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 suggestion 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 Nr 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”
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”

Comparison of 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

<table>
<thead>
<tr>
<th>Species</th>
<th>Phenomenological model</th>
<th>Duration</th>
<th>Model resolution</th>
<th>Region evaluated</th>
<th>NMB value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH3</td>
<td>CAMx</td>
<td>Jan, Jul 2002</td>
<td>12km</td>
<td>GYA</td>
<td>-45%</td>
<td>this study</td>
</tr>
<tr>
<td></td>
<td>CMAQ-CAMx</td>
<td>Feb, Sep 2002</td>
<td>3km</td>
<td>Colorado</td>
<td>1%</td>
<td>Zhang et al. (2013)</td>
</tr>
<tr>
<td>HNO3</td>
<td>CAMx</td>
<td>Mar, Sep 2002</td>
<td>12km</td>
<td>GYA</td>
<td>10%</td>
<td>this study</td>
</tr>
<tr>
<td></td>
<td>CMAQ-CAMx</td>
<td>Aug, Sep 2002</td>
<td>3km</td>
<td>Colorado</td>
<td>25%</td>
<td>Zhang et al. (2013)</td>
</tr>
<tr>
<td>NO25</td>
<td>CAMx</td>
<td>Nov, Dec 2002</td>
<td>12km</td>
<td>GYA</td>
<td>3%</td>
<td>this study</td>
</tr>
<tr>
<td></td>
<td>CMAQ-CAMx</td>
<td>Jan, Feb 2003</td>
<td>3km</td>
<td>Colorado</td>
<td>1%</td>
<td>Zhang et al. (2013)</td>
</tr>
<tr>
<td>NO25</td>
<td>CAMx</td>
<td>Mar, Sep 2003</td>
<td>12km</td>
<td>GYA</td>
<td>31%</td>
<td>this study</td>
</tr>
<tr>
<td></td>
<td>CMAQ-CAMx</td>
<td>Jun, Aug 2003</td>
<td>3km</td>
<td>Colorado</td>
<td>3%</td>
<td>Zhang et al. (2013)</td>
</tr>
<tr>
<td>NO3 wet</td>
<td>CAMx</td>
<td>Nov, Dec 2003</td>
<td>12km</td>
<td>GYA</td>
<td>49%</td>
<td>this study</td>
</tr>
<tr>
<td></td>
<td>CMAQ-CAMx</td>
<td>Jan, Feb 2004</td>
<td>3km</td>
<td>Colorado</td>
<td>1%</td>
<td>Zhang et al. (2013)</td>
</tr>
</tbody>
</table>

We also add the following citations to the reference list:


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:

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

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:

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

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:

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%.

*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/IMPROVE 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:

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:

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:
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 it 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:

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.

<table>
<thead>
<tr>
<th>Tagged region</th>
<th>Total emissions for nitrogen species (ton/yr)</th>
<th>NH3</th>
<th>NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AG</td>
<td>OG</td>
<td>Fire</td>
</tr>
<tr>
<td>NW Colorado (Southwest)</td>
<td>4,000</td>
<td>0</td>
<td>55</td>
</tr>
<tr>
<td>NE Colorado (Southwest)</td>
<td>37,041</td>
<td>415</td>
<td>3,157</td>
</tr>
<tr>
<td>NE Colorado (Southwest)</td>
<td>20,280</td>
<td>0</td>
<td>227</td>
</tr>
<tr>
<td>SW Colorado (Southwest)</td>
<td>8,672</td>
<td>0</td>
<td>73</td>
</tr>
<tr>
<td>Upper Green River, Wyoming</td>
<td>2,358</td>
<td>0</td>
<td>523</td>
</tr>
<tr>
<td>Jettison, Wyoming</td>
<td>2,765</td>
<td>0</td>
<td>359</td>
</tr>
<tr>
<td>Eastern Wyoming (Other WY)</td>
<td>7,200</td>
<td>0</td>
<td>1,623</td>
</tr>
<tr>
<td>Western Wyoming (Other WY)</td>
<td>10,646</td>
<td>4,011</td>
<td>847</td>
</tr>
<tr>
<td>Yellowstone (Other WY)</td>
<td>3,111</td>
<td>0</td>
<td>316</td>
</tr>
<tr>
<td>Northern Idaho (Northwest)</td>
<td>10,837</td>
<td>0</td>
<td>219</td>
</tr>
<tr>
<td>Snake River Valley, Idaho</td>
<td>43,695</td>
<td>0</td>
<td>567,256</td>
</tr>
<tr>
<td>Northern Utah</td>
<td>12,945</td>
<td>0</td>
<td>69</td>
</tr>
<tr>
<td>Southern Utah (Southwest)</td>
<td>10,093</td>
<td>0</td>
<td>54</td>
</tr>
<tr>
<td>Nevada</td>
<td>5,580</td>
<td>0</td>
<td>825</td>
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<tr>
<td>Montana</td>
<td>54,343</td>
<td>0</td>
<td>7,381</td>
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<td>Washington (Northwest)</td>
<td>44,118</td>
<td>0</td>
<td>825</td>
</tr>
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<td>Oregon (Northwest)</td>
<td>43,825</td>
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<td>8,856</td>
</tr>
<tr>
<td>California</td>
<td>203,204</td>
<td>155</td>
<td>3,054</td>
</tr>
<tr>
<td>Mexico (Non U.S.)</td>
<td>246,344</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>New Mexico (Southwest)</td>
<td>35,827</td>
<td>0</td>
<td>4,374</td>
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<td>Arizona</td>
<td>32,247</td>
<td>0</td>
<td>9,041</td>
</tr>
<tr>
<td>Texas (Southwest)</td>
<td>256,853</td>
<td>44</td>
<td>24,481</td>
</tr>
<tr>
<td>Canada (Non U.S.)</td>
<td>411,850</td>
<td>0</td>
<td>2,090</td>
</tr>
<tr>
<td>North Dakota (Eastern U.S. + Great Plains)</td>
<td>93,163</td>
<td>0</td>
<td>952</td>
</tr>
<tr>
<td>Far East U.S. (Eastern U.S. + Great Plains)</td>
<td>292</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>SD_SO2_NY (Eastern U.S. + Great Plains)</td>
<td>498,678</td>
<td>4</td>
<td>6,048</td>
</tr>
</tbody>
</table>

Total: 5,125,972 | 16,891,875

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 SO2 - NOx - NH3 is accounted for in the model. For example, with the decreases in SO2 emissions there should be more NH3 available to neutralize HNO3 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:


Evans, M.J., and Jacob, D.J., 2005. Impact of new laboratory studies of N2O5 hydrolysis on global model budget 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.

<table>
<thead>
<tr>
<th>Species</th>
<th>Network</th>
<th>Duration</th>
<th>OBS</th>
<th>SIMC</th>
<th>Site</th>
<th>NOy (ppb)</th>
<th>R²</th>
<th>NMB (NH₃)</th>
<th>NMFC</th>
<th>NMB (PNH₄)</th>
<th>FIP</th>
<th>FE</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃ (ppb)</td>
<td>AMeN</td>
<td>Sep 22-Dec 12</td>
<td>0.49</td>
<td>0.30</td>
<td>1</td>
<td>2.10 (0.96)</td>
<td>0.20</td>
<td>-16%</td>
<td>47%</td>
<td>-35%</td>
<td>35%</td>
<td></td>
</tr>
<tr>
<td>RNO₃ (ppb)</td>
<td>CASTN</td>
<td>Jan 4-Dec 27</td>
<td>0.23</td>
<td>0.47</td>
<td>2</td>
<td>83.8 (9.5)</td>
<td>0.72</td>
<td>108%</td>
<td>117%</td>
<td>60%</td>
<td>73%</td>
<td></td>
</tr>
<tr>
<td>PNH₄ (µg m⁻³)</td>
<td>CASTN</td>
<td>Jan 4-Dec 27</td>
<td>0.19</td>
<td>0.25</td>
<td>2</td>
<td>83.8 (9.5)</td>
<td>0.42</td>
<td>5%</td>
<td>76%</td>
<td>26%</td>
<td>64%</td>
<td></td>
</tr>
<tr>
<td>PNH₄ (µg m⁻³)</td>
<td>IMPROV</td>
<td>Jan 3-Dec 30</td>
<td>0.14</td>
<td>0.22</td>
<td>4</td>
<td>321 (13.5)</td>
<td>0.35</td>
<td>19%</td>
<td>108%</td>
<td>31%</td>
<td>89%</td>
<td></td>
</tr>
<tr>
<td>NH₄ (µg m⁻³)</td>
<td>GrandTRENDS</td>
<td>Apr 9-Sep 21</td>
<td>0.13</td>
<td>0.15</td>
<td>3</td>
<td>43 (0.9)</td>
<td>0.43</td>
<td>11%</td>
<td>71%</td>
<td>14%</td>
<td>60%</td>
<td></td>
</tr>
<tr>
<td>NH₄ (µg m⁻³)</td>
<td>AMeN</td>
<td>Sep 22-Dec 12</td>
<td>0.17</td>
<td>0.18</td>
<td>2</td>
<td>83.8 (9.5)</td>
<td>0.38</td>
<td>3%</td>
<td>59%</td>
<td>7%</td>
<td>41%</td>
<td></td>
</tr>
<tr>
<td>NH₄ (µg m⁻³)</td>
<td>CASTN</td>
<td>Jan 4-Dec 27</td>
<td>0.08</td>
<td>0.63</td>
<td>3</td>
<td>42 (9.5)</td>
<td>0.26</td>
<td>7%</td>
<td>48%</td>
<td>72%</td>
<td>46%</td>
<td></td>
</tr>
<tr>
<td>NH₄ (µg m⁻³)</td>
<td>CASTN</td>
<td>Jan 4-Dec 27</td>
<td>0.11</td>
<td>0.10</td>
<td>2</td>
<td>83.8 (9.5)</td>
<td>0.81</td>
<td>12%</td>
<td>159%</td>
<td>77%</td>
<td>82%</td>
<td></td>
</tr>
<tr>
<td>RNO₃ (ppb)</td>
<td>CASTN</td>
<td>Jan 4-Dec 27</td>
<td>0.06</td>
<td>0.06</td>
<td>3</td>
<td>83 (19)</td>
<td>0.66</td>
<td>26%</td>
<td>250%</td>
<td>101%</td>
<td>123%</td>
<td></td>
</tr>
<tr>
<td>PNH₄ (µg m⁻³)</td>
<td>CASTN</td>
<td>Jan 4-Dec 27</td>
<td>0.02</td>
<td>0.23</td>
<td>2</td>
<td>83.8 (9.5)</td>
<td>0.14</td>
<td>9%</td>
<td>148%</td>
<td>80%</td>
<td>97%</td>
<td></td>
</tr>
<tr>
<td>NH₄ (µg m⁻³)</td>
<td>CASTN</td>
<td>Jan 4-Dec 27</td>
<td>0.10</td>
<td>0.10</td>
<td>3</td>
<td>43 (0.9)</td>
<td>0.01</td>
<td>9%</td>
<td>15%</td>
<td>1%</td>
<td>15%</td>
<td></td>
</tr>
<tr>
<td>NH₄ (µg m⁻³)</td>
<td>CASTN</td>
<td>Jan 4-Dec 27</td>
<td>0.06</td>
<td>0.07</td>
<td>2</td>
<td>43 (0.9)</td>
<td>0.1</td>
<td>-3%</td>
<td>66%</td>
<td>28%</td>
<td>35%</td>
<td></td>
</tr>
<tr>
<td>NH₄ (µg m⁻³)</td>
<td>CASTN</td>
<td>Jan 4-Dec 27</td>
<td>0.07</td>
<td>0.08</td>
<td>3</td>
<td>42 (9.5)</td>
<td>0.12</td>
<td>49%</td>
<td>95%</td>
<td>12%</td>
<td>73%</td>
<td></td>
</tr>
<tr>
<td>NH₄ (µg m⁻³)</td>
<td>CASTN</td>
<td>Jan 4-Dec 27</td>
<td>0.08</td>
<td>0.12</td>
<td>5</td>
<td>64 (10.2)</td>
<td>0.5</td>
<td>49%</td>
<td>142%</td>
<td>39%</td>
<td>209%</td>
<td></td>
</tr>
<tr>
<td>NH₄ (µg m⁻³)</td>
<td>CASTN</td>
<td>Apr 9-Sep 21</td>
<td>0.13</td>
<td>0.14</td>
<td>3</td>
<td>42 (0.9)</td>
<td>0.48</td>
<td>42%</td>
<td>15%</td>
<td>10%</td>
<td>64%</td>
<td></td>
</tr>
</tbody>
</table>

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 NH₄, 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 NH₄ 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 Nr 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.
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.

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


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.

<table>
<thead>
<tr>
<th>base (kg N/ha)</th>
<th>DV_0.1 (kg N/ha)</th>
<th>difference(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>Wet</td>
<td>Total</td>
</tr>
<tr>
<td>BC</td>
<td>0.033</td>
<td>0.040</td>
</tr>
<tr>
<td>Agriculture</td>
<td>0.038</td>
<td>0.030</td>
</tr>
<tr>
<td>Oil&amp;Gas</td>
<td>0.004</td>
<td>0.001</td>
</tr>
<tr>
<td>Other+Fire</td>
<td>0.149</td>
<td>0.056</td>
</tr>
<tr>
<td>Total</td>
<td>0.224</td>
<td>0.128</td>
</tr>
</tbody>
</table>

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:
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\textsubscript{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 deposition, the Comprehensive Air Quality Model with extensions (CAMx), using Western Air Quality Study (WAQS) emission and meteorology inputs, was used to simulate N\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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
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 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 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 30%); 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 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.

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) compounds in air, rain, and snowpack samples over the GYA have been reported in the past 30 years and linked to N 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 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 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 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 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.

Total N 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\(_x\)), and other compounds. Reduced N arises primarily from ammonia (NH\(_3\)) gas emissions from
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) 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 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 24), 62% of the N deposited was from reduced N and about equally split between dry and wet deposition, and oxidized N only accounted for 27% of the N 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 m) 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, 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 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 zero-out sensitivity simulations and found that in 2006 natural sources, including lightning and wildfires, contributed more than 10% of the total N deposition over the Teton area. Lee et al. (2016) used the adjoint version of GEOS-Chem to quantify the sources of N 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 deposition in remote
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 NOx and livestock NH3 were also found to be major sources of N 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 Nr deposition. In a hybrid modeling technique, Malm et al. (2016) combined the source attribution results from Thompson et al. (2015) with measured Nr concentrations and found that Nr 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 Nr constituted 66% of the total deposition budget.

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, 2014). The final source apportionment results are then interpreted within the context of the identified model bias and uncertainties.
2 Modeling system for N, 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 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, non-surface 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: 1) agriculture (AG), 2) oil and gas activity (OG), 3) 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...
natural sources such as lightning. Table S2 provides the estimated annual NH3 and NOx 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 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 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 NOx, 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 sectors contributions to N 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). To differentiate the possible source impacts from urban activity in Jackson 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) 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 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 NH3; particulate ammonium (PNH3); reactive gaseous nitrogen (RGN), which includes primary emissions of NOx, nitrous acid (HONO), nitrate radical (NO3), and dinitrogen pentoxide (N2O5); gaseous nitric acid (HNO3); gaseous peroxy nitrogen (TPN), including peroxyacetyl nitrate (PAN) and peroxyacetyl nitric acid (PNA); gas-phase organic nitrate (NTR); and particulate nitrate (PNO3). PSAT maintains the source-group identity (i.e., source region and source sector) by apportioning the secondary species to the precursor emissions (ENVIORN, 2014). In the source apportionment comparison results, we report the reduced N deposition as the sum of NH3 and PNH3 and the oxidized N deposition as the sum of RGN, HNO3, PNO3, TPN, and NTR in units of kg N ha⁻¹.

### 3 Evaluation of CAMx-simulated N 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.slb.wisc.edu), total deposition maps (TDEP), hybrid modeling results (Schwede and Lear, 2014). Performance metrics recommended by the EPA’s modeling guidance for ozone, PM2.5, and regional haze attainment demonstrations (Yu et al., 2006; EPA, 2014) were used (see Table 1).
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/tnanet1/speciepg.html); PNO$_3$ concentrations from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network; and wet-deposited inorganic oxidized (NO$_x$) and reduced (NH$_4^+$) nitrogen and associated precipitation rates from the 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 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 alkyperoxy 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 for the western United States. A subset of these results is presented in Supplement File S1 for reference. Model performance statistics for the Nitrates 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$_3$ may be due to the uncertainty for the excessive N$_2$O$_5$ uptake coefficient setting for heterogeneous reactions (Foley hydrolysis in the model (Heald et al., 2010)). The poor NH$_3$ results may be related to dealing with the high uncertainty in the NH$_3$ emission inventory (Clarisse et al., 2009) and missing important emissions.
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 (Thompson et al., 2015; Zhu et al., 2015).

For PNOx and PNHx simulations in the GYA, the CAMx overestimated both species, with better performance for PNHx than PNOx (3% versus 37%, respectively, in terms of NMB normalized mean bias (NMB) and better agreement for PNOx 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 measurements from the five NTN sites with sufficient data were available from within the GYA (Figure S2). Comparisons to CAMx showed that the model captured the general trends in these data with \( r = 0.32-0.34 \) and but were somewhat biased, with NMB = 31% for NOx and NMB = 49% for NH3. 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 NAPD 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). The significant overestimation of HNO3 and HN3 in all seasons. Also evident is the poor simulation of the seasonality in N 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 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 N deposition within the GYA.
3.2 Evaluation against GrandTReNDS data

The GrandTReNDS campaign provides a unique opportunity to evaluate the capability of CAMx to simulate the N compounds and deposition budget. Detailed measurements, including NH₃, 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 2A). Figure 4A 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 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. The primary cause of this bias was the overestimation in the HNO₃ dry deposition rates, which were 2–3 times larger than those derived from the measured data. This is consistent with the systematic overestimation of HNO₃ concentrations (NMB = 106\% in Table 1). Other biases also exist, including an underestimation in the NH₃ dry deposition, which was somewhat balanced by an overestimation in the NH₃ wet deposition (NMB = 60\%). 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 NH₄⁺ (NH₃ = NH₄⁺ + PNH₄) 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 4B, 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 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
Model) (Daly et al., 1994) for high-resolution precipitation estimates for 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 deposition and N concentration data into the TDEP results, they are expected to be less biased than the deposition results from a pure CAMX simulation.

The TDEP total N 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 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 deposition, which was more spatially heterogeneous than the corresponding TDEP results, with significantly higher N deposition in the agricultural lands to the west of the GYA and hotspots due to wildfires that are not evident in the TDEP results. Both sets of results showed higher N wet deposition at the higher-elevation sites in the interior of the GYA, which was associated with higher precipitation rates. However, the TDEP N wet deposition was generally higher throughout the GYA, with an annual average N, wet deposition rate of 2.0 N ha\(^{-1}\) yr\(^{-1}\) versus 1.3 N ha\(^{-1}\) yr\(^{-1}\) from CAMX. Precipitation maps across the GYA generated by WRF and PRISM 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 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 54. The reported CAMX dry and wet N deposition values at the eight Class I areas in Figure 54 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 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 deposition at the western side of the GYA and relatively low values at Fitzpatrick Wilderness. Also, both models showed the importance of reduced N in the GYA, with a nearly 50% or higher contribution to the total N deposition budget. However, the two models differed on the ratio of dry versus wet N deposition, with CAMX simulating a higher fraction from dry N deposition than TDEP.

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

The seasonal modeled N deposition budgets averaged over the GYA are presented in Figure 65. As shown, the total N 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
measured and modeled data presented in Figure 34. In total, the annual model N 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 deposition, suggesting a small but significant 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, 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 7a, while Figure 8a 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 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 7a). In terms of geographic impact (Figure 8a), AG emissions contributed as much as 80% of the total N 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 24). 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 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 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 deposition could be more than 90%, as seen in
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). 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 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 deposition over the GYA are summarized in Figure 9a. 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 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 deposition over the GYA are shown in Figures 7a and 9a. Compared to the results for total N deposition, the dry N 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 deposition from Wyoming were 15% compared to 12% for total N 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 deposition to 12% for dry N deposition.

The opposite pattern is seen for wet N 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 deposition was different from dry and total N 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 deposition levels (Spaulding et al., 2015; Nanus et al., 2017). Figure 10a presents the source attribution results for 100 sites within the GYA where either ecosystem response studies or deposition monitoring have 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- and upper-end estimates of the annual total inorganic N deposition values (Lynch et al., 2015) with confidence levels (Pardo et al.,...
The simulated N\textsubscript{ deposi}on exceeded the lower CL values at three of the ten sites, specifically, Tower Falls, Holly Lake, and Pinedale, and Tower Falls. Comparatively, the 2011 TDEP N\textsubscript{ deposition} results exceeded the CL in 6 out of 10 sites (Black Joe Lakesites at Pinedale, Holly Lake Twin Island, Biscuit Basin, Holly Lake, Jedediah Smith Wilderness, Pinedale, and Twin IslandBlack Joe Lake). As shown in Figure 109, the sites that exceeded the CL tend to be in high-alti\textsubscript{ue} location\textsubscript{s}, 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\textsubscript{ deposition} CL thresholds, with the greatest impacts in sensitive high-elevation basins, including areas within national parks, National Parks, and Wild\textsubscript{ernesses}.

In terms of emission sectors and source regions contributing to the total annual N\textsubscript{ deposition} at CL exceedance sites, emission sources from the Snake River valley were the largest contributo\textsubscript{r}s (27–32\%), and AG emissions were the largest source of this subset. The next three largest contributo\textsubscript{r}s 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\textsubscript{ 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\textsubscript{ deposi}on to source sue regions and sectors is\textsubscript{r} sensitive to NH\textsubscript{3} dry deposition rates; the relative contributo\textsubscript{r}s of dry and wet deposition; and the concentrations of N compounds from the BC. However, the model evaluation revealed a significant underestimation of NH\textsubscript{3} concentrations and overestimation of HNO\textsubscript{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 contributions to changes in NH\textsubscript{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\textsubscript{3} dry deposition rates, the deposition velocities were reduced by increasing the NH\textsubscript{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\textsubscript{3} and NH\textsubscript{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\textsubscript{3} deposition velocity from 2.5–4 cm \textsuperscript{s} to 1–1.5 cm \textsuperscript{s} over the GYA, resulting in values more comparable to those used in the GrandTRENdS study (Benedict et al., 2013; Prenni et al., 2014). The simulated NH\textsubscript{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\textsubscript{3} measurements at the Grand Targhee and NOAA Climate Station sites but...
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 11A, 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 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\(_3\) (Zhang et al., 2010; Whaley et al., 2013). 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 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\(_3^-\) 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\(_3^-\) wet deposition improved (Figure S7). Within the GYA, however, the scaled N\(_3^-\) wet deposition underestimated
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$_x$ deposition overestimation. However, its impact on source apportionment results was not conducted here due to unclear reasons for the model bias.

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$_x$ 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 BC resulted in higher relative contributions of oxidized N to the total N$_x$ deposition rate compared to the MOZART BCs (51% and 45%, respectively). The poor correspondence in the oxidized to reduced N$_x$ split is reflective of the large uncertainties in the BC contributions to the N$_x$ 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 12, 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 was 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$_x$ 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$_x$ 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. Fire and the BC were a mix of reduced and oxidized N compounds. This assessment focused on only the inorganic N$_x$ fraction. There is measured evidence that organic N (Prenti et al., 2014; Benedict et al., 2013; Prenti et al., 2014) is a significant contributor to N$_x$ deposition, and the inability to assess its origin in the current CTM is an important uncertainty in this work. Nevertheless, this N$_x$ source apportionment work is the first thorough analysis of the origin of inorganic N$_x$ 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 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<sub>e</sub> deposition levels throughout the GYA. However, the model simulation underestimated the available measured NH<sub>3</sub> concentrations by 65% on average, and measured HNO<sub>3</sub> concentrations were overestimated the measured HNO<sub>3</sub> 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<sub>e</sub> deposition. In addition, both reduced and oxidized N<sub>e</sub> 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<sub>e</sub> deposition over the GYA in 2011 was 3.13 kg N ha<sup>-1</sup> yr<sup>-1</sup> 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<sub>e</sub> deposition to Class I areas for 2006 and showed that the simulated total N<sub>e</sub> deposition at GTNP (2.9 kg N ha<sup>-1</sup> yr<sup>-1</sup>) and YNP (2.6 kg N ha<sup>-1</sup> yr<sup>-1</sup>) exceeded the low end of CL for lichens (2.5 kg N ha<sup>-1</sup> yr<sup>-1</sup>).

Emissions from the AG sector within the modeling domain were the largest contributor to the GYA total N<sub>e</sub> 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<sub>e</sub> 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 S2). 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<sub>e</sub> 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
for 23%, Wyoming 17%, and northern Utah, California, and the northwestern United States accounting for 14–16% of the N deposition.

Long-range transport of N species from the BC, which primarily originated from international sources, contributed 21% of the total N 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 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 PNO₃ and possibly other N compounds was overestimated (Figure 1244), clearly suggesting that more research is needed on the role of distant emission sources on impacting N 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 NH₄ may be a more important contributor to total N deposition during spring than that observed during GrandTRENDs. Also, considering that the wet deposition in the GYA tended to be underestimated and the precipitation amount in 2011 was anomalously high, the source regions identified as having a higher weighting on the annual wet N 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, 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 NH₄ emissions from agricultural operations, the occurrence of wildfires, and the difficulty in simulating the NH₃ bidirectional flux and the deposition flux of the other N 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 deposition over the GYA, with >90% of the NH₃ emissions originating from agriculture sources. In addition, the Snake River valley in Idaho accounted for 74% of the agricultural contribution to the total N deposition. Significant contributions from more distant sources, e.g., California and international sources, to both oxidized and reduced N deposition illustrate the regional nature of the N deposition problem. Emissions of oxidized N compounds are projected to continue to decrease,
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 N$_r$ deposition below the CL in some GYA ecosystems.

Acknowledgments

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References


Environmental Protection Agency (EPA), Preparation of emissions inventories for version 6.2, 2011 emission modeling platform,


Figure captions


Figure 2. Annual NH₃ emission for the 12-km inner modeling domain at focused tagged regions (see Table S2 and Figure 1S2 for the details of the 27 source region partition) as well as locations of the monitoring sites at different networks (1Ammonia Monitoring Network; 2Clean Air Status and Trends Network; 3Grand Teton Reactive Nitrogen Deposition Study; 4Interagency Monitoring of Protected Visual Environments; 5National 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 (NH₃) 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. Rockefeller 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. Model performance for (a-b) seasonal average Nᵣ concentration, (c-d) seasonal accumulated Nᵣ deposition budget as well as (e-f) seasonal accumulated precipitation amount at collocated location sites (YNP and Pinedale) over the GYA in 2011. 1Clean Air Status and Trends Network; 2Comprehensive Air Quality Model with extensions; 3National Trend Network; 4Parameter-elevation Relationships on Independent Slopes Model; 5Weather Research and Forecasting model.

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

Figure 5. Annual nitrogen deposition budgets in absolute (Figure 5a) and in percentage (Figure 5b) as well as annual precipitation amounts (Figure 5c) from the NADP Total Deposition Map (TDEP) and corresponding CAMx (Comprehensive Air Quality Model with extensions) and WRF (Weather Research and...
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 24. The reported CAMx dry and wet N deposition values at the eight Class I areas are the average of the simulation values at corresponding grid cells for each area.).

**Figure 65.** Seasonal CAMx simulated N deposition budgets averaged over the GYA in 2011. The left axis is the relative contribution of different N species to seasonal N deposition while the right axis is corresponding to the black diamonds for seasonal total N deposition in absolute (kg N ha⁻¹).

**Figure 76.** Contributions of source sectors to the mean total N deposition, dry N deposition, and wet N deposition over the GYA at different seasons in 2011. Figure 76a is the source sectors contributions in absolute and Figure 76b is the corresponding contributions in percentage.

**Figure 87.** 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 deposition over the GYA in 2011. The first column is the seasonal total N deposition patterns in Kg N ha⁻¹ while the following five columns are the seasonal patterns of relative contributions from different source sectors.

**Figure 98.** Contributions of source regions to the mean total N deposition, dry N deposition, and wet N deposition over the GYA at different seasons in 2011. Figure 98a is the source regions contributions in absolute and Figure 98b is the corresponding contributions in percentage.

**Figure 109.** Contributions of different source sectors as well as boundary conditions for total N 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 1140.** The sensitivity of NH₃ dry deposition velocity (left: “base” case, right: “DV_0.1” case with NH₃ dry deposition velocity slowing down) to source apportionment results over the GYA during July–August 2011. Figure 1140a and 1140c are the contributions by source regions in absolute and in percentage while Figure 1140b and 1140d are the contributions by source sectors.

**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.
1Model for Ozone and Related chemical Tracers; 2Interagency Monitoring of Protect Visual Environments.
Figure 1
Figure 2
Figure 7
<table>
<thead>
<tr>
<th>Season</th>
<th>Total N deposition (kg N/ha)</th>
<th>Agriculture Contribution (%)</th>
<th>Oil &amp; Gas Contribution (%)</th>
<th>Fire Contribution (%)</th>
<th>Other Contribution (%)</th>
<th>Boundary Contribution (%)</th>
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</tbody>
</table>
Figure 9
Figure 11

(a) and (b) show the distribution of kilogram of nitrogen per hectare (kg N/ha) for different months and average conditions. The legend indicates various regions and categories such as Wyoming, Washington, Utah, and others.

(c) and (d) display the percentage distribution across the same categories for different months and average conditions.
Simulated NO₃ / Measured NO₃

Boundary Condition NO₃ / Simulated NO₃
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.

<table>
<thead>
<tr>
<th>Species</th>
<th>Network</th>
<th>Duration</th>
<th>OBS(^a)</th>
<th>SIM(^b)</th>
<th>#Site (^c)</th>
<th>N (^d) (%) completeness</th>
<th>R(^e)</th>
<th>NMB(^f)</th>
<th>NME(^g)</th>
<th>FB(^h)</th>
<th>FE(^i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH(_3) (ppb)</td>
<td>AMoN(^1)</td>
<td>Sep 22-Dec 12, 2011- weekly</td>
<td>0.49</td>
<td>0.30</td>
<td>1</td>
<td>7 (100%)</td>
<td>0.20</td>
<td>-65%</td>
<td>67%</td>
<td>-52%</td>
<td>53%</td>
</tr>
<tr>
<td></td>
<td>GrandTReND S(^2)</td>
<td>Apr 5-Sep 21</td>
<td>0.55</td>
<td>0.46</td>
<td>3</td>
<td>434 (97.7%)</td>
<td>0.30</td>
<td>-16%</td>
<td>57%</td>
<td>-42%</td>
<td>63%</td>
</tr>
<tr>
<td>HNO(_3) (ppb)</td>
<td>CASTNet(^2)</td>
<td>Jan 4-Dec 27, 2011- weekly</td>
<td>0.23</td>
<td>0.47</td>
<td>2</td>
<td>83 (98.8%) (^{153})</td>
<td>0.72</td>
<td>108%</td>
<td>117%</td>
<td>60%</td>
<td>71%</td>
</tr>
<tr>
<td></td>
<td>GrandTReND S(^2)</td>
<td>Apr 5-Sep 21</td>
<td>0.28</td>
<td>0.54</td>
<td>3</td>
<td>435 (97.9%)</td>
<td>0.60</td>
<td>106%</td>
<td>109%</td>
<td>63%</td>
<td>68%</td>
</tr>
<tr>
<td>PNO(_3) (µ g m(^{-3}))</td>
<td>CASTNet(^2)</td>
<td>Jan 4-Dec 27, 2011- weekly</td>
<td>0.19</td>
<td>0.25</td>
<td>2</td>
<td>83 (98.8%) (^{153})</td>
<td>0.42</td>
<td>37%</td>
<td>76%</td>
<td>26%</td>
<td>64%</td>
</tr>
<tr>
<td></td>
<td>IMPROVE(^2)</td>
<td>Jan 3-Dec 29, 2011- every 3 days</td>
<td>0.14</td>
<td>0.22</td>
<td>4</td>
<td>332 (68.5%)</td>
<td>0.35</td>
<td>58%</td>
<td>108%</td>
<td>51%</td>
<td>80%</td>
</tr>
<tr>
<td></td>
<td>GrandTReND S(^2)</td>
<td>Apr 5-Sep 21</td>
<td>0.13</td>
<td>0.15</td>
<td>3</td>
<td>435 (97.9%)</td>
<td>0.45</td>
<td>15%</td>
<td>71%</td>
<td>14%</td>
<td>60%</td>
</tr>
<tr>
<td>PNH(_3) (µ g m(^{-3}))</td>
<td>CASTNet(^2)</td>
<td>Jan 4-Dec 27, 2011- weekly</td>
<td>0.17</td>
<td>0.18</td>
<td>2</td>
<td>83 (98.8%) (^{153})</td>
<td>0.28</td>
<td>3%</td>
<td>39%</td>
<td>7%</td>
<td>41%</td>
</tr>
<tr>
<td></td>
<td>GrandTReND S(^2)</td>
<td>Apr 5-Sep 21</td>
<td>0.14</td>
<td>0.17</td>
<td>3</td>
<td>433 (97.7%)</td>
<td>0.12</td>
<td>23%</td>
<td>64%</td>
<td>34%</td>
<td>61%</td>
</tr>
<tr>
<td>NH(_x) (µ g m(^{-3}))</td>
<td>GrandTReND S(^2)</td>
<td>Apr 5-Sep 21</td>
<td>0.68</td>
<td>0.63</td>
<td>3</td>
<td>427 (96.2%)</td>
<td>0.26</td>
<td>-7%</td>
<td>48%</td>
<td>-22%</td>
<td>46%</td>
</tr>
<tr>
<td>HNO(_x) dry (kg N ha(^{-1}))</td>
<td>CASTNet(^2)</td>
<td>Jan 4-Dec 27, 2011- weekly</td>
<td>0.0071</td>
<td>0.0187</td>
<td>2</td>
<td>83 (98.8%) (^{153})</td>
<td>0.81</td>
<td>153%</td>
<td>156%</td>
<td>77%</td>
<td>82%</td>
</tr>
<tr>
<td></td>
<td>GrandTReND S(^2)</td>
<td>Apr 5-Sep 21</td>
<td>0.016</td>
<td>0.049</td>
<td>3</td>
<td>435 (97.9%)</td>
<td>0.66</td>
<td>204%</td>
<td>209%</td>
<td>101%</td>
<td>104%</td>
</tr>
<tr>
<td>Compartment</td>
<td>Source</td>
<td>Collection Period</td>
<td>Mean (µmol N m⁻² s⁻¹)</td>
<td>SD</td>
<td>Median (µmol N m⁻² s⁻¹)</td>
<td>Mode (µmol N m⁻² s⁻¹)</td>
<td>Percent of Data (%)</td>
<td>Percent Bias (%)</td>
<td>Percent Error (%)</td>
<td>Percent Fractional Bias (%)</td>
<td>Percent Fractional Error (%)</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------</td>
<td>------------------------</td>
<td>-----------------------</td>
<td>-----</td>
<td>-------------------------</td>
<td>-----------------------</td>
<td>---------------------</td>
<td>-------------------</td>
<td>-----------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>NO₃ dry (kg N ha⁻¹)</td>
<td>CASTNet</td>
<td>Jan 4-Dec 27, 2011</td>
<td>0.0012</td>
<td>0.0023</td>
<td>83 (98.8%)</td>
<td>153</td>
<td>0.14</td>
<td>96</td>
<td>148</td>
<td>48</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>GrandTReNDS</td>
<td>Apr 5-Sep 21</td>
<td>0.010</td>
<td>0.011</td>
<td>3</td>
<td>435 (97.9%)</td>
<td>0.61</td>
<td>8</td>
<td>58</td>
<td>1</td>
<td>65</td>
</tr>
<tr>
<td>NH₄ dry (kg N ha⁻¹)</td>
<td>CASTNet</td>
<td>Jan 4-Dec 27, 2011</td>
<td>0.0018</td>
<td>0.0019</td>
<td>83 (98.8%)</td>
<td>153</td>
<td>0.1</td>
<td>7</td>
<td>57</td>
<td>22</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>GrandTReNDS</td>
<td>Apr 5-Sep 21</td>
<td>0.006</td>
<td>0.004</td>
<td>3</td>
<td>433 (97.7%)</td>
<td>0.1</td>
<td>-33</td>
<td>46</td>
<td>-28</td>
<td>53</td>
</tr>
<tr>
<td>NO₃ wet (kg N ha⁻¹)</td>
<td>NTN</td>
<td>Jan 4-Dec 27, 2011</td>
<td>0.0079</td>
<td>0.0097</td>
<td>214 (82.3%)</td>
<td>214 (82.3%)</td>
<td>0.34</td>
<td>31</td>
<td>126</td>
<td>12</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>GrandTReNDS</td>
<td>Apr 5-Sep 21</td>
<td>0.051</td>
<td>0.083</td>
<td>3</td>
<td>427 (96.2%)</td>
<td>0.15</td>
<td>60</td>
<td>94</td>
<td>42</td>
<td>71</td>
</tr>
<tr>
<td>NH₄ wet (kg N ha⁻¹)</td>
<td>NTN</td>
<td>Jan 4-Dec 27, 2011</td>
<td>0.0088</td>
<td>0.0126</td>
<td>214 (82.3%)</td>
<td>214 (82.3%)</td>
<td>0.32</td>
<td>49</td>
<td>142</td>
<td>19</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>GrandTReNDS</td>
<td>Apr 5-Sep 21</td>
<td>0.103</td>
<td>0.147</td>
<td>3</td>
<td>427 (96.2%)</td>
<td>0.48</td>
<td>42</td>
<td>72</td>
<td>30</td>
<td>64</td>
</tr>
<tr>
<td>Precipitation (cm)</td>
<td>NTN</td>
<td>Jan 4-Dec 27, 2011</td>
<td>0.77</td>
<td>2.34</td>
<td>214 (82.3%)</td>
<td>214 (82.3%)</td>
<td>0.54</td>
<td>215</td>
<td>242</td>
<td>64</td>
<td>118</td>
</tr>
<tr>
<td></td>
<td>GrandTReNDS</td>
<td>Apr 5-Sep 21</td>
<td>0.33</td>
<td>0.95</td>
<td>3</td>
<td>427 (96.2%)</td>
<td>0.42</td>
<td>187</td>
<td>207</td>
<td>69</td>
<td>94</td>
</tr>
</tbody>
</table>

Note: ¹AMoN samples are collected for 2 weeks; ²CASTNet samples are collected for 1 week; ³GrandTReNDS samples are collected daily; ⁴IMPROVE samples are collected every 3 days; ⁵NH₄=NH₃+PNH₄; ⁶NTN samples are collected for 1 week; ⁷average observation; ⁸average simulation; ⁹number of sites; ¹⁰number of samples, the values in the parentheses are the percentage of valid samples used for model performance evaluation; ¹¹Pearson’s correlation coefficient; ¹²normalized mean bias; ¹³normalized mean error; ¹⁴fractional bias; ¹⁵fractional errors.
Table 2. Total reactive nitrogen (N<sub>r</sub>) deposition and critical loads for receptor points in the Greater Yellowstone Area in Wyoming.

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

Note: Comprehensive Air Quality Model with extensions; <sup>1</sup>NADP Total Deposition maps. <sup>2</sup>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. <sup>3</sup>The CL values were for lichen response at sites with snow pack as a sensitive ecosystem.