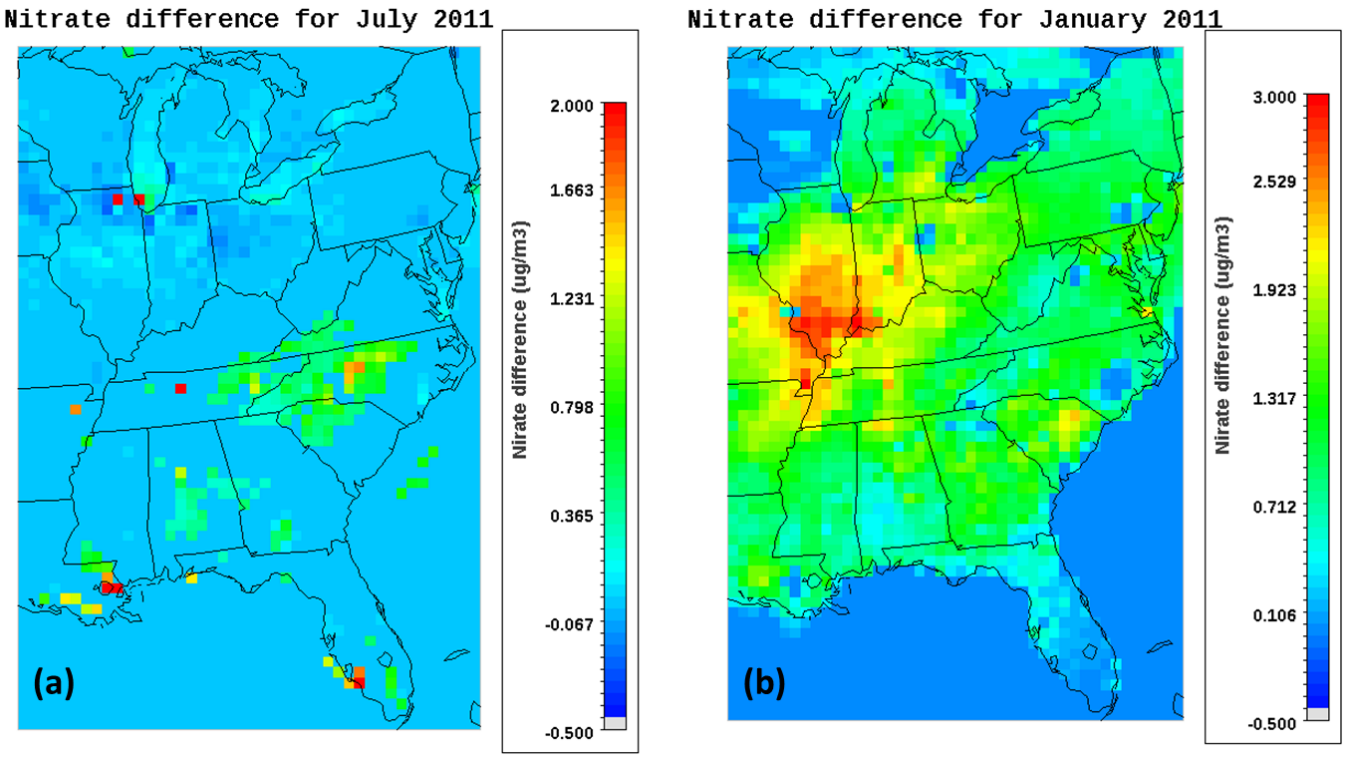
143 **Figure S9** - Scatter plots of ISORROPIA predicted pH over the Eastern US study domain, for the
144 winter (a) and summer (b), with and without NVCs.



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146 **Figure S10** – Difference in nitrate over the Eastern US, between ISORROPIA predicted nitrate
147 when NVCs are included in calculations, and when they are excluded, for July (a) and January (b)
148 of 2011.

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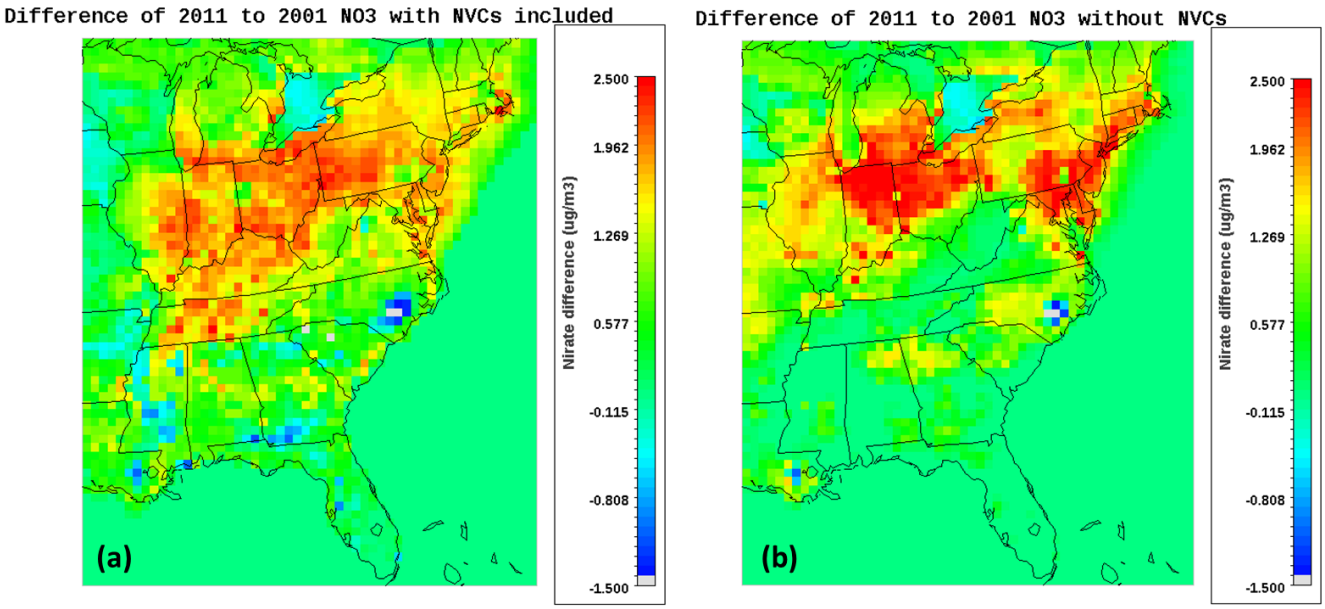

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151 **Figure S11** – Difference in predicted nitrate over the Eastern US between 2011 and 2001 when
152 NVCs are included in calculations (a), and when they are excluded (b).

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