Response to review #2 on acp-2018-116

Long-term trends in total inorganic nitrogen and sulfur deposition in the U.S. from 1990 to 2010

Yuqiang Zhang, Rohit Mathur, Jesse O. Bash, Christian Hogrefe, Jia Xing, Shawn J. Roselle

We thank referee #1 for the positive comments and constructive suggestions, which have helped us improve the manuscript. All referee comments (in blue below) have been carefully addressed, and changes incorporated in the revised manuscript are shown using the track-changes option.

The manuscript discussed twenty year trends in nitrogen (N) and sulfur (S) deposition in the U.S. based on the WRF-CMAQ model simulations. The article identified the current limitations of modeling nitrogen and sulfur deposition and discussed spatial distributions and trends of those species in the U.S. Those results confirmed that reduced nitrogen had dominated the total nitrogen deposition in the U.S. and highlighted the necessity of controlling reduced N. The structure of the manuscript, the results and the presentation of the material are reasonably good. The topic is relevant and certainly deserves publication in Atmospheric Chemistry and Physics.

There are, however, several changes and additions required before publication.
Specific comments:
Page 2, Line 5-6: Please split up these references so that they are associated with the specific impacts being discussed, rather than all placed at the end of the sentence. And, I do not think increased sulfur deposition could cause aquatic eutrophication.
Response: We thank the reviewer for pointing this out. We now split the references. The revised sentence is:
"Increased nitrogen and sulfur deposition is detrimental to ecosystems, since it leads to decreased biological diversity (Clark and Tilman, 2008; Clark et al., 2013; Stevens et al., 2004), increased terrestrial and aquatic eutrophication (Bouwman et al., 2002; Bowman et al., 2008; Fisher et al., 2011) and acidification (Greaver et al., 2012; Savva and Berninger, 2010)."

Page 2, Line 20: Change "pattern" to "patterns".
Response: We made the change following the reviewer' comment.

Page 2, Line 26: Please explain "complexity" more.
Response: We thank the reviewer for pointing this out. Complexity was intended to convey the challenges in spatial interpolation of dry deposition estimates both due to limited availability of observations as well as representativeness of the interpolated fields. To clarify, we have rewritten the sentence as:
"however cannot be easily spatially interpolated due to limited availability of sufficient number of sites in a region as well as the representativeness of the derived fields due to assumptions in the spatial interpolation method (Schwede and Lear, 2014)"

Page 3, Line 20: Change "description" to "descriptions".
Response: Thank you for catching the typo. We have revised the sentence as:

"Interested readers are referred to Gan et al. (2015, 2016) for a detailed description of the settings of the CMAQ model"

Page 3, Line 22: Add "supporting" in the front of "Table S1".
Response: We thank the reviewer for pointing this out. We now add "supporting" in the front of "Table S1".

Page 3, Line 22: O_3 and $PM_{2.5}$ should be defined at first mention.
Response: We thank the reviewer for pointing this out. We now added the definition of O_3 and $PM_{2.5}$ in the paper:
"The performance of the coupled WRF-CMAQ model for major trace gases, aerosol species and meteorological variables such as ozone (O_3), fine particular matter ($PM_{2.5}$)"

Page 3, Line 24-25: Provide some references.
Response: We now rewrite the sentence to add the right references to them:
"at both the hemispheric and regional scale has been extensively evaluated in previous studies, and has shown skill in simulating the magnitudes and long-term trends of these variables (Xing et al., 2015a, b; Mathur et al., 2017; Gan et al., 2015, 2016; Astitha et al., 2017)."

Page 3, in section 2.1: The authors should specify how the dry depositions were estimated.
Response: We thank the reviewer for the suggestion. The dry deposition for each species is calculated by multiplying the concentration in the lowest model layer by the dry deposition velocity (V_d). The dry deposition velocity is calculated as the reciprocal of the sum of the atmospheric (R_a, the resistance to transport through the atmosphere above the surface receptors), quasi-laminar boundary layer (R_b, the resistance to transport across the thin layer of air that is in contact with the surface and varies with the diffusion of the pollutant transported), and surface resistances (R_s, the resistance to the uptake of the pollutant by the surface receptor, typically vegetation or soil). We now add this information on Page 3 line 25:

"The dry deposition of each species in the CMAQ model is calculated by multiplying the concentration in the lowest model layer by the dry deposition velocity (V_d). The V_d is calculated as the reciprocal of the sum of the atmospheric (R_a, the resistance to transport through the atmosphere above the surface receptors), quasi-laminar boundary layer (R_b, the resistance to transport across the thin layer of air that is in contact with the surface and varies with the diffusion of the pollutant transported), and surface resistances (R_s, the resistance to the uptake of the pollutant by the surface receptor, typically vegetation or soil)."

Page 4, Line 11: I am not sure whether the 110th meridian west is appropriate to divide east and west. There are more sites in the east than the west if 110°W is used. A map with 110°W and all the sites should be included in the supplement.
Response: We agree that the use of the 110th meridian to define the East vs West U.S. is somewhat arbitrary. It was used primarily because the majority of the SO_2 and NO_x emissions in the U.S. are east of this meridian. We now include a map of the distribution of observation sites in the supplement. Please see supporting Fig. S1.

Page4, Line 13: How did the authors get the value of 0.984?

Response: 0.984 is the ration of molecular weight of NO_3^- to the molecular wieght of HNO_3 (62/63) and is used to convert the mass of HNO_3 deposited to that of NO_3^-, as also previously discussed in Appel et al. (2011).

Page 5, In 3.1, Could the authors be more specific about the improvements since Appel et al (2011)?

Response: There are numerous differences between the model configuration and versions used in this analysis and those previously used by Appel et al. CMAQv5.0 was used here and included the AERO6 aerosol module, while Appel et al. used CMAQv4.7 that employed the AERO5 aerosol module. Specific process differences between model versions can be found at: https://www.epa.gov/cmaq/cmaq-models-0. In the revised manuscript we point interested users to specifics of these model versions by including the following sentence after Pg 6 line 20:
"There are numerous differences between the model configuration and versions used in this analysis and those previously used by Appel et al. (2011). Specific model process representation differences between CMAQv5.0 used here and CMAQv4.7 used in Appel et al. (2011) can be found at: https://www.epa.gov/cmaq/cmaq-models-0."

Page 5, It seems like the authors only did model evaluation and model justification for wet deposition. How was model performance for dry deposition? The authors could use data from AMON, IMPOROVE and EPA CASTNET to do this work.

Response: The reviewer raises an interesting point related to evaluation of dry deposition estimates. The U.S. CASTNET (Clean Air Status and Trends Network) did provide the dry deposition data. However, these values are not measured but instead derived using the inferential method, pairing the measured air pollutants concentration with a modeled deposition velocity from the MLM model (Meyers et al, 1998). So rather than comparing the two model values between CMAQ and MLM, we chose to compare CMAQ estimated ambient concentrations of both gaseous (SO_2) and particulate (SO_4^{2-}, TNO_3^-, NH_4^+) species with measurements from CASTNET.
We change the title in section 2.2 "Wet deposition observations in the U.S." to "Deposition observations in the U.S.".

On Page 5 line 7, we add the description for the dry deposition from the U.S. CASTNET:
"The U.S. CASTNET provides long-term observation of atmospheric concentrations as well as the dry deposition (https://www.epa.gov/castnet, accessed May 7, 2018). However, the dry deposition values reported are not directly measured, but estimated using the inferential method, pairing the measured air pollutant concentration with a modeled deposition velocity from the MLM model (Meyers et al, 1998). So rather than comparing dry deposition estimates from two models, we choose to evaluate the model's performance in simulating the ambient air concentrations (sulfur dioxide (SO_2), sulfate (SO_4^{2-}), total nitrate ($TNO_3 = NO_3^- + HNO_3$), and ammonium (NH_4)). The detailed site information and the number of years of observational data used for the model evaluation can be found in supporting Table S3. We apply the same criteria in selecting valid observation sites as the NADP/NTN."

In the revised manuscript we further discuss the evaluation of these air concentrations on Page 6 line 21:

"To evaluate the model's performance in simulating the DDEP, we compare the model simulated concentration with the observations from CASTNET. Comparisons of annual average simulated concentrations with corresponding measurements at the CASTNET sites show strong correlation for SO_2 (R of 0.88), SO_4 (0.95), TNO_3 (0.94), and NH_4 (0.94). Some underestimation for SO_4, and overestimation in other species ambient concentrations is noted (supporting Fig. S4). The model also captures the trends for these species with very high R, but the magnitude of the decreasing trends is underestimated by the model (supporting Fig. S5)."

Page 5, Line 19: Change "models" to "model results"

Response: We thank the reviewer for pointing this out. We now changed the word "model" to "model results".

Page 6, Line 15: It should be "Table S3"

Response: We now corrected from "supporting Table 3" to "supporting Table S3".

Page 6, Line 26 – Page 7, Line 2: Please explain the reasons for those results.

Response: The discrepancies for the trends of the TIN TDEP over U.S. ecoregion regions are caused by the combination of the decrease of the NO_x emissions, and unregulated but increased NH_3 emissions at different places. We now clarify this on Page 6 line 26-Page 7 line 2:
"During the period from 1990 to 2010, TIN TDEP has significantly decreased (with $p < 0.05$ for the standard two-tailed Student's t-test) over several ecoregions, including Eastern Temperate Forests, Northern Forests, Mediterranean California and Marine West Coast Forest (decreasing trend of 0.12, 0.071, 0.038 and 0.017 kg N ha^{-1} yr^{-1} respectively) as a result of significant reductions in anthropogenic NO_x emissions (Xing et al., 2013)."

Page 7, Line 11- 20: Which one dominates the decrease of TSOx, SO_4^{2-} or SO_2?

Response: We thank the reviewer for pointing this out. After performing additional calculations, we determined that the decrease of TSO_X is dominated by SO_4^{2-}. We now add this information in Page 7 line 17:
"All the ecoregions experienced statistically significant decreases of TS TDEP over the past two decades which was dominated by the decreases in SO_4^{2-}, except for the Mediterranean California ecoregion which showed an insignificant decreasing trend (Table 6)."

Page 26, The legend of Fig 8 (a) needs to be fixed.

Response: We thank the reviewer for pointing this out. We have now fixed the legend on Fig. 8(a). Please see the updated plot in our revised manuscript.

Response to review #2 on acp-2018-116

Long-term trends in total inorganic nitrogen and sulfur deposition in the U.S. from 1990 to 2010

Yuqiang Zhang, Rohit Mathur, Jesse O. Bash, Christian Hogrefe, Jia Xing, Shawn J. Roselle

We thank referee #2 for the positive comments and constructive suggestions, which have helped us improve the manuscript. Summarized below are our detailed response to the reviewer comments (shown in blue). All comments have been carefully addressed here (blue colors are for referee's comments), and we have tracked all changes in the revised manuscript.

This paper examines trends in inorganic nitrogen and sulfur deposition from 1999 to 2010 across the U.S. This analysis is performed using WRF-CMAQ model simulations. The results from the model are compared to data from the NADP (National Atmospheric Deposition Program) Network. The trends and spatial patterns observed are discussed. Overall, this is a good paper.

Response: We thank the reviewer for the overall positive assessment of our paper.

But I do have some concerns. I feel a large part of the methods section is missing as the authors do not actually discuss the dry deposition data being used.

Response: We thank the reviewer for raising this issue. The U.S. CASTNET (Clean Air Status and Trends Network) does provide an estimate of long-term trends of dry deposition data. However, these values are not measured but instead derived using the inferential method, pairing the measured air pollutants concentration with a modeled deposition velocity from the MLM model (Meyers et al, 1998). So rather than comparing two model values from CMAQ and MLM, we chose to compare CMAQ outputs to ambient concentrations of both gaseous (SO_2) and particulate (SO_4^{2-}, TNO_3^-, NH_4^+) species with measurements from the CASTNET. We have added descriptions of the observation dataset from CASTNET and evaluation into manuscript, as also detailed in our response to a similar query by Reviewer 1. Please see section 2.2 and section 3.1.

We have also addressed the reviewer's similar comments in the specific comments below.

References:

Meyers, T. P., Finkelstein, P., Clarke, J. and Ellestad, T. G.: A multilayer model for inferring dry deposition using standard meteorological measurements, J. Geophys. Res. Atmos., 103(D17), 22645–22661, 1998.

General Comments: -I am a bit surprised that the abbreviation TSOx is used for sulfur deposition rather than TS. TS to me seems more fitting, but I understand if the other is more traditionally used as I am not as familiar with that literature as I am with nitrogen deposition. However, that being said it seems that the paper goes back and forth using TSOx and TSO_4 to represent sulfur deposition. This is true throughout the main text, figures, and supporting information. This should be checked.

Response: We thank the reviewer for pointing this out and agree that consistency is needed in the use of the abbreviation. We agree with the reviewer that TS is a better abbreviation since total

sulfur deposition (expressed in mass of S) is analyzed and compared between the model and observations. In the revised manuscript we have replaced "TSO_x" and "TSO_4" in all the text, figures and tables as well as in the supporting information, with the abbreviation "TS".

Specific Comments: Abstract Page 1, Line 12 – The abbreviation WRF-CMAQ is not defined.

Response: In the revised manuscript, we have revised the text as:
"Here, we use long-term model simulations from the coupled Weather Research and Forecasting and the Community Multiscale Air Quality (WRF-CMAQ) model"

We also updated the sentence on line 16, Page 3:
"The long term simulations were previously performed using the coupled Weather Research and Forecasting and the Community Multiscale Air Quality (WRF-CMAQ model, Wong et al., 2012)"

Page 1, Lines 15-17 – The authors mention that the model generally underestimates the wet deposition. But they do not provide any reasons why this is. This should be added to the abstract.

Response: The underestimation of the wet deposition likely arises due to a combination of factors including coarse model grid resolution, missing emissions of lightning NO_x, as well as the poor temporal and spatial representation of NH_3 emissions. Now we add the explanation in Page 1 line 17:
"The underestimation of the wet deposition by the model is mainly caused by the coarse model grid resolution, missing lightning NO_x emissions, as well as the poor temporal and spatial representation of NH_3 emissions."

Page 1, Line 19 – Suggest changing decrease of TNO_3 to decreases in TNO_3?

Response: Following the reviewer's suggestion, we have modified the sentence as:
"The decreasing trends of TIN TDEP are caused by decreases in TNO_3"

Page 1, Line 20 – The authors mention there are increasing trends in TIN deposition over the Tropical Wet Forest. This is the only region type listed in the text that does not have a geographic location included in its title. I think this makes it hard for readers to understand where it is. I would suggest adding a phrase such as southern Florida to aid the reader.

Response: We thank the reviewer for pointing this out. We have incorporated the reviewer's suggestions in Page 1 line 20:
"in the Tropical Wet Forests (Southern Florida Coastal Plain)"

Page 1, Line 22 – Suggest removing the words region of before Eastern
Page 1, Line 23 – Suggest removing the words region of before Tropical

Response: We followed the reviewer's comments and removed the words "region of" for the sentence from line 22-line 24. Now the new sentence is:
"TIN DDEP shows significant decreasing trends in the Eastern Temperate Forests, Northern Forests, Mediterranean California and Marine West Coast Forest, and significant increasing trends in the Tropical Wet Forests, Great Plains and Southern Semi-arid Highlands"

Page 1, Line 28 – Suggest adding an a before combination.

Response: We made the change following the reviewer's comments. The new sentence is:
"TDEP of TIN over the U.S. was dominated by deposition of TNO_3 during the first decade, which then shifts to reduced nitrogen (NH_X) dominance after 2003 resulting from a combination of NOx emission reductions and NH_3 emission increases."

1.Introduction Page 2, Line 12 – Suggest changing twice higher than to twice as high as

Response: We made change following the reviewer's comments. The new sentence is:
"Another possible source of NH_3 emissions are from vehicles which may be twice as high as the emission estimates in the current NEI (Sun et al., 2016)."

Page 2, Line 13 – Suggest removing the the before sulfur.
Page 2, Line 14 – form fossil-fuel should be from fossil-fuel

Response: We removed word "the" in the sentence, and also corrected the word "form". The new sentence is:
"The primary emission source for sulfur deposition is sulfur dioxide (SO_2) which also mainly originates from fossil-fuel combustion (Smith et al., 2011)"

Page 2, Lines 15-20 – Here the authors discuss the wet deposition national networks. But they do not actually tell how the measurements are made. I would suggest adding some text telling how the samples are collected and then measured by ion chromatography to provide the data.

Response: Following the reviewer's suggestion in the revised manuscript we include a brief description of the NADP measurements in section 2.2 (Page 4 line 6):
"The deposition is measured by wet-only samples, which are triggered by precipitation. The deposition of sulfate and nitrate are analyzed by ion chromatography, and ammonium by flow injection analysis (http://nadp.slh.wisc.edu/educ/sample.aspx, accessed May 4, 2018)."

Page 2, Line 21 – Suggest adding the words e.g., before EEA. Also a comma is missing after EEA
Page 2, Line 22 – Suggest removing the comma and phrase to name a few after 2015

Response: We have incorporated the reviewer's suggestion by modifying the sentence as:
"These data have been extensively used to quantity the sources, pattern, and temporal trends of WDEP of major species worldwide (e.g., EEA, 2011; Jia et al., 2014; Cheng and Zhang, 2017; Lajtha and Jones, 2013; Du et al., 2014; Sickles II and Shadwick, 2007a, 2007b, 2015)."

Page 3, Line 2 – There is an extra period after loss

Response: We thank the reviewer for catching the typo. The extra period has been removed in the revised text.

Page 3, Line 5 – Suggest removing the second Zhao et al.

Response: Actually, the first Zhao et al., 2009, and the second Zhao et al., 2015, 2017 are not the same first author, even though they share the same last name and initials. To made it clear, now we rewrite this:
"Zhao Y. et al., 2009; Zhao Y. H. et al., 2015, 2017"

Page 3, Line 8 – Suggest changing process to processes

Response: We made the change following the reviewer's comments. The new sentence now is:
"CTMs can link the sources to the deposition through atmospheric chemistry and transport processes"

2.Methods 2.1.Model setup Page 3, Line 16 – The abbreviation WRF-CMAQ is not defined

Response: We thank the reviewer for pointing this out. Now we add the abbreviation:
"The long term simulations were previously performed using the coupled Weather Research and Forecasting and the Community Multiscale Air Quality (WRF-CMAQ model, Wong et al., 2012)"

Page 3, Line 20 – There is an extra comma after Gan et al. Also suggest adding an a before detailed

Response: We made the change following the reviewer's comments. The new sentence now is:
"Interested readers are referred to Gan et al. (2015, 2016) for a detailed description of the settings of the CMAQ model and physical configurations of the WRF model (Table S1)."

Page 3, Line 22 – The chemical abbreviation used are not defined

Response: In the revised manuscript we have added the chemical abbreviation as:
"The performance of the coupled WRF-CMAQ model for major trace gases, aerosol species and meteorological variables such as ozone (O_3), fine particulate matter ($PM_{2.5}$) and aerosol optical depth at both the hemispheric and regional scale …"

Page 3, Line 24 – Suggest changing was shown to has shown

Response: We have corrected this as:
"and has shown skill in simulating the magnitudes and long-term trends of these variables."

2.2.Wet deposition observations in the U.S. Page 4, Line 11 – Suggest changing observation data used for to observational data used for the

Response: We modified the sentence following the reviewer's suggestion as:
"The detailed site information and the number of years of observational data used for the model evaluation"

Page 4, Line 13 – Suggest changing combine WDEP to combines WDEP and with 0.984 to by 0.984

Response: We have incorporated the reviewer's suggestion in the revised sentence as:
"In pairing the observed and modeled TNO_3 WDEP values (which combines WDEP of NO_3^- and HNO_3), we multiply the model estimated HNO_3 WDEP by 0.984 to account for the transformation of HNO_3 to NO_3^- in solution in the measurements"

Page 4, Line 15 – Suggest changing combine WDEP to combines WDEP and with 1.06 to by 1.06

Response: We have incorporated the reviewer's suggestion in the revised sentence as:
"In pairing the observed and modeled NH_X WDEP values (which combines WDEP of NH_4^+ and NH_3), we multiply the model estimated NH_3 WDEP by 1.06"

Page 4, Line 17 - Suggest changing combine WDEP to combines WDEP and with 1.50 to by 1.50

Response: We have incorporated the reviewer's suggestion in the revised sentence as:
"In pairing the observed and modeled TSO_X WDEP values (which combines WDEP of SO_4^{2-} and SO_2), we multiply the model estimated SO_2 WDEP by 1.50"

Page 4, Lines 2-26 – Why is there no section on dry deposition in the Methods section? The authors explicitly state in the introduction that there are no direct measurements of this, but that they are calculated at some sites. So then information on how they are calculated and what is used here should be provided to the reader so that they fully understand the analysis that is being performed.

Response: The reviewer raises an interesting point related to evaluation of dry deposition estimates. The U.S. CASTNET (Clean Air Status and Trends Network) did provide the dry deposition data. However, these values are not measured but instead derived using the inferential method, pairing the measured air pollutants concentration with a modeled deposition velocity from the MLM model (Meyers et al, 1998). So rather than comparing the two model values between CMAQ and MLM, we chose to compare CMAQ estimated ambient concentrations of both gaseous (SO_2) and particulate (SO_4^{2-}, TNO_3^-, NH_4^+) species with measurements from CASTNET.
We change the title in section 2.2 "Wet deposition observations in the U.S." to "Deposition observations in the U.S.".

On Page 5 line 7, we add the description for the dry deposition from the U.S. CASTNET:
"The U.S. CASTNET provides long-term observation of atmospheric concentrations as well as the dry deposition (https://www.epa.gov/castnet, accessed May 7, 2018). However, the dry deposition values reported are not directly measured, but estimated using the inferential method, pairing the measured air pollutant concentration with a modeled deposition velocity from the MLM model (Meyers et al, 1998). So rather than comparing dry deposition estimates from two models, we choose to evaluate the model's performance in simulating the ambient air concentrations (sulfur dioxide (SO_2), sulfate (SO_4^{2-}), total nitrate ($TNO_3 = NO_3^- + HNO_3$), and ammonium (NH_4)). The detailed site information and the number of years of observational data used for the model evaluation can be found in supporting Table S3. We apply the same criteria in selecting valid observation sites as the NADP/NTN."

In the revised manuscript we further discuss the evaluation of these air concentrations on Page 6 line 21:
"To evaluate the model's performance in simulating the DDEP, we compare the model simulated concentration with the observations from CASTNET. Comparisons of annual average simulated concentrations with corresponding measurements at the CASTNET sites show strong correlation for SO_2 (R of 0.88), SO_4 (0.95), TNO_3 (0.94), and NH_4 (0.94). Some underestimation for SO_4, and overestimation in other species ambient concentrations is noted (supporting Fig. S4). The model also captures the trends for these species with very high R, but the magnitude of the decreasing trends is underestimated by the model (supporting Fig. S5)."

Page 4, Lines 2-26 – The authors do not actually explain how the data from the network is collected. I understand the model analysis is the point of the paper. But since these

observational data are used to evaluate the model then the authors should provide at least some text to give the readers context.

Response: We have now included a brief description of the NADP measurement in Page 4 line 6: "The wet deposition is measured by wet-only samples, which are triggered by precipitation. The deposition of for sulfate, nitrate are analyzed by ion chromatography, and ammonium by flow injection analysis (http://nadp.slh.wisc.edu/educ/sample.aspx, accessed May 4, 2018)."

Page 5, Line 5 – There is an extra comma after equation 2

Response: We thank the reviewer for pointing this out. Now we removed the extra comma.

Page 3, Line 14 to Page 5, Line 6 – In the methods section there is no discussion of the trend analysis that is used throughout the paper. What is this analysis? How is it done? This should be added to the paper.

Response: Thanks the reviewer for pointing this out. We now added the descriptions how we performed the trends analysis in Page 4 line 26:

"For the trend analysis, we focus on the linear trends (Colette et al., 2011; Xing et al., 2015a), in which the linear least square fit method is employed, and significance of trends is examined with a Student t-test at the 95% confidence level (p=0.05)"

References:

Colette, A., Granier, C., Hodnebrog, Ø., Jakobs, H., Maurizi, A., Nyiri, A., Bessagnet, B., D'Angiola, A., D'Isidoro, M., Gauss, M., Meleux, F., Memmesheimer, M., Mieville, A., Rouïl, L., Russo, F., Solberg, S., Stordal, F., and Tampieri, F.: Air quality trends in Europe over the past decade: a first multi-model assessment, Atmos. Chem. Phys., 11, 11657–11678, doi:10.5194/acp-11-11657-2011, 2011.

Xing, J., Mathur, R., Pleim, J., Hogrefe, C., Gan, C.-M., Wong, D. C., Wei, C., Gilliam, R., and Pouliot, G.: Observations and modeling of air quality trends over 1990–2010 across the Northern Hemisphere: China, the United States and Europe, Atmos. Chem. Phys., 15, 2723-2747, doi:10.5194/acp-15-2723-2015, 2015a.

3.Results 3.1.Model evaluation of WDEP

Page 5, Line 16 – Suggest changing increases for all the three to increase for all three. Also exhibit should be exhibited. Also suggest changing in east than that in west to in the east than the west

Response: We followed the reviewer's comments, and have rewritten the sentence:

"After performing the precipitation adjustment, the NMB values increase for all three species (Table 1). The model exhibited better performance for WDEP in the east than the west"

Page 5, Line 17 – A period is missing after (Appel et al., 2011)

Response: We thank the reviewer for pointing this out and have corrected it in the revised manuscript.

Page 5, Line 19 – Suggest changing both observations and models to both the observations and model results

Response: We thank the reviewer for pointing this out. Now we have corrected this:

"as seen from both the observations and model results (Table 2)"

Page 5, Line 20 – Suggest adding a the before Tropical
Response: Now we added the word "the" before Tropical.

Page 6, Line 11 – I am not sure I understand the phrase but a slightly distinctions in trends for different ecoregions. Is it maybe but with slight distinctions in the trends for each ecoregion?
Response: We now rewrite the sentence as the reviewer suggested:
"and the model is also able to capture these very well but a slightly distinctions in the trends for each ecoregion"

Page 6, Lines 11-13 – The authors mentions that the model generally underestimates decreasing WDEP trends for all sites, but for NH_x they see increasing WDEP trends. Why is this? The authors need to tell why they think this might be the case for the model.
Response: The magnitude of the decreasing trends in TNO_3 and TS wet deposition are slightly underestimated by the model and result from both the coarse model grid resolution and uncertainties in the emission inventories. We have add this in Page 6 line 12:
"We see that the model generally underestimates the magnitude of the decreasing WDEP trends at many sites for TNO_3 and TS (Tables 2 and 4), which may be caused by the coarse model grid resolution (36km), and uncertainties in the emission inventories."

Page 6, Line 14 – Suggest removing the word results before model
Response: We removed the repeat "results" as suggested:
"our model results indicate larger bias"

Page 6, Line 15 – Suggest changing increases for all the three to increase for all three. Also why are the authors only looking at the data from 2002-2006 when they discuss the NMB increase observed? This needs to be clarified.
Response: We now modified the sentence based on the reviewer's comments:
"The NMB increase for all three species in our results from 2002 to 2006"
The reason why we looked at the data from 2002-2006 only as Appel et al. (2011) only has the simulations from 2002 to 2006. Here we want to compare the performance between the model runs using a newer version of the CMAQ model which was used in our study, with older version of the CMAQ from previous study.
Page 6, Line 18 – Suggest changing are more to have more
Page 6, Line 19 – Suggest changing challenging to challenges
Response: We made the changes following the reviewer's these two comments:
"coarse resolution models (e.g. 36km in our study) have more challenges to simulate"

Page 5, Line 8 to Page 6, Line 20 – Why is there no matching section on the model evaluation for DDEP? The remainder of the results section discusses the trends in total, wet, and dry deposition so it seems that it should be established how the model compares with the calculated dry deposition values provided by NADP.
Response: We thank the reviewer for pointing this out. Please see our reply above for the similar question.

3.2.Spatial patterns of modelled total deposition of nitrogen and sulfur Page 6, Line 21 – modelled should be written as modeled to be consistent with how it is used throughout the rest of the text

Response: We thank the reviewer for pointing this out. We now kept consistent with the words we used, and made the following changes:

Page 6 line 21: "Spatial patterns of modeled total deposition of nitrogen and sulfur"

Page 5 line 2-3: "account for biases in modeled precipitation by adjusting the modeled WDEP"

Page 7, Line 18 – Suggest removing the and after showed

Page 7, Line 19 – Believe that Table 4 should be Table 6

Response: We reply the reviewers' above two comments together. We now removed the word "and" after the word "showed", and change "Table 4" to "Table 6". The new sentence is:

"which showed insignificant decreasing trend (Table 6)".

3.3.Wet versus dry nitrogen and sulfur deposition trends in the U.S.

Page 7, Line 25 –Suggest adding a the before Eastern

Page 7, Line 26 – Suggest adding a the before Northern and Great

Response: We thank the reviewer for pointing this out. We reply the reviewers' above two comments together. Now we have add the word "the" as the reviewer suggested:

"The most significant decreasing region is the Eastern Temperate Forests, with an annual decrease of -0.070 kg N ha^{-1} yr^{-1}, followed by the Northern Forests (-0.037 kg N ha^{-1} yr^{-1}) and the Great Plains (-0.023 kg N ha^{-1} yr^{-1})"

Page 7, Line 27 – Suggest changing was mainly to were mainly

Response: We thank the reviewer for pointing this out. Now we have corrected this.

"The decreasing trends of TIN WDEP were mainly caused"

Page 7, Line 28 – The authors mention that there are no significant changes for WDEP of NHx. However, in Table S4 the values for Tropical Wet Forests are in bold, which is what indicates a significant trend. Also there is light blue being shown in Figure S4b. This needs to be clarified.

Response: We thank the reviewer for pointing this out. There are actually no significant trends for WDEP of NH_X in the majority of U.S. Now we have rewrote this sentence:

"There are no significant changes for WDEP of NH_X in the majority of U.S. except for the region Tropical Wet Forests (supporting Fig. S4b),"

Page 8, Line 8 – Suggest adding an a before distinct and changing value to values

Response: We have made the changes following the reviewer's comments:

"Fig. 7 shows a distinct spatial distribution for both the WDEP and DDEP of sulfur, with much higher values in the eastern U.S."

Page 8, Line 9 – Suggest adding a the before vicinity and changing source to sources

Response: We have made the changes following the reviewer's comments:

"in the vicinity and downwind of major sources"

3.4.Deposition budget in U.S.

Page 8, Line 18 – Suggest changing were estimated to was estimated

Response: We modified the sentence following the reviewer's comment:
"The TNO_3 WDEP was estimated to decrease"

Page 8, Line 19 – Suggest removing the hyphen after 2010
Response: We removed the hyphen as suggested.

Page 8, Line 21 – Suggest changing changes to changed
Response: Changed as suggested:

Page 8, Line 22 – Suggest changing till to until and removing the the before NHx
Response: We thank the reviewer for pointing this out. Now we have modified the sentence:
"TNO_3 deposition dominates TIN TDEP until the early 2000s. After 2003, however, NHx dominates the TIN TDEP over the U.S."

Page 8, Line 26 – Suggest changing 1999-2010 to 1999 to 2010
Response: We have changed "1990-2010" to "1990 to 2010":

Page 8, Line 27 – Suggest changing emission to emissions
Response: We made the change following the reviewer's comment:
"due to regulations and growth in NH_3 emissions"

Page 8, Line 28 – The reference is written in blue
Response: We have reformatted the reference.

Page 9, Line 2 - The references are written in blue
Response: We have reformatted the reference.

Page 9, Lines 1-5 – I believe that this section is in reference to Figure 8, but there is citation to Figure 8 listed here.
Response: We now add the reference to Figure 8 in the Page 9 line 1:
"Similar to TIN TDEP, the TSO_X TDEP has also decreased, from 6.85 kg S ha^{-1} yr^{-1} in 1990 to 3.26 kg S ha^{-1} yr^{-1} in 2010 (Fig. 8 (b)),"

Conclusions Page 9, Line 10 – Suggest changing observation to observations
Response: We made the change as suggested.

Page 9, Line 25 – Suggest adding a the before Eastern
Response: We add the word "the" as suggested.

Page 10, Line 9 – It should be aerosol-phase
Response: We change the word "aerosol phase" to "aerosol-phase".

Data availability Page 10, Line 18 – Suggest changing shared to obtained
Response: We changed the word "shared" to "obtained" as the reviewer suggested.

Competing interests Page 10, Line 21 – Suggest changing conflict to conflicts

Response: We changed "no conflict of interest" to "no conflicts of interest".

Page 10, Line 26 – Suggest adding a the before U.S. and removing the phrase improvements of after suggestions on the
Response: We made the changes following the reviewer's comments, and the new sentence is: "We greatly acknowledge James Kelly and Kristen Foley from the U.S. EPA for their comments and suggestions on the initial version of this manuscript."

Disclaimer Page 10, Line 28 – Suggest changing view to views
Response: We changed the word "view" to "views".

References Page 11, Line 26 – Believe the accent marks in Muller should be over the u
Response: Now we changed to "Müller" as the reviewer suggested.

Tables and Figures
Table 1 -In first line of caption – Suggest changing for all the annual to for the sum of the annual -In second line of caption - Suggest adding a the before model -What is the difference between R and R for trends? There is no discussion about this in the main text so it is hard to understand why the two set of values are being shown.
Response: We have modified the sentence following the reviewer's comments and also explain what the second R means. The "R for the trends" are the correlation coefficient for the 21-yr changes of the wet deposition (TNO_3, NH_X and TSO_x) between the model and the observations Now the new caption is:
"Correlation coefficient (R), mean bias (MB, kg ha^{-1}), and normalized mean bias (NMB, %) for the sum of the annual accumulated wet deposition (WDEP) between the model and NADP sites from 1990 to 2010, including both the model values with and without applying monthly/annual precipitation adjustment. The R for trends are the correlation coefficient for the 21-yr changes of the wet deposition (TNO_3, NH_X and TS) between the model and the observations."

Table 2 -In first line of caption – Suggest adding a the before 10 -In third line of caption – There should be a hyphen in t-test -Second column heading – Suggest changing Regions to Region -Third column heading – Suggest changing # sites to # of sites
Response: We changed the caption as the reviewer's suggested, and also made the changes to the Table. Please see our new draft.

Table 3 -Second column heading – Suggest changing Regions to Region -Third column heading – Suggest changing # sites to # of sites
Table 4 -Second column heading – Suggest changing Regions to Region -Third column heading – Suggest changing # sites to # of sites
Table 5 -Second column heading – Suggest changing Regions to Region
Table 6 -In third line of caption – There should be a hyphen in t-test -Second column heading – Suggest changing Regions to Region
Response: We answer the reviewers' above comments about Table 3 to Table 6 together. As suggested, we have made the changes in the tables' captions. Please see our new draft.

Figure 1 -In second line of caption – To match the figure between observations and precipitation-adjusted model results should be switched -In third line of caption – Suggest changing Each NADP to The data at each NADP site -Letters should be added to each plot and the caption updated to indicate this -Suggest making a symbol indicating that green is for East sites and red is for West sites as currently this is only indicated from the small text at the top of each plot -It should be indicated in the caption what the solid and dashed lines in each plot represent -There are no subscripts in the abbreviations used on both the x and y-axes for all plots

Response: Following the review's comments, we have made the following changes. The new captions reads as:

"Scatter plots for the annual accumulated WDEP (total oxidized nitrogen (TNO_3, a), reduced nitrogen (NH_X, b), and total sulfate (TS, c)) between precipitation-adjusted model results and observations from 1990 to 2010 for 170 valid sites with 3531 valid data points. The data at each NADP is assumed to be valid for our analysis only if at least 18 years of observation data are available at that site and the data coverage is at least 75% for each year. Each point in the plots represents the annual accumulated WDEP for a given site and year. Note that the annual accumulated WDEP values used in this analysis may not be the actual annual totals due to missing data in the observations. The green color is for the eastern U.S., and the red color is for the western U.S., with the dashed line for the 1:2 and 2:1 ratio, and the solid line for the 1:1 ratio."

We also add subscripts for abbreviations at both the x, y-axes of all the plots. Please see our updated figures.

Figure 2 -In first line of caption – Suggest changing of (a) TNO3 to for (a) TNO3 - In second line of caption – Suggest removing the phrase annual accumulated before precipitation. -In second, third, and fourth lines of caption - US should be U.S. -There are no x-axis labels -The legend for plots a, b, and c are incorrect as they indicate the data for the East is red and West is green

Response: We have corrected the legends for plots a, b, and c. Please see our updated draft.

Figure 3 -In first line of caption – Suggest changing adding a the before observations -In first line of caption – To match the figure between observations and precipitationadjusted model valves should be switched -In second line of caption – Suggest changing observation to observational -Letters should be added to each plot and the caption updated to indicate this -It should be indicated in the caption what the solid and dashed lines in each plot represent -There are also no subscripts in the abbreviations used on both the x and y-axes for all plots

Response: We have made the changes to the captions, and also added the letters for the plots. Please see the new plots from our updated draft.

The new caption is:

"Figure 3. Comparison of the WDEP trend for each valid site between the precipitation-adjusted model values and observational for total oxidized nitrogen (TNO_3, a), reduced nitrogen (NH_X, b), and total sulfate (TS, c). Each NADP site is assumed to be valid for our analysis only if at least 18 years of observation data are available at that site and the data coverage is at least 75% for

each year. The green color is for the eastern U.S., and the red color is for the western U.S., with the dashed line for the 1:2 and 2:1 ratio, and the solid line for the 1:1 ratio. ”

Figure 4 -In first and second lines of caption – Suggest changing panel to panels -In third line of caption – Suggest changing plot show p value to plots show p values -In fourth line of caption – Suggest adding a comma after i.e. -There are no x and y-axes labels

Response: We have made changes to the captions according to the reviewer’ comments.

Figure 5 -In second line of caption – Suggest changing the right plot show p value great than to both plots show p values greater than -In third line of caption – T-test should be t-test. Also suggest adding a comma after i.e. -Letters should be added to each plot and the caption updated to indicate this -There are no x and y-axes labels

Figure 6 -In first line of caption – Suggest changing (top panel) and DEP (bottom panel) to (top panels) and DDEP (bottom panels) -In second line of caption – Suggest changing plot show p value great than to plots show p values greater than -In third line of caption – T-test should be t-test. Also suggest adding a comma after i.e. -There are no x and y-axes labels

Response: We have now corrected this. Please see our updated draft for the new plots.

Figure 8 -In caption – It should be mentioned in the caption that the percent contribution is being indicated on each bar -In first line of caption – US should be U.S. -On the yaxis for both plots, US should be U.S. -Suggest in legend for plot a calling Oxid as NO3 instead and Red as NHx instead so that it matches the main text

Response: We now mention the percentiles in the caption, and also updated our plots.

“Interannual variability of the TDEP for inorganic nitrogen (a), and sulfur (b) in the U.S. from 1990 to 2010, including their fractions labelled as percent contributions for WDEP of oxidized nitrogen (NO_3), WDEP of reduced nitrogen (NH_X), DDEP of oxidized nitrogen (NO_3) and DDEP of reduced nitrogen (NH_X) deposition for the nitrogen, and WDEP versus DDEP for sulfur. ”

Figure 9 -In second line of caption – Suggest changing an NHx to a NHx -In third line of caption – Suggest removing the comma after 0.5 -There are no x and y-axes labels -Title for plot a – Suggest changing NHx ratio over TIN 1990 to TDEP NHx to TIN ratio 1990 -Title for plot b – Suggest changing NHx ratio over TIN 2010 to TDEP NHx to TIN ratio 2010 -Title for plot c – I am not sure I understand this plot title. What is (/year) indicating? Should the title maybe be TDEP NHx to TIN ratio Overall Trend?

Response: We have made the changes suggested by the reviewer in the revised manuscript. Please see our new draft for the updated plots.

Supporting Information Figure S1 -In caption – Suggest changing all the ofs to equal signs (e.g., 5 of Northern Forests to 5 = Northern Forests) -There are no x and y-axes labels -In plot title – US should be U.S. Also what does mask mean? It is not indicated in the caption or text.

Response: We have made the changes following the reviewer’s comments, and also update the plot caption as “U.S. ecoregion Level 1”. Please see the plot in our updated draft.
The new caption is:

"The 10 Level I ecoregions in the continental U.S.: 5 = Northern Forests, 6 = Northwestern Forested Mountains, 7 = Marine West Coast Forest, 8 = Eastern Temperate Forests, 9 = Great Plains, 10 = North American Deserts, 11 = Mediterranean California, 12 =Southern Semi-arid Highlands, 13 = Temperate Sierras, and 15 = Tropical Wet Forests."

Figure S2 -In first line of caption – Suggest changing plot to plots. Also the words observation and model should be switched to match what is actually plotted. -In second line of caption – Suggest changing data. The site in NADP is assumed to data points. The data at each NADP site is assumed -In third line of caption – Suggest changing valid if only at to valid only if at, changing is available to are available, and changing for the to for that -In fourth line of caption – suggest changing plot to plots -In fifth line of caption – Suggest removing the the before missing -In sixth line of caption – Suggest changing observation to observations -It should be indicated in the caption what the solid lines in the plot represent. Also should this be like the other plots and have two dashed lines and one solid line?

Response: We made the changes following the reviewer's comments.

Figure S3 -Letters should be added to each plot and the caption updated to indicate this -Suggest making a symbol indicating that green is for East sites and red is for West sites as currently this is only indicated from the small text at the top of each plot -It should be indicated in the caption what the solid and dashed lines in each plot represent -There are no subscripts in the abbreviations used on both the x and y-axes for all plots

Response: We add letters for each plot, and update the captions to indicate this. We also add descriptions for the two dashed and solid lines. The new captions is:

"Scatter plots for the annual accumulated deposition (total oxidized nitrogen (TNO_3, a), reduced nitrogen (NH_X, b), and total sulfate (TS,c)) without considering the precipitation adjustment between observation and model results from 1990 to 2010 for 170 valid sites with 3531 valid data. The site in NADP is assumed valid if only at least 18 years of observation data is available with 75% annual coverage for the site. Note that the annual accumulated deposition may not be the actual annual totals because of the missing data in the observation. The green color is for the eastern U.S., and the red color is for the western U.S., with the dashed line for the 1:2 and 2:1 ratio, and the solid line for the 1:1 ratio."

Figure S4 -There are no x and y-axes labels -There are no subscriptions in the abbreviations used in the titles for all plots

Response: We now add the subscriptions for all the abbreviations. Please see the new plots in our updated draft.

Figure S5 -In first line of caption – Suggest adding a the before US. Also US should be U.S. -There are no x-axis labels -Suggest changing y-axis labels to Fraction of the Total -Suggest pointing out on both plots somehow 2003 since this is an important year in terms of trends and so that it corresponds with the discussion in the main text. Maybe add a vertical dashed line.

Response: We add a red arrow to point the year 2003, and description in the caption.

"The red arrow points to the year 2003."

Table S1 -Either the comma or the parenthesis should be removed from Xing et al. reference. Both are not needed.
Response: We removed the comma for both the Xing et al. (2013) and Xing et al. (2015a).

Table S3 -In third line of caption – Suggest removing the and with at the end of the sentence
Response: We removed the "and with" as suggested. Please see our new draft.

Table S4 -In fourth line of caption - There should be a hyphen in t-test -Second column heading – Suggest changing Regions to Region
Response: We made the changes as the reviewer suggested. Please see our new draft.

Table S5 -Second column heading – Suggest changing Regions to Region
Response: We made the change as the reviewer suggested. Please see our new draft.

Long-term trends in total inorganic nitrogen and sulfur deposition in the U.S. from 1990 to 2010

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Abstract. Excess deposition (including both wet and dry deposition) of nitrogen and sulfur are detrimental to ecosystems. Recent studies have investigated the spatial patterns and temporal trends of nitrogen and sulfur wet deposition, but few studies have focused on dry deposition due to the scarcity of dry deposition measurements. Here, we use long-term model simulations from the coupled Weather Research and Forecasting and the Community Multiscale Air Quality (WRF-CMAQ) model covering the period from 1990 to 2010 to study changes in spatial distribution as well as temporal trends in total (TDEP), wet (WDEP) and dry deposition (DDEP) of total inorganic nitrogen (TIN) and sulfur (TS). We first evaluate the model's performance in simulating WDEP over the U.S. by comparing the model results with observational data from the U.S. National Atmospheric Deposition Program. The coupled model generally underestimates the WDEP of both TIN (including both the oxidized nitrogen deposition-TNO_3, and the reduced nitrogen deposition-NH_X) and TS, with better performance in the eastern U.S. than the western U.S. The underestimation of the wet deposition by the model is mainly caused by the coarse model grid resolution, missing lightning NO_x emissions, as well as the poor temporal and spatial representation of NH_3 emissions. TDEP of both TIN and TS show significant decreases over the U.S., especially in the east due to the large emission reductions that occurred in that region. The decreasing trends of TIN TDEP are caused by decreases in TNO_3, and the increasing trends of TIN deposition over the Great Plains and Tropical Wet Forests (Southern Florida Coastal Plain) regions are caused by increases in NH_3 emissions although it should be noted that these increasing trends are not significant. TIN WDEP shows decreasing trends throughout the U.S., except for the Marine West Coast Forest region. TIN DDEP shows significant decreasing trends in the Eastern Temperate Forests, Northern Forests, Mediterranean California and Marine West Coast Forest, and significant increasing trends in the Tropical Wet Forests, Great Plains and Southern Semi-arid Highlands. For the other three regions (North American Deserts, Temperate Sierras and Northwestern Forested Mountains), the decreasing or increasing trends were not significant. Both the WDEP and DDEP of TS have decreases across the U.S., with a larger decreasing trend in the DDEP

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than that in the WDEP. Across the U.S. during the 1990-2010 period, DDEP of TIN accounted for 58-65% of TDEP of TIN. TDEP of TIN over the U.S. was dominated by deposition of TNO_3 during the first decade, which then shifts to reduced nitrogen (NH_X) dominance after 2003 resulting from a combination of NO_x emission reductions and NH_3 emission increases. The sulfur DDEP is usually higher than the sulfur WDEP until recent years, as the sulfur DDEP has a larger decreasing trend than WDEP.

1 Introduction

Increased nitrogen and sulfur deposition is detrimental to ecosystems, since it leads to decreased biological diversity (Clark and Tilman, 2008; Clark et al., 2013; Stevens et al., 2004), increased terrestrial and aquatic eutrophication (Bouwman et al., 2002; Bowman et al., 2008; Fisher et al., 2011) and acidification (Greaver et al., 2012; Savva and Berninger, 2010). The primary sources for nitrogen deposition are nitrogen oxides (NO_x≡NO + NO_2) and ammonia (NH_3), which both have anthropogenic and natural sources. The major source for NO_x is from the combustion of fossil fuels in industry and energy use (Elliott et al., 2007; Lamarque et al., 2010). For NH_3, 80% of the total emissions are from livestock manure management and chemical fertilizer in 2005 as estimated from the U.S. National Emission Inventory (Reis et al., 2009), which are not regulated under current legislation and underwent significant increases over the past decades (Xing et al., 2013; Warner et al., 2017). Another possible source of NH_3 emissions are from vehicles which may be twice as high as the emission estimates in the current NEI (Sun et al., 2016). The primary emission source for sulfur deposition is sulfur dioxide (SO_2) which also mainly originates from fossil-fuel combustion (Smith et al., 2011).

The ultimate fate for NO_x, NH_3 and SO_2 is removal by wet scavenging and uptake by terrestrial and aquatic ecosystems (Greaver et al., 2012). Wet deposition (WDEP), in the form of rain or snow, is relatively easy to measure. Several observation networks were established to provide reliable long-term records of WDEP, such as the European Monitoring and Evaluation Programme (EMEP) in Europe, the National Acid Deposition Monitoring Network (NADMN) in China, the Canadian Air and Precipitation Monitoring Network (CAPMoN) in Canada, and the National Atmospheric Deposition Program's National Trends Network (NADP/NTN) in the U.S. (Xu et al., 2015). These data have been extensively used to quantity the sources, patterns, and temporal trends of WDEP of major species worldwide (e.g., EEA, 2011; Jia et al., 2014; Cheng and Zhang, 2017; Lajtha and Jones, 2013; Du et al., 2014; Sickles II and Shadwick, 2007a, 2007b, 2015). However, the majority of these studies discussed WDEP based on the measurements only, and neglected the discussion of the spatial distribution and trends of dry deposition (DDEP), as no direct DDEP measurements are available at these networks. The calculated values at some sites, such as for the Clean Air Status and Trends Network (CASTNET) and CAPMoN, however cannot be easily spatially

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interpolated due to limited availability of sufficient number of sites in a region as well as the representativeness of the derived fields due to assumptions in the spatial interpolation method (Schwede and Lear, 2014). DDEP can contribute up to two-thirds of total deposition (TDEP) of nitrogen, and neglecting it can lead to substantial underestimation of the total flux (Flechard et al., 2011; Vet et al., 2014). Also, accurate estimates of TDEP are usually required to assess the impacts of excess nitrogen and sulfur deposition on ecosystem health, such as critical load exceedances and species loss (Simkin et al., 2016).

To address these challenges, global and regional chemical transport models (CTMs) have been extensively used in recent years to quantify the sources and distribution of both WDEP and DDEP (Mathur and Dennis, 2003; Galloway et al., 2008; Paulot et al., 2013; Sanderson et al., 2008; Zhang et al., 2012; Zhao Y. et al., 2009; Zhao Y. H. et al., 2015, 2017), to study the projected deposition changes in the future (Dentener et al., 2006; Larmarque et al., 2013; Ellis et al., 2013; Kanakidou et al., 2006; Sun et al., 2017), and also its effect on ecosystems (Simkin et al., 2016). CTMs can link the sources to the deposition through atmospheric chemistry and transport processes, and can provide insights on the trends of TDEP and its components. In this study we quantify the long-term geographical patterns and temporal trends of TDEP, WDEP, and DDEP of total inorganic nitrogen and sulfur over the continental U.S. based on a 21-year model simulation from 1990 to 2010 at 36km×36km. The paper is organized as follows. Section 2 describes the model configuration and observation datasets as used for model evaluation. The model evaluation results and the patterns and trends of inorganic nitrogen and sulfur deposition are presented in Section 3, followed by the conclusions in Section 4.

2 Methods

2.1 Model setup

The long term simulations were previously performed using the coupled Weather Research and Forecasting and the Community Multiscale Air Quality (WRF-CMAQ model, Wong et al., 2012) with WRFv3.4 coupled with CMAQv5.02 driven by internally consistent U.S. emission inventories (Xing et al., 2013) covering the Continental U.S. (CONUS) domain discretized with a grid of 36 km horizontal resolution. Spatial and time varying chemical lateral boundary conditions were provided by the hemispheric WRF-CMAQ (Mathur et al., 2017) running over the same period (Xing et al., 2015). Interested readers are referred to Gan et al. (2015, 2016) for a detailed description of the settings of the CMAQ model and physical configurations of the WRF model (supporting Table S1). The performance of the coupled WRF-CMAQ model for major trace gases, aerosol species and meteorological variables such as ozone (O_3), fine particular matter ($PM_{2.5}$) and aerosol optical depth at both the hemispheric and regional scale has been extensively evaluated in previous studies (Xing et al., 2015a, b; Mathur et

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al., 2017; Gan et al., 2015, 2016; Astitha et al., 2017), and has shown skill in simulating the magnitudes and long-term trends of these variables. The dry deposition of each species in the CMAQ model is calculated by multiplying the concentration in the lowest model layer by the dry deposition velocity (V_d). The V_d is calculated as the reciprocal of the sum of the atmospheric (R_a, the resistance to transport through the atmosphere above the surface receptors), quasi-laminar boundary layer (R_b, the resistance to transport across the thin layer of air that is in contact with the surface and varies with the diffusion of the pollutant transported), and surface resistances (R_s, the resistance to the uptake of the pollutant by the surface receptor, typically vegetation or soil).

2.2 Deposition observations in the U.S.

A previous study using the offline CMAQ model has demonstrated moderate skill simulating WDEP from 2002 to 2006 (Appel et al., 2011). Here we evaluate the coupled WRF-CMAQ model's ability to simulate WDEP of nitrate (TNO_3), ammonium (NH_X) and sulfate (TS) during 1990 – 2010 over the U.S., including both the interannual variability as well as long-term trends. This is accomplished by comparing the model results with observations from the U.S. National Atmospheric Deposition Program (NADP, http://nadp.sws.uiuc.edu/ntn/), which measures total weekly wet deposition of these species. The deposition is measured by wet-only samples, which are triggered by precipitation. The deposition of sulfate and nitrate are analyzed by ion chromatography, and ammonium by flow injection analysis (http://nadp.slh.wisc.edu/educ/sample.aspx, accessed May 4, 2018). We first pair the wet deposition data between the observation and the model results in time and space, and then extract the annual deposition for the sites matching our criteria (at least 18 available years with 75% annual coverage for each year). Model data during periods of missing observations were not considered in either the statistical evaluation or the trends analysis. By applying the criteria, we use information at 170 of 359 sites, with 141 sites in the eastern U.S. (east of 110°W longitude) and 29 sites in the western U.S. (west of 110°W longitude). The detailed site information and the number of years of observational data used for the model evaluation can be found in supporting Table S2. In pairing the observed and modeled TNO_3 WDEP values (which combines WDEP of NO_3^- and HNO_3), we multiply the model estimated HNO_3 WDEP by 0.984 to account for the transformation of HNO_3 to NO_3^- in solution in the measurements. In pairing the observed and modeled NH_X WDEP values (which combines WDEP of NH_4^+ and NH_3), we multiply the model estimated NH_3 WDEP by 1.06 to account for the transformation of NH_3 to NH_4^+ in the rainwater in the measurements. In pairing the observed and modeled TS WDEP values (which combines WDEP of SO_4^{2-} and SO_2), we multiply the model estimated SO_2 WDEP by 1.50 to account for the fact that SO_2 will be fully oxidized into SO_4^{2-} during sampling (Appel et al., 2011).

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For the model evaluation, we examine the correlation coefficients (R), Mean Bias (MB) as well as the normalized mean bias (NMB):

$$NMB = \frac{\sum_1^N (Model - Obs)}{\sum_1^N Obs} \quad (1)$$

When discussing the model evaluation and deposition trends, we divide the U.S. into 10 ecological regions, following the North America Level I ecoregion definition (https://www.epa.gov/eco-research/ecoregions-north-america, accessed 08/01/2017), including Northern Forests, Northwestern Forested Mountains, Marine West Coast Forest, Eastern Temperate Forests, Great Plains, North American Deserts, Mediterranean California, Southern Semi-arid Highlands, Temperate Sierras, and Tropical Wet Forests (supporting Fig. S1). For the trend analysis, we focus on the linear trends (Colette et al., 2011; Xing et al., 2015a), in which the linear least square fit method is employed, and significance of trends is examined with a Student t-test at the 95% confidence level (p=0.05).

Errors in the simulated meteorology and precipitation in particular, can lead to errors in estimating WDEP in the CMAQ model. We follow the previous approach of Appel et al. (2011) to account for biases in modeled precipitation by adjusting the modeled WDEP as:

$$Bias\ Adjusted\ WD_{mod} = \frac{Precip_{Obs}}{Precip_{mod}} \times WD_{mod} \quad (2)$$

In equation 2, WD_{mod} represents the WDEP from the model, $Precip_{Obs}$ represents annual or monthly accumulated observed precipitation, and $Precip_{mod}$ represents the corresponding annual or monthly accumulated precipitation from the model.

The U.S. CASTNET provides long-term observation of atmospheric concentrations as well as the dry deposition (https://www.epa.gov/castnet, accessed May 7, 2018). However, the dry deposition values reported are not directly measured, but estimated using the inferential method, pairing the measured air pollutant concentration with a modeled deposition velocity from the MLM model (Meyers et al, 1998). So rather than comparing dry deposition estimates from two models, we choose to evaluate the model's performance in simulating the ambient air concentrations (sulfur dioxide (SO_2), sulfate (SO_4^{2-}), total nitrage ($TNO_3 = NO_3^- + HNO_3$), and ammonium (NH_4)). We apply the same criteria in selecting valid observation sites as the NADP/NTN. By doing this, we have chosen 39 valid sites out of total 145 sites. The detailed site information and the number of years of observational data used for the model evaluation can be found in supporting Table S3.

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3 Results

3.1 Model evaluation for WDEP and DDEP

The coupled WRF-CMAQ model generally overestimates the precipitation throughout U.S. (Fig. 2(d), supporting Fig. S2), consistent with previous findings (Ran et al., 2015). After performing the annual precipitation adjustment for model simulated WDEP, we see that the correlation coefficients (R) are slightly improved relative to using the unadjusted WDEP values (Table 1), increasing from 0.89 to 0.92 for TNO_3, from 0.77 to 0.81 for NH_X, and from 0.92 to 0.94 for TS (supporting Fig. S3). There are no significant changes for R when we use the monthly precipitation adjustment compared with the annual precipitation adjustment (Table 1). The model generally underestimates WDEP for both the eastern and western U.S., except for TS where the model tends to overestimate WDEP in the western U.S. (Figs. 1 and 2). After performing the precipitation adjustment, the NMB values increase for all three species (Table 1). The model exhibited better performance for WDEP in the east than the west, considering both the R and the NMB, largely because of the complex terrain in the western U.S. (Appel et al., 2011).

The 21-yr average TNO_3 WDEP is highest in the Eastern Temperate Forest region, and lowest in the Southern Semi-arid Highlands, as seen from both the observations and model results (Table 2). The model generally underestimates the TNO_3 deposition for all the regions with MB values ranging from -1.11 kg ha^{-1} in the Southern Semi-arid Highlands to -3.73 kg ha^{-1} in the Tropical Wet Forests, except for the Marine West Coast Forest region where the model overestimates the TNO_3 WDEP, with MB values of 0.79 kg ha^{-1}. The correlation coefficients between the model and observations are generally much higher in the eastern U.S. (R larger than 0.80), than the western U.S. (R less than 0.70). The 21-yr average NH_X WDEP is also highest in the Eastern Temperate Forest region, and lowest in the Southern Semi-arid Highlands (Table 3). The model generally underestimates the NH_X WDEP with MB values ranging from -0.26 kg ha^{-1} yr^{-1} in the Northwestern Forested Mountains to -0.81 kg ha^{-1} in Tropical Wet Forests, and overestimates in the Marine West Coast Forest with MB of 0.24 kg ha^{-1}. The correlation coefficients between model and observations for NH_X WDEP share similar spatial patterns with TNO_3 WDEP but have lower R values. The 21-yr average TS deposition is highest in the Eastern Temperate Forests region, and lowest in the North American Desserts. Similar to TNO_3 and NH_X, the model underestimates the TS WDEP over most of the regions, but overestimates observed values in the Marine West Coast Forest and Mediterranean California. The R between the model and the observations are generally larger than 0.9 in the eastern U.S. but range from 0.46 to 0.79 in the western U.S.

Clear downward trends are seen for TNO_3 and TS WDEP from both the observations and model in Fig.2 (a, c), while NH_X deposition exhibits much larger interannual fluctuations (Fig.2 (b)). From Fig. 3, we see much larger decreasing trends for TNO_3 and TS WDEP in the eastern U.S. than those in the western U.S. This is due to the fact that the emission reductions

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mostly occurred in the eastern U.S. (Xing et al., 2013) and the model captures this trend very well especially for TNO_3 and TS WDEP with R values of 0.94 and 0.95, respectively. A stronger decreasing trend over the Northern Forests and Eastern Temperate Forests regions compared to other regions is observed for both TNO_3 and TS WDEP, and the model is also able to capture these very well but a slightly distinctions in the trends for each ecoregion (Tables 2 and 4). We see that the model generally underestimates the decreasing WDEP trends for all the sites for TNO_3 and TS (Tables 2 and 4). We see that the model generally underestimates the magnitude of the decreasing WDEP trends at many sites for TNO_3 and TS (Tables 2 and 4), which may be caused by the coarse model resolution (36km), and uncertainties in the emission inventories. For NH_X, we see increasing WDEP trends for most of the sites but the trends are not statistically significant (Table 3).

Compared with Appel et al. (2011), our model results indicate larger bias for WDEP for both the eastern and western U.S. (supporting Table S4). The NMB increase for all three species in our results from 2002 to 2006 after applying the precipitation-adjustment, which was also seen in Appel et al. (2011), except for TS, which Appel et al. (2011) reported decreased bias after the precipitation adjustment. The discrepancies for the model performances between our study and Appel et al. (2011) could be caused by the grid resolutions, in which coarse resolution models (e.g. 36km in our study) have more challenges to simulate various chemical and physical processes compared with fine resolution (e.g. 12km used in Appel et al., 2011). There are numerous differences between the model configuration and versions used in this analysis and those previously used by Appel et al. (2011). Specific model process representation differences between CMAQv5.0 used here and CMAQv4.7 used in Appel et al. (2011) can be found at: https://www.epa.gov/cmaq/cmaq-models-0.

To evaluate the model's performance in simulating the DDEP, we compare the model simulated concentration with the observations from CASTNET. Comparisons of annual average simulated concentrations with corresponding measurements at the CASTNET sites show strong correlation for SO_2 (R of 0.88), SO_4 (0.95), TNO_3 (0.94), and NH_4 (0.94). Some underestimation for SO_4, and overestimation in other species ambient concentrations is noted (supporting Fig. S4). The model also captures the trends for these species with very high R, but the magnitude of the decreasing trends is underestimated by the model (supporting Fig. S5).

3.2 Spatial patterns of modeled total deposition of nitrogen and sulfur

Table 5 shows that modeled TDEP of total inorganic nitrogen (TIN), i.e. the sum of TNO_3 and NH_X, is much higher in the Eastern Temperate Forests than any other ecoregion (regional average of 10.08 and 7.95 kg N ha^{-1} in 1990 and 2010, respectively), followed by the Northern Forests and Mediterranean California regions. The hotspot for TIN TDEP has shifted from the eastern U.S. in 1990 to the north central U.S. in 2010, with relative higher values in North Carolina (NC) and

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Pennsylvania (PA) (Fig. 4). During the period from 1990 to 2010, TIN TDEP has significantly decreased (with $p < 0.05$ for the standard two-tailed Student's t-test) over several ecoregions, including Eastern Temperate Forests, Northern Forests, Mediterranean California and Marine West Coast Forest (decreasing trend of 0.12, 0.071, 0.038 and 0.017 kg N ha^{-1} yr^{-1} respectively) as a result of significant reductions in anthropogenic NO_x emissions (Xing et al., 2013). Slightly increasing but not statistically significant trends are estimated in TIN TDEP for the Great Plains and the Tropical Wet Forests while the remaining regions show statistically insignificant decreasing trends (Table 6). We see statistically significant increasing trends of TIN TDEP in eastern North Carolina (larger than 0.2 kg N ha^{-1} yr^{-1}), which is mainly caused by the increase in NH_X TDEP (Fig. 5) arising from increased NH_3 emission from hog farming (Xing et al., 2013; Paulot et al., 2014). There are also significant increasing trends of TIN TDEP over Iowa, Minnesota and South Dakota (larger than 0.04 kg N ha^{-1} yr^{-1}) because of the increased NH_X TDEP related to animal foster and corn plantation (Figs. 4 and 5). From Fig. 5, we see that the TIN TDEP decreasing trends predominantly result from the TNO_3 TDEP decreases across the U.S., with larger decreasing rates in the east than the west. The increasing TIN TDEP trends over the east and central states (such as North Carolina, Pennsylvania, and Virginia) were caused by the NH_X TDEP increases which in turn arise from increases in NH_3 emissions (Paulot et al., 2013).

Similar to TIN TDEP, TDEP of total sulfur (TS), i.e. the sum of SO_2 and SO_4^{2-}, shows a distinct spatial gradient from the east (usually larger than 9 kg S ha^{-1}) compared to the west (lower than 3 kg S ha^{-1}) (Fig. 4). In 1990, the TS was even higher than 30 kg S ha^{-1}in some states of the central U.S., such as Indiana, Ohio, Pennsylvania, and West Virginia. In 2010, TS TDEP is still higher in the east than the west, but TS TDEP in the east has decreased by half (to lower than 15 kg S ha^{-1}) for most regions. From 1990 to 2010, the estimated TS TDEP exhibits significant trends across the U.S., with decreasing trends generally larger in the east (larger than 0.4 kg S ha^{-1} yr^{-1}) and lower in the west (less than 0.2 kg S ha^{-1} yr^{-1}) as a result of SO_2 decreases from the passage of the Clean Air Act Amendments of 1990. All the ecoregions experienced statistically significant decreases of TS TDEP over the past two decades which was dominated by the decreases in SO_4^{2-} except for the Mediterranean California ecoregion which showed an insignificant decreasing trend (Table 6). The largest decreasing trend was seen in the Eastern Temperate Forests region (-0.51 kg S ha^{-1} yr^{-1}), followed by the Northern Forests (-0.23 kg S ha^{-1} yr^{-1}) and the Great Plains (-0.082 kg S ha^{-1} yr^{-1}).

3.3. Wet versus dry nitrogen and sulfur deposition trends in the U.S.

Fig. 6 shows that the TIN WDEP is higher in the east than the west, due to both greater precipitation (Fig. 2 (d)) and higher atmospheric burden of airborne reactive nitrogen in the east (Xing et al., 2013). In addition, estimated TIN WDEP shows widespread significant decreasing trends in the eastern U.S. while trends in the western U.S. generally have smaller magnitudes

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and often are not statistically significant. The most significant decreasing region is the Eastern Temperate Forests, with an annual decrease of -0.070 kg N ha^{-1} yr^{-1}, followed by the Northern Forests (-0.037 kg N ha^{-1} yr^{-1}) and the Great Plains (-0.023 kg N ha^{-1} yr^{-1}) (supporting Table S5). The decreasing trends of TIN WDEP were mainly caused by the WDEP of TNO_3 (supporting Fig. S6a, and Table S5). There are no significant changes for WDEP of NH_X in the majority of U.S. except for the region Tropical Wet Forests (supporting Fig. S6b), consistent with previous findings (Lajtha and Jones, 2013). TIN DDEP is higher in the eastern U.S. and lower in the northwestern and central U.S. Significant decreasing trends for the TIN DDEP were seen over the Eastern Temperate Forests (-0.049 kg N ha^{-1} yr^{-1}), Northern Forests (-0.033 kg N ha^{-1} yr^{-1}), Mediterranean California (-0.032 kg N ha^{-1} yr^{-1}), and Marine West Coast Forest regions (-0.022 kg N ha^{-1} yr^{-1}) (supporting Table S6). The decreases of TIN DDEP over these regions were dominated by the DDEP of TNO_3 (supporting Fig. S6c, and Table S6). In contrast, there are significant increasing trends of TIN DDEP over the Tropical Wet Forests (0.027 kg N ha^{-1} yr^{-1}), Great Plains (0.026 kg N ha^{-1} yr^{-1}), and Southern Semi-arid Highlands (0.009 kg N ha^{-1} yr^{-1}). These increases are caused by the DDEP of NH_x (supporting Fig. S6d, and Table S6).

Fig. 7 shows a distinct spatial distribution for both the WDEP and DDEP of sulfur, with much higher values in the eastern U.S. in the vicinity and downwind of major sources. Significant decreasing trends are noted for both the wet and dry TS deposition for all the ecoregions, except for the Marine West Coast Forest and Mediterranean California where TS WDEP were estimated to increase, though the trend was not statistically significant (supporting Tables S4 and S5). TS DDEP trends were larger or comparable to TS WDEP trends for the majority of the regions, except for Southern Semi-arid Highlands, Temperate Sierras and Tropical Wet Forests where the magnitude of the decreasing trends for DDEP were lower than those for WDEP.

3.4 Deposition budget in U.S.

Fig 8 (a) shows that the U.S. domain average TDEP of TIN generally decreased over the past two decades, from 5.55 kg N ha yr^{-1} in 1990 to 5.00 kg N ha yr^{-1} in 2010. The decrease in TIN TDEP is mainly caused by reductions in TNO_3. The TNO_3 WDEP was estimated to decrease from 1.26 kg N ha yr^{-1} to 0.76 kg N ha yr^{-1}, and TNO_3 DDEP decreased from 1.98 kg N ha yr^{-1} to 1.35 kg N ha yr^{-1}, during the same period. DDEP accounts for large fractions of TDEP for TIN over the entire 1990 to 2010 time period, 58%-65% of TDEP over the U.S. (supporting Fig. S7). The relative proportions of TNO_3 over the TDEP have also changed over the past 2 decades in response to changes in precursor emissions. TNO_3 deposition dominates TIN TDEP until the early 2000s. After 2003, however, NHx dominates the TIN TDEP over the U.S. (supporting Fig. S7). This is consistent with Li et al. (2016) who showed that the U.S. TIN deposition has transitioned from being dominated by TNO_3 to NH_x as a

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result of NOx emission reductions and increases of unregulated NH_3 emissions. The increasing contributions of NH_X to the TIN TDEP can also be seen from Fig. 9, which shows increasing proportions of NH_X contributions across larger regions of the continental U.S. during the 1990 to 2010 period (significant increasing trend ($p < 0.05$) for the NHx fraction of the total TIN across the U.S.). This has resulted from the significant NO_X reduction due to regulations and growth in NH_3 emissions (Warner et al., 2017).

Similar to TIN TDEP, the TS TDEP has also decreased, from 6.85 kg S ha^{-1} yr^{-1} in 1990 to 3.26 kg S ha^{-1} yr^{-1} in 2010 (Fig. 8 (b)), as a result of the decreasing anthropogenic SO_2 emissions (Smith et al., 2011; Xing et al., 2013). The TS DDEP dominates the TS TDEP during the first decade, but TS WDEP becomes dominant after the year 2004. The dry sulfur deposition has decreased by 58% from 1990 to 2010, from 3.65 kg S ha^{-1} yr^{-1} to 1.55 kg S ha^{-1} yr^{-1}, while the wet sulfur deposition has decreased by 47%, from 3.20 kg S ha^{-1} yr^{-1} to 1.70 kg S ha^{-1} yr^{-1} during the same period.

4 Conclusion

In this study, we used model simulations spanning a 21-year period from 1990-2010 to investigate the spatial distribution and temporal trends in the total inorganic nitrogen (TIN) and total sulfur (TS) deposition across the U.S., including changes in chemical composition of the deposition as well as relative importance of the wet (WDEP) and dry deposition (DDEP) components. By evaluating the model's performance against observations from the NADP network, we found that the model generally underestimated the WDEP for both the oxidized nitrogen (TNO_3) deposition and reduced nitrogen (NH_X) deposition across the U.S. The model underestimated TS WDEP in the eastern U.S., but overestimated it in the western U.S. The model exhibited better performance in simulating the WDEP in the eastern U.S. than in the western U.S. The 21-yr model simulations captured the spatial pattern of decreasing trends for the WDEP of TNO_3 and TS very well, with a correlation coefficient typically larger than 0.9. However, the model generally underestimated the decreasing trends of the TNO_3 and TS WDEP. The model performance is worse in simulating the spatial distribution and trends of the NH_X deposition compared with TNO_3 and TS, which may be caused by uncertainties in the representation of NH_3 emissions in the model. The underestimation of the NH_X deposition could also be caused by uncertainties in temporal and spatial representation of emissions associated with fertilizer applications and bi-directional exchange of NH_3 between the air and underlying soil and vegetation surfaces. Applying the bi-directional NH_3 exchange mechanism in the coupled model could improve the model's ability in simulating NH_X deposition (Appel et al., 2011; Bash et al., 2013).

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The modeled total deposition (TDEP) of TIN and TS is higher in the eastern U.S. and lower in the western U.S. For TIN, it is highest in the Eastern Temperate Forests and lowest in the Northwestern Forested Mountains. For TS it is also highest in the Eastern Temperate Forests but lowest in the North American Deserts. The TDEP of TIN has seen significant decreasing trends over the Eastern Temperate Forests, Northern Forests, Mediterranean California and Marine West Coast Forest, and results from decreases in both wet and dry deposition of TNO_3. Modeled TDEP of TS was found to be decreasing over the entire U.S., with larger decreasing trends for the dry deposition compared with the wet deposition.

The TDEP of TIN over the entire U.S. domain was dominated by DDEP, accounting from 58%-65% of the total from 1990 to 2010. TDEP of oxidized nitrogen dominated TIN deposition in the U.S. in the first decade but a shift occurred in 2003 when TDEP of reduced nitrogen became the dominant factor. The DDEP of TS dominates the total sulfur deposition in the first decade while WDEP becomes the dominant factor after the year 2004.

Our analysis as well as others (Li et al., 2016; Kharol et al., 2017) show that reduced nitrogen has dominated the total nitrogen deposition budget in the U.S. in recent years. Additionally, model calculations show strong increasing trends in dry deposition amounts of NH_x across the U.S. which arise both from increasing NH_3 emissions but also perhaps from reduced transport distances. Reductions in SO_2 and NO_x emissions (and consequently their oxidation products) have decreased the amounts of NH_x partitioning to the aerosol-phase where scavenging by rain is the primary sink. Consequently, more NH_x remains in the gas-phase and dry deposits closer to the source regions. The study highlights the growing importance of NH_X deposition as emissions of NO_X and SO_2 have been reduced substantially over the years. We conclude that it is urgent to acquire accurate NH_3 emissions inventories and maintain additional measurements of NH_X, not only for improving the air quality model's performance, but also for controlling the nitrogen deposition in the U.S. In addition, dry deposition of TNO_3 and TS is a large fraction of the total deposition in the U.S., demonstrating the need for accurate dry deposition measurements, as well as more robust characterization of dry deposition in air quality models.

Data availability: The wet deposition data from the U.S. National Atmospheric Deposition Programm can be downloaded from the website (http://nadp.sws.uiuc.edu/). The 21-yrs model outputs for the coupled WRF-CMAQ model can be obtained by contacting the corresponding author (Y. Zhang, zhang.yuqiang@epa.gov, yuqiangzhang.thu@gmail.com).

Competing interests. The authors declare that they have no conflicts of interest.

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Tables and Figures

Table 1. Correlation coefficient (R), mean bias (MB, kg ha^{-1}), and normalized mean bias (NMB, %) for the sum of the annual accumulated wet deposition (WDEP) between the model and NADP sites from 1990 to 2010, including both the model values with and without applying monthly/annual precipitation adjustment. The R for trends are the correlation coefficient for the 21-yr changes of the wet deposition (TNO_3, NH_X and TS) between the model and the observations.

		TNO_3	NH_X	TS
R[1]	No adjustment	0.89	0.77	0.92
	Monthly Precip-adjust	0.91	0.81	0.94
	Annual Precip-adjust	0.92	0.81	0.94
MB	No adjustment	-1.92	-0.50	-0.37
	Monthly Precip-adjust	-1.89	-0.52	-0.53
	Annual Precip-adjust	-2.16	-0.56	-0.77
NMB	No adjustment	-31.6	-30.9	-5.1
	Monthly Precip-adjust	-32.1	-33.7	-7.5
	Annual Precip-adjust	-35.6	-35.1	-10.5
R for trends[2]	No adjustment	0.85	0.35	0.86
	Monthly Precip-adjust	0.94	0.64	0.95
	Annual Precip-adjust	0.94	0.66	0.95

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Table 2. Evaluation results for the 10 ecoregions for TNO_3 WDEP. The units for the means and MB are kg ha^{-1}, and kg ha^{-1} yr^{-1} for the trends. The bolded values indicate trends that are statistically significant with the P value less than 0.05 for the standard Student's t-test.

ID	Region Name	# of sites	Mean		MB	NMB	R	Trends	
			Obs	Mod				Obs	Mod
5	Northern Forests	18	7.56	4.97	-2.59	-0.34	0.93	**-0.22**	**-0.16**
6	Northwestern Forested Mountains	28	3.23	1.28	-1.95	-0.60	0.70	-0.03	**-0.01**
7	Marine West Coast Forest	3	1.55	2.34	0.79	0.51	0.44	**-0.02**	0.01
8	Eastern Temperate Forests	72	8.77	6.14	-2.63	-0.30	0.97	**-0.20**	**-0.17**
9	Great Plains	24	4.73	2.62	-2.11	-0.45	0.87	**-0.05**	**-0.04**
10	North American Deserts	17	1.81	0.66	-1.15	-0.63	0.82	**-0.02**	**-0.01**
11	Mediterranean California	4	2.34	2.39	0.05	0.02	0.76	**-0.09**	-0.03
12	Southern Semi-arid Highlands	1	1.59	0.49	-1.11	-0.69	0.85	-0.02	-0.01
13	Temperate Sierras	2	2.49	0.80	-1.68	-0.68	0.61	-0.01	0.00
15	Tropical Wet Forests	1	5.80	2.07	-3.73	-0.64	0.88	**0.11**	**0.04**

Table 3. The same as Table 2 but for NH_X.

ID	Region Name	# of sites	Mean		MB	NMB	R	Trends	
			Obs	Mod				Obs	Mod
5	Northern Forests	18	1.92	1.22	-0.7	-0.37	0.83	-0.01	-0.01
6	Northwestern Forested Mountains	28	0.64	0.39	-0.26	-0.4	0.36	0.00	**0.00**
7	Marine West Coast Forest	3	0.45	0.69	0.24	0.54	0.16	0.00	**0.01**
8	Eastern Temperate Forests	72	2.13	1.58	-0.55	-0.26	0.66	0.00	0.00
9	Great Plains	24	2.03	0.91	-1.12	-0.55	0.86	**0.03**	**0.01**
10	North American Deserts	17	0.58	0.19	-0.38	-0.66	0.62	0.00	0.00
11	Mediterranean California	4	1.01	0.64	-0.38	-0.37	0.82	-0.02	0.00
12	Southern Semi-arid Highlands	1	0.42	0.13	-0.29	-0.69	0.76	0.00	0.00
13	Temperate Sierras	2	0.63	0.26	-0.37	-0.59	0.75	0.00	0.00
15	Tropical Wet Forests	1	1.14	0.33	-0.81	-0.71	0.75	**0.04**	**0.01**

Table 4. The same as Table 2 but for TS.

ID	Region Name	# of sites	Mean		MB	NMB	R	Trends	
			Obs	Mod				Obs	Mod
5	Northern Forests	18	7.76	7.33	-0.42	-0.06	0.95	**-0.29**	**-0.23**
6	Northwestern Forested Mountains	28	2.15	1.88	-0.27	-0.13	0.70	**-0.05**	**-0.01**
7	Marine West Coast Forest	3	3.35	6.08	2.73	0.82	0.46	-0.02	0.04
8	Eastern Temperate Forests	72	11.78	11.04	-0.70	-0.06	0.97	**-0.34**	**-0.29**
9	Great Plains	24	4.16	2.95	-1.21	-0.29	0.91	**-0.07**	**-0.04**
10	North American Deserts	17	1.38	0.81	-0.58	-0.41	0.79	**-0.04**	-0.01
11	Mediterranean California	4	1.40	3.15	1.75	1.25	0.67	**-0.03**	0.01
12	Southern Semi-arid Highlands	1	1.45	0.89	-0.56	-0.39	0.91	**-0.07**	**-0.04**
13	Temperate Sierras	2	2.30	1.05	-1.25	-0.54	0.76	**-0.08**	-0.01
15	Tropical Wet Forests	1	7.41	2.94	-4.47	-0.60	0.73	0.09	0.04

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Table 5. TDEP (WDEP+DDEP, units of kg N ha^{-1} for nitrogen deposition including TNO_3, NH_X and TIN, and kg S ha^{-1} for TS) in 1990 and 2010 for the 10 ecoregions.

ID	Region Name	TNO_3		NH_X		TIN		TS	
		1990	2010	1990	2010	1990	2010	1990	2010
5	Northern Forests	4.21	2.19	2.35	2.56	6.56	4.74	9.86	3.56
6	Northwestern Forested Mountains	1.36	1.12	0.91	1.26	2.27	2.38	1.75	1.47
7	Marine West Coast Forest	1.07	1.35	2.00	2.43	3.7	3.78	5.03	3.95
8	Eastern Temperate Forests	6.12	3.27	3.96	4.68	10.08	7.94	17.54	6.66
9	Great Plains	2.45	1.84	2.77	3.97	5.22	5.81	3.36	2.16
10	North American Deserts	1.49	1.12	0.83	1.01	2.32	2.13	1.34	1.05
11	Mediterranean California	3.15	2.08	2.68	3.36	5.84	5.44	1.68	1.74
12	Southern Semi-arid Highlands	1.68	1.10	1.18	0.93	2.86	2.03	2.87	0.92
13	Temperate Sierras	2.00	1.48	0.91	1.02	2.91	2.5	2.33	1.2
15	Tropical Wet Forests	4.11	3.35	1.27	2.05	5.38	5.41	5.15	3.77

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Table 6. Trends for total deposition (WDEP+DDEP, units of kg N ha^{-1} yr^{-1} for nitrogen deposition including TNO_3, NH_X and TIN, and kg S ha^{-1} yr^{-1} for TS) over the ten ecoregions. The bolded values indicate trends that are statistically significant with the P value less than 0.05 for the Student's t-test.

ID	Region Name	TNO_3	NH_X	TIN	TS
5	Northern Forests	**-0.087**	**0.016**	**-0.071**	**-0.23**
6	Northwestern Forested Mountains	**-0.013**	**0.011**	-0.002	**-0.021**
7	Marine West Coast Forest	**-0.018**	0.002	**-0.017**	**-0.053**
8	Eastern Temperate Forests	**-0.15**	**0.034**	**-0.12**	**-0.51**
9	Great Plains	**-0.041**	**0.044**	0.003	**-0.082**
10	North American Deserts	**-0.016**	**0.008**	-0.008	**-0.023**
11	Mediterranean California	**-0.051**	0.013	**-0.038**	-0.013
12	Southern Semi-arid Highlands	**-0.014**	0.002	-0.012	**-0.074**
13	Temperate Sierras	**-0.016**	**0.009**	-0.006	**-0.054**
15	Tropical Wet Forests	**-0.026**	**0.041**	0.015	**-0.055**

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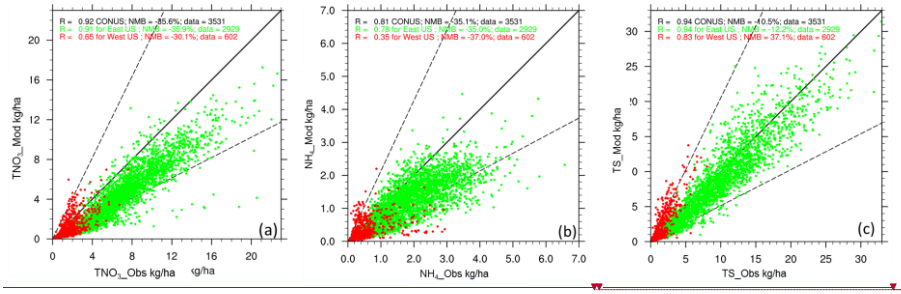
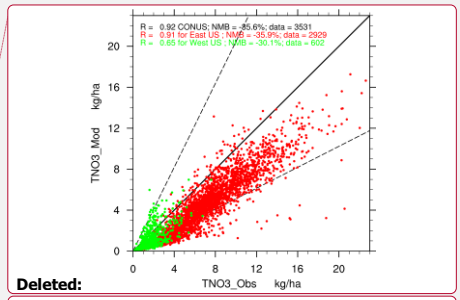


Figure 1. Scatter plots for the annual accumulated WDEP (total oxidized nitrogen (TNO_3, a), reduced nitrogen (NH_X, b), and total sulfate (TS, c)) between precipitation-adjusted model results and observations from 1990 to 2010 for 170 valid sites with 3531 valid data points. The data at each NADP is assumed to be valid for our analysis only if at least 18 years of observation data are available at that site and the data coverage is at least 75% for each year. Each point in the plots represents the annual accumulated WDEP for a given site and year. Note that the annual accumulated WDEP values used in this analysis may not be the actual annual totals due to missing data in the observations. The green color is for the eastern U.S., and the red color is for the western U.S., with the dashed line for the 1:2 and 2:1 ratio, and the solid line for the 1:1 ratio.



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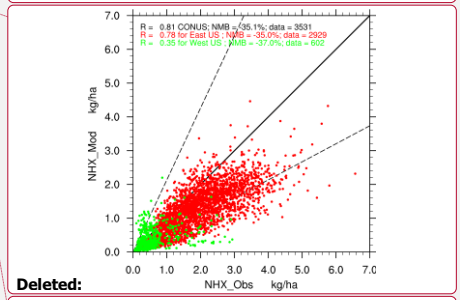

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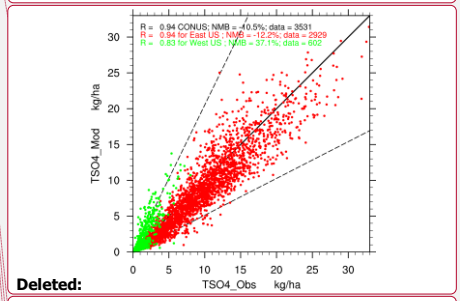

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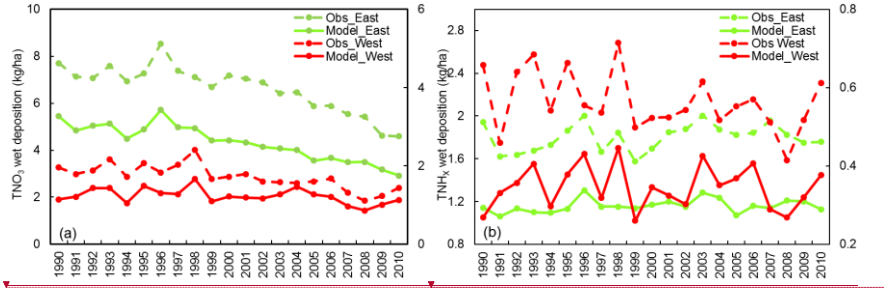


Figure 2. Comparison of the temporal trends for the annual accumulated WDEP (across all the 170 valid sites) for (a) TNO_3, (b) TNH_X, (c) TS, and (d) precipitation, for the eastern U.S. (green, averaged over 141 sites) and western US (red, average over 29 sites) between observation (dashed lines) and annual precipitation-adjusted model values (solid lines). The scale shown on the left is for the eastern U.S., and on the right for the western U.S.

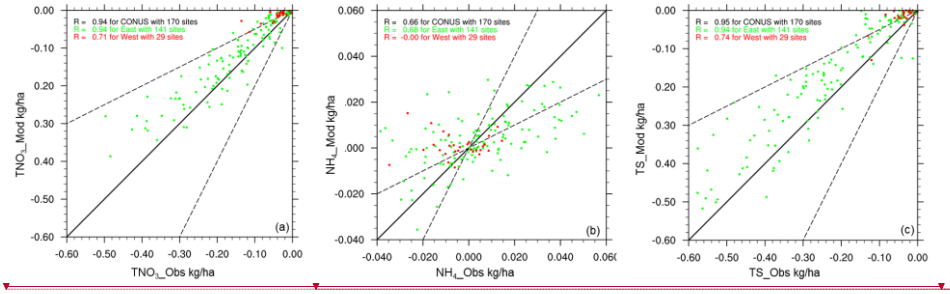
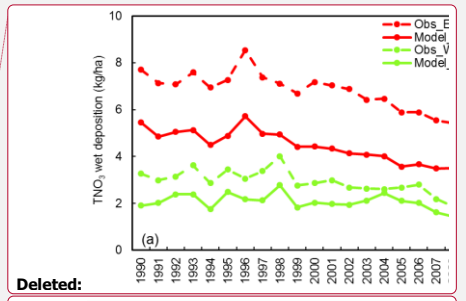


Figure 3. Comparison of the WDEP trend for each valid site between the precipitation-adjusted model values and observational for total oxidized nitrogen (TNO_3, a), reduced nitrogen (NH_X, b), and total sulfate (TS, c). Each NADP site is assumed to be



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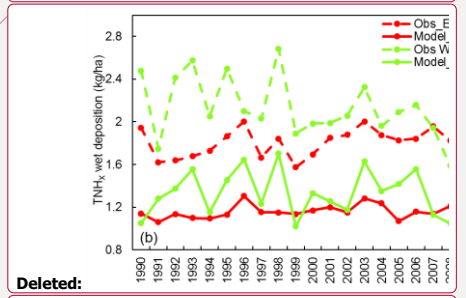

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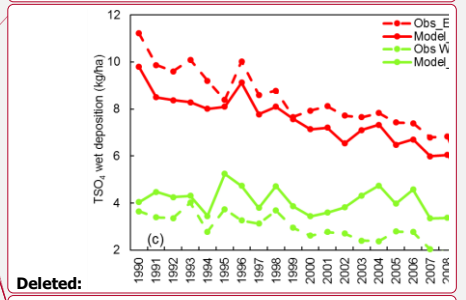

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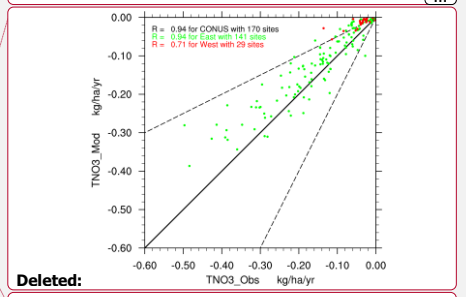

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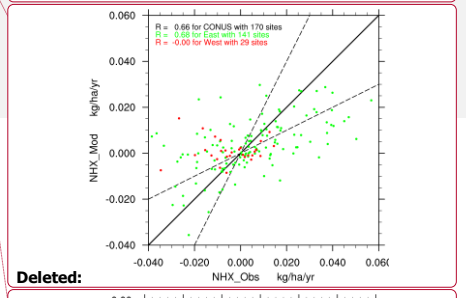

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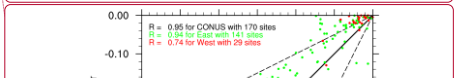


valid for our analysis only if at least 18 years of observation data are available at that site and the data coverage is at least 75% for each year. The green color is for the eastern U.S., and the red color is for the western U.S., with the dashed line for the 1:2 and 2:1 ratio, and the solid line for the 1:1 ratio.

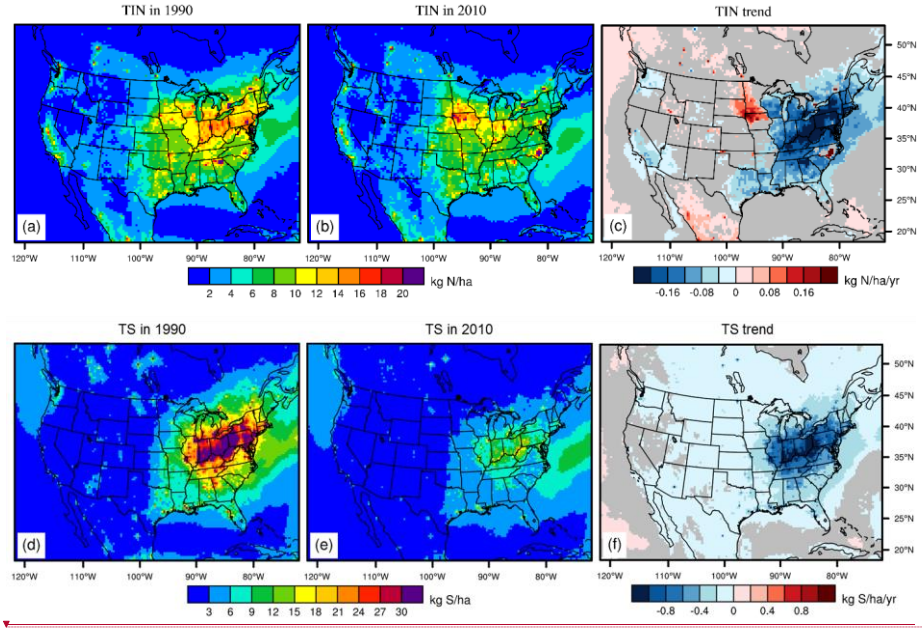
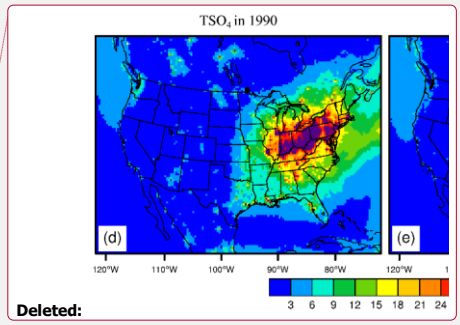


Figure 4. Spatial distribution of annual TDEP of total inorganic nitrogen (TIN, kg N/ha, top panels) and sulfur (kg S/ha, bottom panels) in 1990 (a, d), 2010 (b, e), and the simulated trends of the TIN (c, kg N ha^{-1} yr^{-1}) and total sulfur (f, kg S ha^{-1} yr^{-1}) TDEP changes over the 2 decades. Grey areas on the right plots show p value for the standard two-tailed Student *t*-test greater than 0.05 (i.e., areas where trend estimates were not significant at the 95% confidence level).



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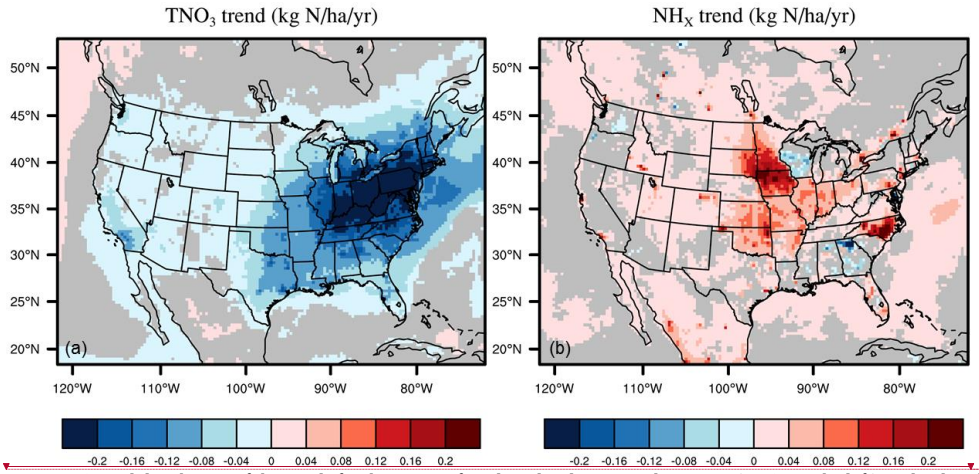
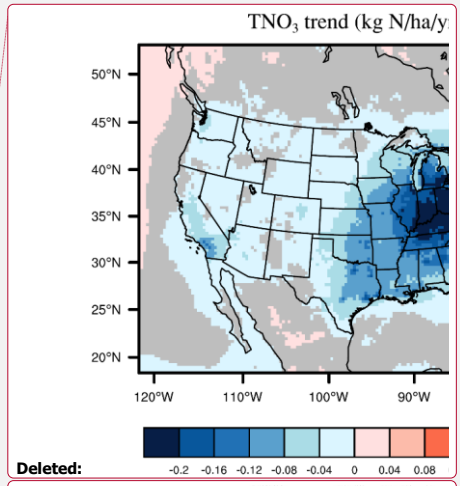


Figure 5. Spatial distribution of the trends for the TDEP of total oxidized nitrogen deposition (TNO_3 on the left), and reduced nitrogen (NH_X on the right) from 1990 to 2010. Grey areas on the both plots show p value great than 0.05 for the standard two-tailed Student *t*-test (i.e. areas where trend estimates were not significant at the 95% confidence level).



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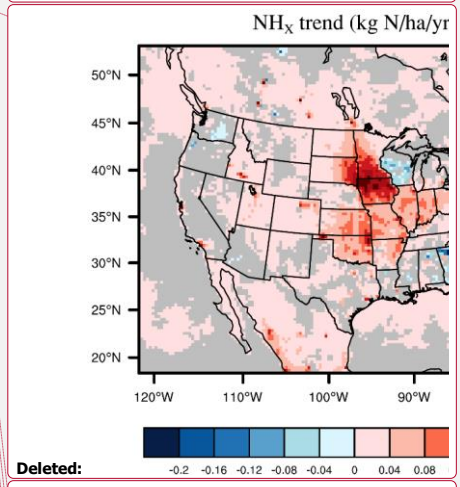

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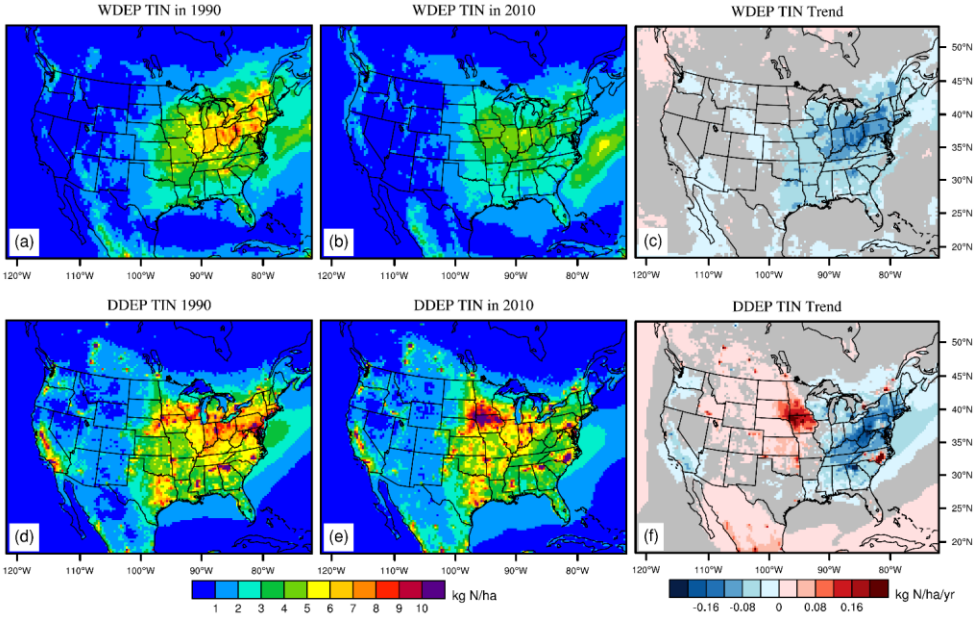

Figure 6. Spatial distribution of WDEP (top panel) and DEP (bottom panel) of TIN (kg N ha^{-1}) in 1990 (a, d), 2010 (b, e), and the simulated trends (c, f, kg N ha^{-1} yr^{-1}) over the 2 decades. Grey areas on the right plot show p value great than 0.05 for the standard two-tailed Student t-test (i.e. areas where trend estimates were not significant at the 95% confidence level).

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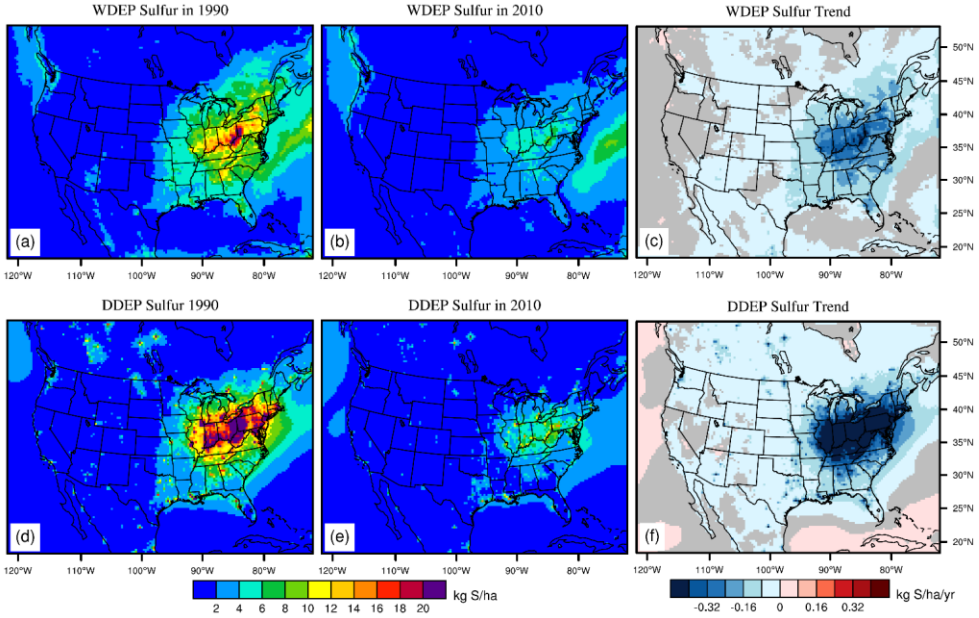

Figure 7. As in Fig. 6 but for sulfur. The units are kg S ha^{-1} for (a, b, d, e) and kg S ha^{-1} yr^{-1} for (c, f).

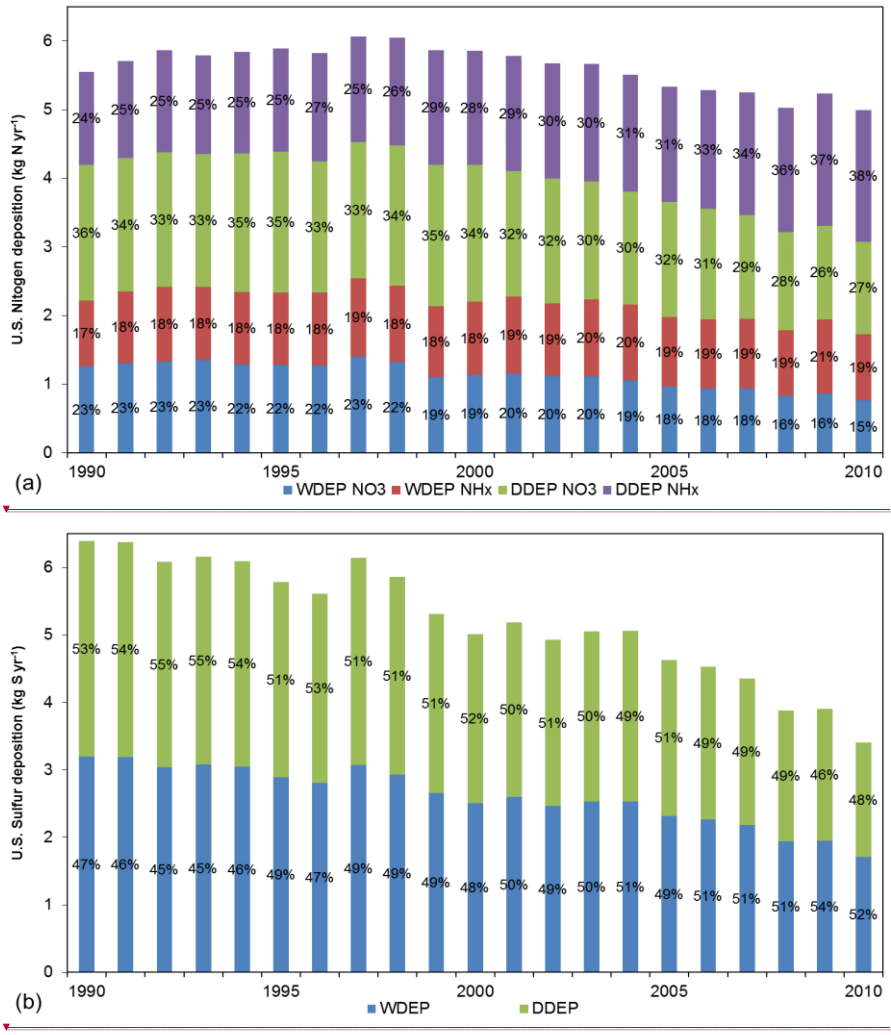

Figure 8. Interannual variability of the TDEP for inorganic nitrogen (a), and sulfur (b) in the U.S. from 1990 to 2010, including their fractions labelled as percent contributions for WDEP of oxidized nitrogen (NO_3), WDEP of reduced nitrogen (NH_X),

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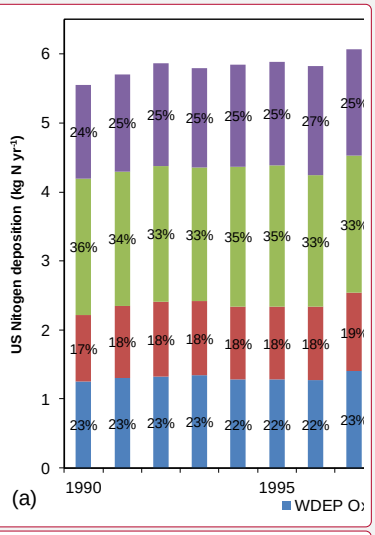

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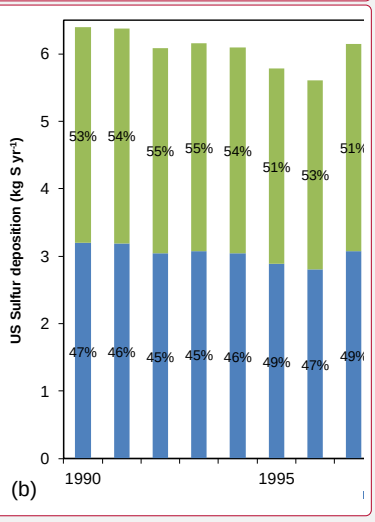

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DDEP of oxidized nitrogen (NO_3) and DDEP of reduced nitrogen (NH_X) deposition for the nitrogen, and WDEP versus DDEP for sulfur.

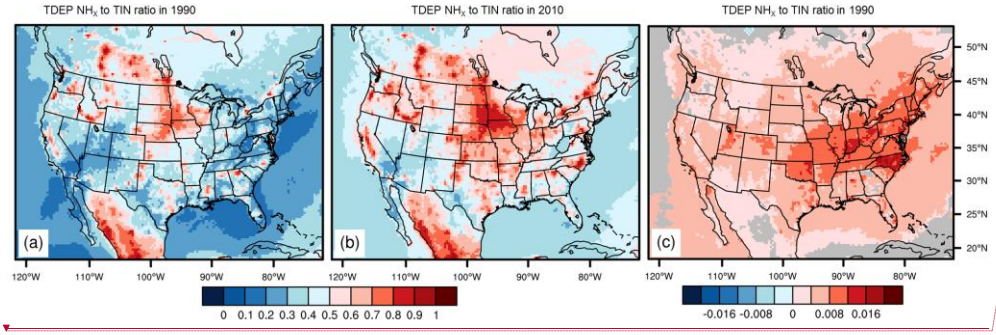

Figure 9. The ratio of TDEP of NH_X over the TDEP of TIN in 1990 (a), 2010 (b), and the trend (c). The blue color in (a,b) indicates a NHx ratio less than 0.5 which means TNO_3 dominates the total nitrogen deposition, while the red color indicates a ratio larger than 0.5 and NH_X dominates the total nitrogen deposition.

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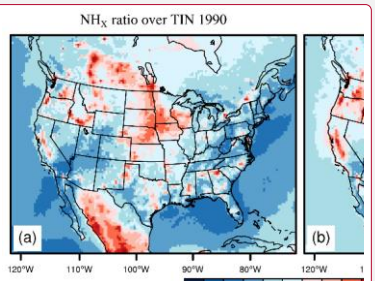

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