Comments from anonymous referee #1

General comments

This manuscript reports on a modelling study, whereby the source sectors and regions of reactive nitrogen (Nr) are determined for the Greater Yellowstone Area in the United States. The model was evaluated thoroughly, and then used for quantifying source contributions to Nr deposition via a tagged model method. Agriculture from the Snake River Valley was determined to be the largest source. They took model error into account by doing a sensitivity study to give approximate uncertainties on the source contributions. This study represents new work as there is a lack of source attribution studies for Nr deposition for this region, however, I feel that they could emphasize further how their study is new, different, and important compared to previous studies.

Response:

Thanks for the recognition of the value of this modeling study and providing the opportunity for us to revise the manuscript accordingly. In order to emphasize the importance and new findings compared with previous modeling studies targeting nitrogen deposition in remote areas of the United States, we follow the suggestions of the reviewer to add a few sentences to emphasize how our study stands out compared with previous similar source apportionments. The detailed changes can be seen in the "track changes" version of the revised manuscript as well as in the responses to the specific comments below.

Specific and technical comments below.

Specific comments

p2, line 21: state where the 40% of NH3 emissions from mobile applies? U.S. urban areas? A national average?

Response:

The sentence: "Mobile sources are also an important source of NH3 and can be the primary emitter in urban areas. A recent study found the increasing importance of on-road emissions of NH3, which at 40% exceed agricultural emissions (Fenn et al., 2018)."

Was modified to:

"Mobile sources are also an important source of NH3 and can be the primary emitter in urban areas (Sun et al., 2014; Sun et al., 2017). Emissions from this sector have large uncertainties and a recent study suggests that on-road NH3 emissions in the 2011 National Emissions Inventory (NEI) were underestimated by a factor of 2.9 (Fenn et al., 2018)."

p4, first paragraph: can you emphasize more what's new from your study? It simply says that it "add to a growing body of Nr modeling source apportionment studies"? For example; is your study more detailed than that of Zhang et al (2012) and Lee et al (2016)?

Does yours use a different technique (e.g., tagged model vs. zero-out scenario and adjoint model)? Is your study at higher resolution or does your model contain more detailed processes than GEOS-Chem? Etc. Emphasize why it was important to do this particular work despite the previous publications. Please also add to Section 6 to emphasize the importance of what's new in this study.

Response:

Based on the reviewer's suggestion, we revised this paragraph to the following:

"In this work, we add to the growing body of Nr modeling source apportionment studies by conducting a detailed analysis using the Particulate Source Apportionment Technology (PSAT) module within the CAMx (Comprehensive Air Quality Model with extensions) (Ramboll Environ, 2014) CTM to quantify the seasonal contributions from different source regions and source sectors to Nr throughout the GYA. Compared with previous Nr deposition simulation studies in United States, this work uses tagged reactive tracers to attribute the contributions from four designated emission sectors and 27 designated emission regions to Nr deposition in the GYA with a much higher horizontal grid resolution (12 km) and an up-to-date emission inventory instead of using a zero-out approach (e.g., Zhang et al., 2012) or an adjoint model (e.g., Lee et al., 2016). The model simulation of Nr and its constituents were first evaluated against routine measured data as well as the unique data measured during the GrandTReNDS campaign period (Benedict et al., 2013a; Prenni et al., 2014). Nr deposition from CAMx simulations was also compared with total deposition maps (TDEP), which were developed for deposition trend analysis and ecological impact assessment (Schwede and Lear, 2014). The detailed source apportionment results are presented here, focusing on seasonal variations and the relative importance to CL exceedance in sensitive ecosystems within the GYA. The discussion of identified model bias and uncertainties to source apportionment results interpretation, including the model lateral boundary conditions, the impact of model precipitation to wet deposition simulation, and the impact of ammonium dry deposition velocity to dry deposition are also presented."

Also, in section 6, the first paragraph, we added a sentence to emphasize the uniqueness or the importance of our modeling work here:

"Nevertheless, this N_r source apportionment work is the first thorough analysis of the origin of inorganic Nr in the GYA using a regional air quality modeling platform. The detailed source sector and source region configurations in PSAT enabled quantitative, though uncertain, estimates of their relative importance. This is needed information by stakeholder and regulator groups to understand the causes of excess Nr deposition in the GYA, monitor changes in Nr deposition and develop possible future mitigation strategies"

p4, line5: The sensitivity tests you did are an important part of this paper. I suggest emphasizing this more here in the introduction that this was done, given the large model biases.

Response:

We changed the sentence from "The final source apportionment results are then interpreted within the context of the identified model bias and uncertainties" to "The discussion of identified model bias and uncertainties to source apportionment results interpretation, including the model lateral boundary conditions, the impact of model precipitation to wet deposition simulation, and the impact of ammonium dry deposition velocity to dry deposition are also presented"

p7, line 8: Comparing Table 1 in this paper to Figures 8, 11, and 12 in Simon et al, (2012), and it seems like CAMx model performance is within the range reported in Simon et al. However, just because it is within the range of what other models do, it doesn't necessarily follow that the model results are "adequate". Also the Simon et al. (2012) paper summarizes results published between 2006-2012, whereas model publications 2013-2017 may have improvements. Can you please add a few more recent references which have similar model biases as yours, and add some further justification to what is meant by "adequate"?

Response:

We do not explicitly use the word "adequate" in the description of the base model performance from CAMx in 2011. As requested, we added additional citations from the model publications from 2013 to 2017 with similar model biases to justify that the modeling platform we were working with has the capability to capture the general spatial and temporal variations of the reactive nitrogen in the atmosphere and that the model performance is in line with the peer modeling results applied for the continental United States using regional photochemical models (e.g., CMAQ and CAMx). Also, we provided Table S3 in the supplementary material to summarize model performance of series simulations with nitrogen-deposition-related species.

We deleted the sentence referring only to the Simon et al. (2012) study and added the new description at the end of this section as follows:

"Table S3 provides a comparison of regional air quality model, N- related species performance, evaluated by observations over the United States from peer-reviewed studies in recent years (e.g., Simon et al., 2012; Bash et al., 2013; Zhang et al., 2013; Yu et al., 2014; Thompson et al., 2015; Li et al., 2017), and it shows that our results are comparable, with some similar model biases such as overestimation of HNO3 and underestimation of NH3. Overall, the CAMx results provide a reasonable platform for evaluation of the contribution of sources to Nr deposition throughout the GYA."

Table S3. Summary of regional air quality model nitrogen related species performance in terms of normalized mean bias (NMB) evaluated by observations over the continental United States

Species	Photochemical model	Duration	Model resolution	Region evaluated	NMB value	Reference
NH3	CAMx	2011 full year	12km	GYA	-65%	this study
	CMAQ,CAMx	Jan, Jul 2002	4km	Southwest US	[-23% -79%]	Zhang et al. (2013)
	CAMx	2009 full year	36km/12km	Colorado	-55%	Thompson et al. (2015)
	CAMx	Summer 2011	4km	Colorado	[-83% 46%]	Li et al. (2017)
HNO3	CAMx	2011 full year	12km	GYA	108%	this study
	CAMx	2009 full year	36km/12km	Colorado	23%	Thompson et al. (2015)
	CMAQ,CAMx	Jan, Jul 2002	4km	Southwest US	[-17% 45%]	Zhang et al. (2013)
PM25 nitrate	CAMx	2011 full year	12km	GYA	[37% 58%]	this study
	CAMx,CMAQ, WRF-Chem (n=34)	varies, case study to full year simulation	9-45km	varies, states to CONUS	[-49% 11%]	Simon et al. (2012)
	CMAQ,CAMx	Jan, Jul 2002	4km	Southwest US	[-92% -103%]	Zhang et al. (2013)
	CAMx	2009 full year	36km/12km	Colorado	57%	Thompson et al. (2015)
	CMAQ	2002 full year	12km	CONUS	[-24% 45%]	Bash et al. (2013)
	CMAQ	1990-2010	108km	CONUS	[-41% 106%]	Xing et al. (2015)
	WRF-CMAQ	Aug, Sep 2006	12/4km	CONUS/Texas	[-82% 83%]	Yu et al. (2014)
PM25 ammonia	CAMx	2011 full year	12km	GYA	3%	this study
	CMAQ,CAMx	Jan, Jul 2002	4km	Southwest US	[-57% 61%]	Zhang et al. (2013)
	CAMx,CMAQ, WRF-Chem (n=31)	varies, case study to full year simulation	9-45km	varies, states to CONUS	[-17% 7%]	Simon et al. (2012)
	CAMx	2009 full year	36km/12km	Colorado	-31%	Thompson et al. (2015)
	CMAQ	1990-2010	108km	CONUS	[-54% 23%]	Xing et al. (2015)
	WRF-CMAQ	Aug, Sep 2006	12/4km	CONUS/Texas	[-75% 48]	Yu et al. (2014)
NOx wet deposition	CAMx	2011 full year	12km	GYA	31%	this study
	CAMx,CMAQ, WRF-Chem (n=16)	varies, case study to full year simulation	9-45km	varies, states to CONUS	[-45% 19%]	Simon et al. (2012)
	CMAQ,CAMx	Jan, Jul 2002	4km	Southwest US	[-94% 52%]	Zhang et al. (2013)
NH4 wet deposition	CAMx	2011 full year	12km	GYA	49%	this study
	CAMx,CMAQ, WRF-Chem (n=16)	varies, case study to full year simulation	36km/12km	varies, states to CONUS	[-33% 28%]	Simon et al. (2012)
	CMAQ,CAMx	Jan, Jul 2002	4km	Southwest US	[-51% 19%]	Zhang et al. (2013)
	CMAQ	2002 full year	12km	CONUS	[-16% 18%]	Bash et al. (2013)

We also add the following citations to the reference list:

Bash, J.O., Cooter, E.J., Dennis, R.L., Walker, J.T., and Pleim, J.E. (2013), Evaluation of a regional air-quality model with bidirectional NH3 exchange coupled to an agroecosystem model, Biogeoscience, 10, 1635-1645, doi:10.5194/bg-10-1635-2013.

Li, Y., Thompson, T.M., Damme, M.V., Chen, X., Benedict, K.B., Shao, Y., Day, D., Boris, A., Sullivan, A.P., Ham, J. and Whitburn, S.: Temporal and spatial variability of ammonia in urban and agricultural regions of northern Colorado, United States, Atmos. Chem. Phys., 17(10), 6197-6213, 2017.

Thompson, T.M., Rodriguez, M.A., Barna, M.G., Gebhart, K.A., Hand, J.L., Day, D.E., Malm, W.C., Benedict, K.B., Collett, J.L. and Schichtel, B.A.: Rocky Mountain National Park reduced nitrogen source apportionment, J. Geophys. Res., 120(9), 4370-4384, 2015.

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, 2015.

Yu, S., Mathur, R., Pleim, J., Wong, D., Gilliam, R., Alapaty, K., Zhao, C. and Liu, X., Aerosol indirect effect on the grid-scale clouds in the two-way coupled WRF-CMAQ: model description, development, evaluation and regional analysis, 14, 11247-11285, Atmos. Chem. Phys., 2014.

Zhang, Y., Olsen, K.M. and Wang, K., Fine scale modeling of agricultural air quality over the southeastern United States using two air quality models. Part I. Application and evaluation. Aerosol Air Qual. Res., 13(4), 1231-1252, 2013.

p10, line 12: it is mentioned above this that NH3 from agriculture is emitted into the first model layer and therefore doesn't get transported as far. Can you please also discuss the fire emissions – specifically how high they get put into the model? It is described a bit on p4, lines 19-20, but can you mention here approximately how high the fires spread in the vertical, and thus how it would affect deposition at some distance downwind?

Response:

We used the fire emissions developed from the Particulate Matter Deterministic and Empirical Tagging and Assessment of Impacts on Levels (PMDETAIL) study (Moore et al., 2012). The emissions for fire activities include prescribed fires and wildfires. In the PMDETAIL fire plume rise methodology (Mavko and Morris, 2013), three parameters were defined to provide the release heights of fire smoke emissions as hourly inputs to CAMx, namely (1) height above ground of plume top (P_{top}), (2) height above ground of plume bottom (P_{bot}), and (3) the fraction of emissions emitted near the ground (f_{Lay1}). When allocating the fire emissions to different vertical layers according to the CAMx vertical layer setting, the PMDETAIL methodology included the WRF estimated hourly planetary boundary layer (PBL) in the grid cell containing the fire emissions and injected the fire emissions near the surface between the CAMx model layer 1 and the maximum of P_{bot} and PBL values:

Fire emission (f_{Lay1}) = ground to max.(P_{bot}, PBL)

For the elevated fire emissions, the PMDETAIL methodology released the emissions in layers between P_{bot} and the maximum of P_{top} and PBL value for the hour and grid cell of the fire:

Fire emission (1-f_{Lay1}) = P_{bot} to max.(P_{top}, PBL)

We did not have the detailed information for those three parameters for each fire accounted for in the PMDETAIL and used in the 2011 CAMx modeling. However, looking at the attached figure below, we can deduce that those three fire plumes in summer within the GYA were injected into the vertical layer between P_{bot} and the model PBL height so that it may be mostly mixed within the PBL and has the dominant impact to adjunct grids where the fire emission occurs. It has little chance to disperse higher and impact N deposition at a longer distance downwind.

We changed page 4, lines 19–20, from “PMDETAIL developed 2011 fire emissions using satellite data, ground detects, and burn scar and estimated the plume rise depending on fire size and type (Mavko and Morris, 2013).” to “PMDETAIL developed 2011 fire emissions using satellite data, ground detects, and burn scar and estimated the plume rise, depending on fire size and type. The hourly, nonsurface fire emissions were allocated to the proper CAMx vertical layers based on the model-predicted planetary boundary layer (PBL) height and the spanning of the plume top and bottom above the ground (Mavko and Morris, 2013).”

We added Figure S4 to the supplementary file to show that the fires occurring during summer 2011 near the GYA predominantly impacted the adjacent grids. Now the sentences on page 12, line 12 that describe the fire emission impact to seasonal N deposition in the GYA read as “The footprint of fire emission impacts depends on the simulated injection height of the fire plumes. The emissions from fires that occurred within the GYA during the summer and fall likely remained within the mixed layer and had less chance to be transported far downwind to impact more distance areas (Figure S4).”

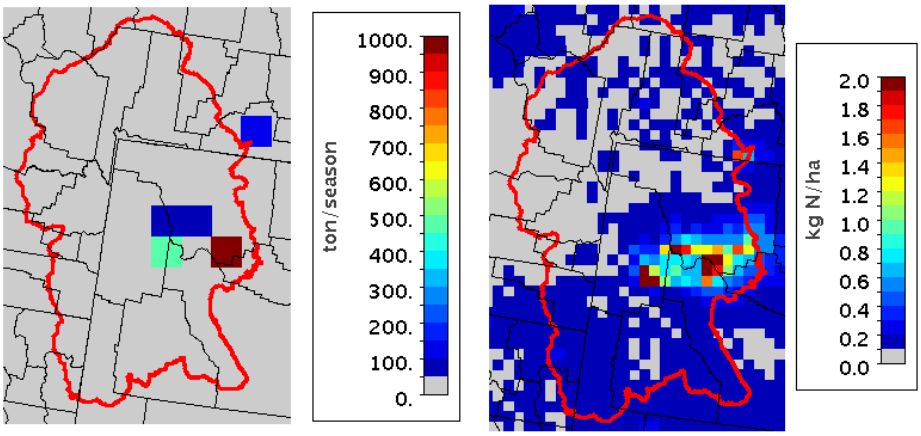


Figure S4. (left) Spatial pattern of total NOx emission from Fire emission sectors during summer (June, July, August) 2011 near the Greater Yellowstone Area (GYA). (right) the Spatial pattern of total N deposition attributed to Fire emission during summer 2011.

References:

Mavko, M. and Morris, R., DEASCO3 project updates to the fire plume rise methodology to model smoke dispersions. Air Science Inc. Portland, Oregon and ENVIRON International Corporation, Novato, California. December 3, 2013. http://wraptools.org/pdf/DEASCO3_Plume_Rise_Memo_20131210.pdf

Moore, C.T., Randall, D., Mavko, M., Morris, R., Koo, B., Fitch, M., George, M., Barna, M., Vimont, J., Anderson, B. and Acheson A., Deterministic and empirical assessment of smoke's contribution to ozone (DEASCO3), final report, 2012, Joint Fire Science, Program Project #11-1-6-6, https://www.firescience.gov/projects/11-1-6-6/project/11-1-6-6_final_report.pdf.

Technical corrections

p2, line 18: particulate nitrate (NO3), and other...

Response:

To be consistent with the notation in other places in the manuscript, such as page 5, line 14, and Table 1, we changed the sentence from "Atmospheric reactions of NOx result in nitric acid (HNO3), particulate nitrate, and other compounds." to "Atmospheric reactions of NOx result in nitric acid (HNO3), particulate nitrate (PNO3), and other compounds."

p6, line 22: may be related with the high: : :

Response:

Changed from "The poor NH3 results may related with the high …" to "The poor NH3 results may be related to the high …".

p10, line 19: There is no "Table S4" in the supplement document. The table on the last page of the supplement has no label, and doesn't seem to be what you're talking about here. I think you may mean Table S3.

Response:

We corrected the sentence to "Most (74%) of the Nr from this region was from the AG source sector and was composed of reduced N (Table S3)." The last table in the supplemental material belongs with the supplementary File S1 in the section "regional evaluation of CAMx nitrogen deposition in 2011" and is therefore not assigned a label.

p24, line 4: (caption to Fig 1) National Trend Network: typo in National

Response:

Corrected the typo from "Natiaonl" to "National".

p5, line 4: I expected to see the 24 tagged regions in Fig 1 given the text here, but actually that map is Fig S2. Text should be clarified. And I feel that knowing where those tagged regions are is important enough to be included in the main paper, rather than the supplemental material.

Response:

We followed the suggestion to move the Figure S2, including the 27 tagged regions, from supplemental material into the main content. The caption in old Figure 1 (now Figure 2) has been changed to clarify that the source region partition for the CAMx PSAT

simulation shown here is only for the 12-km inner modeling domain. The number of the figures in main document and supplemental material has changed accordingly.

p.14, line 9-10: It wasn't measured HNO3 concentrations were overestimated by 108%. Modelled HNO3 was overestimated.

Response:

Changed the sentence from "However, the model simulation underestimated available measured NH3 concentrations by 65% on average, and measured HNO3 concentrations were overestimated by 108%." to "However, the model simulation underestimated the measured NH3 concentrations by 65% on average and overestimated the measured HNO3 by 108%."

Fig 9: the Oil and Gas pattern is difficult to see in the legend – looks very similar to the Other pattern in the legend, and doesn't seem to be as dark as in the pies. In the pies, the Oil and Gas is (I think) the gray, but the legend looks much lighter. This doesn't seem to be a problem in Figs. 6 and 10 which has the same system.

Response:

We double-checked Figure 10 (previously Figure 9) and made sure the legend, color map setting, as well as notation are consistent with Figure 7 (previously Figure 6) and Figure 11 (previously Figure 10). The updated Figure 9 is attached here for reference.

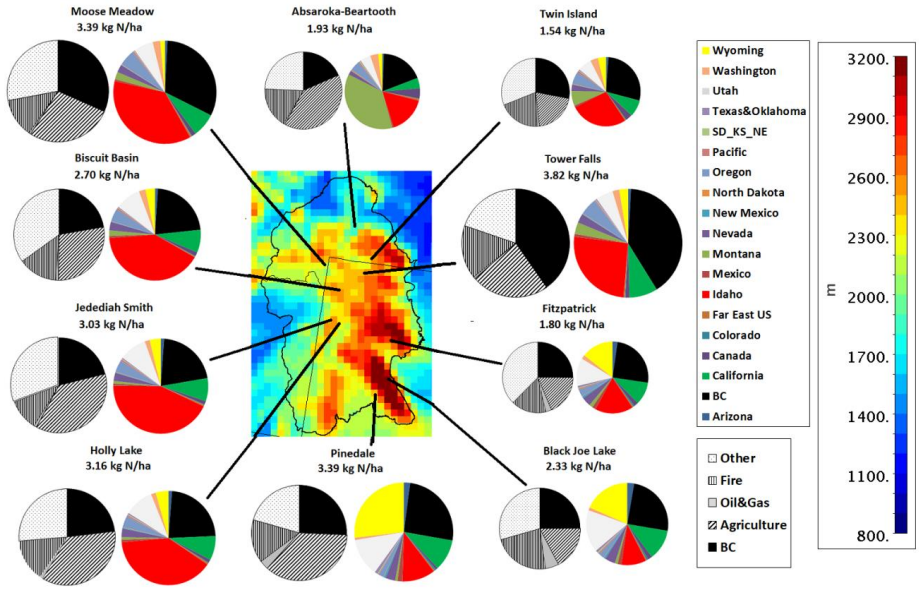
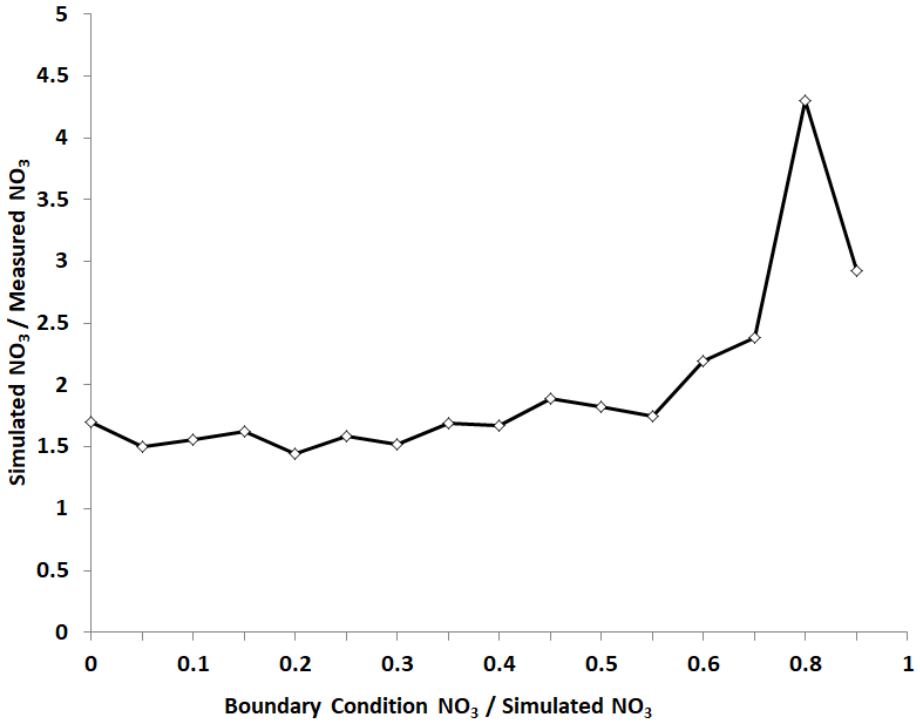


Fig 11: I think the legend at the bottom should be removed because seeing MOZART/IMRPOVE next to the red square with the line through it is confusing and doesn't really make sense. It's not needed since in the text we know that the BC came from MOZART, and from the caption we know that the simulation was sampled at IMPROVE sites.

Response:

We accepted this suggestion to revise the caption for Figure 12 (previously Figure 11) as: "Figure 12. Ratio of simulated versus measured particulate nitrate (PNO3) concentrations against the boundary contributions to simulated PNO3 at IMPROVE sites over a 12-km domain."

The revised figure attached below.



Comments from anonymous referee #2

General comments

The manuscript by Zhang et al. considers the sources of reactive nitrogen deposition in the Greater Yellowstone Area (GYA). The topic is timely and of relevance to this journal. The paper is in general clearly organized, well written, and is easy to read; the figures and tables are descriptive and appropriate. In terms of findings, the authors do a thorough job of first evaluating their modeling results compared to available measurements and other modeling studies in the literature. An issue is that they find very significant overestimation of HNO3 and underestimating of NH3. They then present source attribution results. Overall, findings of sources being from oxidized vs reduced nitrogen, different sectors, and different source reasons are interesting and seem sensible. They also consider a sensitivity study to try to address some of the modeling shortcomings.

My major criticism in this regard though is that such analysis or consideration of model biases is not reflected in the reporting of results elsewhere in the manuscript nor the abstract given the rather significant model biases it seems results should be presented much more cautiously throughout. It would be useful if the authors could estimate some uncertainty ranges to their source attribution results at for example do they think they are accurate to within 1%? 10% an order of magnitude? Detailed comments along this line as well as a few other minor points are described in detail below. Addressing these would amount to minor revisions.

Response:

We appreciate the favorable overall sentiment and the opportunity to revise our manuscript in response to those comments. We have addressed each comment and suggestion as described below. Note that we do not know the uncertainties in the source attribution (SA) results, but suspect that they are large based on the model performance evaluation. This is why the results are discussed in more general and semi-quantitative terms in section 5. However, in response to the comment we have made a greater effort to convey the uncertainties and potential biases where appropriate. For example, in the abstract we included the sentences: "These uncertainties appear to result in an overestimation of distant source regions including California and BC and an underestimation of closer agricultural source regions including the Snake River valley. Due to these large uncertainties the relative contributions from the modelled sources and their general patterns are the most reliable results."

Also, the discussions on the change of deposition velocity of NH3 in CAMx to SA results showed that less than 10% change of the contributions for each source sectors/regions for the conducted 2 month sensitivity simulations (Figure 11). Also, the SA results due to different boundary conditions usage didn't change much (less than 10%, see Figure S8). The detailed comment below further address this issue.

Specific comments:

Abstract: The model biases for NH3 and HNO3 are significant. Suggest adding some material to the abstract to address how modeled SA results should be interpreted, given these biases. Suggest referring to SA results as they pertain to the model (i.e., "largest source contributions in the model. . .), unless this disconnect between measured and modeled values is resolved.

Response:

We agree with the reviewer and added the following sentences to the abstract:
"These uncertainties appear to result in an overestimation of distant source regions including California and BC and an underestimation of closer agricultural source regions including the Snake River valley. Due to these large uncertainties the relative contributions from the modelled sources and their general patterns are the most reliable results."

Abstract: importance of boundary conditions is not clear without having stated where these boundaries are. Nor is it clear that influence across the boundary would be international in origin (as opposed to natural oceanic emissions, recirculated domestic Nr, etc).

Response:

The following sentence was added to the abstract: "The BC were outside the conterminous United States and thought to represent international anthropogenic and natural contributions."

1.26: I thought it was already established that Nr deposition is already in excess (see first sentence of the abstract), thus it is odd here to say that the "results suggest that Nr deposition …was above critical loads".

Response:

We deleted this sentence as suggested.

2.17: Worth indicating that these numbers are approximate and perhaps specific to a particular time period given trends in emissions from these sectors.

Response:

Based on the suggestion, this sentence now read as:
"These compounds arise from a variety of sources, with inorganic oxidized N primarily emitted as nitrogen oxides (NOx) from fossil fuel combustion, with approximately 25% from power plants, 50% from automobiles, and 10% from other mobile sources on annual based county level estimation (EPA, 2015)."

2.20: Missing some references here, e.g. work from Zondlo's group.

Response:

We added two highly cited references from Zondlo's group regarding the on-road NH3 emissions (Sun et al., 2014; Sun et al., 2017). The sentence now read as "Mobile sources are also an important source of NH3 and can be the primary emitter in urban areas (Sun et al., 2014; Sun et al., 2017)."

References:

Sun, K., Tao, L., Miller, D.J., Khan, M.A. and Zondlo, M.A.: On-road ammonia emissions characterized by mobile, open-path measurements. Environ. Sci. Tech., 48(7), 3943-3950, 2014.

Sun, K., Tao, L., Miller, D.J., Pan, D., Golston, L.M., Zondlo, M.A., Griffin, R.J., Wallace, H.W., Leong, Y.J., Yang, M.M. and Zhang, Y. Vehicle emissions as an important urban ammonia source in the United States and China. Environ. Sci. Tech., 51(4), 2472-2481, 2017.

3.14: for zero-out –> using zero-out

Response:

Changed.

3.17: "found the importance of emissions from California" is a bit vague. Were these found to be more important than local sources? Or more important than otherwise expected?

Response:

Lee et al. (2016) used the adjoint of GOES-Chem to investigate the spatial and sectoral distribution of annual Nr deposition contributed by different sources. As expected, NH3 emissions from livestock and NOx emissions from mobile sources are the major contributors to Nr deposition in nearly all selected Class I areas in the United States. Nr deposition in the mountain regions in the western U.S (Grand Teton and Rocky Mountain NPs) are ~50% from nearby sources (<400 km) and the rest from sources as far away as California (~1300 km). To avoid the ambiguity, we rewrote this sentence as:

"Lee et al. (2016) used the adjoint version of GEOS-Chem to quantify the sources of Nr deposition in eight selected federal Class I areas in 2010 and found a nonnegligible footprint (>20%) of Nr deposition in western United States, including GTNP and Rocky Mountain National Park (RMNP), attributed to long-range transport from sources in California, especially during summer time."

Reference:

Lee, H. M., Paulot, F., Henze, D. K., Travis, K., Jacob, D. J., Pardo, L. H., and Schichtel, B. A.: Sources of nitrogen deposition in Federal Class I areas in the US, Atmos. Chem. Phys., 16(2), 2016.

3.19: This paragraph feels rather tangential and could be removed from the introduction or significantly shortened so only the content as it relates to understanding Nr dep in GYA.

Response:

We significantly shortened this paragraph into one sentence and combined it with the previous paragraph to show the similarity of source apportionment modeling studies' focus on Rocky Mountain to the GYA area. Now the new sentence read as:

"Similar modeling studies focusing on RMNP also suggested the important contributions of distant sources including those from California and other counties and the fact that the contributions from source of reduced Nr were larger than those from sources of oxidized Nr (Thompson et al., 2015; Malm et al., 2016)."

4.13 - 20: several studies in the past year have identified an overestimation of mobile NOx emissions in the NEI2011 inventory. How were these addressed in the present work?

Response:

The mobile emissions we used in this modeling study were from the NEI 2011 inventory, which used MOVES2010 to generate emission inventories or emission rate lookup tables for on-road mobile sources (UNC-Chapel Hill and ENVIRON, 2014). We notice there are reports commenting that the NEI may overestimate the mobile NOx emission. For example, Anderson et al. (2014) estimated the NEI may overestimate mobile NOx emissions by 51–70%, based on the observed molar CO/NOx emission ratios from the DISCOVER-AQ campaign data. They argue that "the NEI overestimate of NOx emissions could indicate that engines produce less NOx and catalytic converters degrade more slowly than assumed by MOVES2010. MOVES2010 likely fails to capture dependence of NOx emissions on vehicle age accurately." We didn't explicitly explore the uncertainty of mobile NOx emission to the source apportionment results.

References:

UNC-Chapel Hill and ENVIRON International Corporation, Three-State Air Quality Modeling Study (3SAQS) – Final modeling protocol: 2011 emissions & air quality modeling platform, http://vibe.cira.colostate.edu/wiki/Attachments/Modeling/3SAQS_2011_WRF_MPE_v8_draft_Aug04_2014.pdf

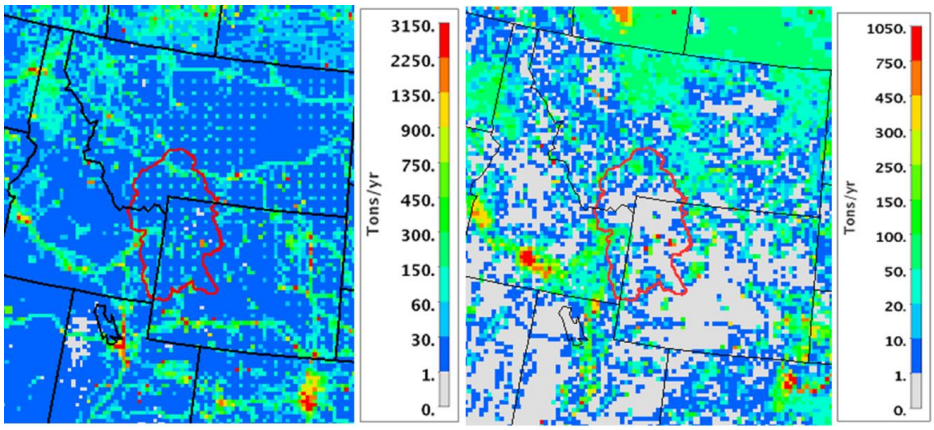
Anderson, D.C., Loughner, C.P., Diskin, G., Weinheimer, A., Canty, T.P., Salawitch, R.J., Worden, H.M., Fried, A., Mikoviny, T., Wisthaler, A. and Dickerson, R.R.,

Measured and modeled CO and NOy in DISCOVER-AQ: An evaluation of emissions and chemistry over the eastern US. Atmos. Environ., 96, 78-87, 2014.

4.13 - 20: Does the inventory here contain the amount of NH3 from mobile sources mentioned in the introduction, or is if felt that this inventory under-represents this source?

Response:

As mentioned in the previous response, the on-road mobile source is provided by MOVE2010, and it does account for the NH3 emissions from the mobile sources; see the attached picture below. However, these emissions are likely underestimated since recent work by Fenn et al., (2018), which was discussed in the manuscript, estimates that the 2011 NEI underestimates mobile NH3 emissions by a factor of 2.9.



Reference:

Fenn, M.E., Bytnerowicz, A., Schilling, S.L., Vallano, D.M., Zavaleta, E.S., Weiss, S.B., Morozumi, C., Geiser, L.H. and Hanks, K.: On-road emissions of ammonia: An underappreciated source of atmospheric nitrogen deposition, Sci. Total Environ., 625, 909-919, 2018.

4.13 - 20: It would be very useful for answering these questions and others if the emissions totals by sector and species for the different tagged regions could be included in the supporting information and summarized in the text (as opposed to the summaries mentioned in the introduction, which reflect values in the literature but do not specifically refer to the values used in the modeling for this work).

Response:

For this work, we used the 2011 NEI version 2 inventory from the EPA and updated the oil and gas sector at western U.S. based on the local survey data. As requested, we

provided the designated table (Table S2) in the supplemental material to provide the summary of 27 tagged regions in CAMx PSAT in this study and annual emissions for NH3 and NOx. The table is attached for reference.

Table S2. Summary of 27 tagged regions in CAMx PSAT in this study and their corresponding annual emissions for NH3 and NOx with agriculture (AG), oil and gas OG), wildfires and prescribed fires (fire), and remaining emission source sectors (Other). The items in the parentheses are aggregate regions based on prevailing wind patterns over the GYA for the source apportionment results reported in Figures 9–11.

Tagged region	Total emission for nitrogen species (tons/yr)									
	NH3					NOx				
	AG	OG	Fire	Other	total	AG	OG	Fire	Other	total
NW Colorado (Southwest)	4,900	0	55	418	5,373	0	12,046	564	54,827	67,437
NE Colorado (Southwest)	37,041	0	415	3,157	40,613	0	16,002	749	72,830	89,581
SE Colorado (Southwest)	20,281	0	227	1,728	22,237	0	20,869	976	94,980	116,825
SW Colorado (Southwest)	6,672	0	75	569	7,315	0	5,504	258	25,051	30,812
Upper Green River, Wyoming	2,358	0	525	110	2,993	0	11,412	3,016	43,523	57,952
Jackson, Wyoming	2,375	0	529	111	3,015	0	477	126	1,817	2,420
Eastern Wyoming (Other WY)	7,298	0	1,625	342	9,265	0	3,013	796	11,490	15,299
Western Wyoming (Other WY)	18,046	0	4,018	845	22,910	0	10,925	2,887	41,662	55,474
Yellowstone (Other WY)	1,511	0	336	71	1,918	0	761	201	2,902	3,864
Northern Idaho (Northwest)	16,887	0	2,193	910	19,991	0	669	6,906	47,036	54,612
Snake River Valley, Idaho	43,696	0	5,674	2,356	51,726	0	682	7,030	47,882	55,594
Northern Utah	12,946	0	69	2,163	15,178	0	10,235	200	92,312	102,747
Southern Utah (Southwest)	10,083	0	54	1,685	11,822	0	8,907	174	80,338	89,419
Nevada	5,569	0	825	2,533	8,926	0	189	2,725	107,900	110,814
Montana	54,343	0	7,531	1,313	63,187	0	13,806	11,510	153,220	178,537
Washington (Northwest)	44,118	3	825	7,400	52,345	0	467	2,458	268,831	271,757
Oregon (Northwest)	43,626	0	8,858	5,164	57,649	0	925	28,231	146,062	175,218
California	203,204	155	3,056	111,240	317,655	0	8,806	9,457	669,421	687,684
Mexico (Non U.S.)					246,344					782,600
New Mexico (Southwest)	35,327	0	4,374	2,673	42,374	0	71,863	15,197	170,550	257,609
Arizona (Southwest)	33,247	0	9,041	8,520	50,808	0	1,489	26,817	250,201	278,506
Texas&Oklahoma (Southwest)	364,835	44	24,481	39,179	428,539	0	410,736	35,635	1,450,095	1,896,465
Canada (Non U.S.)					421,830					934,900
North Dakota (Eastern U.S. + Great Plains)	93,163	0	952	6,995	101,110	0	8,408	1,407	171,869	181,683
Pacific (Non U.S.)					292					251,698
Far East U.S. (Eastern U.S. + Great Plains)					2,627,200					9,296,000
SD_KS_NE (Eastern U.S. + Great Plains)	480,670	4	6,245	9,439	496,359	0	96,945	25,572	666,950	789,467
Total:					5,128,972					16,834,975

Also, we added a summary in the text about the emissions we used in this modeling study: "Table S2 provides the annual NH3 and NOx emissions used in this modeling study with a breakdown by tagged source regions and source sectors. Figure 2 provides the annual emissions of NH3 in the inner 12-km domain as well as the monitoring sites or receptor areas used for the model evaluation and analysis. For NH3 emissions, the AG sector contributed 84.1% of the total emissions within 12-km domain, while the OG, Fire, and Other sectors contributed 0.1%, 4.5%, and 11.4%, respectively (Table S2). In the Snake River valley, the AG sector emissions dominate the emission budget. For NOx emissions, the contribution rankings from the four tagged emission sources are Other (83.8%), OG (12.8%), Fire (3.2%), and AG (0%)."

5.14: As anthropogenic SO2 emissions have declined in the US, the role of NOx and NH3 in forming ammonium nitrate aerosol has increased. How would PSAT account for the influence of the EGU sector via SO2 on deposition of PNH4 and PNO3, or is this not accounted for?

Response:

We are not completely clear as to exactly what the reviewer is asking in this question. However, CAMx contains relatively complete chemical and thermodynamic mechanisms for inorganic sulfur and nitrogen gases and particles. Therefore, the interplay between SO_2 - NO_x - NH_3 is accounted for in the model. For example, with the decreases in SO_2 emissions there should be more NH_3 available to neutralize HNO_3 forming particulate ammonium nitrate. The CAMx chemical and thermodynamic mechanism can account for these and other shifts and their impact on nitrogen deposition and be reflected in the PSAT source attribution results.

6.9: Could the authors clarify what constituted questionable data, such that their results could be more reproducible?

Response:

Questionable data refers to the measurements used to evaluate the model. There are certain protocols used by the measurement community to report their data and the associated credentials. For instance, for the wet deposition data reported by the NTN, a series of codes are assigned to samples that are considered invalid by the NTN for the purposes of computing weighted-mean concentrations, depositions, and data completeness estimates. The common reasons are contaminated samples, inadequate volume collected in the bucket for analysis, and lab error, for example. To make this statement clear, we changed the sentence from "All data flagged as questionable were removed from the analysis" to "All measurement data flagged as questionable, either due to maloperation or due to insufficient samples to calculate representative values, were excluded from the analysis. In Table 1, we also reported the percentage of validate measurements used for statistical analysis during evaluation time. For most of the nitrogen species, the percentage of validate samples are more than 80%."

We also added the percentages of measurement data completeness in the model performance evaluation table (Table 1) for reference.

6.22: Does the mechanism for formation of N2O5 in CAMx match that in GEOS-Chem? If not, it's not clear how the reference to Heald et al. (2012) is relevant here.

Response:

Thanks for pointing this out. The reference here is not proper. In GEOS-Chem, the inorganic chemistry mechanism used to model the pollutants' evolution from surface to

the stratopause is called the "tropchem" mechanism and is based on the NASA/JPL publication 10-6 for chemical kinetics and photochemical data for use in atmospheric studies. In total, 236 reactions were included in this mechanism, and reaction #225 has the parameterization of heterogeneous N2O5 reaction to form HNO3 based on the ambient aerosol type, relative humidity, and temperature (Evans and Jacob, 2005). In CAMx, we used the CB6r2 mechanism, and it also includes consideration of this heterogeneous HNO3 formation with the initial parameterization protocol as in Evans and Jacob (2005) but with revisions (Foley et al., 2010). However, since GEOS-Chem is a global photochemical model and the "tropchem" is different from a carbon bond mechanism, it is unfair to quote the evaluation statements regarding GEOS-Chem to the CAMx simulation results here. Therefore, we deleted this statement. Instead, we added two additional citations for reporting the same HNO3 overestimation problem using regional air quality models (e.g., CMAQ, CAMx). Now this sentence read as:

"The overestimation of HNO3 has also been reported in other regional-scale modeling simulations over the United States (e.g., Barker and Scheff. 2007, Foley et al., 2010; Thompson et al., 2015) with the carbon bond mechanism used in this study. The possible reason for the overestimation of HNO3 may be due to the uncertainty for the N2O5 uptake coefficient setting for heterogeneous reactions (Foley et al., 2010)."

References:

Baker, K. and Scheff, P.: Photochemical model performance for PM2. 5 sulfate, nitrate, ammonium, and precursor species SO2, HNO3, and NH3 at background monitor locations in the central and eastern United States, Atmos. Environ., 41, 6185-6195, 2007.

Foley, K.M., Roselle, S.J., Appel, K.W., Bhave, P.V., Pleim, J.E., Otte, T.L., Mathur, R., Sarwar, G., Young, J.O., Gilliam, R.C. and Nolte, C.G., Incremental testing of the Community Multiscale Air Quality (CMAQ) modeling system version 4.7. Geosci. Model Dev., 3(1), 205-226, 2010.

Evans, M.J. and Jacob, D.J., 2005. Impact of new laboratory studies of N2O5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH. Geophysical Research Letters, 32(9).

7.2: Is a unidirectional NH3 emission model expected to lead to larger NH3 concentrations in this region of the US than a bidirectional flux model?

Response:

Currently, there is no bidirectional flux model for NH3 implemented in CAMx. The bidirectional flux model calculates the compensation point of NH3 between canopy and land-surface terrain and allows a portion of deposited NH3 to be emitted back into the atmosphere based on the emission potential of the soil NH3 pool. Conceptually, given the occurrence of re-emittance of certain amounts of NH3 into the atmosphere, the NH3

ground concentrations at the surrounding modeling grids (especially downwind grids) should be increased. The GYA area is adjacent and downwind of the Snake River valley and northern Utah, both of which have significant portions of agricultural sources (see Table S2). Therefore, it is a logical expectation that if the bidirectional NH3 model was implemented in CAMx, the bias in the simulated NH3 concentrations in this region would be decreased. Furthermore, in section 5, we discussed the potential benefit of including NH3 bidirectional parameterization into the CAMx model and the difficulties for implementation. To specifically address the reviewer's comment, we added the following statement:

"The poor NH3 results may be related to the high uncertainty in the NH3 emission inventory (Clarisse et al., 2009) and important missing physical mechanisms in the model, including the lack of bidirectional NH3 deposition (Zhang et al., 2010; Bash et al., 2013; Zhu et al., 2015). The GYA area is located downwind of the major agriculture sources in the Snake River valley and northern Utah (Table S2). The incorporation of the bidirectional NH3 flux mechanism in the model should increase ambient NH3 concentrations in the GYA and thus decrease the large model underestimation of NH3 concentrations."

7.2: I would suspect that another possible factor leading to poor correlation and underestimation for NH3 is the overestimation of HNO3, which would promote excessive partitioning of NH3 to the particle phase. Did the authors consider evaluating NHx, or HNO3+PNO3, to get around the issues of partitioning (and thus hone in on issues related to sources and sinks)?

Response:

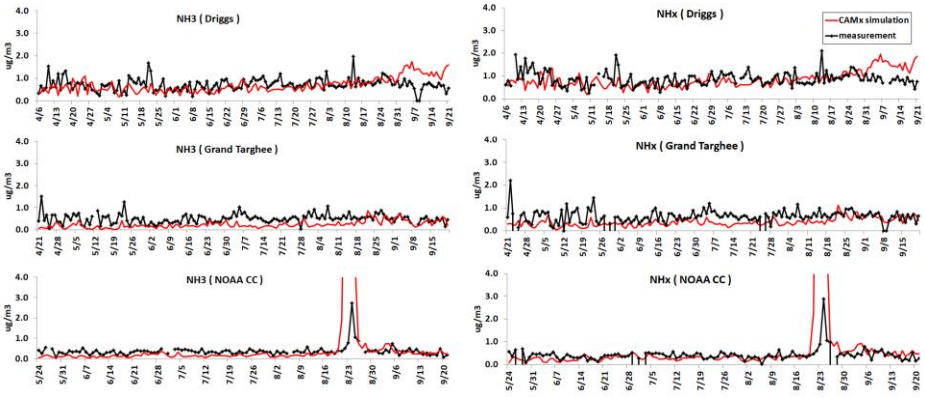
It is possible that the poor model performance for NH3 may relate to the overestimation of HNO3 in the model, which would push excessive partitioning of NH3 into the particle phase. CAMx uses ISORROPIA to calculate the inorganic gas–particle thermodynamic equilibrium. From the old Table 1, we also see a slight overestimation of PNH4 in conjunction with the large underestimation of NH3 at CASTNET sites within the GYA. Therefore, we followed the suggestion of the reviewer to evaluate NHx to try to get around the possible bias in gas-particle partitioning. However, only a few locations existed within the GYA where a network has concurrent measurements of nitrogen gas and particulate species. We added the statistics for NH3, PNH4, and NHx model performance during the GrandTReNDS campaign at the three sites in the updated Table 1 (attached below).

Table 1. CAMx model performance for nitrogen species concentrations as well as nitrogen dry/wet depositions evaluated at sites in AMoN, CASTNet, IMPROVE, NTN

networks as well as the 3 sites during GrandTRENDS campaign over the GYA region (see Figure 1 for site locations) in 2011.

Species		Network	Duration	OBS[a]	SIM[b]	#Site[c]	N[d] (% completeness)	R[e]	NMB[f]	NME[g]	FB[h]	FE[i]
concentration	NH_3 (ppb)	AMoN[1]	Sep 22-Dec 12	0.49	0.30	1	7 (100%)	0.20	-65%	67%	-52%	53%
		GrandTReNDS[2]	Apr 5-Sep 21	0.55	0.46	3	434(97.7%)	0.30	-16%	57%	-42%	63%
	HNO_3 (ppb)	CASTNet[3]	Jan 4-Dec 27	0.23	0.47	2	83(98.8%)	0.72	108%	117%	60%	71%
		GrandTReNDS[2]	Apr 5-Sep 21	0.28	0.54	3	435(97.9%)	0.60	106%	109%	63%	68%
	PNO_3 ($\mu g\ m^{-3}$)	CASTNet[3]	Jan 4-Dec 27	0.19	0.25	2	83(98.8%)	0.42	37%	76%	26%	64%
		IMPROVE[4]	Jan 3-Dec 29	0.14	0.22	4	332(68.5%)	0.35	58%	108%	51%	80%
		GrandTReNDS[2]	Apr 5-Sep 21	0.13	0.15	3	435(97.9%)	0.45	15%	71%	14%	60%
	PNH_4 ($\mu g\ m^{-3}$)	CASTNet[3]	Jan 4-Dec 27	0.17	0.18	2	83(98.8%)	0.28	3%	39%	7%	41%
		GrandTReNDS[2]	Apr 5-Sep 21	0.14	0.17	3	433(97.7%)	0.12	23%	64%	34%	61%
	NH_x ($\mu g\ m^{-3}$)[4]	GrandTReNDS[2]	Apr 5-Sep 21	0.68	0.63	3	427(96.2%)	0.26	-7%	48%	-22%	46%
N Deposition	HNO_3 dry ($kg\ N\ ha^{-1}$)	CASTNet[3]	Jan 4-Dec 27	0.071	0.187	2	83(98.8%)	0.81	153%	156%	77%	82%
		GrandTReNDS[2]	Apr 5-Sep 21	0.016	0.049	3	435(97.9%)	0.66	204%	209%	101%	104%
	PNO3 dry ($kg\ N\ ha^{-1}$)	CASTNet[3]	Jan 4-Dec 27	0.012	0.023	2	83(98.8%)	0.14	96%	148%	48%	97%
		GrandTReNDS[2]	Apr 5-Sep 21	0.010	0.011	3	435(97.9%)	0.61	8%	58%	1%	65%
	PNH_4 dry ($kg\ N\ ha^{-1}$)	CASTNet[3]	Jan 4-Dec 27	0.018	0.019	2	83(98.8%)	0.1	7%	57%	22%	61%
		GrandTReNDS[2]	Apr 5-Sep 21	0.006	0.004	3	433(97.7%)	0.1	-33%	46%	-28%	53%
	NO_3^- wet ($kg\ N\ ha^{-1}$)	NTN[5]	Jan 4-Dec 27	0.079	0.097	5	214(82.3%)	0.34	31%	126%	12%	100%
		GrandTReNDS[2]	Apr 5-Sep 21	0.051	0.083	3	427(96.2%)	0.15	60%	94%	42%	71%
	NH_4^+ wet ($kg\ N\ ha^{-1}$)	NTN[5]	Jan 4-Dec 27	0.088	0.126	5	214(82.3%)	0.32	49%	142%	19%	106%
		GrandTReNDS[2]	Apr 5-Sep 21	0.103	0.147	3	427(96.2%)	0.48	42%	72%	30%	64%
Precipitation (cm)		NTN[5]	Jan 4-Dec 27	0.77	2.34	5	214(82.3%)	0.54	215%	242%	64%	118%
		GrandTReNDS[2]	Apr 5-Sep 21	0.33	0.95	3	427(96.2%)	0.42	187%	207%	69%	94%

The time series plots with the daily mean concentration comparisons are also given below. The CAMx model still underestimates the NH3 concentration (NMB = -16%) and overestimates PNH4 concentration (NMB =23%) at the three sites, but if we evaluate NHx, the model bias is smaller (NMB = -7%).



Also, we added a sentence in the first paragraph of section 3.2 as:

"The underestimation of NH3 concentration still existed (NMB = -16%), and one of the possible reasons may be due to the overestimation of HNO3 in the model pushing excessive partitioning of NH3 into the particle phase, which can be shown by the better model performance for NHx simulation (NMB = -7%) without splitting the gas-particle partition bias."

7.7: Are the performance metrics referenced here relevant for a study focusing on Nr source attribution? I could imagine if a studies goal was to forecast total PM2.5 concentrations, then opposing large biases in e.g. NH3 vs HNO3 would be of little concern; here, these issues seem much more considerable in terms of their impact on the final conclusions. Overall, I think the authors need to do more work in this regards to convince the readers of the merits of the application of the model so SA in the presence of such errors and biases.

Response:

The performance metrics referenced here from Simon et al. (2012) are the compilation of 69 peer-reviewed articles published between 2006 and 2012 focusing on regional air quality model performance evaluation for total PM2.5, speciated PM2.5, and wet deposition of sulfate, nitrate, and ammonium over the United States and Canada. None of the simulations compiled by the authors focus on the N_r source attribution. Reviewer #1 also has suggestions on this sentence. In here we just want to demonstrate that our CAMx base case modeling performance is in line with the peer modeling results and provides a good platform for further source attribution analysis. We provided Table S3 in the supplemental material to summarize the collected recent model performance evaluations for nitrogen species and revised this sentence to:

"Table S3 provides a comparison of regional CTM performance evaluations against measured N- containing species over the United States from peer-reviewed studies in recent years (e.g., Simon et al., 2012; Bash et al., 2013; Zhang et al., 2013; Yu et al., 2014; Thompson et al., 2015; Li et al., 2017). The model performance results in this study are comparable to these past studies including the overestimation of HNO3 and underestimation of NH3. Resolution of these biases requires additional research and these biases need to be taken into account when interpreting the source attribution of Nr deposition within the GYA."

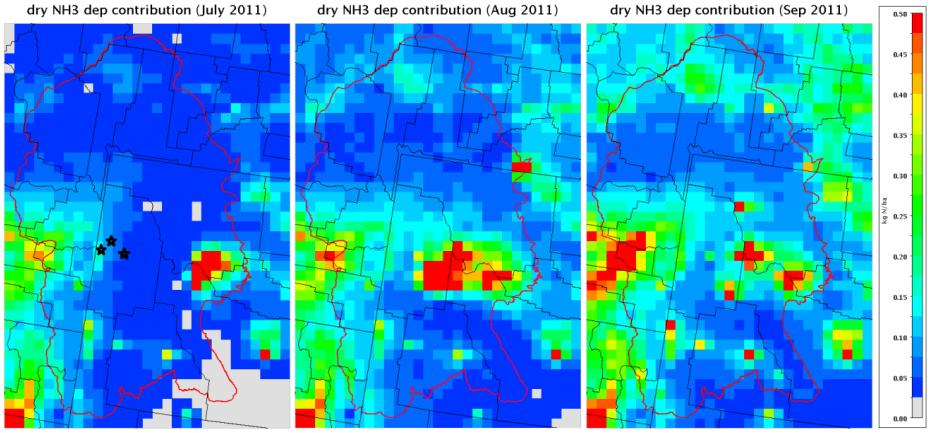
Fig 3: I find it interesting that the measurements at each site show a distinct reduction in NH3 dry dep in September, whereas CAMx shows a maximum in September for Driggs and Grand Targhee. Can authors comment on this?

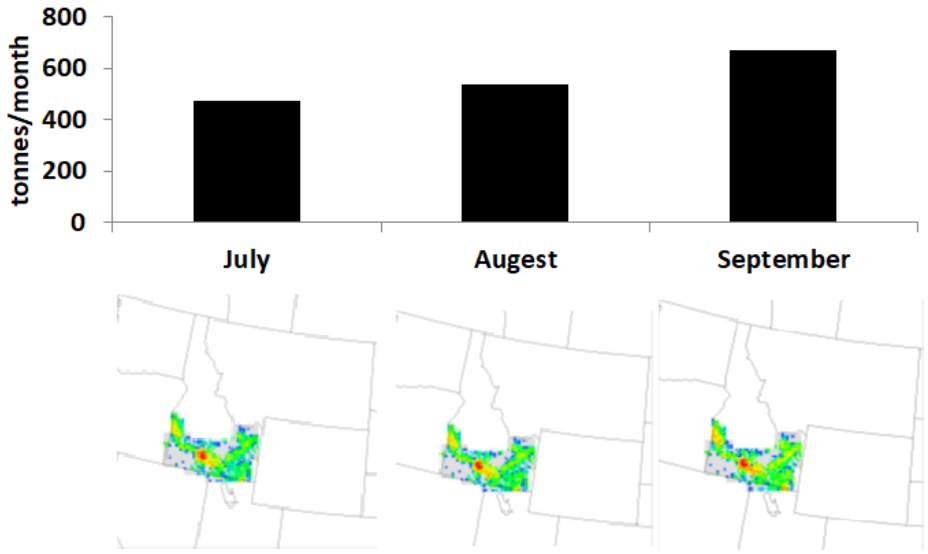
Response:

The monthly dry NH3 deposition values at the three sites associated with Figure 3 (now Figure 4) are attached below as a Table for clarification. It is true that the NH3 dry deposition (light blue in the figure) in September at each site shows a distinct reduction compared with the previous month (0.094 versus 0.209 in Driggs, 0.074 versus 0.147 in Grand Targhee, and 0.049 versus 0.113 in NOAA), but the corresponding CAMx results have the opposite trend for the Driggs and Grand Targhee sites.

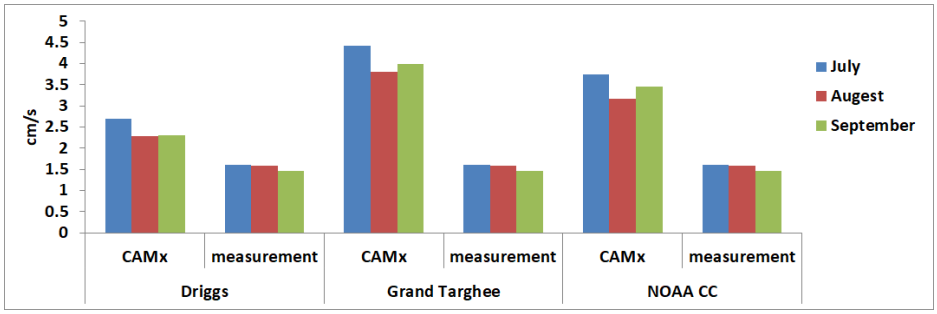
		GrandTReNDS (kg N/ha)	CAMx (kg N/ha)
Driggs	Apr	0.114	0.142
	May	0.158	0.104
	Jun	0.156	0.104
	Jul	0.194	0.101
	Aug	0.209	0.134
	Sep	0.094	0.194
Grand Targhee	Jul	0.018	0.071
	Aug	0.147	0.101
	Sep	0.074	0.119
NOAA CC	May	0.018	0.043
	Jun	0.076	0.050
	Jul	0.085	0.049
	Aug	0.113	0.102
	Sep	0.049	0.088

Back trajectory analysis shows that during the GrandTReNDS campaign period, the dominant source origins impacting the Nr in the GYA are from Snake River valley and northern Utah (Prenni et al., 2015). The high NH3 deposition at the three sites in September in the CAMx simulation results is also verified with the spatial plots attached below. The high deposition is associated with the high NH3 emission rates in September from the Snake River valley.





More importantly, if we compare the monthly mean dry deposition velocities used to calculate the measured NH3 dry deposition with the corresponding CAMx values, we find that there is a steep jump from August to September from the GrandTReNDS calculations, while the deposition velocity values from the models keep steady. Therefore, we believe this discrepancy is mainly due to the different variation trend of dry deposition velocity between the measurements and the model.



We revised the corresponding sentences in section 3.2 as:

"As shown, the simulation does a poor job of reproducing the total Nr deposition rates both in the month-to-month variation as well as across the sites. The difference in the dry NH3 deposition monthly variation between measurements and simulation is mainly due to the difference in associated dry deposition velocity used for calculation. However, consistent with the observations, the simulation shows that wet deposition is larger than dry and that the contribution from reduced N deposition was larger than from the

oxidized N deposition at all three sites, although the observed range of 70–80% reduced N was more than the 55–68% simulated in CAMx."

Reference:

Prenni, A.J., Levin, E.J.T., Benedict, K.B., Sullivan, A.P., Schurman, M.I., Gebhart, K.A., Day, D.E., Carrico, C.M., Malm, W.C., Schichtel, B.A. and Collett, J.L., Gas-phase reactive nitrogen near Grand Teton National Park: Impacts of transport, anthropogenic emissions, and biomass burning. Atmos. Environ., 89, 749-756, 2014.

12: How much did reducing the NH3 dry deposition change the total NH3 deposition amounts and their underestimation compared to observations mentioned in previous sections?

Response:

In the supplemental material, Figure S6, we updated the change of spatial patterns of the simulated total NH3 deposition over the GYA during July–August 2011 due to the change of NH3 deposition velocity in CAMx (the middle panel in the attached figure below).

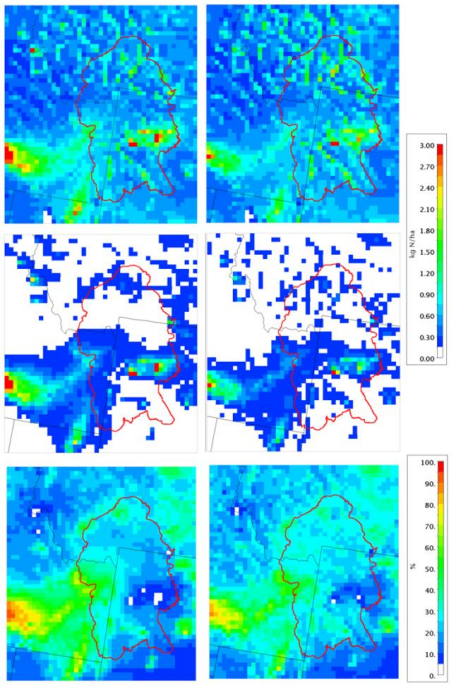


Figure S6. Change of spatial patterns of the simulated total Nr deposition (top panel), total NH3 deposition (middle panel) as well as contributions from agricultural emissions

sector to total Nr deposition budget (bottom panel) over the Greater Yellowstone Area (GYA) during July–August 2011 due to the change of NH3 deposition velocity in CAMx.

Attached table shows the dry and wet nitrogen deposition change at the GYA due to changing NH3 deposition velocity in CAMx during July-August 2011. Decreasing the NH3 deposition velocity will increase the NH3 surface concentration and improve the model bias for underestimation (see Figure S5). Still, the total NH3 dry deposition in the GYA will decrease by 3%. However, the NH3 wet deposition in the GYA is significantly increased (73%) due to longer NH3 lifetime since emit and further deposition into the GYA during precipitation events. On average, a 31% increase for total Nr deposition from the agriculture source sector (which is dominated by NH3 emissions) can be seen by decreasing the NH3 dry deposition velocity.

	base (kg N/ha)			DV_0.1 (kg N/ha)			difference(%)		
	Dry	Wet	Total	Dry	Wet	Total	Dry	Wet	Total
BC	0.033	0.040	0.073	0.029	0.045	0.074	-12.5%	14.3%	2.1%
Agriculture	0.038	0.030	0.069	0.037	0.052	0.090	-2.7%	73.1%	30.8%
Oil&Gas	0.004	0.001	0.005	0.004	0.002	0.005	-1.2%	14.1%	3.2%
Other+Fire	0.149	0.056	0.206	0.130	0.070	0.200	-13.2%	25.6%	-2.7%
Total	0.224	0.128	0.352	0.199	0.170	0.369	-11.2%	33.2%	4.9%

13.1: It seems like earlier there were several possible reasons for this, such as overestimated HNO3 concentrations, and yet here only precipitation biases are considered?

Response:

Due to the limited amount of computational resources, we didn't conduct the HNO3 sensitivity study or quantify its impact to source apportionment results. It is true that the overestimation of HNO3 concentration is a major uncertainty for the simulated nitrogen deposition budgets (see Figure 3 and Figure 4). Heald et al. (2012) used GOES-Chem to simulate inorganic aerosol loading and NH3 concentrations over the United States. They also reported significant overestimation of HNO3 concentrations and found that by reducing HNO3 concentrations to 75% of their simulated values, the model can correct the bias in nitrate as well as in ammonium simulation. They didn't pinpoint the mechanism underneath this model performance improvement but provided a general statement that it may be due to "a combination of errors in chemistry, deposition and sub-grid near-surface gradients." However, the findings from Heald et al. (2012) using GEOS-Chem are hard to refer here to justify the similar impact from CAMx given the differences of those two photochemical models in terms of implementation scales (regional versus global) and chemical mechanism (carbon bond versus tropchem). We expect the decrease of deposition of oxidized nitrogen in the GYA by decreasing the HNO3 concentrations in the model and we suspect the impact from further source regions with high NOx emissions will become smaller to the GYA.

We added a sentence at the section 5 as:
"The overestimation of HNO3 concentrations in the GYA is another reason for the wet Nr deposition overestimation. However, its impact on source apportionment results was not conducted here due to unclear reasons for the model bias (emission, chemistry, meteorology, deposition scheme) and limited computational resources."

Reference:
Heald, C.L., Collett Jr, J.L., Lee, T., Benedict, K.B., Schwandner, F.M., Li, Y., Clarisse, L., Hurtmans, D.R., Van Damme, M., Clerbaux, C. and Coheur, P.F., Atmospheric ammonia and particulate inorganic nitrogen over the United States. Atmos. Chem. Phys., 12(21), 10295-10312, doi:10.5194/acp-12-10295-2012, 2012.

Source regions contributing to excess reactive nitrogen deposition in the Greater Yellowstone Area (GYA) of the United States

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Abstract.

Research has shown that excess reactive nitrogen (N_r) deposition in the Greater Yellowstone Area (GYA) of the United States has passed critical load (CL) thresholds and is adversely affecting sensitive ecosystems in this area. To better understand the sources causing excess N_r deposition, the Comprehensive Air Quality Model with extensions (CAMx), using Western Air Quality Study (WAQS) emission and meteorology inputs, was used to simulate N_r deposition in the GYA. CAMx's Particulate Source Apportionment Technology (PSAT) was employed to estimate contributions from agriculture (AG), oil and gas (OG), fire (Fire), and other (Other) source sectors from 27 regions, including the model boundary conditions (BC) ~~representative of international contributions,~~ to the simulated N_r for 2011. The BC were outside the conterminous United States and thought to represent international anthropogenic and natural contributions. Emissions from the AG and Other source sectors are predominantly from reduced N and oxidized N compounds, respectively. The model evaluation revealed a systematic underestimation in ammonia (NH_3) concentrations by 65% and overestimation in nitric acid concentrations by 108%. The measured inorganic N wet deposition at National Trend Network sites in the GYA was overestimated by 31–49%, due at least partially to an overestimation of precipitation. These uncertainties appear to result in an overestimation of distant source regions including California and BC and an underestimation of closer agricultural source regions including the Snake River valley. Due to these large uncertainties the relative contributions from the modelled sources and their general patterns are the most reliable results. Source apportionment results showed that the AG sector was the single largest contributor to the GYA total N_r deposition, contributing 34% on an annual basis. Seventy-four percent of the AG contributions originated from the Idaho Snake River valley, with Wyoming, California, and northern Utah contributing another 7%, 5%, and 4%~~,%~~ respectively. Contributions from the OG sector were small at about 1% over the GYA, except in the

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southern Wind River Mountain Range during winter where they accounted for more than 10%, with 46% of these contributions coming from OG activities in Wyoming. Wild and prescribed fires contributed 18% of the total N_r deposition, with fires within the GYA having the highest impact. The Other source category was the largest winter contributor (44%) with high contributions from California, Wyoming and northern Utah~~The five largest source area contributions to the annual total N_r deposition in the GYA were 1) the Snake River valley (38% with AG 68%, OG 2%, Fire 15%, and Other 16%); 2) BC (21%); 3) Wyoming (12% with AG 19%, OG 5%, Fire 38%, and Other 39%); 4) California (7% with AG 26%, OG 1%, Fire 14%, and Other 59%); and 5) northern Utah (6% with AG 25%, OG 2%, Fire 10%, and Other 63%). These results suggest that N_r deposition over the GYA, especially in the western region, was above the critical loads for sensitive ecosystems, and AG from the Snake River valley was the largest contributor. Distant source regions were also important, with large contributions from the BC, i.e., international source regions~~.

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1 Introduction

The Greater Yellowstone Area (GYA) (see Figure 1) of the United States, with Yellowstone National Park (YNP) and Grand Teton National Park (GTNP) at its core, is one of the largest remaining intact ecosystems in the northern temperate zone and features diverse wildlife, alpine lakes, forests, and geologic wonders (Keiter and Boyce, 1994; NPS, 2017). Increasing concentrations of reactive nitrogen (N_r) compounds in air, rain, and snowpack samples over the GYA have been reported in the past 30 years and linked to N_r emissions from human activities (Clow et al., 2003; Blett et al., 2011; IMPROVE, 2011; Sullivan et al., 2011; USGS, 2014; NADP, 2016; Nanus et al., 2017; also, see Figure S1). The inorganic wet N_r deposition rates measured at high-elevation National Trend Network (NTN) sites within the GYA in 2010 were 2.5–3.5 kg N ha^{-1} yr^{-1}, compared with 1.5–2.5 kg N ha^{-1} yr^{-1} in 2000 (NADP, 2016). This is relevant to the long-term conservation of the area because as N_r deposition levels increase, they can cross critical load (CL) thresholds, at which negative effects to sensitive ecosystem components can occur (Porter et al., 2005; Pardo et al., 2011). Additional concerns posed by enhanced N_r deposition include lake acidification, loss of lichen biodiversity, and eutrophication (Baron, 2006; Blett et al., 2011; NADP, 2016). While ecosystem changes due to excess N_r deposition over Class I areas including the GYA have been documented (e.g., Baron et al., 2011; Saros et al., 2011; Sullivan et al., 2011; Spaulding et al., 2015; Nanus et al., 2017), the origins, chemical composition, and spatial and temporal changes in the deposition over this region are not as well understood.

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Total N_r is a mix of oxidized and reduced inorganic nitrogen (N) and organic N compounds that are chemically and biologically active in the Earth's biosphere and atmosphere and ~~are~~ deposited through wet and dry processes. These compounds arise from a variety of sources, with inorganic oxidized N primarily emitted as nitrogen oxides (NO_x) from fossil fuel combustion, with approximately 25% from power plants, 50% from automobiles, and 10% from other mobile sources, based on annual county-level estimations (EPA, 2015). Atmospheric reactions of NO_x result in nitric acid (HNO_3), particulate nitrate (PNO_3)~~,~~ and other compounds. Reduced N arises primarily from ammonia (NH_3) gas emissions from

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agricultural activities, which can react with acidic aerosols to form ammonium (NH_4^+) compounds (Galloway et al., 2004). Mobile sources are also an important source of NH_3 and can be the primary emitter in urban areas (Sun et al., 2014; Sun et al., 2017). Emissions from this sector have large uncertainties and a recent study suggests that on-road NH_3 emissions in the 2011 National Emissions Inventory (NEI) were underestimated by a factor of 2.9~~. A recent study found the increasing importance of on-road emissions of NH_3, which at 40% exceed agricultural emissions~~ (Fenn et al., 2018). There are hundreds of organic N compounds, including reduced (e.g., amines) and oxidized forms (e.g., alkyl nitrates)~~.) forms.~~ Sources of organic N are less well known, but increasing evidence suggests that biomass burning and agriculture are significant contributors, as are atmospheric reactions of NO_x with volatile organic compounds (Cape et al., 2011; Reay et al., 2012). With the steady decline of NO_x emissions in the United States during past decades as a result of the implementation of the Clean Air Act, the importance of reduced N to the total N deposition budget has increased (Li et al., 2016). Specific to the GYA, local anthropogenic emissions are small, but upwind sources, including agricultural activities in the Snake River valley and northern Utah, wildfires throughout the western United States, energy development in the Upper Green River Basin, and anthropogenic activities at urban centers such as Salt Lake City, are larger and likely to be significant contributors to regional N emissions (Prenni et al., 2014).

To better understand the levels and composition of the N_r compounds deposited in the GYA and to help guide strategies to reduce N deposition, the National Park Service (NPS) initiated the Grand Teton Reactive Nitrogen Deposition Study (GrandTReNDS), which included spatially and temporally detailed measurements of N compounds during April to September 2011 (Benedict et al., 2013a; Prenni et al., 2014). It was found that during summer months at the high-elevation sites (e.g., Grand Targhee; see Figure 2~~1~~), 62% of the N~~itrogen~~ deposition was from reduced N and about equally split between dry and wet deposition, and oxidized N only accounted for 27% of the N~~itrogen~~ deposition budget, with the remaining in the form of wet-deposited, organic N. Study findings indicate a significant west-to-east gradient in atmospheric NH_3 concentrations, with higher concentrations west of the Teton mountain range. Concurrently measured concentrations of HNO_3~~, and~~ $PM_{2.5}$ (particulate matter with aerodynamic diameter less than 2.5 μm) nitrate, and NH_4^+ showed relatively small west-to-east gradients inside GTNP (Benedict et al., 2013a; Prenni et al., 2014).

The origins of N_r transported to the GYA and other remote locations in the western United States have been examined in past modeling studies. Back trajectory analyses have shown that air mass~~airmass~~ transport to GTNP is predominantly from the west through the Snake River valley and from the southwest through northern Utah (Prenni et al., 2014). Zhang et al. (2012) applied the global Chemical Transport Model (CTM) GEOS-Chem (Bey et al., 2001) using~~for~~ zero-out sensitivity simulations and found that in 2006 natural sources, including lightning and wildfires, contributed more than 10% of the total N_r deposition over the Teton area. Lee et al. (2016) used the adjoint version of GEOS-Chem to quantify the sources of N_r deposition in eight selected federal Class I areas in 2010~~, including GTNP,~~ and found a nonnegligible footprint (>20%)~~the importance~~ of ~~emissions from California to~~ N_r deposition in ~~remote~~

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~~areas in the~~ western United States, including GTNP and Rocky Mountain National Park (RMNP), attributed to long-range transport from sources in California, especially during summertime.~~,~~ Mobile NO_x and livestock NH_3 were also found to be major sources of N_r deposition in GTNP. Similar modeling studies focusing on RMNP also suggested the important contributions of distant sources including those from California and other counties and the fact that the contributions from source of reduced Nr were larger than those from sources of oxidized Nr (Thompson et al., 2015; Malm et al., 2016).

~~Rocky Mountain National Park (RMNP), located in the Intermountain West, has been the focus of several Nr deposition studies. This area has many similarities to the GYA, although the intense agricultural activity and large population centers are located to the east of RMNP as opposed to the west as is the case for the GYA. In one 2009 modeling study, Thompson et al. (2015) found that 40% of the reduced N deposition originated from ammonia sources within Colorado. The emissions from more distant sources in California and the Snake River valley in Idaho as well as international sources each contributed 7–15% of the total N_r deposition. In a hybrid modeling technique, Malm et al. (2016) combined the source attribution results from Thompson et al. (2015) with measured N_r concentrations and found that N_r contributions to RMNP were also predominantly from the sources within Colorado, with a significant portion (27%) originating from sources along the Front Range of Colorado. Furthermore, they pointed out that reduced N_r constituted 66% of the total deposition budget.~~

In this work, we add to the growing body of N_r modeling source apportionment studies by conducting a detailed analysis using the Particulate Source Apportionment Technology (PSAT) module within the CAMx (Comprehensive Air Quality Model with extensions) (Ramboll Environ, 2014) CTM to quantify the seasonal contributions from different source regions and source sectors to N_r throughout the GYA. Compared with previous Nr deposition simulation studies in United States, this work uses tagged reactive tracers to attribute the contributions from four designated emission sectors and 27 designated emission regions to N_r deposition in the GYA with a much higher horizontal grid resolution (12 km) and an up-to-date emission inventory instead of using a zero-out approach (e.g., Zhang et al., 2012) or an adjoint model (e.g., Lee et al., 2016). The model simulation of N_r and its constituents were first evaluated against routine measured data as well as the unique data measured during the GrandTReNDS campaign period (Benedict et al., 2013a; Prenni et al., 2014). N_r deposition from CAMx simulations was also compared with total deposition maps (TDEP), which were developed for deposition trend analysis and ecological impact assessment (Schwede and Lear, 2014). The detailed source apportionment results are presented here, focusing on seasonal variations and the relative importance to CL exceedance in sensitive ecosystems within the GYA. The discussion of identified model bias and uncertainties to source apportionment results interpretation, including the model lateral boundary conditions, the impact of model precipitation to wet deposition simulation, and the impact of ammonium dry deposition velocity to dry deposition are also presented. ~~2014). The final source apportionment results are then interpreted within the context of the identified model bias and uncertainties.~~

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2 Modeling system for N_r source apportionment

Modeling simulations for 2011 were conducted using the CAMx version 6.10 (ENVIRON, 2014) with two nested grids. The outer domain (36 km) covered the contiguous United States (CONUS), as well as portions of Canada and Mexico, while the inner domain (12 km) encompassed the western United States and focused on states within the Western Regional Air Partnership (WRAP) (see Figure 1).

The hourly meteorological inputs for 2011 were generated by the Weather Research and Forecasting (WRF) model (WRF-ARW, version 3.5.1) (Skamarock et al., 2008) and were obtained from the Intermountain West Data Warehouse (IWDW) (http://views.cira.colostate.edu/tsdw/). This meteorological simulation performed comparably to other recent prognostic model applications used in air quality planning (UNC-Chapel Hill and ENVIRON, 2014a).

The emission inventory used by CAMx was primarily derived from the 2011 NEI~~National Emissions Inventory~~ version 2 (NEI2011v2) (EPA, 2015) with the Sparse Matrix Operator Kernel Emissions (SMOKE) processing system version 3.0 (Houyoux et al., 2002) for anthropogenic emissions, the Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2.10 (Guenther et al., 2012) for biogenic emissions, and the WRAP Windblown Dust Model (WRAP-WBD) to estimate wind-driven dust emissions (UNC-Chapel Hill and ENVIRON, 2014b). Emissions from the oil and gas sector were further updated by the IWDW to represent the best available inventory for oil and gas activity in the western United States at the time of modeling (UNC-Chapel Hill and ENVIRON, 2014b). The emissions for fire activities include agricultural fires, prescribed fires, and wildfires and were generated by the Particulate Matter Deterministic and Empirical Tagging and Assessment of Impacts on Levels (PMDETAIL) study (Moore et al., 2012). PMDETAIL developed 2011 fire emissions using satellite data, ground detects, and burn scar and estimated the plume rise, depending on fire size and type. The hourly, nonsurface fire emissions were allocated to the proper CAMx vertical layers based on the model-predicted planetary boundary layer (PBL) height and the spanning of the plume top and bottom above the ground (Mavko and Morris, 2013).

The boundary conditions for the 36-km domain were estimated from a 2011 global model run using the Model for Ozone and Related chemical Tracers (MOZART) version 4.6 (Emmons et al., 2010). The simulation year of 2011 was preceded by 15 days of "spin-up" time to minimize the effects of initial conditions. A more detailed description of the WRF-SMOKE-CAMx modeling platform applied in this study is summarized in Table S1 as well as the 2011 Three-State Air Quality Study (3SAQS) (UNC-Chapel Hill and ENVIRON, 2014b).

For the source apportionment estimates, 27 source regions (Figure 1), as well as the lateral boundary conditions (BC), were "tagged" in the CAMx PSAT simulation. ~~Figure 1 provides the source region partition map of the inner 12-km domain emissions.~~ In addition, the emissions for each region were further subdivided into four source sectors: ~~of~~ 1) agriculture (AG), 2) oil and gas activity (OG), 4) fire activity, including wildfires and prescribed fires (Fire), and 4) the remaining sources labeled as Other. The Other source sector primarily comes from mobile and large point sources, with smaller contributions from

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natural sources such as lightning. Table S2 provides the ~~estimated~~ annual NH_3 and NO_x emissions used in this modeling study with a breakdown by tagged~~the corresponding~~ source regions and source sectors. Figure 2 provides the annual emissions of NH_3 in the inner 12-km domain as well as the monitoring sites or receptor areas used for the model evaluation and analysis. For NH_3 emissions, the AG sector contributed 84.1% of the total emissions within the 12-km domain, while the OG, Fire, and Other sectors contributed 0.1%, 4.5%, and 11.4%, respectively (Table S2). In the Snake River valley, the AG sector emissions dominate the emission budget. For NO_x emissions, the contribution rankings from the four tagged emission sources are Other (83.8%), OG (12.8%), Fire (3.2%), and AG (0%). The regions were selected to highlight important source sector~~s~~ contributions to N_r deposition in the GYA. For example, the state of Wyoming ~~(WY)~~ was partitioned into five regions (YNP, Jackson, Upper Green River, ~~and~~ Eastern Wyoming, and Western Wyoming~~WY~~) to differentiate the possible source impacts from urban activity in Jackson from~~as compared to~~ energy development in southwestern Wyoming (Blett et al., 2011; NPS, 2017). Significant agricultural operations in the Snake River valley in Idaho, northern Utah, and northeastern Colorado were tagged due to their high ammonia emissions (see Figure 2~~1~~) associated with fertilizer application and confined animal feeding operations (Fenn et al., 2003; Clarisse et al., 2009; Prenni et al., 2014). Lastly, wildfires are episodic events (http://wrapfets.org/map.cfm) that can have large intermittent contributions to N_r deposition, but they can mask important contributions from other sources that are significant in nonfire years.

CAMx-PSAT treats nitrogen-containing compounds as one of seven species: gaseous NH_3; particulate ammonium (PNH_4); reactive gaseous nitrogen (RGN), which includes primary emissions of NO_x, nitrous acid (HONO), nitrate radical (NO_3), and dinitrogen pentoxide (N_2O_5); gaseous nitric acid (HNO_3); gaseous peroxy nitrogen (TPN), including peroxyacetyl nitrate (PAN) and peroxynitric acid (PNA); gas-phase organic nitrate (NTR); and particulate nitrate (PNO_3). PSAT maintains the source ~~-~~group identity (i.e., source region and source sector) by apportioning the secondary species to the precursor emissions (ENVIRON, 2014). In the source apportionment comparison results, we report the reduced N_r deposition as the sum of NH_3 and PNH_4 and the oxidized N_r deposition as the sum of RGN, HNO_3, PNO_3, TPN, and NTR in units of kg N ha^{-1}.

3 Evaluation of CAMx-simulated N_r concentration and deposition rates

Acceptable model performance of the regional air quality modeling system is a prerequisite for a credible source apportionment interpretation (Boylan and Russell, 2006; EPA, 2014; Emery et al., 2017). In this work, the CAMx simulation was extensively evaluated against routine monitoring data as well as data collected in the GrandTReNDS special field study (Benedict et al., 2013a; Prenni et al., 2014) and against the nitrogen deposition estimates from the National Atmospheric Deposition Program (NADP, nadp.slh.wisc.edu) ~~total deposition maps (~~TDEP) hybrid modeling results (Schwede and Lear, 2014). Performance~~The performance~~ metrics recommended by~~from~~ the EPA's modeling guidance for ozone, $PM_{2.5}$, and regional haze attainment demonstrations (Yu et al., 2006; EPA, 2014) were used (see Table 1).

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The variables and routine monitoring networks used in the model evaluation were NH_3 concentrations from the Ammonia Monitoring Network (AMoN) (http://nadp.sws.uiuc.edu/AMoN/); nitric acid (HNO_3), PNO_3, and PNH_4 concentrations as well as estimated dry deposition fluxes from the Clean Air Status and Trends Network (CASTNet) (https://www.epa.gov/castnet); PNO_3 and PNH_4 concentrations from the Chemical Speciation Network (CSN) (https://www3.epa.gov/ttnamti1/speciepg.html); PNO_3 concentrations from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network; and wet-deposited inorganic oxidized (NO_3^-) and reduced (NH_4^+) nitrogen and associated precipitation rates from the ~~at National Atmospheric Deposition Program (~~NADP~~)~~ NTN sites. Each network had a unique sampling frequency and duration (Table 1). The hourly CAMx outputs were aggregated to match the timescales of the measured data. All measurement data flagged as questionable, either due to maloperation or to insufficient samples to calculate representative values, were excluded~~removed~~ from the analysis. Table 1 reports the percentage of valid measurements used for statistical analysis during evaluation time. For most of the N species, the percentage of valid samples is more than 80%. In general, the ~~Clean Air Status and Trends Network (~~CASTNet~~),~~ IMPROVE, AMoN, and NADP networks sample in rural areas, while the data from the CSN network primarily represent the air quality in urban and suburban settings. Although organic N species were also measured in the GrandTReNDS campaign, we focus on the inorganic N budget comparison, given the large uncertainties for organic N prediction (Jickells et al., 2013) and its incomplete treatment in the model's chemical mechanism. For example, the modeling system does not account for primary emissions of organic N compounds but does include the formation of organic N from the alkylperoxy radical and secondary alkoxy radical (ENVIRON, 2014).

3.1 Evaluation against data in the GYA

The 3SAQS study performed photochemical grid modeling using the same modeling platform and input files as this study (UNC and ENVIRON, 2014b) and evaluated the model performance fo~~ve~~r the western United States. A subset of these results is presented in Supplement File S1 for reference.~~;~~ Model performance statistics for the N~~nitrogen~~ species within the GYA area at AMoN, CASTNet, IMPROVE, and NTN network sites (Figure 1) at different periods in 2011 are presented in Table 1. The biases at the GYA sites are similar to those throughout the West (Table in File S1) in that the CAMx simulation significantly overestimated ~~the~~ HNO_3 with a normalized mean bias (NMB) of ~~=~~ 108% and significantly underestimated ~~the~~ NH_3 concentrations with NMB = -65%. While the model had skill in reproducing the daily variation in HNO_3, with a correlation coefficient of $r = 0.71$, it had little skill for NH_3, with $r = 0.2$. The overestimation of HNO_3 has also been reported in other regional-scale modeling simulations over the United States~~studies~~ (e.g., Barker and Scheff, 2007; Foley~~Zhang~~ et al., 2010; Thompson~~2012; Lee~~ et al., 2015) with the carbon bond mechanism used in this study. The possible reason for the overestimation of HNO_3 ~~2016) and~~ may be due to the uncertainty for the~~excessive~~ N_2O_5 uptake coefficient setting for heterogeneous reactions (Foley~~hydrolysis in the model (Heald~~ et al., 2010~~2~~).~~.~~ The poor NH_3 results may be related to~~realted with~~ the high uncertainty in the NH3 emission inventory (Clarisse et al., 2009) and ~~missing~~ important missing

physical mechanisms in the model, including the lack of bidirectional NH3 deposition (Zhang et al., 2010; Bash et al., 2013; Zhu et al., 2015). The GYA area is located downwind of the major agriculture sources in the Snake River valley and northern Utah (Table S2). The incorporation of the bidirectional NH_3 flux mechanism in the model should increase ambient NH_3 concentrations in the GYA and thus decrease the large model underestimation of NH3 concentrations. ~~Thompson et al., 2015; Zhu et al., 2015).~~

For PNO_3 and PNH_4 simulations in the GYA, ~~the~~ CAMx ov~~und~~erestimated both species, with better performance for PNH_4 than PNO_3 (3% versus 37%, respectively, in terms of NMB) ~~normalized mean bias (NMB))~~ and better agreement for PNO_3 at CASTNet sites versus IMPROVE sites (37% versus 58% for NMB, respectively). The errors and biases in the dry deposition fluxes compared to CASTNet values follow the same patterns as in the ambient concentrations, but it should be noted that CASTNet and CAMx use different algorithms to estimate dry deposition velocities, and these model-to-model discrepancies will manifest themselves in the performance evaluations. ~~Overall, the CAMx model performance for the concentrations of gaseous and PM nitrogen components in the GYA fall within the range of reported regional air quality model performance metrics from other peer-reviewed studies (Simon et al., 2012).~~

Wet deposition measurement~~s~~ from the five NTN sites with sufficient data were~~was~~ available from within the GYA (Figure S2). ~~,~~ Comparisons to CAMx showed that the model captured the general trends in these data with $r \sim 0.32–0.34$ ~~and~~ but were somewhat biased, with NMB = 31% for NO_3^- and NMB = 49% for NH_4^+. The precipitation simulations were consistently 100–200% higher than the rain gauge measurements at the NTN sites, showing that WRF overestimated the frequency and intensity of precipitation events over the GYA in 2011 (Table 1). ~~,~~ However, note that 2011 was a large snowpack year; by May, much of the GYA was sitting at 100–180% of normal snow weather equivalent (USGS, 2014). Precipitation measurements tend to be low during high~~-~~snow events.

The seasonal, simulated ambient concentrations and deposition rates are compared against measured CASTNet and NADP data at the YNP and Pinedale monitoring sites in Figure 3. Seasons refer to winter (December, January, February, DJF), spring (MAM), summer (JJA), and fall (SON). ~~2.~~ The significant overestimation of~~in~~ HNO_3 is evident in all seasons. Also evident is the poor simulation of the seasonality in N_r deposition, primarily due to the poor reproduction of ~~the~~ wet deposition, which is at least partly due to the large errors in the simulated precipitation.

Table S3 provides a comparison of regional CTM performance evaluations against measured N- containing species over the United States from peer-reviewed studies in recent years (e.g., Simon et al., 2012; Bash et al., 2013; Zhang et al., 2013; Yu et al., 2014; Thompson et al., 2015; Li et al., 2017). The model performance results in this study are comparable to these past studies including the overestimation of HNO_3 and underestimation of NH_3. Resolution of these biases requires additional research and these biases need to be taken into account when interpreting the source attribution of N_r deposition within the GYA.

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3.2 Evaluation against GrandTReNDS data

The GrandTReNDS campaign provides a unique opportunity to evaluate the capability of CAMx to simulate the N_r compounds and deposition budget. Detailed measurements, including NH_3, were made at three sites that crossed GTNP from west to east: Driggs, in the foothills just west of GTNP (43.74 °N, -111.87 °W, elevation 1947m); Grand Targhee, an upper-elevation site on the western edge of GTNP (43.78 °N, -110.94 °W, elevation 2722m); and the National Oceanic and Atmospheric Administration (NOAA) Climate Station site on the eastern edge of GTNP (43.66 °N, -110.71 °W, elevation 1978m) (also see Figure 2~~1~~). Figure 4~~3~~ presents the monthly deposition budgets for these three sites during the sampling periods, and Table 1 provides the model performance statistics for the N species concentration and deposition. As shown, the simulation does a poor job of reproducing the total N_r deposition rates both in the month-to-month variation as well as across the sites. The difference in the dry NH_3 deposition monthly variation between measurements and simulation is mainly due to the difference in associated dry deposition velocity used for calculation. However, consistent with the observations, the simulation shows that wet deposition is larger than dry and that the contribution from reduced N deposition was larger than from the oxidized N deposition at all three sites, although the observed range of 70–80% reduced N was more than the 55–68% simulated in CAMx. The primary cause of this bias was the overestimation in the HNO_3 dry deposition rates, which were 2–3 times larger than those derived from the measured data. This is consistent with the systematic overestimation of HNO_3 concentrations (NMB = 106% in Table 1). Other biases also exist, including an underestimation in the NH_3 dry deposition, which was somewhat balanced by an overestimation in the NH_4^+ wet deposition (NMB = 60%). The underestimation of NH_3 concentration still existed (NMB = -16%), and one of the possible reasons may be due to the overestimation of HNO_3 in the model pushing excessive partitioning of NH_3 into the particle phase, which can be shown by the better model performance for NH_x ($NH_x = NH_3 + PNH_4$) simulation (NMB = -7%) without splitting the gas-particle partition bias.

An additional challenge that affected model performance was the difficulty in estimating precipitation rates. This is shown in Figure 4~~3~~, where the simulated precipitation rates do not reproduce the month-to-month variation and generally were highly overestimated. For example, on average the simulated precipitation at Driggs was more than double the measured precipitation, and it was more than a factor of 4 higher at the NOAA Climate Station site.

3.3 Evaluation against NADP -TDEP

TDEP maps (Schwede and Lear, 2014) are widely used in the land management community to assess total N_r deposition throughout the United States and estimate the critical load exceedances in sensitive ecosystems (Saros et al., 2011; Nanus et al., 2017). TDEP employs a hybrid approach to integrate measurements from multiple networks, including CASTNet and NTN, with Community Multiscale Air Quality (CMAQ) modeling (Byun and Schere, 2006) results for deposition velocities and unmeasured species' dry deposition, as well as PRISM (Parameter-elevation Relationships on Independent Slopes

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Model) (Daly et al., 1994) ~~for~~ high-resolution precipitation estimates for~~to~~ mapping total deposition in the United States (Schwede and Lear, 2014). Both the CAMx simulation in this study and the TDEP results are derived from model simulations and subject to similar errors in emissions and physical and chemical processes. However, with the incorporation of measured wet N_r deposition and N concentration data into the TDEP results, they are expected to be less biased than the deposition results from a purely~~pure~~ CAMx simulation.

The TDEP total N_r deposition and the CAMx 2011 simulation in this work exhibited similar spatial and temporal patterns across the western United States; for example, both sets of results show high N_r deposition in the Snake River valley, northern Utah, and across the Wyoming state border area near GTNP, with values >5 kg N $ha^{-1}yr^{-1}$. Within the GYA (Figure S3~~S4~~), the CAMx simulation had higher dry N_r deposition, which was more spatially heterogeneous than the corresponding TDEP results, with significantly higher N_r deposition in the agricultural lands to the west of the GYA and hotspots~~hot spots~~ due to wildfires that are not evident in the TDEP results. Both sets of results showed higher N_r wet deposition at the higher-elevation sites in the interior of the GYA, which was associated with higher precipitation rates. However, the TDEP N_r wet deposition was generally higher throughout the GYA, with an annual average N_r wet deposition rate of 2.0 N $ha^{-1}yr^{-1}$ versus 1.3 N $ha^{-1}yr^{-1}$ from CAMx. Precipitation~~Both precipitation~~ maps ~~across the GYA~~ generated by WRF and PRISM across the GYA had similar spatial patterns, with hotspots located in high-elevation mountain ranges, though the WRF annual precipitation rates were on average 73% higher than the PRISM estimates.

The annual N_r deposition budget and the annual precipitation rate from TDEP and the CAMx simulations at eight Class I areas over the GYA ~~area~~ are compared in Figure 5~~4~~. The reported CAMx dry and wet N_r deposition values ~~at the eight Class I areas~~ in Figure 5~~4~~ are the averages of the simulation values at corresponding grid cells for each area. Generally, results from the CAMx model agreed well with TDEP results in terms of replicating ~~the~~ spatial gradients and ~~the~~ ratios of oxidized versus reduced N deposition. The TDEP 2011 annual N_r deposition at the GYA receptor sites was in the range of 2.8–5.4 kg N $ha^{-1}yr^{-1}$, while the corresponding values for CAMx were 2.2–4.3 kg N $ha^{-1}yr^{-1}$. Both results showed the west-to-east gradient (Prenni et al., 2014) with higher N_r deposition at the western side of the GYA and relatively low values at Fitzpatrick Wilderness. Also, both models showed the importance of reduced N_r in the GYA, with a nearly 50% or higher contribution to the total N_r deposition budget. However, the two models differed on the ratio of dry versus wet N_r deposition, with CAMx simulating a higher fraction from dry N_r deposition than TDEP.

4. Source apportionment of N_r deposition over the GYA in 2011

The seasonal modeled N_r deposition budgets averaged over the GYA are presented in Figure 6~~5~~. As shown, the total N_r deposition rates peaked in the summer (1.12 kg N $ha^{-1}season^{-1}$) with somewhat lower rates in the spring (0.91 kg N ha^{-1} $season^{-1}$) and fall (0.81 kg N ha^{-1} $season^{-1}$) and with winter rates (0.29 kg N ha^{-1} $season^{-1}$) being about a factor of 3 smaller than in the other seasons. These patterns are similar to the

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measured and modeled data presented in Figure 3~~2~~. In total, the annual model N_r deposition was 3.13 kg N $ha^{-1}yr^{-1}$, with wet deposition accounting for only ~40%. Reduced N compounds were the largest contributor, except in winter, which is consistent with past studies (Li et al., 2017). Contributions from organic N compounds are not measured in routine monitoring programs. Together they accounted for <10% of the N_r deposition, suggesting a small but significant~~not insignificant~~ contribution. This is also less than has been measured in field studies conducted at GTNP (Benedict et al., 2013a; Prenni et al., 2014) and in RMNP (Benedict et al., 2013b), where the GrandTReNDS study showed on average 8–18% contribution from organic N to total N_r deposition budgets during the whole campaign period and up to 39% in June at the NOAA Climate Station site (Figure 7 in Benedict et al., 2013a).

The relative contributions from the four modeled source sectors (AG, OG, Fire, and Other) and the BC averaged over the GYA are presented in Figure 7~~6~~, while Figure 8~~7~~ presents the seasonal and spatial patterns of their contributions over the GYA. As shown in Table S2, the AG source sector was composed of almost all reduced N compounds (>99%), while the Other source sector was primarily composed (97%) of oxidized N~~itrogen~~ compounds, with about 88% originating from anthropogenic combustion emissions, including point and mobile sources, and the remainder from the natural emissions from soil and lightning. Contributions from the Fire and the BC sectors were more evenly split between reduced and oxidized N contributions.

Reduced N from the AG source sector was the largest contributor in spring (40%) and fall (41%) seasons, while oxidized N from the Other source sector was the largest contributor in summer (29%) and winter (44%) (Figure 7~~6~~). In terms of geographic impact (Figure 8~~7~~), AG emissions contributed as much as 80% of the total N_r deposition in the western portion of the GYA during the spring and fall, which was associated with the outflow from the Snake River valley. In the model, NH_3 from regional agriculture activities was treated as being from surface area sources (i.e., emitted into the first model layer, which is approximately 24 m thick). These low-level emissions can be quickly deposited to the surface unless there is sufficient vertical mixing to inject the NH_3 into the upper levels of the atmosphere (Ferm, 1998; Fenn et al., 2003) or if it reacted with acidic gases and aerosols. Consequently, it is likely that a higher fraction of the modeled NH_3 emissions from the AG sector will be deposited in the lower-elevation periphery of the GYA near the agricultural lands and not impact the more-distant mountainous interior (Figure 2~~1~~). The incorporation of the bidirectional NH_3 flux could extend the NH_3 emission footprint (Bash et al., 2013; Zhu et al., 2015).

The OG source sector contributed only about 1% of the total N_r deposition over the GYA, with contributions of 10% or more occurring during winter in the southeastern corner of the GYA where nearby OG activity in the Jonah Field and Pinedale Anticline was taking place. Wildfires are episodic and their locations and magnitudes vary significantly from year to year (Westerling and Swetnam, 2003; Parisien et al., 2012). In 2011, fire events contributed on average 18% of the total N_r deposition in the GYA. Most of the wildfire happened in summer and fall, while agriculture and prescribed burning occurred in winter and spring. Near the fire activities, the contribution to ~~the~~ N_r deposition could be more than 90%, as seen in

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Figure 8. The footprint of fire emission impacts depends on the simulated injection height of the fire plumes. The emissions from fires that occurred within the GYA during the summer and fall likely remained within the mixed layer and had less chance to be transported far downwind to impact more distance areas (Figure S4).~~7.~~ The Other source sector had relatively uniform contributions throughout the GYA, indicative of contributions from regional sources. The Other sector accounted for 26% of the annual N_r deposition, with its largest absolute contributions in the summer, but had the highest relative contribution in the winter at 44% when AG contributions were at their lowest. Finally, the BC had high contributions, often over 20%, with the highest contributions occurring in the northern part of the GYA and at higher-elevation sites.

The seasonal contributions from the modeled source regions and sectors to the average total N_r deposition over the GYA are summarized in Figure 9~~8~~. As shown, the Snake River valley in Idaho was the largest contributor (in all seasons), with annual mean contributions of 38% and a maximum contribution of 43% in fall. Most (74%) of the N_r from this region was from the AG source sector and was composed of reduced N (Table S4). The next four largest contributors, on average, were the BC (21%), western Wyoming (8%), California (7%), and northern Utah (6%). The impact of emissions from Wyoming to the GYA during summer and fall (14% and 16%, respectively) was more pronounced than winter and spring (5% and 7%, respectively). The contributions of long-range transport from California and the BC were higher during spring and winter.

Seasonal source apportionment results of the average dry and wet N_r deposition over the GYA are shown in Figures 7~~6~~ and 9~~8~~. Compared to the results for total N_r deposition, the dry N_r deposition had higher contributions from closer sources, such as the Snake River valley (46% for dry versus 38% for total), with emissions primarily from AG sources. Similarly, contributions to dry N_r deposition from Wyoming were 15% compared to 12% for total N_r deposition and ranked as the second~~--~~largest contributor. The contributions from distant source regions decreased. For example, the BC decreased from 21% for total N_r deposition to 12% for dry N_r deposition.

The opposite pattern is seen for wet N_r deposition, where the contributions from the distant source regions increased relative to the neighboring ones. The annual contributions from the BC increased to 34% and peaked in spring and summer at 37%, associated with higher precipitation amounts than the other two seasons. Annual contributions from sources in California (10%) and Utah (8%) surpassed Wyoming (7%). Furthermore, the seasonal variation for wet N_r deposition was different from dry and total N_r deposition, with the highest deposition rates occurring in spring as opposed to summer.

The GYA has been the focus of several ecological assessments of the response of ecosystems to changing N_r deposition levels (Spaulding et al., 2015; Nanus et al., 2017). Figure 10~~9~~ presents the source attribution results for 10~~ten~~ sites within the GYA where either ecosystem response studies or deposition monitoring ha~~s~~ve been conducted for lichen diversity, alpine lake chemistry, and snow pack analysis. In Table 2, the ~~critical load (~~CL~~)~~ values are provided as a range of lower~~–~~end and upper-end estimates of the annual total inorganic N_r deposition values (Lynch et al., 2015) with confidence levels (Pardo et al.,

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2011).~~,~~) The simulated N_r deposition exceeded the lower CL values at three~~3~~ of the 10 sites, specifically, ~~Tower Falls,~~ Holly Lake, ~~and~~ Pinedale, and Tower Falls.~~,~~ Comparatively, the 2011 TDEP N_r deposition results exceeded the CL in 6 out of 10 sites (Black Joe Lake~~sites at Pinedale, Holly Lake Twin Island~~, Biscuit Basin, Holly Lake, Jedediah Smith Wilderness, Pinedale, and Twin Island~~Black Joe Lake~~). As shown in Figure 10~~9~~, the sites that exceeded the CL tend to be in high-~~-~~alpine locations, with four of these sites on the western slope of the mountains, which are downwind of the Snake River valley. These results are consistent with another modeling study to access CL exceedances in Class I areas using GEOS-Chem (Ellis et al. 2013; Lee et al., 2016). In addition, in one study (Nanus et al., 2017) over 30% of the GYA was estimated to potentially exceed lower N_r deposition CL thresholds, with the greatest impacts in sensitive high-~~-~~elevation basins, including areas within national parks~~National Parks~~ and w~~W~~ildernesses.

In terms of emission sectors and source regions contributing to the total annual N_r deposition at CL exceedance sites, emission sources from the Snake River valley were the largest contributors (27–32%).~~%)~~ and AG emissions were the largest source of this subset. The next three largest contributors were transport from the BC (23–25%) and emissions from northern Utah (8–15%) and California (7–8%). Wyoming emissions associated with the OG and Fire emission sectors contributed around 3–5% and 14–23%, respectively, of the N_r budget for receptor sites at the southeastern corner of the GYA.

5. The influence of model bias on source apportionment results

It is evident from the results in section 4 that the attribution of total N_r deposition to source ~~the source~~ regions and sectors is~~are~~ sensitive to NH_3 dry deposition rates; the relative contributions of dry and wet deposition; and the concentrations of N compounds from the BC. However, the model evaluation revealed a significant underestimation of NH_3 concentrations and overestimation of HNO_3 concentrations and precipitation rates; thus, these modeling errors could bias the source attribution results. To better understand the potential effects of these biases, sensitivity analyses of the source attributions to changes in NH_3 dry deposition rates and average precipitation rates as well as potential biases in the BC were evaluated.

To test the sensitivity of the apportionment to NH_3 dry deposition rates, the deposition velocities were reduced by increasing the NH_3 resistance scaling factor by 10%, following the methodology used in Thompson et al. (2015). The Zhang et al. (2003) dry deposition scheme was used in the CAMx simulations (Table S1), and this resistance scaling factor is designed to address the rapid removal of "sticky" compounds such as HNO_3 and NH_3 and can yield a nonlinear response in the estimated dry deposition velocity. July and August 2011 were simulated using the modified deposition velocity, and these results will be referred to as "DV_0.1". The 10% change in the resistance factor slowed the NH_3 deposition velocity from 2.5~4 cm s^{-1} to 1~1.5 cm s^{-1} over the GYA, resulting in values more comparable to those used in the GrandTreNDS study (Benedict et al., 2013a; Prenni et al., 2014). The simulated NH_3 concentrations for the DV_0.1 case increased throughout the GYA compared to the base case. This resulted in ~~a~~ better agreement with NH_3 measurements at the Grand Targhee and NOAA Climate Station sites but

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poorer agreement at the Driggs monitoring site (Figure S5). The slower dry deposition velocities result in a longer NH_3 lifetime, allowing it to travel farther from nearby source regions, e.g., the Snake River valley, into the GYA, and cause a more homogeneous concentration pattern throughout the GYA (Figure S6). As shown in Figure 11~~10~~, the slower deposition velocities also somewhat altered the source attribution results. The contribution from the AG emission sector increased with the DV_0.1 simulation to 23% compared to 19% in the base case, with a smaller decrease in the contributions from the Other and the Fire sectors. This change was due to small increases in the contributions from the Snake River valley and northern Utah and decreases from Wyoming. Overall, decreasing the NH_3 dry deposition rate by about a factor of 2 had only a small impact on the N_r deposition budget and source apportionments results in the GYA. It is important to note that, although this was a significant reduction in the simulated dry deposition velocity for NH_3, it still represents a relatively rapid removal rate as compared to other species, and NH_3 is quickly lost from the atmosphere in either case. It is known that NH_3 deposition in many environments is a bidirectional as opposed to a unidirectional process, and modeling the NH_3 flux as a bidirectional process may further decrease the bias for ambient NH_x ~~($NHx=NH_3+PNH_4$)~~ concentration simulations (Bash et al., 2013; Wen et al., 2014; Whaley et al., 2018). The key process in air quality models to represent the re-emission of NH_3 from soil and plants to the atmosphere is the estimation of the available soil NH_x pool and the parameterization of compensation points for the conditions to re-emit NH_3 (Zhang et al., 2010; Whaley et al., 2018). In the CMAQ model, the bidirectional NH_3 deposition was realized by coupling with the United States Department of Agriculture's (USDA) Environmental Policy Integrated Climate (EPIC) agroecosystem model to provide the fertilization timing, rate, and composition (Bash et al., 2013). There is no similar parameterization available in the current CAMx model. Furthermore, the CAMx source apportionment tools cannot properly account for the origin of NH_3 concentrations at a receptor that has been deposited then re-emitted.

The CAMx simulation overestimated the wet N_r deposition at measured sites, which was likely associated with an overestimation in the precipitation rates from WRF, especially at high-elevation sites. This precipitation rate bias was large, with the annual precipitation over the GYA more than 73% higher than the PRISM estimates. We used the Noah land-surface model and Kain-Fritsch scheme cumulus parametrization in the WRF simulations (Table S1), and those physical module configurations were reported to have the tendency to overestimate precipitation (Warrach-Sagi et al., 2013). To evaluate the impact of the overestimation in precipitation on the source attribution results, the seasonal wet deposition rates were scaled to the measured precipitation rates at all NADP-NTN and GrandTReNDS monitoring sites, following the procedures by Appel et al. (2011). This was equivalent to scaling the modeled wet deposition rates by the ratio of the measured to modeled precipitation rates. This approach assumes that the concentrations of N_r in the precipitation were the same in the model and measured data, which was not the case. After the precipitation adjustment, the correlation between the simulated and measured N_r wet deposition improved (Figure S7). Within the GYA, however, the scaled N_r wet deposition underestimated

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the measured by about a factor of 2 and significantly underestimated the ratio of wet to dry deposition. Consequently, scaled wet deposition results were not used in this assessment. The overestimation of HNO_3 concentrations in the GYA is another reason for the wet N_r deposition overestimation. However, its impact on source apportionment results was not conducted here due to unclear reasons for the model bias (emission, chemistry, meteorology, deposition scheme) and limited computational resources.

The BC used in this work was derived from a MOZART global model simulation. An alternative set of BC from the GEOS-Chem global model was also evaluated. Both sets of BC resulted in high contributions to the total N_r deposition in the GYA, with the GEOS-Chem results having a slightly higher average contribution of 23% compared to 21% for MOZART (Figure S8). However, the GEOS-Chem BCs resulted in higher relative contributions of oxidized N to the total N_r deposition rate compared to the MOZART BCs (51% and 45%, respectively). The poor correspondence in the oxidized to reduced N_r split is reflective of the large uncertainties in the BC contributions to the N_r deposition and suggests that more evaluation of the global model results is warranted.

To examine the potential bias in the BC contributions, the simulated PNO_3 concentrations were compared to measurements from the IMPROVE monitoring program over the western United States for 2011. This comparison is shown in Figure 1211, where the ratio of the simulated to measured PNO_3, i.e., an estimate of the bias, is plotted against the relative fraction of the contribution of the BC to the simulated PNO_3. The data were first segregated by the fractional contribution of the BC and then averaged together. As shown, for the MOZART BC, the bias increased with larger relative contributions from the BC, and when the BC fraction wasis 60%, the bias was more than a factor of 2. This suggests that at least the particulate nitrate concentrations from the BC are overestimated and possibly other N_r compounds from the BC as well. In a CMAQ simulation using BC derived from a GEOS-Chem simulation, Baker et al. (2015) also found that the contributions from the BC to PNO_3 were overestimated when compared to IMPROVE data.

6. Summary and Discussion

The CAMx model and its PSAT source apportionment tool were used to examine and quantify the contributions of four different source sectors and 27 source regions and the boundary conditions (BC) to the 2011 total inorganic N_r deposition within the GYA. The source sectors were agriculture (AG), oil and gas activities (OG), wild and prescribed fires (Fire), and remaining contributions labeled as "Other". The Other sector was primarily composed of oxidized N originating from anthropogenic combustion sources, including mobile and point sources, and the AG sector was almost entirely composed of reduced N compounds. Fires and the BC were a mix of reduced and oxidized N compounds. This assessment focused on only the inorganic N fraction. There is measured evidence that organic N (Prenni et al., 2014; Benedict et al., 2013a; Prenni et al., 2014) is a significant contributor to N_r deposition, and the inability to assess its origin in the current CTM is an important uncertainty in this work. Nevertheless, this N_r source apportionment work is the first thorough analysis of the origin of inorganic N_r in the GYA using a regional

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air quality modeling platform. The detailed source sector and source region configurations in PSAT enabled quantitative, though uncertain, estimates of their relative importance. This is needed information by stakeholder and regulators to understand the causes of excess Nr deposition in the GYA, monitor changes in Nr deposition and develop possible future mitigation strategies..

Overall, the model simulation had a reasonable capacity to reproduce the measured seasonal and annual total N_r deposition levels throughout the GYA. However, the model simulation underestimated the~~available~~ measured NH_3 concentrations by 65% on average~~,~~ and ~~measured HNO_3 concentrations were~~ overestimated the measured HNO_3 by 108%. Therefore the model tended to overestimate the contributions from~~contribution of~~ oxidized N compounds and underestimate those from reduced N compounds to ~~the~~ total N_r deposition. In addition, both reduced and oxidized N_r wet depositions were overestimated by 20–30%, which was due, at least partially, to the simulated precipitation frequency and magnitude being too high in the model. These biases suggest that the modeled contributions from the AG emission sector were underestimated, while those from the Other sector's activities were overestimated.

The simulated annual total N_r deposition over the GYA in 2011 was 3.13 kg N ha^{-1} yr^{-1} and exceeded the CL estimates for lichen and lake chemistry primarily at high--elevation sites on the western slope and southern portion of the GYA. This finding is consistent with other studies using global models. Ellis et al. (2013) used the GEOS-Chem model to estimate the N_r deposition to Class I areas for 2006 and showed that the simulated total N_r deposition at GTNP (2.9 kg N $ha^{-1}yr^{-1}$) and YNP (2.6 kg N $ha^{-1}yr^{-1}$) exceeded the low end of CL for lichens (2.5 kg N ha^{-1} yr^{-1}).

Emissions from the AG sector within the modeling domain were the largest contributor to the GYA total N_r deposition budget at 34% per year. The contributions from the Other sector were also large at 26%. The OG emission sector generally had a small contribution, except at the southern edge of the GYA, where it could contribute over 10% of the total N_r deposition during winter months, with almost half of the OG contributions originating from emissions in the neighboring Jonah Field in western Wyoming. The Fire emission sector also had a significant contribution of 18% over the year. This was due to regional contributions from fires throughout the West and large contributions (>90%) at areas within the GYA where several wildfires occurred (Figure 8~~7~~). The large impact from fires within the GYA is notable since the episodic nature of fire will result in differing year-to-year contributions from this uncontrollable sector.

The largest impact from the AG emission sector originated from sources relatively close to the GYA, and the Snake River valley accounted for 74% of the annual agricultural contribution. The agricultural contribution from Wyoming was 7%, and more-distant source regions in northern Utah, California, and the northwestern United States each accounted for 4–5% of the agricultural contribution. Nearly half (45%) of the N_r deposition from the OG emission sector originated within Wyoming, especially the Upper Green River (27%). The largest impact from the Fire emission sector~~, including wildfire and prescribed fires,~~ originated from Snake River valley (33%) and within the GYA (25%). The Other emission sector was more evenly distributed among near and distant regions, with the Snake River valley accounting

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for 23%, Wyoming 17%, and northern Utah, California, and the northwestern United States accounting for 14–16% of the N_r deposition.

Long-range transport of N species from the BC, which primarily originated from international sources, contributed 21% of the total N_r deposition within the GYA during 2011 and had the largest absolute contribution during the summer. Several studies have shown the importance of international source contributions to particulates and N deposition within the continental United States (Park et al., 2004; Brewer and Moore, 2009; Zhang et al., 2012; Fann et al., 2013; Baker et al., 2015; Thompson et al., 2015). However, the BC contribution in this work is on the high end of the reported values. For example, in a similar modeling study by Thompson et al. (2015), the estimated contribution of BC to N_r deposition in Rocky Mountain National Park in 2009 was 13%. Zhang et al. (2012) used the GEOS-Chem model to evaluate N deposition in the United States during 2006–2008 and showed that foreign anthropogenic contributions were generally <~~less than~~ 10% but could rise up to 30% near the Canadian and Mexican borders. In addition, our evaluations of the BC suggest that the contribution of the BC to ambient PNO_3 and possibly other N_r compounds was overestimated (Figure 12~~11~~), clearly suggesting that more research is needed on the role of distant emission sources on impacting N~~nitrogen~~ deposition in remote areas, as well as further investigations into model biases.

The observed precipitation in 2011 was ~30–50% higher than the historical average (NOAA, 2012)~~.~~, with the largest bias occurring at the eastern sites in the GYA (Figure S9). This suggests that dry deposition of NH_3 may be a more ~~-~~important contributor to total N_r deposition during spring than that observed during GrandTReNDS. Also, considering that the wet deposition in the GYA tended to be overestimated and the precipitation amount in 2011 was anomalously high, the source regions identified as having a higher weighting on the annual wet N_r deposition budget (e.g., California) may not have such a significant impact as the current PSAT results suggested.

As discussed, source apportionment assessments of N_r and its deposition to remote, ecologically sensitive areas such as the GYA have large uncertainties. Many of these uncertainties are known to the air quality modeling community, including the challenges of simulating precipitation in complex terrain, adequately characterizing NH_3 emissions from agricultural operations, the occurrence of wildfires, and the difficulty in simulating the NH_3 bidirectional~~bi-directional~~ flux and the deposition flux of the other N_r compounds. Contributions from long-range transport of international emissions can also play a significant role in deposition in remote locations in the western United States. Further refinement in all of these areas is required to better understand and estimate the relative contributions of emission sources to excess N deposition within the GYA. Nevertheless, the modeling assessment showed that ~~the~~ reduced N contributed more than 50% of the total N_r deposition over the GYA, with >90% of the NH_3 emissions originating from agriculture sources. In addition, the Snake River valley in Idaho accounted for 74% of the agricultural contribution to the total N_r deposition. Significant contributions from more-distant sources, e.g., California, and international sources, to both ~~the~~ oxidized and reduced N_r deposition illustrate the regional nature of the N_r deposition problem. Emissions of oxidized N compounds are projected to continue to decrease,

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while emissions of ammonia are projected to remain relatively constant or increase (Li et al., 2016). This will further increase the importance of the AG sector. However, exceedances of CL are still relatively small, and it is possible that decreased oxidized N deposition could reduce the N_r deposition sufficiently to bring total Nr deposition below the CL in some GYA ecosystems.

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Figure 1. Source region partition for CAMx PSAT simulation in this study. The 27 tagged regions are: 1. NW Colorado, 2. NE Colorado, 3. SE Colorado, 4. SW Colorado, 5. Upper Green River, Wyoming, 6. Jackson, Wyoming, 7. Eastern Wyoming, 8. Western Wyoming, 9. Yellowstone, 10. Northern Idaho, 11. Snake River Valley, Idaho, 12. Northern Utah, 13. Southern Utah, 14. Nevada, 15. Montana, 16. Washington, 17. Oregon, 18. California, 19. Mexico, 20. New Mexico, 21. Arizona, 22. Texas & Okalahoma, 23. Canada, 24. North Dakota, 25., Pacific, 26. Far East U.S. 27. South Dakota, Kansas, Nebraska

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Figure 2. Annual NH_3 emission for the 12-km inner modeling domain at focused tagged regions (see Table S2 and Figure 1~~S2~~ for the details of the 27 source region partition) as well as locations of the monitoring sites at different networks ([a]Ammonia Monitoring Network; [b]Clean Air Status and Trends Network; [c]Grand Teton Reactive Nitrogen Deposition Study; [d]~~I~~nteragency Monitoring of Protected Visual Environments; [e]Nati~~a~~onal Trend Network) used in the model performance evaluation of CAMx nitrogen species concentration and dry/wet deposition in the GYA (the black boundary line). ~~The background map is the annual ammonia (NH_3) emission rate.~~ The numbers in the figure are locations for the three sampling sites during GrandTReNDS and the 8 Class I areas in within the area: 1. Driggs, 2. Grand Targhee, 3. NOAA Climate Station station, 4. Grand Teton National Park, 5. John D. Rockfeller Jr. Memorial Parkway, 6. Yellowstone National Park, 7. Teton Wilderness, 8. Washakie Wilderness, 9. North Absaroka Wilderness, 10. Fitzpatrick Wilderness, and 11. Bridger Wilderness.

Figure 3~~2~~. Model performance for (a-b) seasonal average N_r concentration, (c-d) seasonal accumulated N_r deposition budget as well as (e-f) seasonal accumulated precipitation amount at collocated location sites (YNP and Pinedale) over the GYA in 2011. [1]Clean Air Status and Trends Network; [2]Comprehensive Air Quality Model with extensions; [3]National Trend Network; [4]Parameter-elevation Relationships on Independent Slopes Model; [5]Weather Research and Forecasting model.

Figure 4~~3~~. Inorganic nitrogen deposition budgets in absolute (Figure 4a~~3a~~) and in percentage (Figure 4c~~3c~~), as well as precipitation (Figure 4e~~3e~~), measured at the three core sites during the GrandTReNDS study period (April to September in 2011) with corresponding CAMx simulations (Figure 4b~~3b~~, Figure 4d~~3d~~, and Figure 4e~~3e~~). [1]Grand Teton Reactive Nitrogen Deposition Study; [2]Comprehensive Air Quality Model with extensions; [3]Weather Research and Forecasting model.

Figure 5~~4~~. Annual nitrogen deposition budgets in absolute (Figure 5a~~4a~~) and in percentage (Figure 5b~~4b~~) as well as annual precipitation amounts (Figure 5c~~4c~~) from the NADP Total Deposition Map (TDEP) and corresponding CAMx (Comprehensive Air Quality Model with extensions) and WRF (Weather Research and

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Forecasting model) simulation results in 2011 at eight Class I areas across the GYA (the receptor sites on the x-axis are arranged from west to east in the GYA, see Figure 2~~1~~. The reported CAMx dry and wet N_r deposition values at the eight Class I areas are the average of the simulation values at corresponding grid cells for each area.).

Figure 6~~5~~. Seasonal CAMx simulated N_r deposition budgets averaged over the GYA in 2011. The left axis is the relative contribution of different N_r species to seasonal N_r deposition while the right axis is corresponding to the black diamonds for seasonal total N_r deposition in absolute (kg N ha^{-1}).

Figure 7~~6~~. Contributions of source sectors to the mean total N_r deposition, dry N_r deposition, and wet N_r deposition over the GYA at different seasons in 2011. Figure 7a~~6a~~ is the source sectors contributions in absolute and Figure 7b~~6b~~ is the corresponding contributions in percentage.

Figure 8~~7~~. Seasonal patterns of different source sectors' (agriculture, oil and gas activities, fires, others (e.g., anthropogenic, biogenic, lightning, and boundary conditions) contributions to total N_r deposition over the GYA in 2011.The first column is the seasonal total N_r deposition patterns in Kg N ha^{-1} while the following five columns are the seasonal patterns of relative contributions from different source sectors.

Figure 9~~8~~. Contributions of source regions to the mean total N_r deposition, dry N_r deposition, and wet N_r deposition over the GYA at different seasons in 2011. Figure 9a~~8a~~ is the source regions contributions in absolute and Figure 9b~~6b~~ is the corresponding contributions in percentage.

Figure 10~~9~~. Contributions of different source sectors as well as boundary conditions for total N_r deposition in 2011 at 10 points of interest for critical load exceedance (see Table 2 for site locations and ecosystem impacts). The black-and-white pies are the contributions by source sectors while the color pies are the contributions by source regions. The color contour for the GYA boundary is the terrain heights with the legend at rightmost.

Figure 11~~10~~. The sensitivity of NH_3 dry deposition velocity (left: "base" case, right: "DV_0.1" case with NH_3 dry deposition velocity slowing down) to source apportionment results over the GYA during July–August 2011. Figure 1~~0~~a and 1~~0~~c are the contributions by source regions in absolute and in percentage while Figure 1~~0~~b and 1~~0~~d are the contributions by source sectors.

Figure 12. Ratio~~**11. The ratio**~~ of simulated versus measured particulate nitrate (PNO_3) concentrations against the boundary contributions to simulated PNO_3 at IMPROVE sites over a 12-km domain.

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[1]Model for Ozone and Related chemical Tracers; [2]Interagency Monitoring of Protect Visual Environments.

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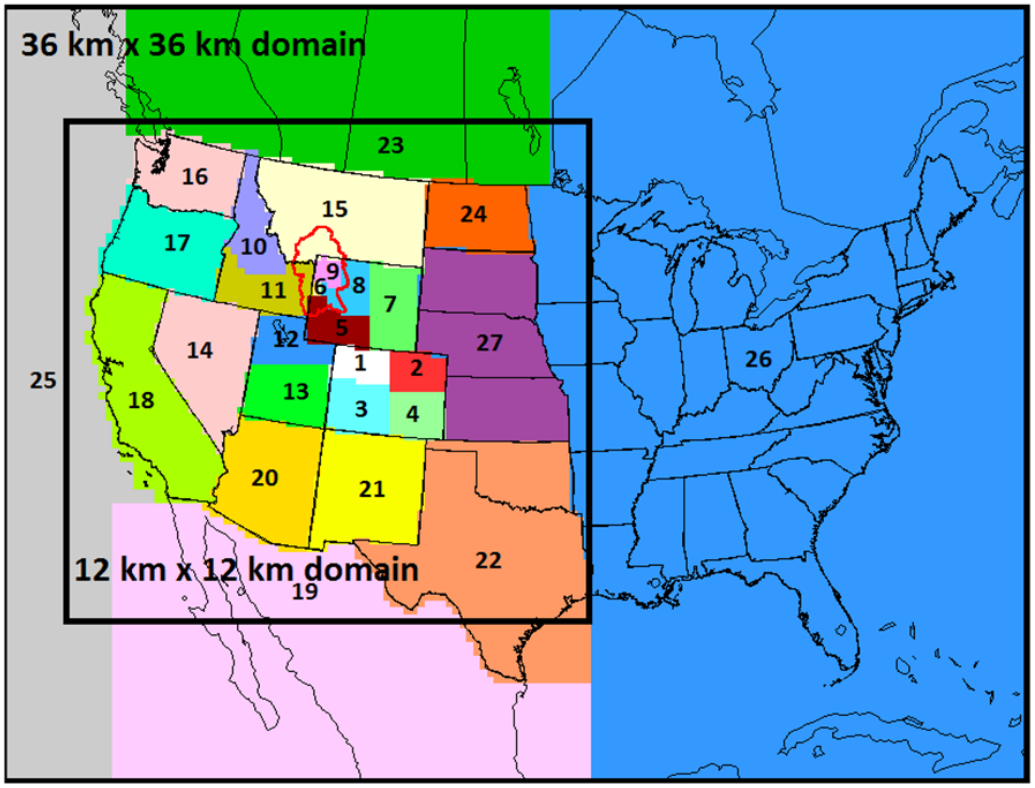

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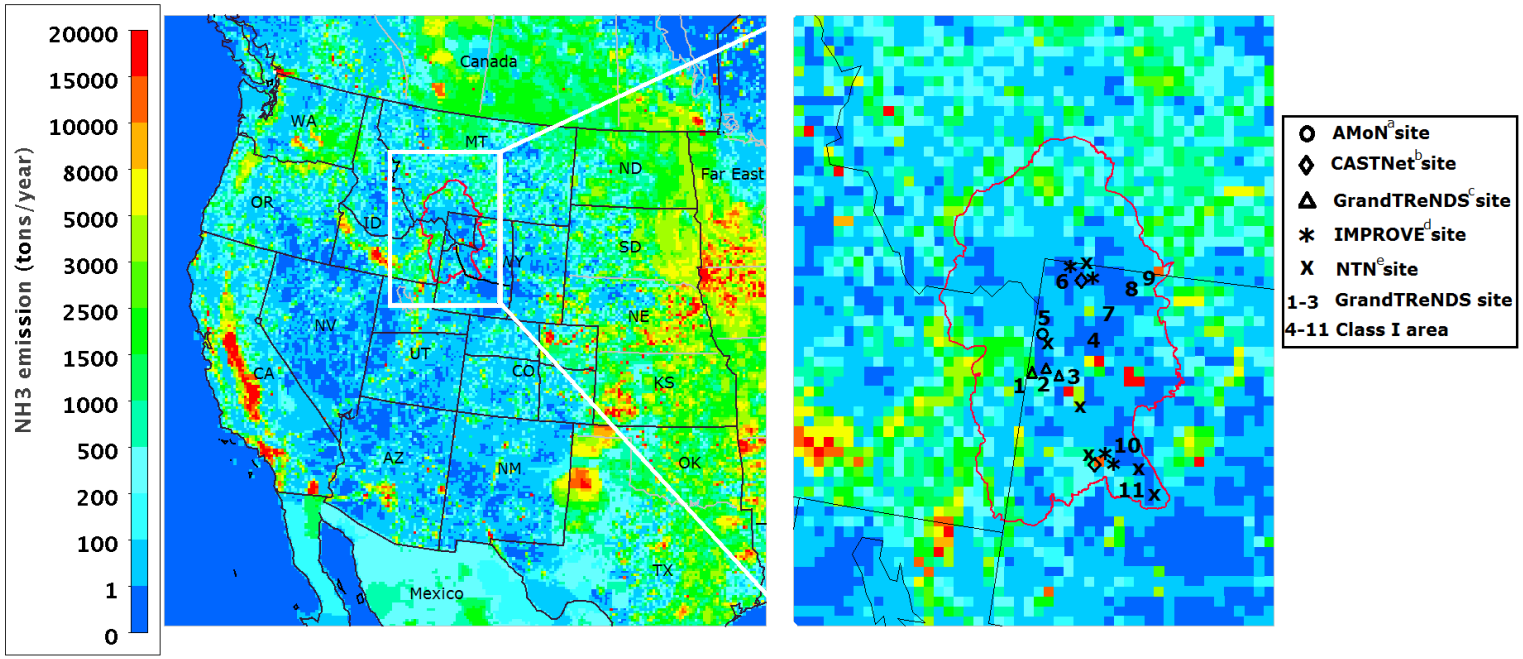

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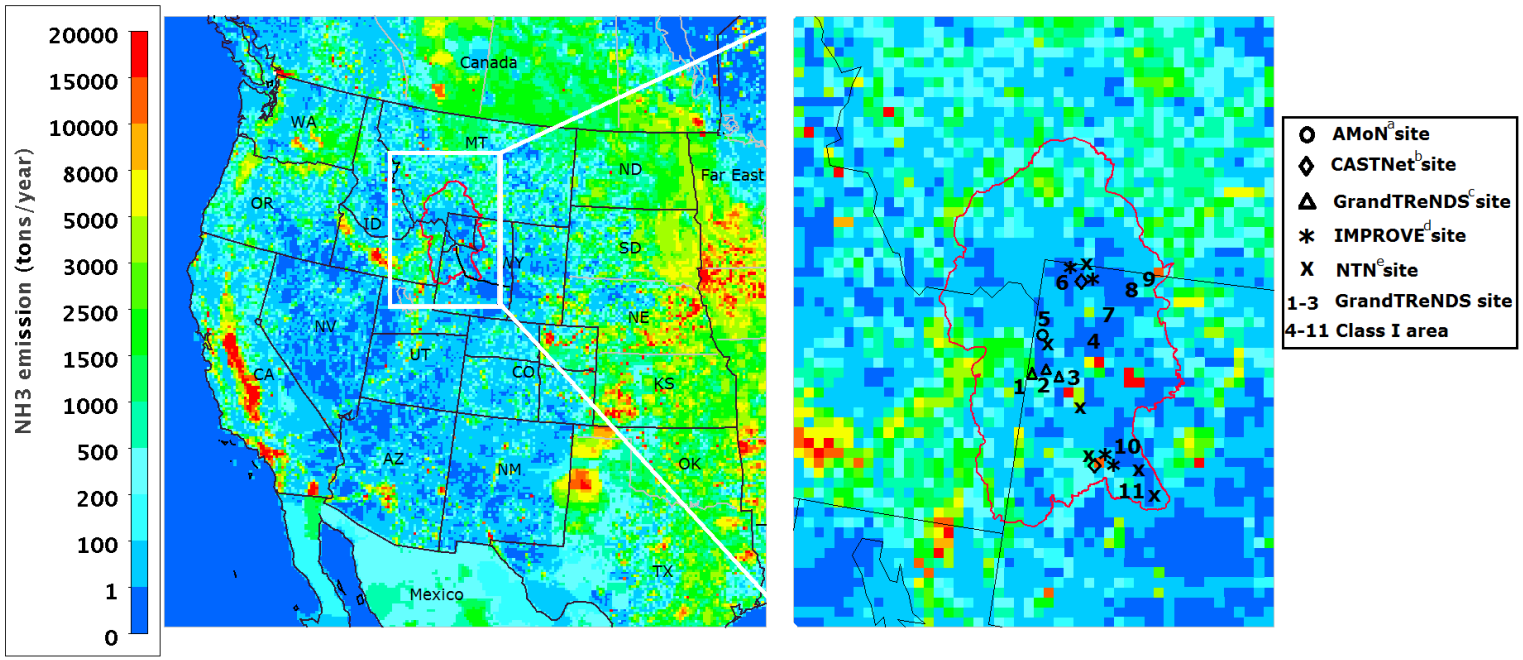

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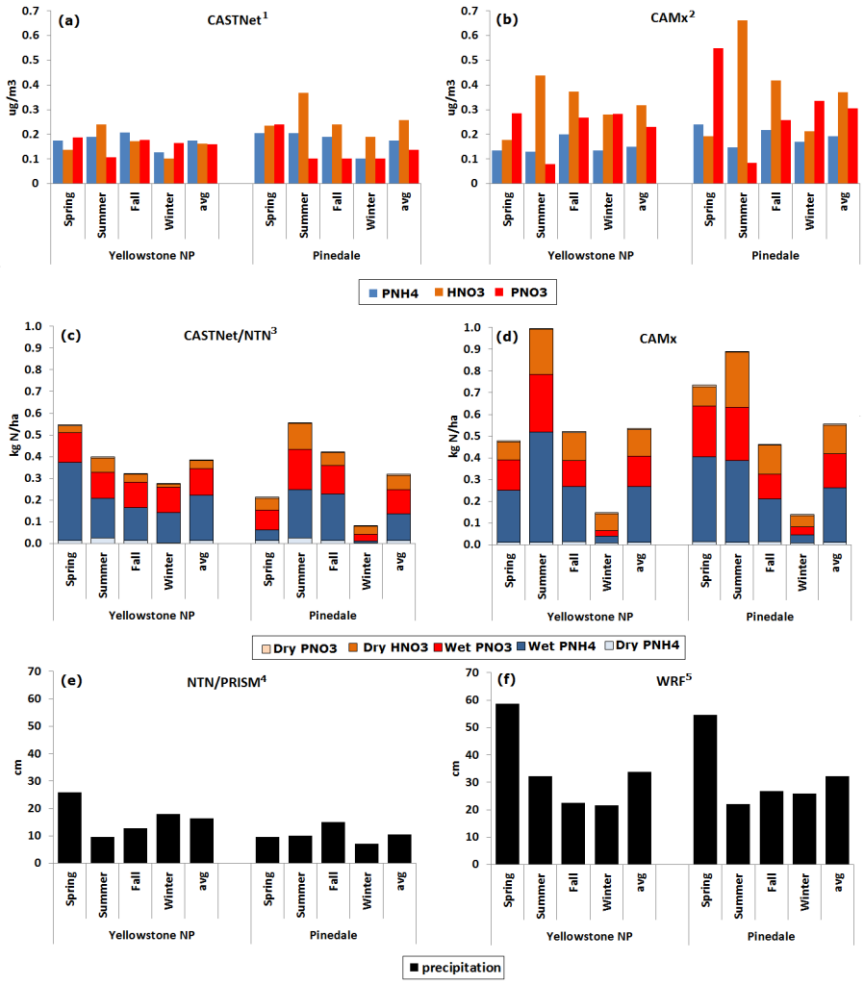

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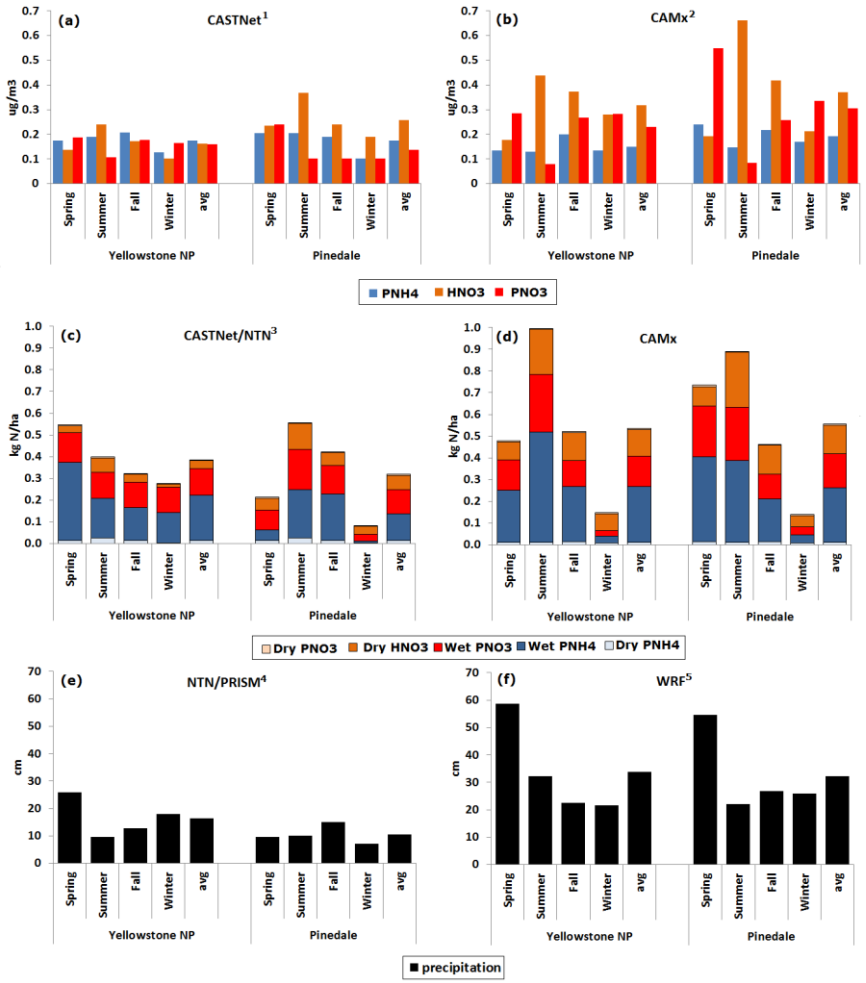

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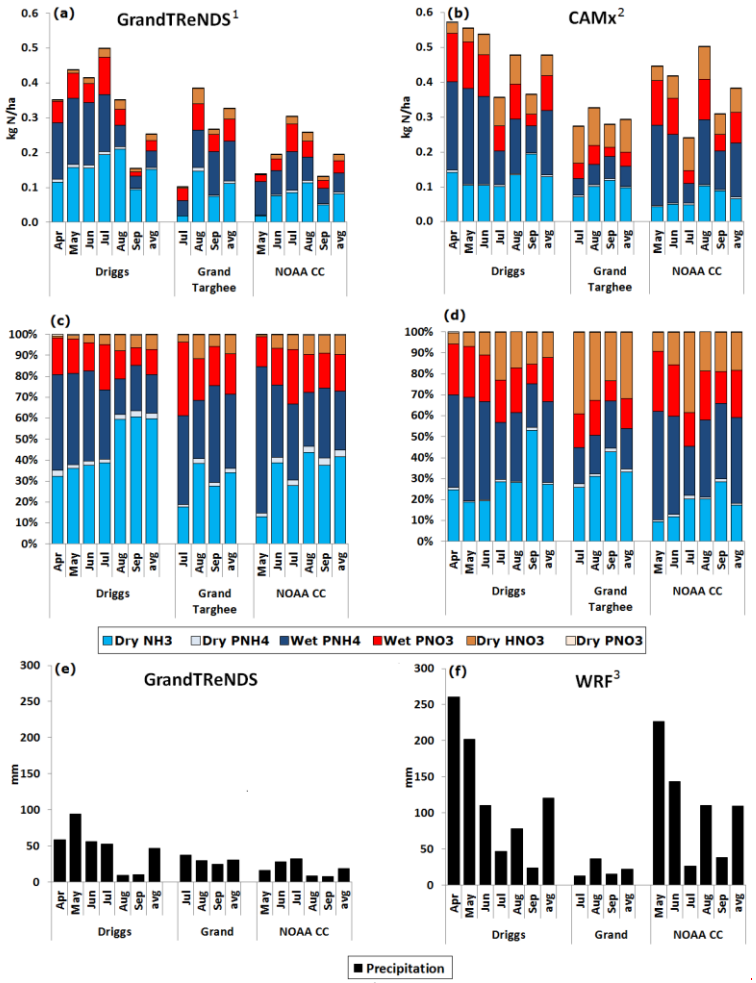

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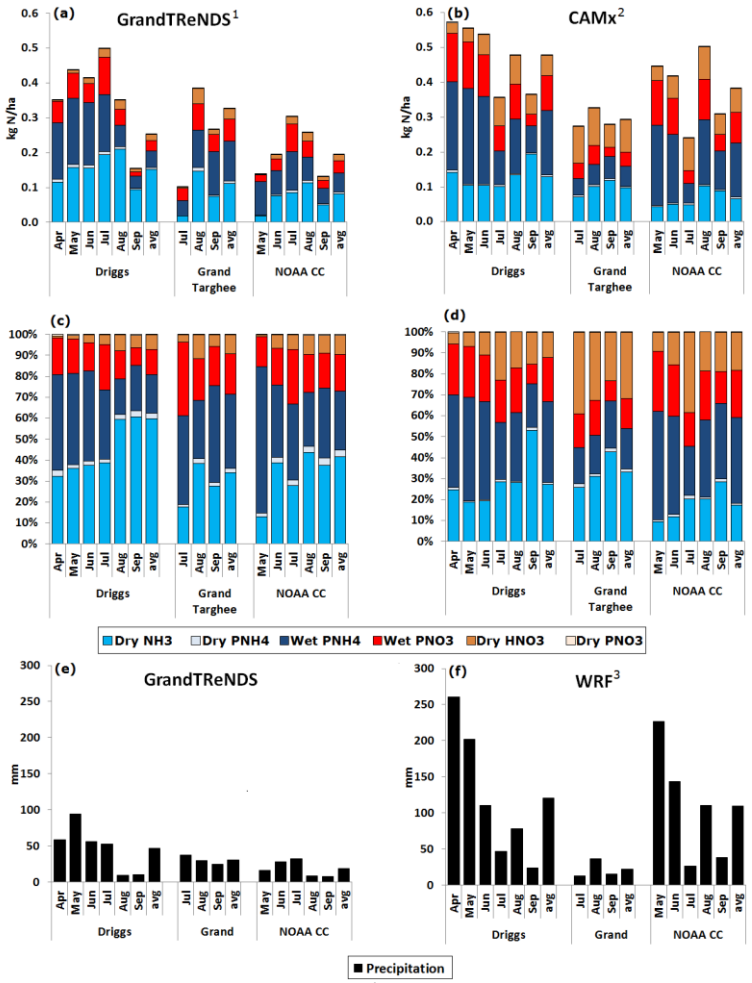

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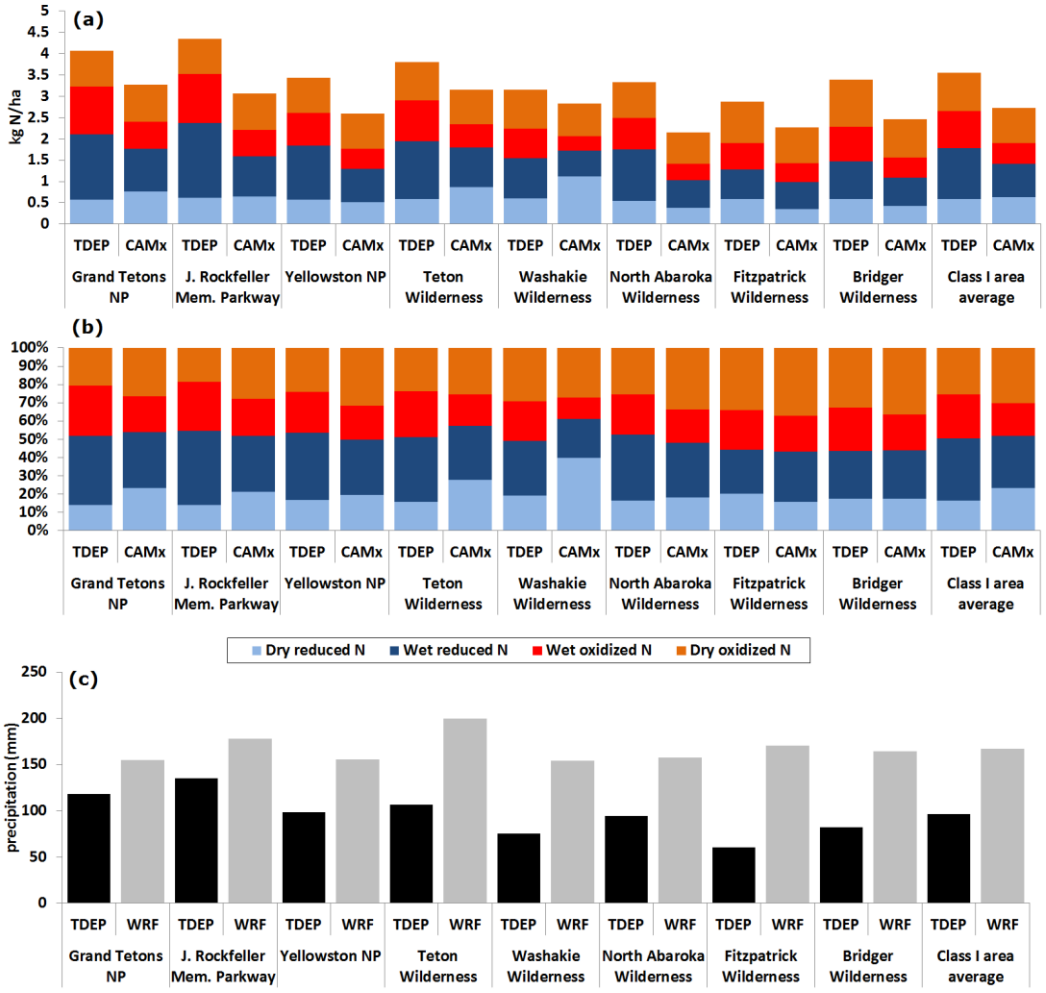

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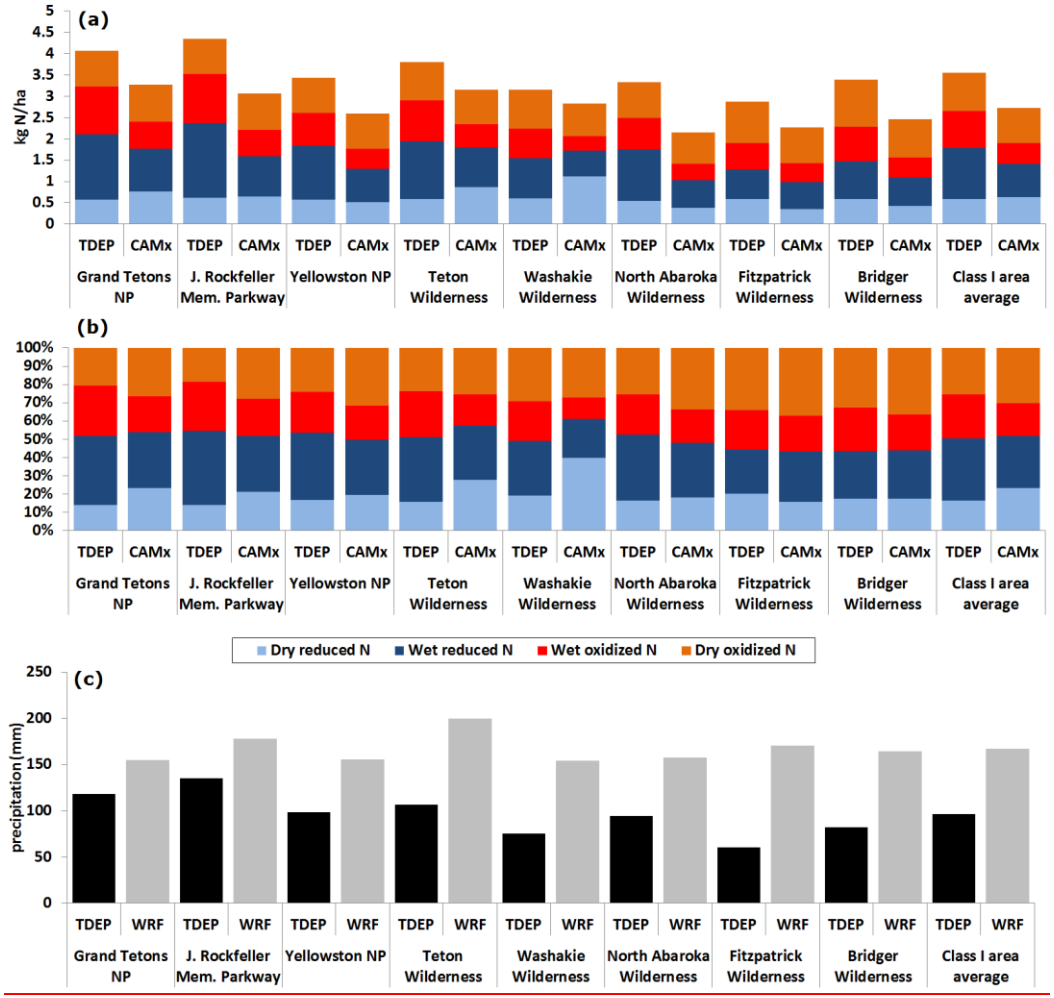

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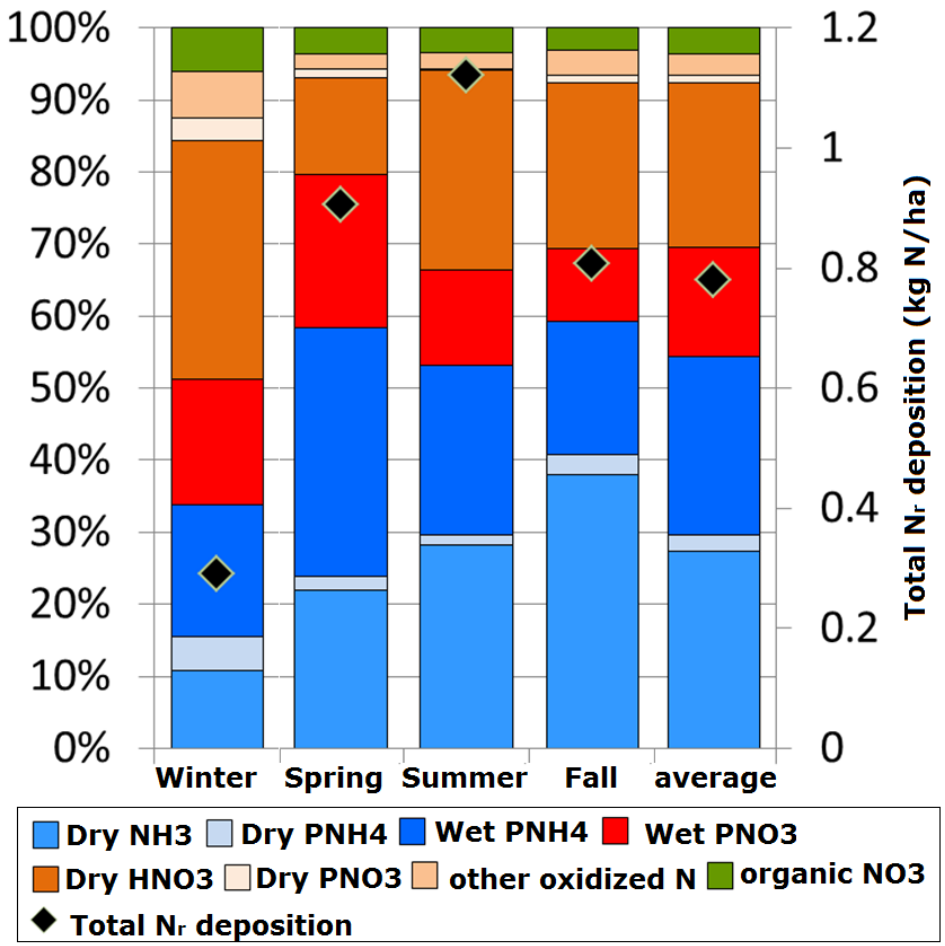

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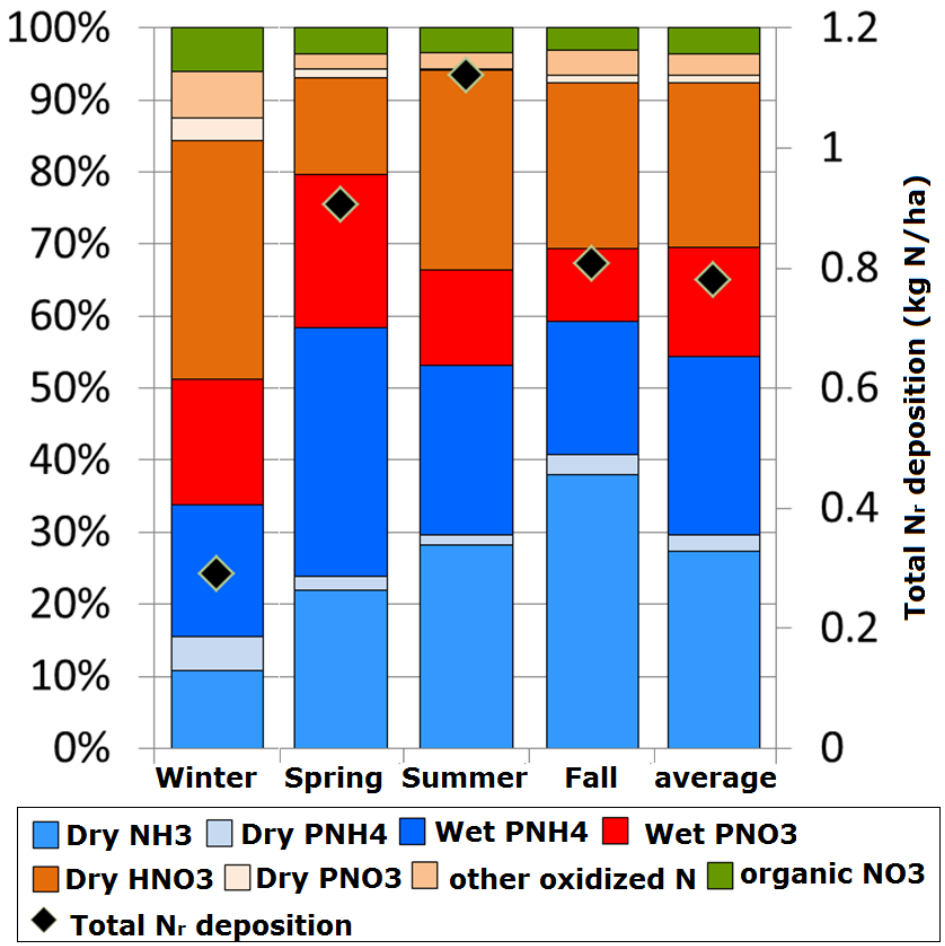

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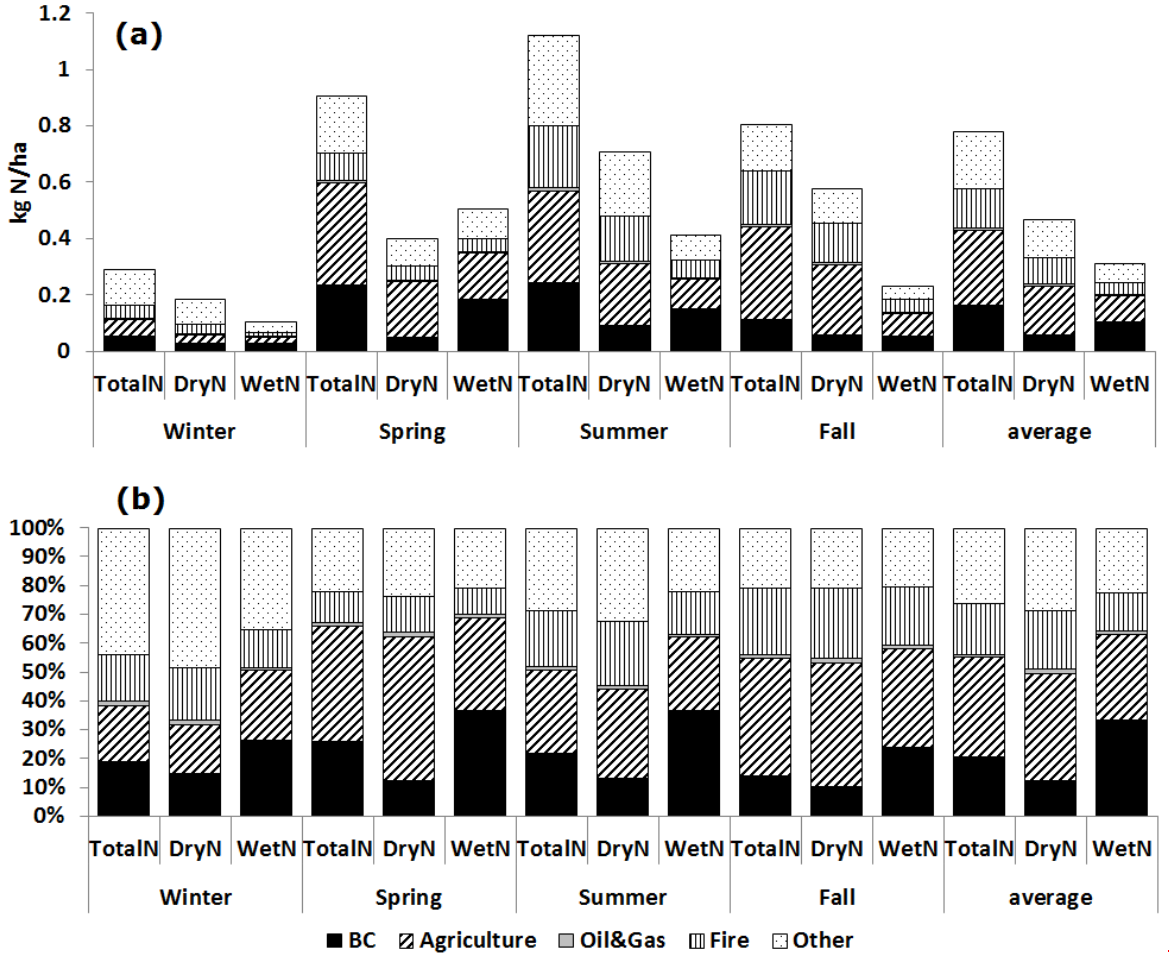

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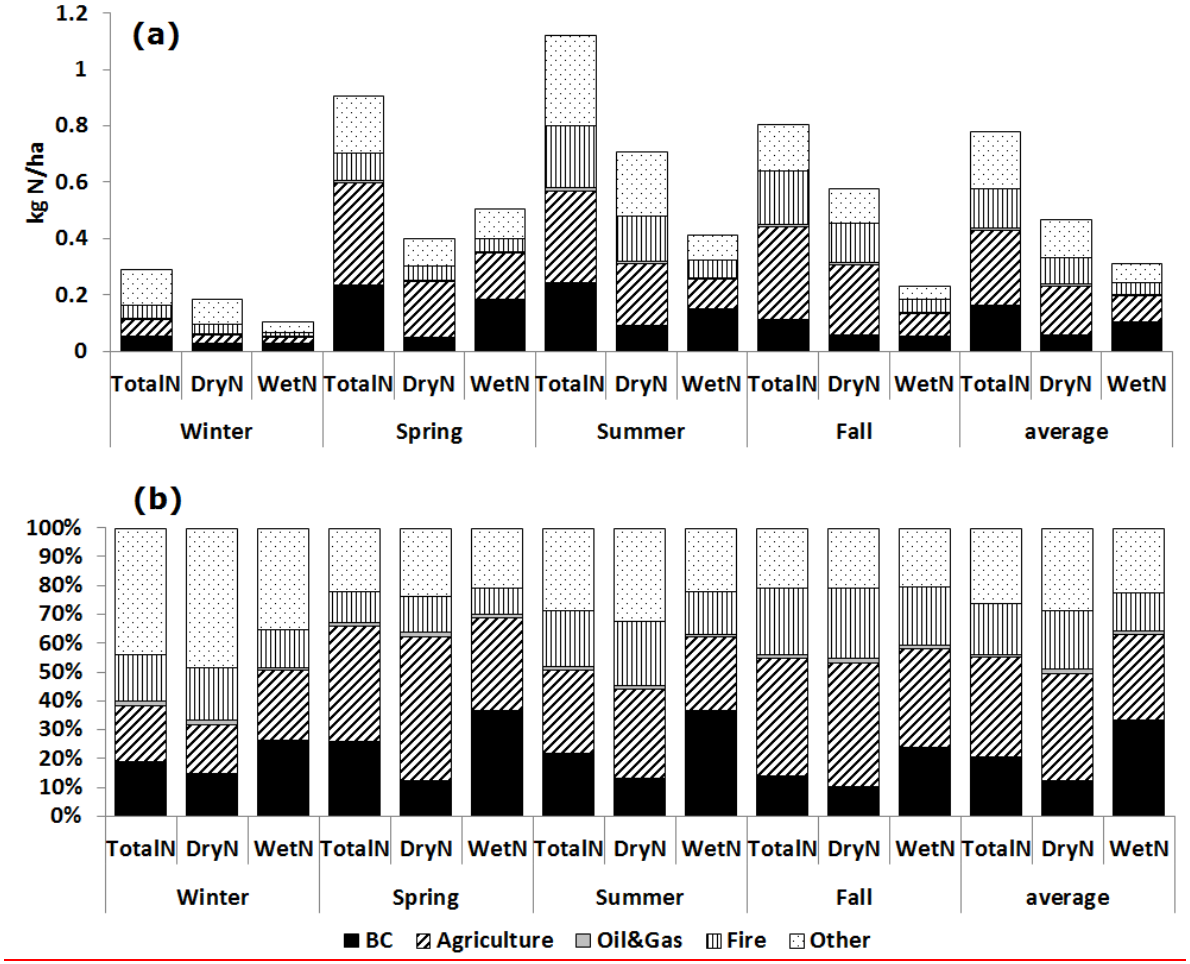

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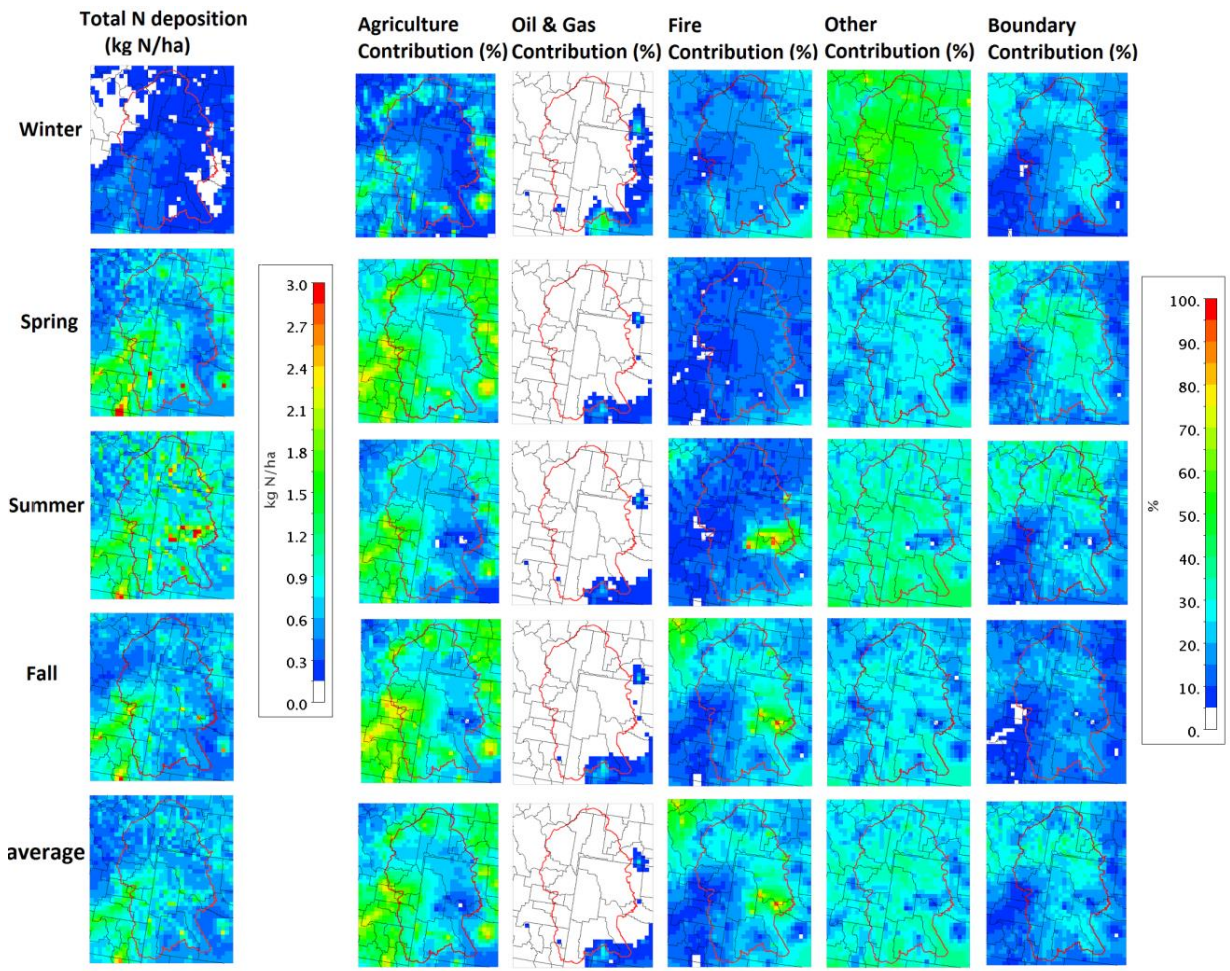

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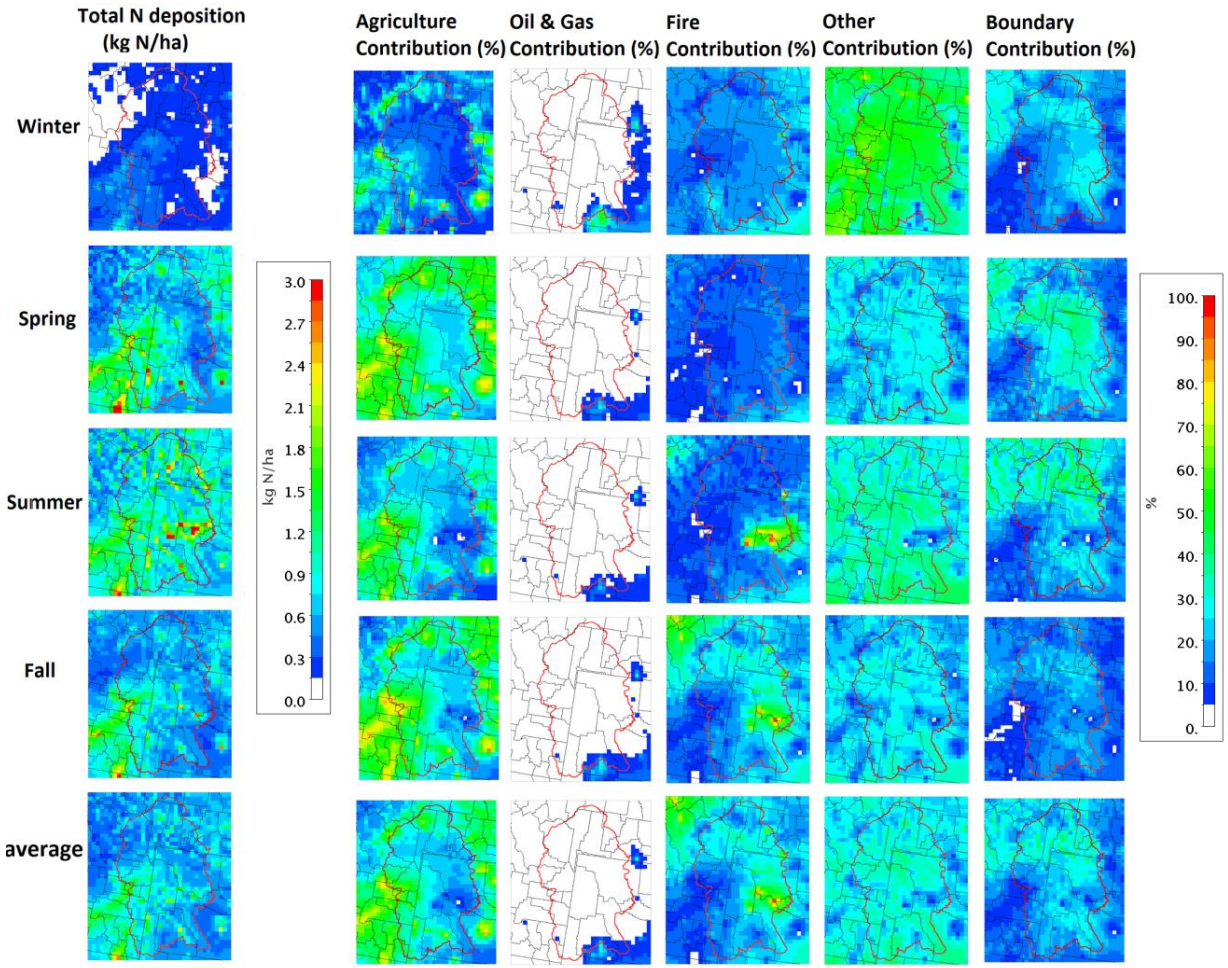

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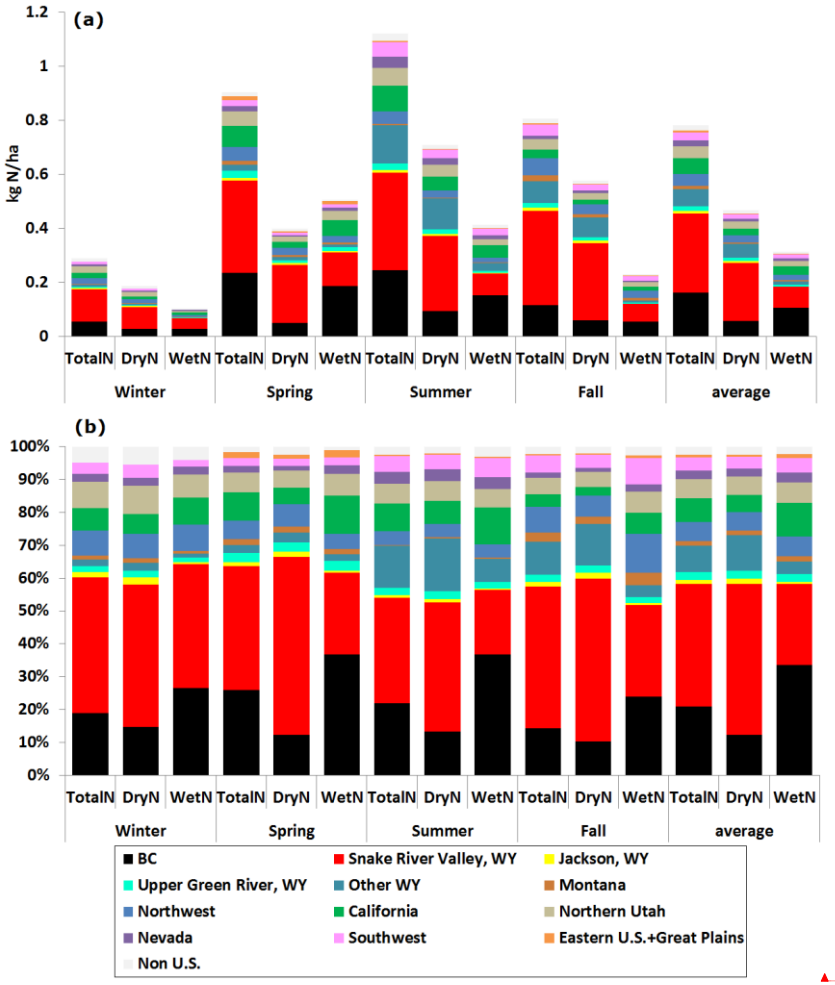

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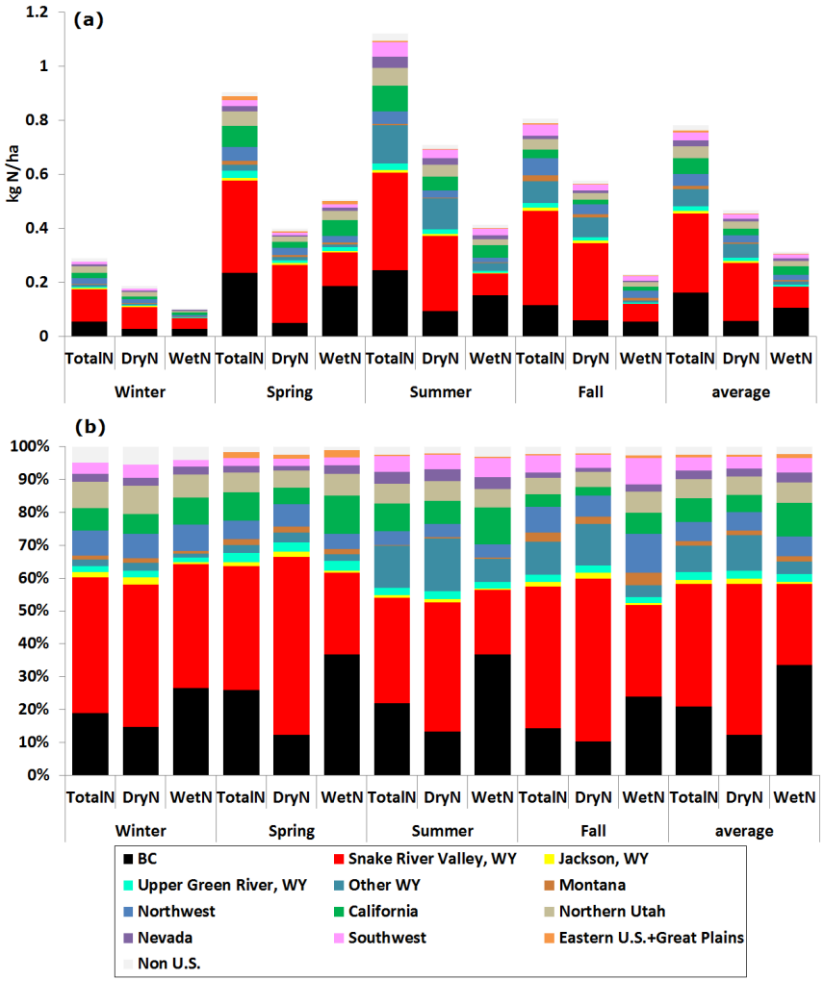

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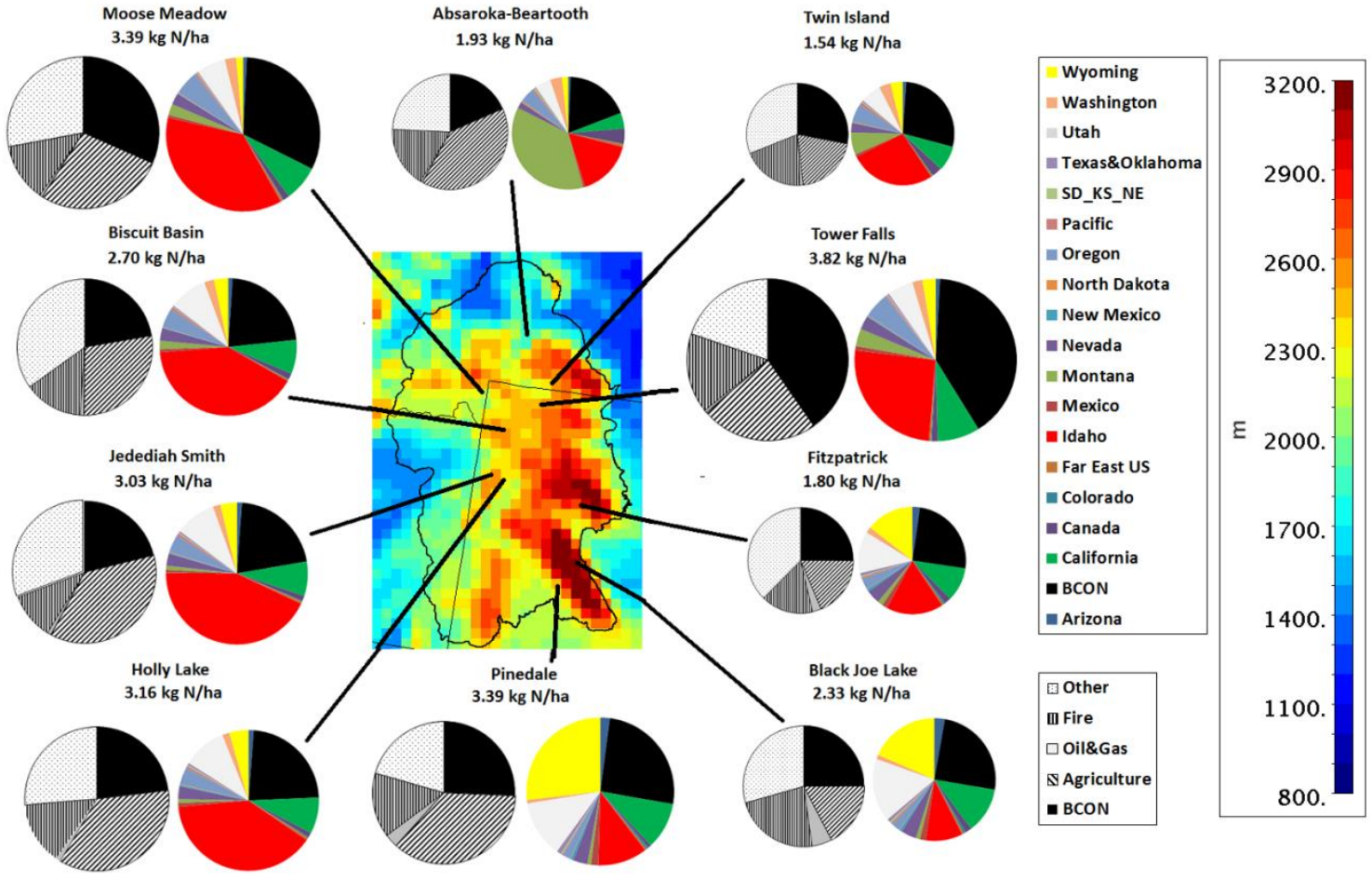

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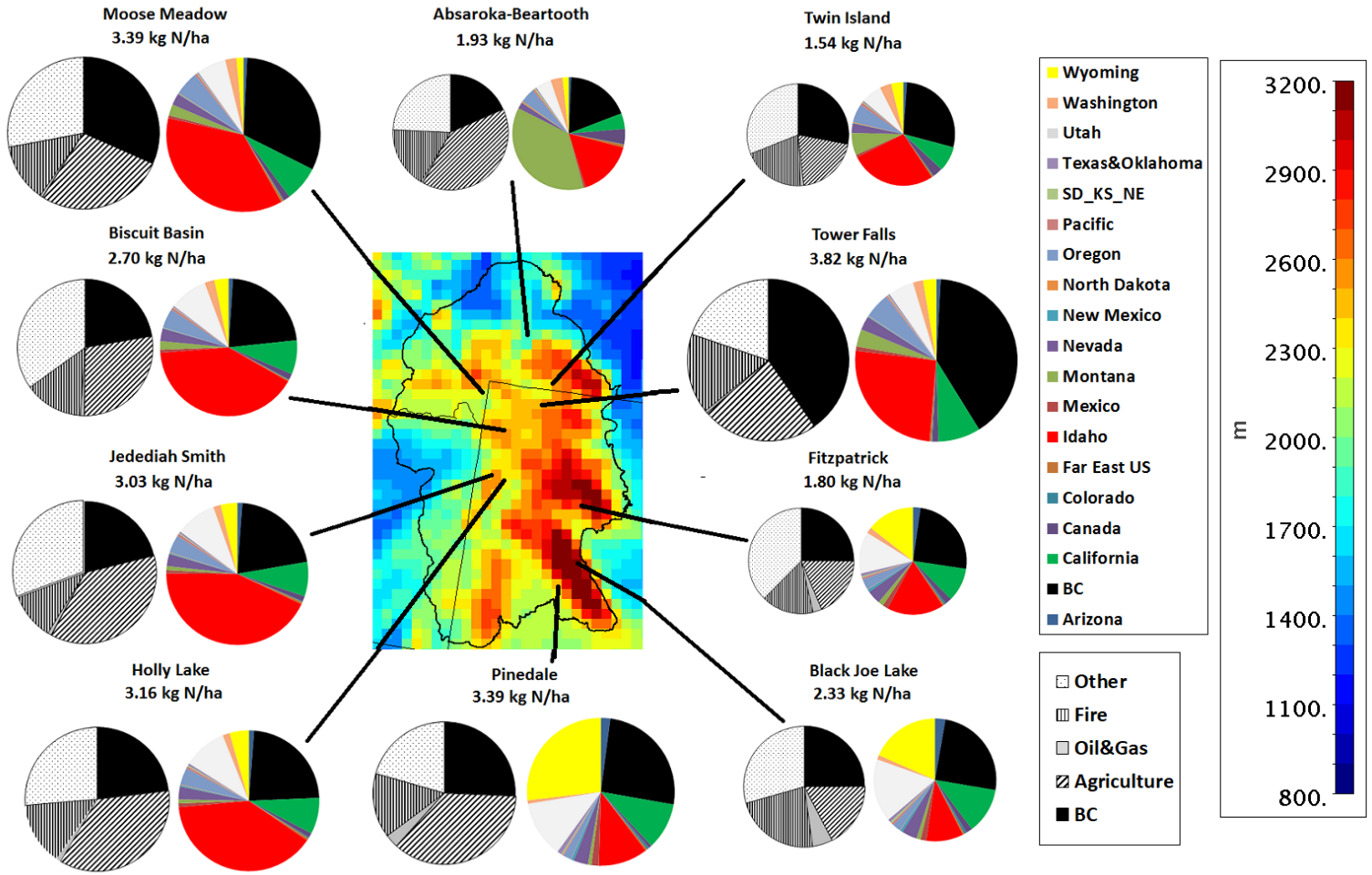

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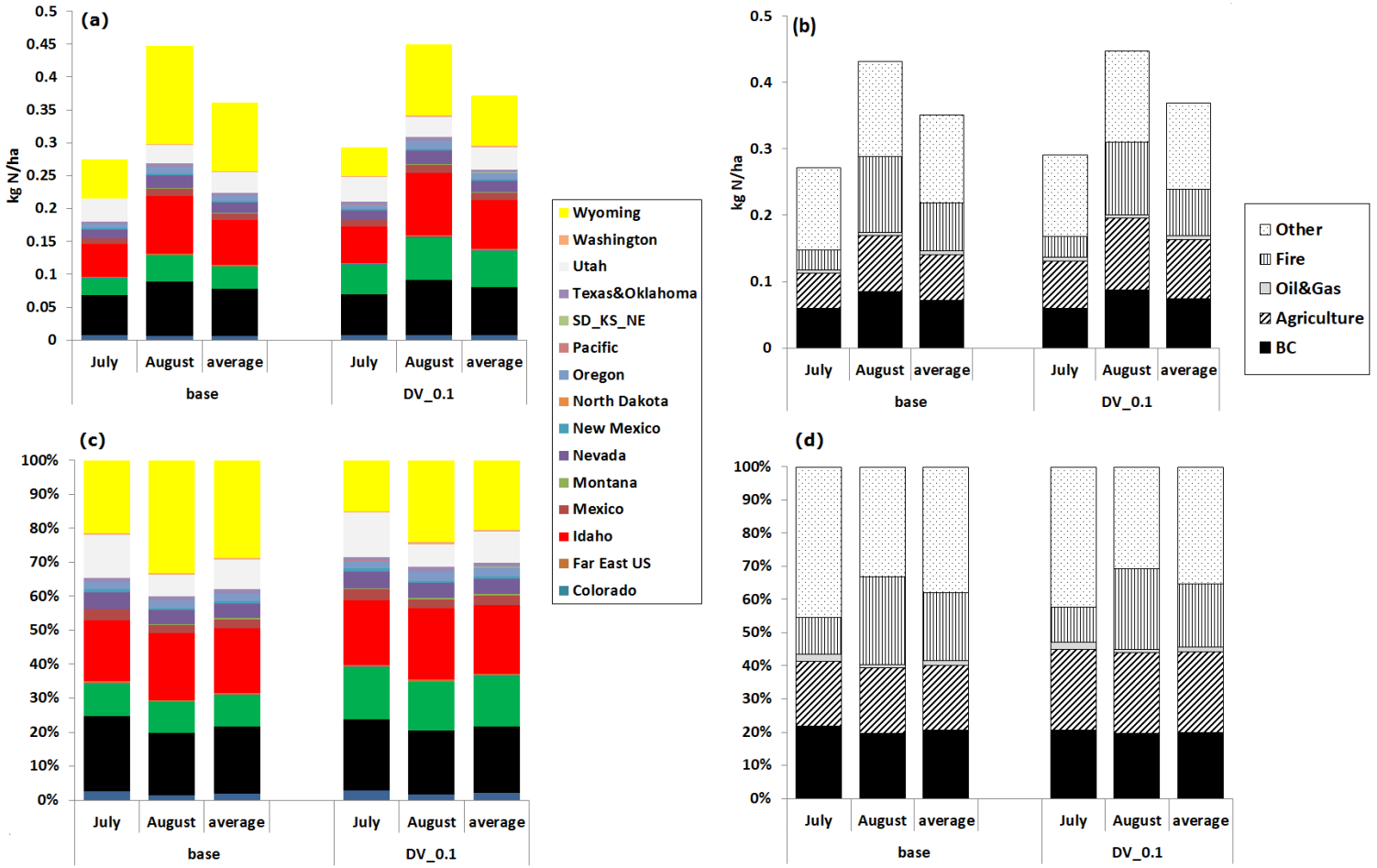

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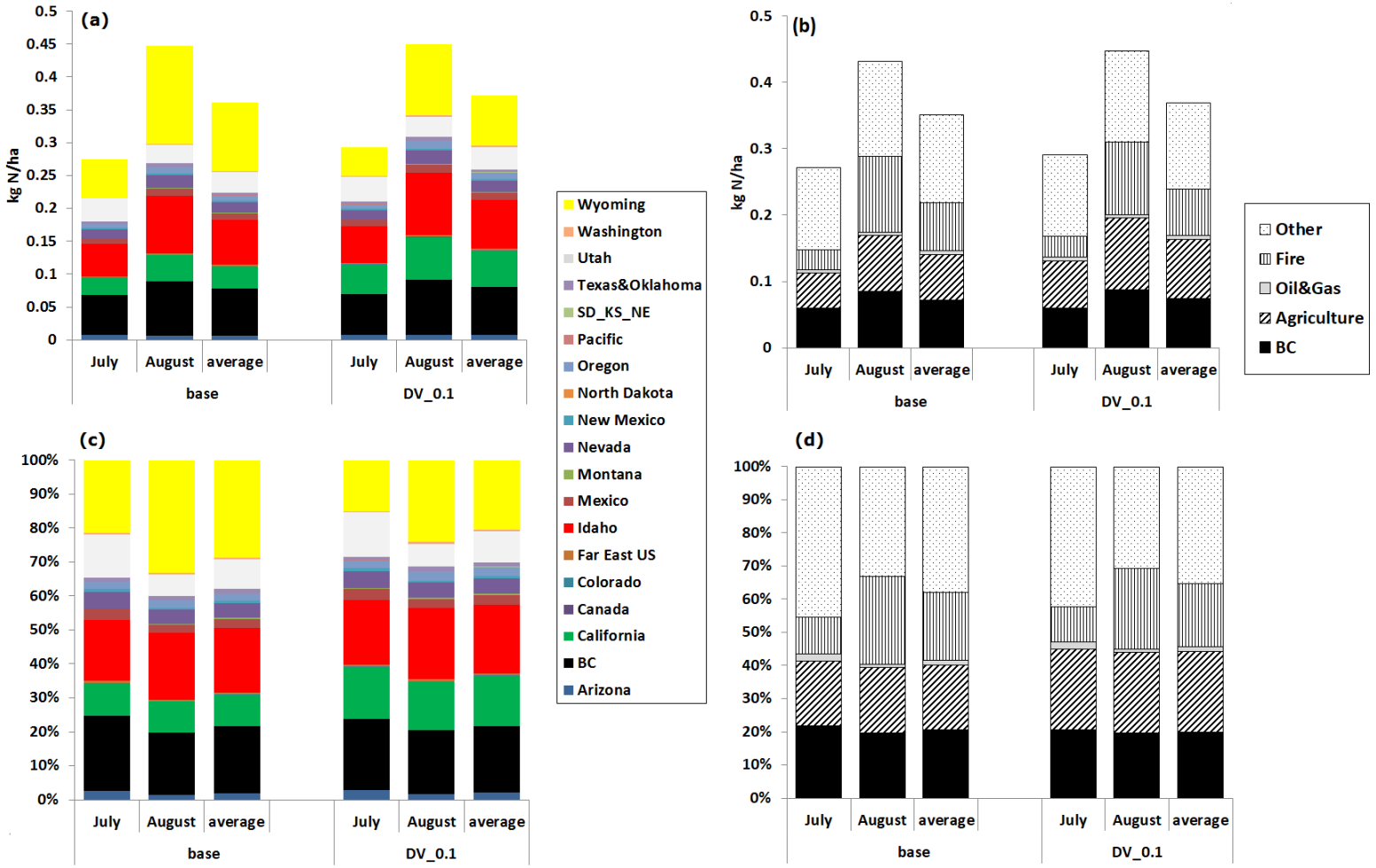

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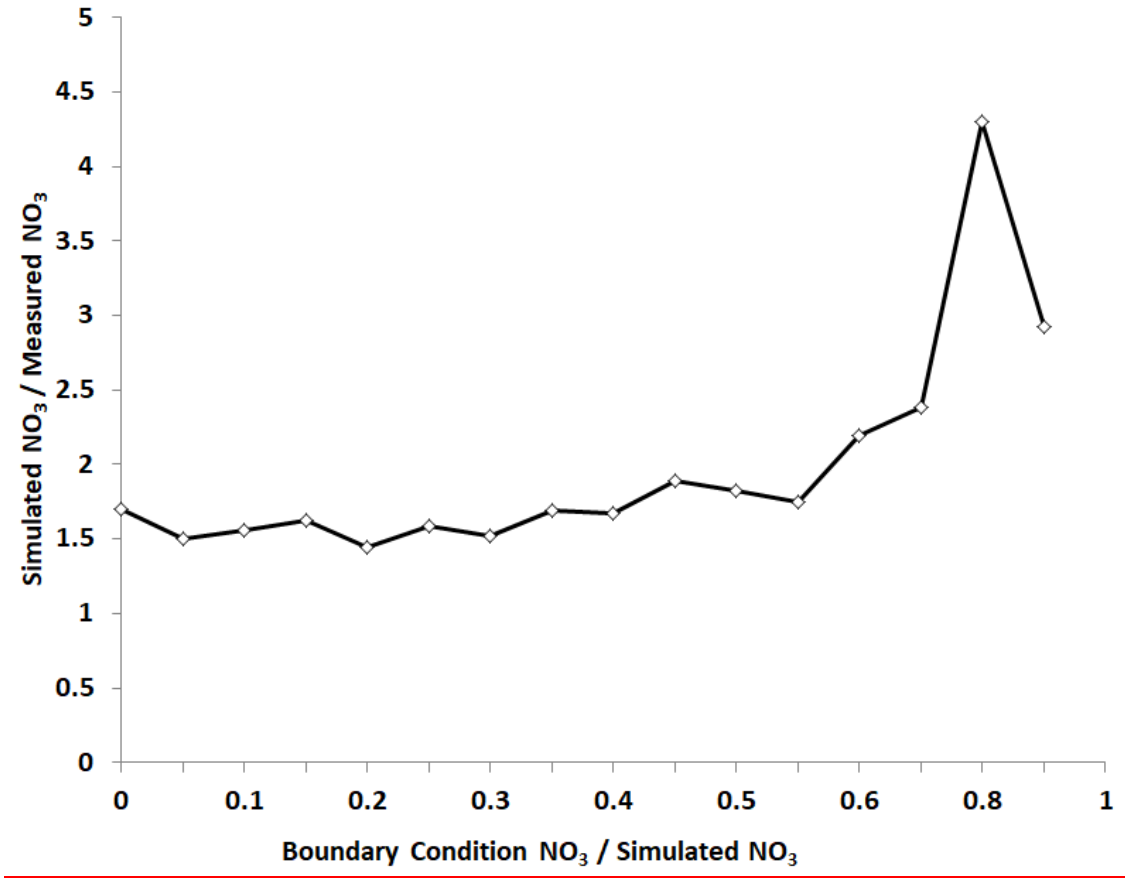

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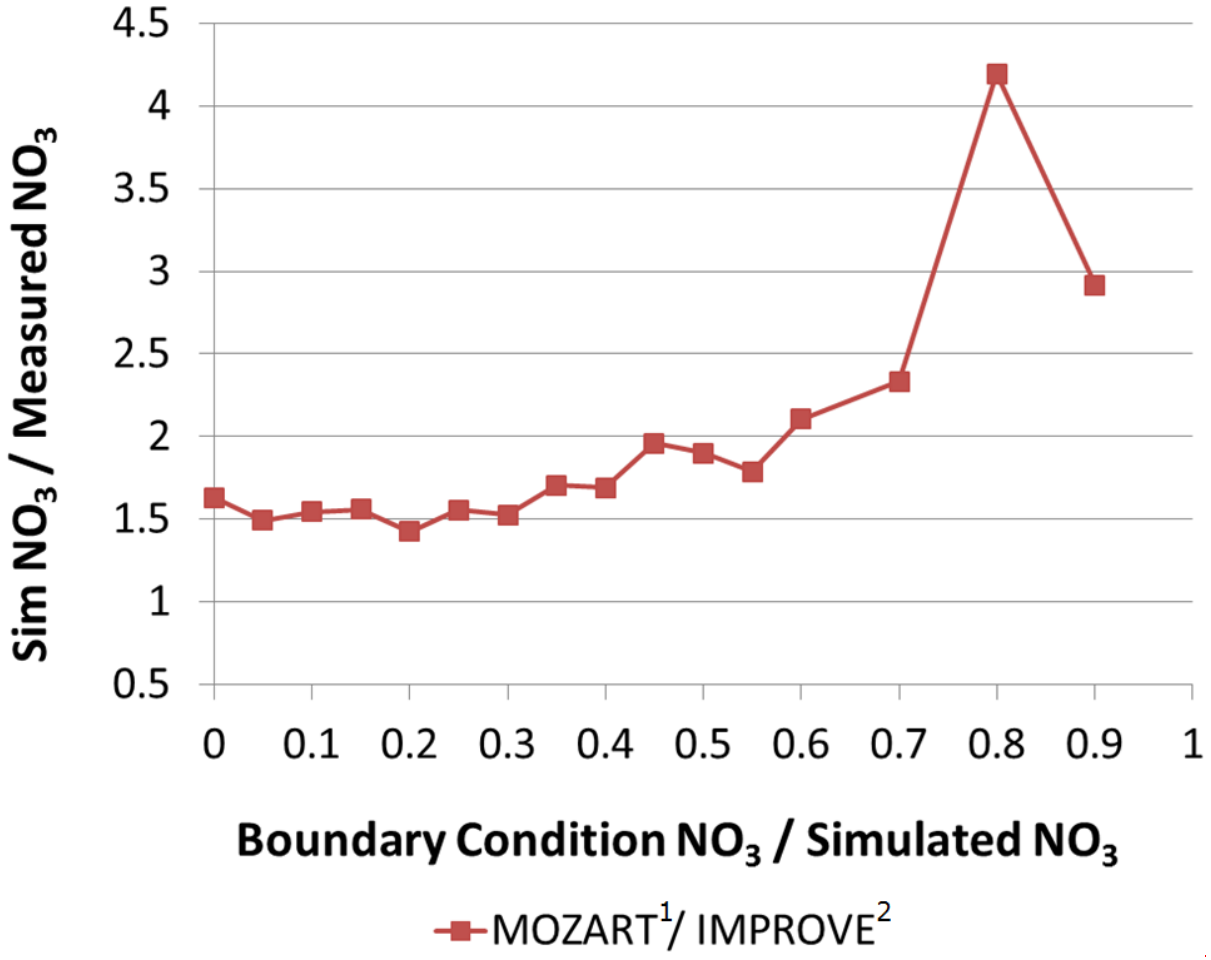

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Table 1. ~~Annual mean~~ CAMx model performance for nitrogen species concentrations as well as nitrogen dry/wet depositions evaluated at sites in AMoN, CASTNet, IMPROVE, ~~and~~ NTN networks as well as the 3 sites during GrandTRENDS campaign over the GYA region (see Figure 1 for site locations) in 2011.

Species		Network	Duration	OBS[a]	SIM[b]	#Site[c]	N[d] (% completeness)		R[e]	NMB[f]	NME[g]	FB[h]	FE[i]
concentration	NH_3 (ppb)	AMoN[1]	Sep 22-Dec 12~~, 2011 bi-weekly~~	0.49	0.30	1	7 (100%)		0.20	-65%	67%	-52%	53%
		GrandTReNDS[2]	Apr 5-Sep 21	0.55	0.46	3	434(97.7%)	0.30	-16%	57%	-42%	63%	
	HNO_3 (ppb)	CASTNet[32]	Jan 4-Dec 27~~, 2011 weekly~~	0.23	0.47	2	83(98.8%)~~153~~		0.72	108%	117%	60%	71%
		GrandTReNDS[2]	Apr 5-Sep 21	0.28	0.54	3	435(97.9%)	0.60	106%	109%	63%	68%	
	PNO_3 ($\mu g\ m^{-3}$)	CASTNet[3]	Jan 4-Dec 27~~, 2011 weekly~~	0.19	0.25	2	83(98.8%)~~153~~		0.42	37%	76%	26%	64%
		IMPROVE[43]	Jan 3-Dec 29~~, 2011 every 3 days~~	0.14	0.22	4	332(68.5%)		0.35	58%	108%	51%	80%
		GrandTReNDS[2]	Apr 5-Sep 21	0.13	0.15	3	435(97.9%)	0.45	15%	71%	14%	60%	
	PNH_4 ($\mu g\ m^{-3}$)	CASTNet[3]	Jan 4-Dec 27~~, 2011 weekly~~	0.17	0.18	2	83(98.8%)~~153~~		0.28	3%	39%	7%	41%
		GrandTReNDS[2]	Apr 5-Sep 21	0.14	0.17	3	433(97.7%)	0.12	23%	64%	34%	61%	
	NH_x ($\mu g\ m^{-3}$)[4]	GrandTReNDS[2]	Apr 5-Sep 21	0.68	0.63	3	427(96.2%)	0.26	-7%	48%	-22%	46%	
N Deposition	HNO_3 dry (kg N ha^{-1})	CASTNet[3]	Jan 4-Dec 27~~, 2011 weekly~~	0.0~~0~~71	0.~~0~~187	2	83(98.8%)~~153~~		0.81	153%	156%	77%	82%
		GrandTReNDS[2]	Apr 5-Sep 21	0.016	0.049	3	435(97.9%)	0.66	204%	209%	101%	104%	

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PNO3 dry (kg N ha^{-1})	CASTNet[3]	Jan 4-Dec 27~~,~~ ~~2011~~ ~~weekly~~	0.0~~0~~12	0.0~~0~~23	2	83(98.8%)~~153~~		0.14	96%	148%	48%	97%
	GrandTReNDS[2]	Apr 5-Sep 21	0.010	0.011	3	435(97.9%)	0.61	8%	58%	1%	65%	
PNH_4 dry (kg N ha^{-1})	CASTNet[3]	Jan 4-Dec 27~~,~~ ~~2011~~ ~~weekly~~	0.0~~0~~18	0.0~~0~~19	2	83(98.8%)~~153~~		0.1	7%	57%	22%	61%
	GrandTReNDS[2]	Apr 5-Sep 21	0.006	0.004	3	433(97.7%)	0.1	-33%	46%	-28%	53%	
NO_3^- wet (kg N ha^{-1})	NTN[5~~4~~]	Jan 4-Dec 27~~,~~ ~~2011~~ ~~weekly~~	0.0~~0~~79	0.0~~0~~97	5	214(82.3%)		0.34	31%	126%	12%	100%
	GrandTReNDS[2]	Apr 5-Sep 21	0.051	0.083	3	427(96.2%)	0.15	60%	94%	42%	71%	
NH_4^+ wet (kg N ha^{-1})	NTN[5]	Jan 4-Dec 27~~,~~ ~~2011~~ ~~weekly~~	0.0~~0~~88	0.~~0~~126	5	214(82.3%)		0.32	49%	142%	19%	106%
	GrandTReNDS[2]	Apr 5-Sep 21	0.103	0.147	3	427(96.2%)	0.48	42%	72%	30%	64%	
Precipitation (cm)	NTN[5]	Jan 4-Dec 27~~,~~ ~~2011~~ ~~weekly~~	0.77	2.34	5	214(82.3%)		0.54	215%	242%	64%	118%
	GrandTReNDS[2]	Apr 5-Sep 21	0.33	0.95	3	427(96.2%)	0.42	187%	207%	69%	94%	

Note: [1]AMoN samples are collected for 2 weeks; [2]CASTNet samples are collected for 1 week; [3]GrandTReNDS samples are collected daily; [4]IMPROVE~~[3]IMPROVE~~ 24-hr samples are collected every 3 days; [4]NH_x=NH_3+PNH_4; [5]NTN~~[4]NTN~~ samples are collected for 1 week; [a]average observation; [b]average simulation; [c]number of sites; [d]number of samples, the values in the parentheses are the percentage of valid samples used for model performance evaluation ; [e]Pearson's correlation coefficient; [f]normalized mean bias; [g]normalized mean error; [h]fractional bias; [i]fractional errors.

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Table 2. Total reactive nitrogen (N_r) deposition and critical loads for receptor points in the Greater Yellowstone Area in Wyoming.

Site ID	Site Name (State)	Latitude /Longitude	Elevation (m)	Sensitive ecosystem	Total N_r deposition (kg N ha^{-1})		Critical load (kg N ha^{-1})[3]	
					CAMx[1]	TDEP[2]	Range	confidence level
1	Absaroka-Beartooth Wilderness (MT)	45.49 ℕ 110.51 ℃W	2536	Lichen	1.93	2.80	3.02–4.89	reliable
2	Twin Island (MT)	45.07 ℕ 109.81 ℃W	2829	Lake chemistry	1.53	3.99	2.5–7.1	Fairly reliable
3	Tower Falls (WY)	44.92 ℕ 110.42 ℃W	2457	Snowpack	3.8	1.87	2.93–4.81[4]	reliable
4	Moose Meadow (ID)	44.63 ℕ 111.24 ℃W	1885	Snowpack	3.38	2.36	3.52–5.40[4]	reliable
5	Biscuit Basin (WY)	44.46 ℕ 110.83 ℃W	2050	Snowpack	2.69	3.49	3.39–5.27[4]	reliable
6	Jedediah Smith Wilderness (WY)	43.79 ℕ 110.94 ℃W	1944	Lichen	3.03	6.36	3.40–5.27	reliable
7	Holly Lake (WY)	43.79 ℕ 110.79 ℃W	2230	Lake chemistry	3.15	5.50	2.5–7.1	Fairly reliable
8	Fitzpatrick Wilderness (WY)	43.40 ℕ 109.66 ℃W	2890	Lichen	1.79	1.86	3.41–5.29	reliable
9	Pinedale (WY)	42.93 ℕ 109.79 ℃W	2246	Lichen	3.39	2.67	2.66–4.53	reliable
10	Black Joe Lake (WY)	42.74 ℕ 109.16 ℃W	3133	Lake chemistry	2.32	3.56	2.5–7.1	Fairly reliable

Note [1]Comprehensive Air Quality Model with extensions; [2]NADP Total Deposition maps. [3]The range of critical loads (CLs) for different effects on the selected sensitive ecosystem receptor is from United State CLAD (Critical Loads for Sulfur and Nitrogen Access Database), version 2.5 (Lynch et al., 2015). The level of confidence is based on the work of Pardo et al. (2011). The lower ends of the range were used in this study as a measured CL. [4]The CL values were for lichen response at sites with snow pack as a sensitive ecosystem.

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