Reviewer #1

This manuscript presents a novel approach to assess NOx emissions by utilizing nitrate wet deposition (NWD) as a potential predictor. The authors used NWD flux data from the United States National Atmospheric Deposition Program (NADP) and the European Monitoring and Evaluation Programme (EMEP). To evaluate the effectiveness of the proposed approach, the authors employed the GEOS-Chem chemical transport model spanning the years 1980 to 2020, comparing simulated and observed NWD fluxes with anthropogenic NOx emissions data derived from the Community Emissions Data System (CEDS) for both the United States and Europe. They further investigated the impact of NOx emissions changes on tropospheric ozone concentrations, using data collected by ozonesondes and by the Tropospheric Ozone Assessment Report (TOAR) Surface Ozone Database.

The analysis reveals that NWD might be used as a predictor for NOx emissions fairly well, and its usage further enabled to reinforce trends such as a decline in anthropogenic NOx emission, and the subsequent reduced sensitivity of NWD to these emissions. Notably, the study also identifies overestimations in anthropogenic NOx emissions, which appear to contribute to an overestimation of surface ozone levels over Europe.

While the methodologies employed are generally suitable for addressing the research objectives, several limitations warrant discussion. Firstly, the methodology does not account for the dry deposition of nitrogen, a process that can significantly contribute to NOx and its chemical products deposition, especially involving chemical products like HNO, and through the dry deposition of aerosols. Additionally, the study does not consider the potential increase in soil NO emissions under elevated temperatures, which becomes particularly relevant in warmer seasons. These limitations should be thoroughly discussed to provide context for the study's findings. Moreover, it should be emphasized that the utility of NWD as a predictor for NOx emissions is expected to be limited in relatively small spatial and temporal scales, such as urban areas. Discussing these limitations is vital in the context of the applicability of the proposed method. Specific comments are included below.

We thank the Reviewer for their positive feedback and insightful comments regarding our method. We have addressed the major and minor concerns below.

Specific comments

Line 19 – "These results suggest that NWD fluxes constrain total NOx emissions well." However, this statement does not fully consider the insights about anthropogenic effect as specified in section 3.2: "Our work underscores the value of measurements of NWD extending into the future for constraining total NOx trends in areas with strict NOx emissions regulations."

NWD fluxes capture total NOx trends that take into account both anthropogenic and background sources. We should not have included the "in areas with strict NOx emissions regulations" in the final sentence in Section 3.2, as NWD is able to capture trends dominated by background emissions (post-2010 flat trends), in addition to the steep decline pre-2010 driven by

anthropogenic emissions. Thus, NWD can be applied in areas with or without strict NOx emissions regulations. We have removed the phrase.

We have edited the sentence in Section 3.2 to say: "Our work underscores the value of measurements of NWD extending into the future for constraining total NO_x trends." We also edit Line 19 to read: "These results suggest that NWD fluxes constrain total NO_x emissions well, whether trends are driven by anthropogenic or background sources."

Lines 21 – 27 Here, you present the evaluation results of the comparison between observed and modeled NWD and NOx emissions using CEDS data for both the US and Europe. It is essential to specify, both here and elsewhere, the spatial and temporal resolution at which this comparison was conducted. These details are of significant importance as they can influence the interpretation of your findings concerning the utility of NWD as a predictor for NOx emissions.

We add in extra clarification here about the timeframe and spatial resolution. Those lines now read: "Over the United States, we find that modeled NWD is overestimated in summer from 1980-2017 by 15-20% on average (interquartile range: 11-31%), with overestimates most prominent in the eastern US after 2000 (20% on average), implying an overestimate of NOx emissions in the CEDS inventory (0.5x0.5-degree resolution). Over Europe, we find that modeled NWD is overestimated in all seasons from 1980-2017, with the strongest average overestimates occurring in summer and fall (175% and 170%, respectively). These overestimates may be reduced by cutting anthropogenic NO_x emissions by 50% in CEDS over Europe (i.e., cutting the 1980-2017 average annual emissions from 8.7 to 4.3 Tg NO), but summertime and fall NO_x may still need to be reduced further for observations and models to align. Overestimates may extend to other inventories such as the EMEP inventory…"

Line 28 – "EMEP" is defined twice

We thank the Reviewer for catching this. We have changed this so EMEP is only defined once in Line 12.

Line 44- "those processes" is not clear in the context of the sentence

We have clarified this to say: "However, the small increase in lifetimes is not expected to substantially impact wet deposition since deposition processes such as rainout occur on longer timescales (e.g., days)."

Lines 120, 150 – multiple definition for "EMEP"

We have fixed this.

Line 160 – only "point sources"?

The sites are also located far away from non-point sources, such as roads. This is stated later in the sentence, but we clarify this to say: "Similar to NADP, most sites are located in areas that are considered representative of the air mass (avoiding inversion areas and mountaintops) away from

sources of pollution including point, road, and agricultural sources. All samplers are required to be placed >1 km away from gravel roads, farmyards, and tilled agricultural fields to limit the impact of dust particles (Tørseth et al., 2012)."

Line 164 – I understand that you don't consider dry deposition in your analysis due to observational limits. Nevertheless, I believe it is important to discuss the potential effects of dry deposition on both your analysis and the resulting conclusions, particularly with regard to seasonal variations, meteorological conditions, and geographical locations. But I think that the potential effect of dry deposition on both your analysis and conclusions, possibly with respect to season/meteorological conditions and location, should be discussed.

We agree with the Reviewer that this should be discussed in more detail and have expanded this paragraph. Both dry and wet deposition peak during summer months, and the % difference between summer and winter months is about the same (45-50% greater during summer). The geographical patterns for dry deposition, wet deposition, and NO_x emissions are all the same (highest values are found in the same regions during the same seasons for all). Thus, since the seasonal variations and geographical distribution are the same, we do not expect the exclusion of dry deposition to contribute substantially to our overall results, especially in regard to trends. It is possible that excluding dry deposition would lead to some biases in our ability to capture anthropogenic trends, as dry deposition is more influenced by urban sources (Dutta and Heald, 2023). On a regional basis as is used in this work, seasonal variations, trends, and geographical patterns are similar between wet and dry deposition. We have included a longer discussion of dry deposition and its impacts in our methods section. In addition, assessing magnitudes with dry deposition introduces more uncertainties due to measurement limitations. We include a discussion of why magnitudes are difficult to assess using dry deposition and why wet deposition is a better choice for this comparison.

"We do not consider dry deposition in this analysis due to observational limits. Dry deposition measurements are available only after 2000 over the CONUS from the Clean Air Status and Trends Network (CASTNET), and there are only four sites over Europe (EMEP) with analysis timeframes long enough to include. There are also many uncertainties with regard to both observations and model representation of dry deposition. Estimates of dry deposition velocities must be made to determine dry deposition fluxes at observation sites. This is typically done by using a multi-layer model (Finkelstein et al., 2000; Meyers et al., 1998), which calculates deposition velocity as a function of chemical composition, meteorology, and vegetation. Limitations to this method include the lack of meteorological measurements co-located with observation sites, requiring the use of a chemical transport model to estimate deposition velocities. These velocities are uncertain, and different velocity estimation methods can result in fluxes that differ by ~1.6x (Schwede & Lear, 2014). A recent study also shows a high bias in GEOS-Chem for nitrate dry deposition that persists throughout seasons and across multidecadal timeframes (Dutta and Heald, 2023), largely due to a model overestimate of dry deposition velocity of HNO_3. The uncertainty inherent to the dry deposition observations, the limitations of the observations, and a known bias in GEOS-Chem makes dry deposition a more uncertain comparator for NO_x trends than wet deposition. Excluding dry deposition may lead to some bias in capturing anthropogenic trends, as dry deposition tends to be more influenced by urban

sources, but seasonal variations, annual trends, and geographic distributions are similar to those found in wet deposition (Dutta and Heald, 2023)."

New References Cited:

Dutta, I. and Heald, C. L.: Exploring Deposition Observations of Oxidized Sulfur and Nitrogen as a Constraint on Emissions in the United States, JGR Atmospheres, 128, e2023JD039610, https://doi.org/10.1029/2023JD039610, 2023.

Finkelstein, P. L., Ellestad, T. G., Clarke, J. F., Meyers, T. P., Schwede, D. B., Hebert, E. O., and Neal, J. A.: Ozone and sulfur dioxide dry deposition to forests: Observations and model evaluation, J. Geophys. Res., 105, 15365–15377, https://doi.org/10.1029/2000JD900185, 2000.

Meyers, T. P., Finkelstein, P., Clarke, J., Ellestad, T. G., and Sims, P. F.: A multilayer model for inferring dry deposition using standard meteorological measurements, J. Geophys. Res., 103, 22645–22661, https://doi.org/10.1029/98JD01564, 1998.

Schwede, D. B. and Lear, G. G.: A novel hybrid approach for estimating total deposition in the United States, Atmospheric Environment, 92, 207–220, https://doi.org/10.1016/j.atmosenv.2014.04.008, 2014.

Line 217 – what is the justification for constraining lightning NOx emissions at ~6 Tg N per year ?

This is the standard constraint for lightning NOx emissions in GEOS-Chem. This value was originally derived in Martin et al. (2007) (https://doi.org/10.1029/2006JD007831) to match NO2 columns from SCIAMACHY, O3 columns from OMI and MLS, and upper tropospheric HNO3 from ACE-FTS. GEOS-Chem was used to identify locations and times in which lightning would dominate trace gas observations. A global total source of 6 Tg N/yr from lightning was thus derived since it best represented satellite observations of tropospheric NO2, O3, and HNO3. We add the Martin et al. (2007) reference to our methods section. The sentence now reads:

"Lightning NO_x emissions were constrained at ~6 Tg N per year to match satellite observations (Martin et al., 2007) and distributed to match satellite climatological observations of lightning flashes while maintaining coupling to deep convection from meteorological fields (Murray et al., 2012)."

New references:

Martin, R. V., Sauvage, B., Folkins, I., Sioris, C. E., Boone, C., Bernath, P., and Ziemke, J.: Space-based constraints on the production of nitric oxide by lightning, J. Geophys. Res., 112, 2006JD007831, https://doi.org/10.1029/2006JD007831, 2007.

Line 277 – "NO2 measurements are commonly used to infer NOx concentrations due to the short lifetime of NO2, which results in robust correlations between NOx emissions and NO2 column amounts (Goldberg et al., 2021)." This argument, which is based on the lifetime of NO2, may be applicable at sufficiently large spatial and temporal scales but may not hold for relatively smaller scales. Therefore, in reference to the preceding statement, it would be valuable to understand whether a strong correlation exists between NO_2 measurements from surface stations or satellites and NWD in urban areas or in proximity to air pollution sources. This aspect warrants further investigation and discussion.

It is difficult to assess the correlations between satellite NO_2 over urban areas and NWD since NWD observations sites are intentionally located away from pollution sources and urban areas. However, we can assess the ability of NWD to capture trends on larger spatial and temporal scales. Previous research over the CONUS has shown that satellite NO_2 measurements and NWD show similar trends, as they are both influenced by background emissions (Silvern et al., 2019; DOI: 10.5194/acp-19-8863-2019). These trends are in contrast with surface NO_2 stations located in urban areas (Silvern et al., 2019). Thus, NWD is a useful constraint on regional spatial scales, as it is influenced by transport. The Reviewer is correct that it may not be as useful for urban areas or small spatial scales, which may be better characterized by other means. We have included that caveat in our discussion:

"We find that over the CONUS, the strongest decreases in NWD occur from 2000-2010 and average -4.1 ± 1.2%/yr (mean ± standard deviation). NO_2 measurements are commonly used to infer NO_x concentrations due to the short lifetime of NO_2, which results in robust correlations between NO_x emissions and NO_2 column amounts (Goldberg et al., 2021). Prior to 2010, there is generally good agreement between NWD and measurements of NO_2 from surface stations and satellites when analyzed on a regional scale. The EPA's Air Quality System (AQS) surface NO_2 trends decrease by -6.6 ± 1.4 %/yr from 2005-2009 and satellite NO_2 trends decrease by -6 ± 0.5%/yr (Silvern et al., 2019), both of which are in good agreement with NWD measurements over that timeframe (-5.7 ± 1.9%/yr). It should be noted NWD is most useful as a constraint on regional spatial scales, as NWD observations are located in rural areas influenced by transport and background emissions, which can show different trends from urban areas (Silvern et al, 2019)."

Line 290- Specify what kind of observations

We clarify this to say "After 2010 over the CONUS, decreases in NWD observations slow down, averaging -1.2 ± 2.9%/yr from 2011-2019."

Line 308 – "solely" – "dominantly" or similar should be more appropriate.

We have erased "solely."

Line 372 – it is not clear to me what do you mean by – "total NOx emissions calculated using GEOS-Chem …"

We have clarified this. It now reads "Figure 5 shows anthropogenic NO$_x$ emissions derived directly from the CEDS inventory (blue solid line) and total NO$_x$ emissions summed using GEOS-Chem (black solid line), which includes all sources of NOx emissions (anthropogenic from CEDS, soil, lightning, and biomass burning)."

Figure 5 – In the text you refer to NOx emissions while in the figure you refer to NO emissions. It should be estimated what bias this can impose on your results and conclusions.

We apologize for the confusion. This is a typo, and the results do actually show NO$_x$ emissions as mentioned in the text. To avoid confusion, we have changed the axes to report NO$_x$ as Tg N per year. We have fixed the figure axes labels and legend to clarify this.
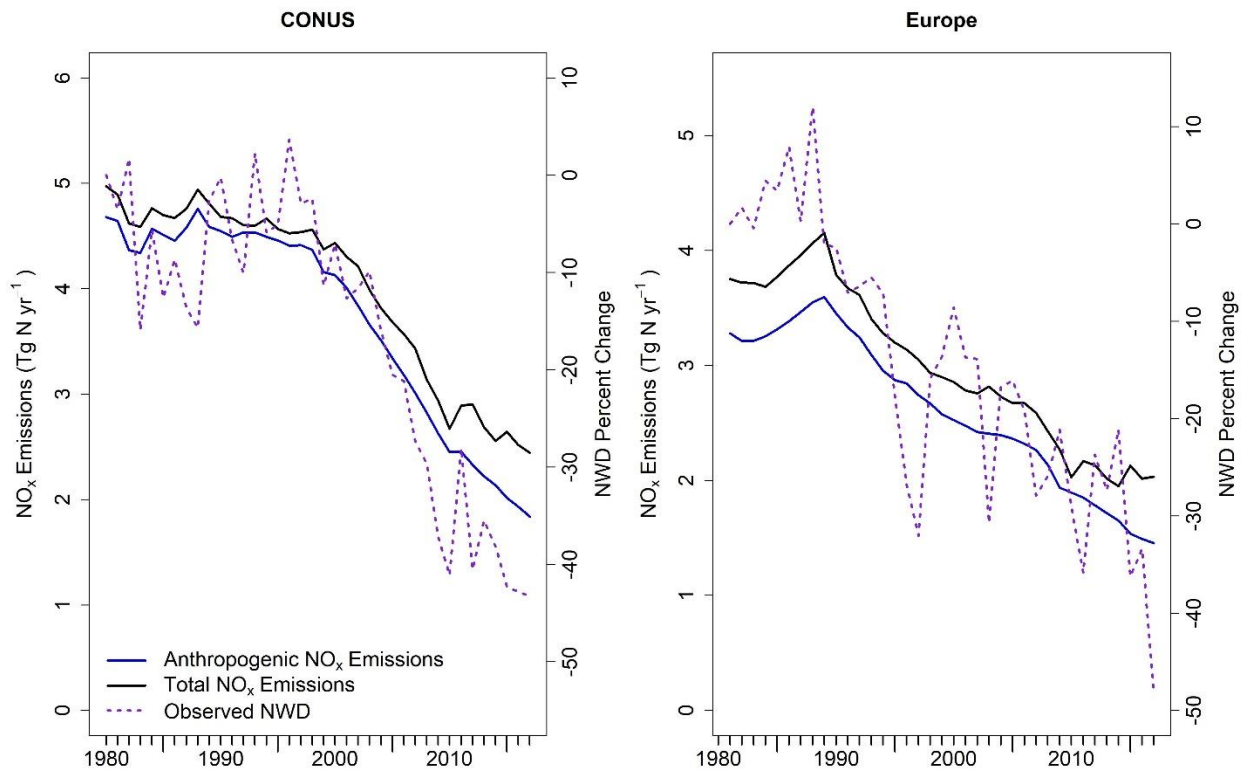
Figure 5. NO$_x$ trends in the CEDS inventory (reported as Tg N), total NO$_x$ emissions (Tg N) estimated by GEOS-Chem, and observed trends in annual NWD data over (a) the CONUS and (b) Europe. Anthropogenic emissions from the CEDS inventory are shown in solid blue, total NO$_x$ emissions are shown in black, and trends from NWD are overlaid with the dashed purple line.

Line 492 – "However, we find that summertime and autumnal NOx is still overestimated by ~36% in the sensitivity simulation, suggesting that further reductions of NOx may be appropriate in certain areas during summer and fall" - Do you estimate that the change in NWD due to reduction in a factor of 2 of the NOx emissions is in line with your earlier statement on line 397?

(:"Our work underscores the value of measurements of NWD extending into the future for constraining total NOx trends in areas with strict NOx emissions regulations").

Can you develop an empirical/mathematical expression to better characterize the correlation between NO_x emission (or mixing ratios) and NWD? this can be highly valuable.

The reduction by a factor of 2 was performed based on annual values averaged across Europe and was not originally meant to apply seasonally. We expect that seasonal factors would need to be derived to bring these estimates closer together. Doing this was beyond the scope of this work, but it is clear that further refinements will be needed for seasonal corrections, which is a source of future work. For example, other sources of NO_x, such as soil NO_x, can be important on a seasonal basis and contribute to overestimates.

Correlations between NO_x and NWD are strongest during spring and summer, when NO_x emissions are highest (R~0.7), but correlations are still strong in all seasons (R>0.6). Seasonal differences do not take away from our overall findings that NO_x emissions are broadly overestimated in certain regions in CEDS, although future work should focus on refining these constraints on seasonal and finer regional scales. Based on our large-scale analysis here, NWD is overestimated by factors ranging from 1.9 to 2.9 over Europe, with overestimates highest during fall and smallest during spring. We add these factors into our analysis:

Line 515: "During summer and fall over the entire domain, we find that NWD is overestimated on average by 176% (50 to >500%, factor of 2.9 on average) and 169% (39 to >500%, factor of 2.7 on average), respectively, by the model. During winter and spring, this overestimate is smaller, but still ~100% (average factor of 2.4 and 1.9, respectively)."

Line 528: "To test the impact of NO_x emissions on model NWD, we perform a sensitivity test that cuts anthropogenic NO_x emissions in the CEDS inventory in half (reducing the 1980-2017 average of 8.7 to 4.3 Tg NO) over Europe using GC at the 4°x5° resolution (Fig. 7), as NO_x and NWD correlate highly in all seasons (R>0.6)."

Later, in Line 533, we add this phrase: "However, we find that summertime and autumnal NO_x is still overestimated by ~36% in the sensitivity simulation, suggesting that further reductions of NO_x may be appropriate in certain areas during summer and fall (Fig. 7), and these seasonal corrections should be a focus of future work."

Line 503 – "with overestimates of 145% in summer and 140%" – the observed overestimation of 145% in summer and 140% raises questions about its underlying causes. Do you have any further insights or speculations regarding the factors that might be contributing to such a significant level of overestimation?

While anthropogenic NO_x emissions are the most likely explanation, as NWD scales directly with changes to anthropogenic emissions in the model, it is possible that discrepancies in some meteorological variables could add to this. We correct for precipitation as part of our analysis, so it is not likely to be due to this. Additionally, other meteorological factors are not likely to be the cause, as our sensitivity simulation that holds emissions constant ("Meteorology" sensitivity

simulation) cannot reproduce NWD trends, instead showing no trend over time (Fig. 4). Soil NO_x is another possibility, the emissions of which are not well accounted for in models. Soil NO_x can make up 23% of total NOx emissions in Europe, and this could be a contributing source of this discrepancy, especially during summer and fall when overestimates of NWD are highest. We discuss this possibility in Section 3.4:

"As discussed previously for the CONUS, it is also possible that this disagreement in NWD magnitudes in Europe during summer stems partially from overestimates of soil NO_x in the model. However, this difference is not large enough to fully explain these overestimates, as soil NO_x emissions range from <2 to 23% of total NO_x emissions over Europe."

While we did not explicitly investigate soil NO_x in our sensitivities, we do find that small perturbations of 5% in soil NO_x emissions leads to a change in NWD of 0.2-0.3% over Europe, a much smaller sensitivity than anthropogenic emissions, where a 5% perturbation leads to a 3.5-4.9% change in NWD (Table 2). Thus, it is most likely that anthropogenic emissions are responsible for the discrepancies we see. Other reports have found large overestimates of anthropogenic NO_x emissions over Europe using satellite measurements (Szymankiewicz et al., 2021, DOI: 10.3390/atmos12111465). Our findings are consistent with their results that anthropogenic emissions are the most likely cause. We discuss this in Section 3.4:

"A recent analysis assessing NO_x emissions over Europe via satellite measurements points out overestimates in Southern Europe during winter and across the entire European domain during summer (Szymankiewicz et al., 2021). The study suggested that EMEP anthropogenic NO_x emissions needed to be reduced by 40% to match observations."

Line 519: "The surface ozone overestimate over Europe is reduced from 14% (6 ppb) to 2% (0.7 ppb) on average, bringing it within agreement of observations." - Does it mean that tropospheric ozone is NOx-limited over Europe? While your analysis is pertinent to larger scales, it's important to note that the relevance of ozone analysis is more substantial on a mesoscale or in urban areas.

The Reviewer is correct that this would imply that Europe, on average, is in the NO_x-limited regime. There will of course be variations on smaller spatial scales, and this can be the focus of future investigations. Our resolutions of 2x2.5 and 4x5 degrees are not appropriate for an urban-scale analysis, but it should be noted that ozone formation regimes can vary between urban areas and the surrounding rural regions. We have added a short discussion of this in Line 570 right before Figure 8:

"It is important to note that this analysis was done on a regional scale. Ozone formation varies between urban and rural regions, where formation regimes can switch between NO_x- and VOC-limited over a short spatial scale. Future analyses should investigate the impact of NO_x constraints on model ozone at the urban scale."

Figure 8 – 1. the reader is referred to panel "a", but "a" is not specified on the figure; 2. Which schemes are used to capture the turbulence in the boundary/surface layer in the model? It seems

to not capture the trend in ozone with height, close to the ground; 3. The averaging period, for both modeling and observation, should be specified for the right-hand side panel.

1 & 3) We have fixed the figure and clarified the averaging period in the caption: "(b) Vertical profiles of ozone observed by WOUDC and HEGIFTOM are shown in black, GC ozone is shown in red, and ozone from our Half-NOₓ simulation is shown in green. The vertical profiles are an average of summertime concentrations from 1990-2017. GC was sampled at the same launch time and location as all ozonesonde launches compiled here."

2) GEOS-Chem using VDIFF non-local mixing for the boundary layer. This scheme considers different states of mixing within the PBL as determined by static instability. During the night, the scheme shrinks to a low mixing scenario. During the day, the PBL is less stable and thus a non-local term is introduced to account for PBL-wide mixing, which typically does not approach full mixing. The PBL height is taken from the meteorological datasets. The model does not capture ozone concentrations close to the ground, and it has been suggested that part of this is due to issues in vertical mixing representation (Travis et al., 2016, DOI: 10.5194/acp-16-13561-2016).
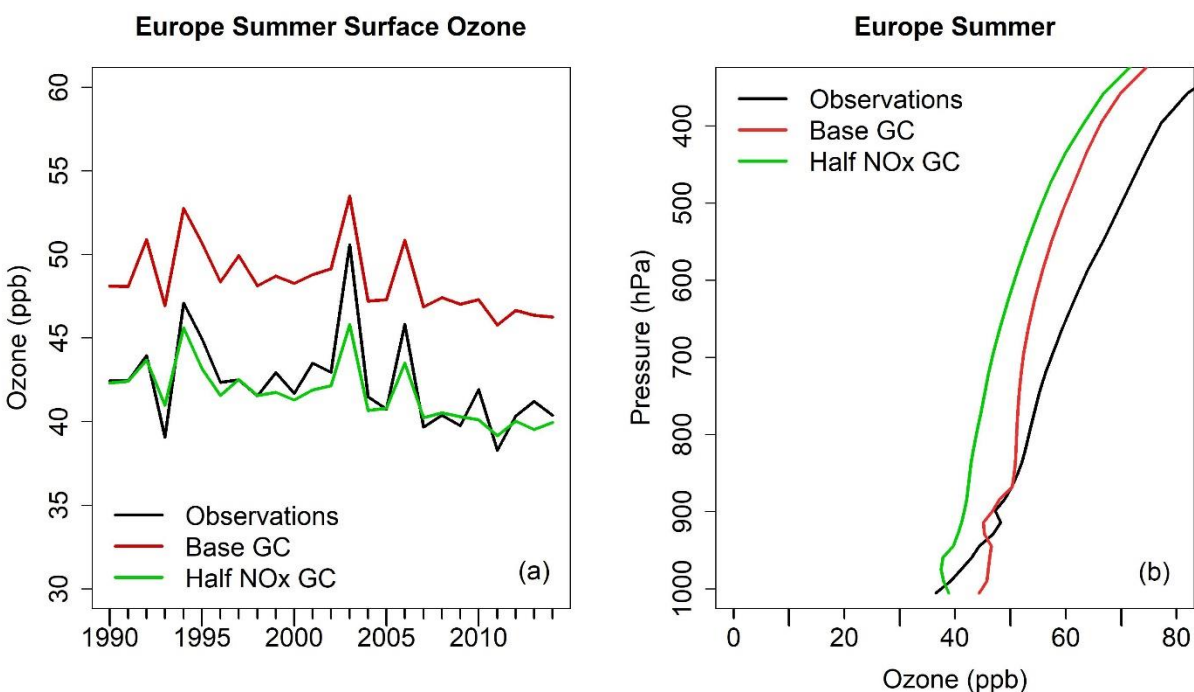
Figure 8. Comparisons between observed and modeled summertime ozone concentrations, averaged over Europe. Results from the Half-NOₓ sensitivity simulation are also shown. (a) Observations of surface ozone compiled by the TOAR Database team (Schultz et al., 2017) are shown in black, GC surface ozone is shown in red, and surface ozone from the Half-NOₓ simulation is shown in green. (b) Vertical profiles of ozone observed by WOUDC and HEGIFTOM are shown in black, GC ozone is shown in red, and ozone from our Half-NOₓ simulation is shown in green. The vertical profiles are an average of summertime concentrations from 1990-2017. GC was sampled at the same launch time and location as all ozonesonde launches compiled here.

Line 547 – multiple definition for "NWD"

We have fixed this.

Line 548 – "total NOx emission trends" should be better defined.

We have clarified this to state that the pre-2010 anthropogenic trends are captured, and the post-2010 background trends are captured. NWD captures the trends of the dominant emissions source driving the overall trend of total (anthro + background) NO_x. This line now reads:

"We found that anthropogenic NO_x trends in the CEDS emissions inventory are reproduced well by NWD until 2010, and that total (i.e., anthropogenic + lightning + soils + biomass burning) NO_x emission trends are well reproduced by NWD after 2010."

Line 563 - which "trends"?

We have removed the "trends" part since we do not discuss ozone trends explicitly in the manuscript.

Line 563 – "Our work shows that NWD fluxes can be a useful constraint on total NOx emissions and their trends…" – not clear to me what do you mean by "trends" here.

We are referring to the total NO_x emissions trends (sum of anthropogenic and background sources). We find that NWD follows the same trends as total NO_x throughout the timeframe. We have clarified the trends we refer to, and it now reads: "Our work shows that NWD fluxes can be a useful constraint on total (anthropogenic + background) NO_x emissions and trends (rapid decrease from 1990-2010, and flattening after 2010)…"

Line 564 – "…emissions and their trends…" – At what scale is the relevance of these findings?

We have performed our analysis at the regional scale. Thus, these findings are most relevant at larger scales, especially given the constraints of our model horizontal resolutions. Future analyses should investigate this constraint on a smaller spatial and seasonal scale, and we have added a sentence to clarify this: "Due to the model resolutions used here, these findings are most relevant at the regional scale, and future analyses should focus on smaller spatial and temporal (e.g., seasonal) scales to further refine NWD as an independent NO_x constraint."

General comments

This manuscript is well written and focuses on a topic that should be of broad appeal to the ACP readership. It pushes forward the use of a robust, publicly available dataset for a novel application—inferring NO_x emissions and trends—with strong utility for atmospheric chemists. Although I agree with the authors' premise that NWD should prove to be a useful dataset for constraining NO_x emissions, I disagree that the magnitude of biases and trends in NWD are directly equivalent to NO_x emissions and trends as implied for results over the USA. I suggest some analyses that I hope may serve as a constructive supplement for addressing this concern. With these additions, I believe that this paper would serve as a wonderful reference for many pressing questions in air quality science.

Excellent attention to detail—I have no suggestions for editing the paper in terms of typography or semantics.

We thank the Reviewer for their positive view of this work and their insightful comments. We have responded to the major and minor comments below.

Minor revisions

In general, the figures in this manuscript are thoughtful, attractive and clear.

General comment related to NEI discussions (for example, bottom of page 2 through Figure 1): I found the comparison among different versions of the NEI confusing. From my understanding, new iterations of the NEI are meant to supersede previous versions, so that they're expected to diverge from one another with availability of improved methods. It was not clear to me what readers are meant to conclude from this comparison across versions and the inclusion of multiple NEI iterations in Figure 1. It would be helpful to either clarify this point, or it could be more constructive to discuss how the NEI has been updated in the most recent version included (2017) and the relationship of those updates to the references cited. If the overall point is that there is uncertainty among NO_x emission estimates, I think that is effectively communicated through the comparison across different inventories without needing to invoke multiple versions of the NEI.

The Reviewer is correct that the NEI updates each iteration with improved methods, so direct comparisons between inventories should not be made. However, it is important to note that these new iterations change the estimated NOx substantially between versions, which serves to highlight the uncertainties involved in estimating NOx emissions. We have included a sentence to clarify this on Page 2 above the figure, and we have included information about how the most recent version has been updated from previous versions.

"Magnitudes do not agree across different estimates, even amongst the EPA NEI from different years, although it should be noted that methods for calculating NEI estimates change from year to year (e.g., NEI 2003 vs. NEI 2007 vs. NEI 2017), and previous NEI version estimates are not changed to reflect these updates. For example, the most recent NEI (2017) used an updated

version of the Motor Vehicle Emissions Simulator (MOVES) model, increasing nonroad NO_x emissions estimates from previous NEIs. While NEI versions are not meant to be used as a time series, the large changes in NO_x magnitudes between NEI versions brought about by updated methods illustrate the uncertainty inherent in NO_x emissions inventories."

L210: Based on a later reference to sector-level emissions, I believe that McDuffie et al. 2020 should also be cited here. McDuffie, E. E., Smith, S. J., O'Rourke, P., Tibrewal, K., Venkataraman, C., Marais, E. A., Zheng, B., Crippa, M., Brauer, M., and Martin, R. V.: A global anthropogenic emission inventory of atmospheric pollutants from sector- and fuel-specific sources (1970–2017): an application of the Community Emissions Data System (CEDS), Earth Syst. Sci. Data, 12, 3413–3442, https://doi.org/10.5194/essd-12-3413-2020, 2020.

Thank you for catching this omission. We have included this reference.

In general (e.g., L248, Figure 2), I didn't understand the motivation for including the v10-01 GEOS-Chem simulation. I think that could be better clarified, or this simulation could be taken out of the analysis. The only point of interpretation that I found was in L345-346, but I believe that this point could be made more simply with other existing comparisons of the two inventories.

The v10-01 simulation gives us another point of comparison. The chemistry has been updated between the two versions (see Section 2.2), but we see that they calculate similar values for NWD. The slight differences we see in NWD between versions is probably due to the differences in emissions inventories. CEDS (GCv12.9.3) and MACCity (GCv10-01) report similar values, but at different resolutions, which leads to some discrepancies. This helps us illustrate that our findings with NWD are not unique to one specific model version that would change upon any updates to the chemical mechanism. We have added language in the methods section (Line 277) to clarify this:

"Including this simulation provides a point of comparison to our GC simulations. We use this to show that the discrepancies between modelled and observed NWD are not unique to a specific model version. Instead, we show that these discrepancies are consistent between model versions that use different settings, different emissions inventories, and contain different chemistry updates. This allows us to assess whether model-observations discrepancies in NWD are due to internal model processes or emissions inventories."

Quantitative results starting on L276: What is the +/- indicating?

This indicates the standard deviation of the relative trend (%/yr). We have included this clarification in the text.

Paragraph starting L315: This paragraph may benefit from a discussion of the differences in spatial distribution between the satellite and ground-based measurements referenced. A greater urban influence in the satellite data could belie differences in the dataset trends.

The Reviewer is correct that an urban bias could influence the satellite trends in ways that would not necessarily be reflected by the NWD measurements. However, on a regional scale, satellite measurements are also strongly influenced by background NO_2, much in the same way that NWD observations are influenced by transport processes and background emissions. Thus, previous analyses have found similar trends over the CONUS between satellite NO_2 and NWD on a regional scale (Silvern et al., 2019). We concede that this may not be true if trends are analyzed more locally, but this work focuses on regional trends, where NWD and satellite NO_2 observations show similar trends influenced by background NO_x. Despite the influence of background NO_x, both NWD and satellite NO_2 measurements can capture large-scale changes in anthropogenic emissions. Our work shows that a drastic change in anthropogenic emissions is captured by NWD, even when those trends are primarily influenced by urban emissions (trends prior to 2010 and during the COVID-19 shutdown). We add a sentence starting in Line 346 to discuss:

"Observed trends in NWD also agree with satellite and surface-derived NO_2 trends during the COVID-19 lockdown period in March and April 2020, lending further evidence to the ability of NWD to capture large changes in NO_x emissions. Satellite measurements may be more influenced by urban emissions than NWD, but satellites are sensitive to background NO_2 similar to how NWD is sensitive to background NO_x, and trends between satellite NO_2 and NWD have been shown to match closely when averaged over a regional scale (Silvern et al., 2019). Despite the influence of background emissions, both NWD and satellite NO_2 observations capture large-scale changes in anthropogenic emissions (Fig. 3; pre-2010 trends)."

L367 (caption of Figure 4): Colors for met and anthropogenic emission simulations seem to differ from figure, please check.

We have clarified this figure caption: "Figure 4. Results of annual NWD (kg N/ha) from each sensitivity simulation over (a) the CONUS and (b) Europe. The base GC simulation is shown in red, the simulation with changing emissions but constant meteorology (Emissions) is shown in green, the simulation with changing meteorology but constant anthropogenic emissions (Meteorology) is shown in blue, and the no biomass burning simulation (No Fires) is shown in gold. See Sect. 2.2 for a detailed description of these sensitivity runs."

Figure 4: My confusion may stem from the legend/caption inconsistency, but based on the figure legend (emissions: green, met: blue)--Some of the conclusions from this figure are not intuitive to me. The trend line changes most when meteorology is held constant: doesn't that imply a larger role for meteorology than anthropogenic emissions? The sentence L356 ("As long as…") doesn't seem correct to me because the anthro-constant simulation largely matches the trendline of the base case. If the legend colors are incorrect/swapped, please ignore this point.

The confusion here seems to stem from the figure caption not being fully explained. We have titled our constant emissions simulation "Meteorology" to show that the trends are driven by changes in meteorology rather than emissions. This line (blue) remains constant throughout the timeframe. In contrast, we name our constant meteorology simulation "Emissions" since those trends will rely entirely on changing emissions. We have updated the figure caption to clarify;

see the response point above. We also include detailed descriptions of the sensitivity simulations in Section 2.2.

L371 starting with "total NO_x…": consider specifying that CEDS is used for anthro and the others described are the ones calculated? consider: "total NO_x emissions, with the natural component calculated using GEOS-Chem..."

We thank the Reviewer for this suggestion and have rephrased: "Figure 5 shows anthropogenic NO_x emissions derived directly from the CEDS inventory (blue solid line) and total NO_x emissions summed using GEOS-Chem (black solid line), which includes all sources of NO_x emissions (anthropogenic from CEDS, soil, lightning, and biomass burning)."

Table 2: The European soil NO_x reduction case doesn't seem to show a larger influence of soil NO_x in later timeframes. Suggest that it's specified in L395-396 that these results relate to the USA. It's also a little unclear to me the role that meteorology has in this analysis. While I understand the NWD results to be precipitation-corrected, isn't there also a role for other met variables (e.g. temperature in soil NO_x, or the loss of NO_x between urban areas and NTN sites)? I realize and respect that this result already required quite a lot of work, so I don't mean to suggest this as a necessary addition, but it may be worth considering bookend cases with incremental reductions within a year (for example, 5% and 10% scenarios in 1985 and 2017) to control for the role of meteorology.

We have specified that our soil NO_x results are more pertinent to the CONUS starting in Line 427: "We find that the sensitivity to anthropogenic NO_x emissions is greatest in the 1980s and 1990s and decreases to its lowest sensitivity in 2017 over both the CONUS and Europe. This is in contrast to similar sensitivity simulations that reduced soil NO_x emissions by 5%. In these simulations, NWD trends become slightly more sensitive to changes in background soil NO_x emissions later in the timeframe, especially over the CONUS."

We can illustrate that the NWD sensitivity is primarily due to changes in anthropogenic NO_x emissions using our Meteorology sensitivity, in which all NO_x emissions were held constant at 1980 values and all meteorological variables were allowed to evolve over time. We see that the trend in NWD does not change in this scenario (Fig. 4), and perhaps even shows slight increases in NWD over both the CONUS and Europe, which implies that meteorological variables (and any NO_x emissions driven by meteorology such as soil NO_x) are not playing a large role in the NWD changes observed. In contrast, in our Emissions simulation (all meteorological variables including temperature, RH, winds, etc. held constant and anthropogenic emissions allowed to evolve normally) closely matches observed changes in NWD, suggesting the dominant role of anthropogenic emissions in determining NWD trends.

It is possible that other meteorological parameters such as temperature play a role in NWD results (we note that we correct for precipitation biases in our calculations, and we do not see a decrease in precipitation over time (Fig. S3)). Table 2 illustrates the decline in the prevalence of anthropogenic emissions in determining NWD over time. We contrast it to soil NO_x since that is a major natural source of NO_x that is influenced by meteorology. We do not mean to imply that it is the only other parameter that can influence NWD; rather, we just use it as a point of

comparison. We also use this to illustrate that soil NO_x is not sufficient to explain the discrepancies noted in the manuscript, as NWD is not nearly as sensitive to soil NO_x changes compared to anthropogenic NO_x throughout this study.

We discuss the above-mentioned items in Section 3.2: "Trends in GC-predicted NWD since 1980 are driven primarily by changes in anthropogenic emissions rather than meteorological factors. Figure 4 shows the results of the three sensitivity simulations that demonstrate the role of anthropogenic emissions, fire emissions, and meteorology in simulated NWD trends. Over both the United States and Europe, the only simulation that does not follow the trendline of the base simulation is the Meteorology simulation. Trends for the Emissions and No Fires simulations are similar to the base simulation in both domains. As long as anthropogenic emissions are allowed to evolve over time, the trendline in NWD can be matched. Further, changes in precipitation are unlikely to be responsible for the observed changes in NWD, as precipitation rates have remained relatively flat, or even increased, in opposition to NWD trends (Fig. S3). This, along with our sensitivity simulations, suggests that the changes in anthropogenic emissions of NO_x are most influential in driving overall NWD trends in GC."

L405-406: It would be helpful to present model bias results. Figure 3 seems to imply that the model aligns well with the observations and, if anything, the model underestimates NWD. It's not clear to me how the model can "agree" over the CONUS domain but that NOx emissions are "overestimated in certain regions and seasons." Wouldn't that imply that there are also underestimates in some regions and seasons also (in order to agree on a spatial average basis)? Should those be explored?

We agree that this would be a helpful discussion to include. Overall, the model agrees well with observations when the CONUS domain is averaged annually, and regional aggregates were the main focus of our work. However, some areas (such as the Eastern US) are overestimated, and others are underestimated. These overestimates in the Eastern US are more prominent during summer, which is shown in Figure 6. However, some sites are underestimated during summer, as well. We have added a short discussion on these regional and seasonal biases, along with an extra supplemental figure (Fig. S6, shown below), but we leave the full exploration of seasonal and regional NO_x constraints based on NWD to future analyses.

We add this paragraph at Line 500: "It should be noted that the model does not overestimate NWD over all regions or seasons in the US. Some regions, such as the eastern US during spring, exhibit model underestimates. On an annual average basis across the CONUS, NWD is slightly overestimated, but certain regions and seasons show more prominent underestimates that should be explored more fully in future analyses (Fig. S6)."
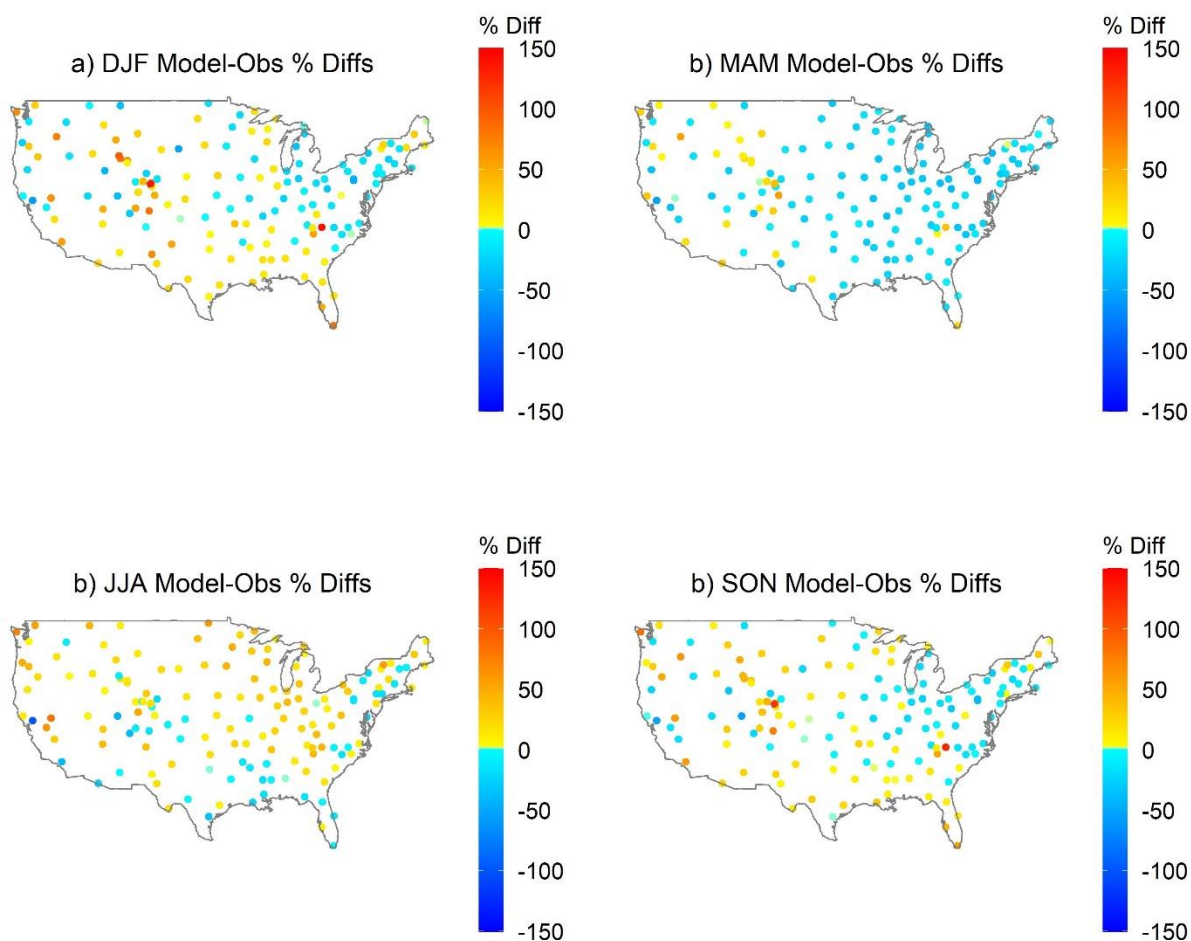
Figure S5. Average model-observation differences (%) in NWD from 1980-2017 during (a) winter, (b) spring, (c) summer, and (d) fall. During summer, many sites in the Eastern US are overestimated by GC, while these same sites tend to be underestimated during spring.

L540: I found the phrase "Such underestimates are not present in other models" to be overly broad—could you please clarify which models?

Here, we are specifically referring to the NASA MERRA2-GMI model and GEOS-Chem v10-01, both of which we explored extensively in a previous paper regarding their ability to reproduce ozone concentrations (Christiansen et al., 2022, DOI: 10.5194/acp-22-14751-2022). We have clarified this and inserted the appropriate reference. It now reads:

"Such underestimates are not present in other chemical transport models, including MERRA2-GMI from NASA (http://acd-ext.gsfc.nasa.gov/Projects/GEOSCCM/MERRA2GMI; last access: 21 Dec 2023) and the previous version of GEOS-Chem explored in this work (v10-01), that do not include these updates (Christiansen et al., 2022)."

Major comments

Lines 21-23: For the sentence beginning, "Over the United States…" is this overestimate intended to reference NWD, rather than NO_x emissions? I believe that this sentence should specify that the overestimate pertains to NWD specifically and not NO_x emissions.

We rephrase this to say: "Over the United States, we find that NWD is overestimated in summer from 1980-2017 by 15-20% on average (interquartile range: 11-31%), with overestimates most prominent in the eastern US after 2000, (20% on average), implying an overestimate of NO_x emissions in the CEDS inventory (0.5x0.5-degree resolution). Over Europe, we find that modeled NWD is overestimated in all seasons from 1980-2017, with the strongest average overestimates occurring in summer and fall (175% and170%, respectively)."

Lines 43-44: This assumption underpins this analysis and merits expansion.

We have clarified this to say: "deposition processes such as rainout occur on longer timescales (e.g., days). This suggests that NWD measurements can be used over long timeframes to track NO_x emissions trends, despite potential changes in NO_x lifetime over decades."

Paragraph lines 164-168:

- I agree that there are greater limitations in the availability of dry deposition (vs wet deposition) measurements, however, the phrase "Dry deposition measurements are available only after 2000 over the CONUS" seems to imply that there is a long-term dry deposition network as part of NADP, which is not true (unless the authors are referencing short-term field studies, which may be clarified). To the extent that dry deposition estimates are made available, to my knowledge they are based on simulations which draw from CASTNet measured concentrations with the Multilayer Model. Overall, the authors' important assertion that dry deposition observational constraints are limited is well supported, but the evidence provided for this should be corrected or clarified.

We have clarified that we mean that CASTNET is only available since 2000, and that there is not a dry deposition network as part of NADP. We have made this sentence clearer: "We do not consider dry deposition in this analysis due to observational limits. Dry deposition measurements are available only after 2000 over the CONUS from the Clean Air Status and Trends Network (CASTNET), and there are only four sites over Europe (EMEP) with analysis timeframes long enough to include."

The Reviewer is correct that dry deposition estimates necessarily include a modeled component, which adds uncertainty to observations. We have added a paragraph discussing the uncertainties in dry deposition and further reasons for excluding those values from this analysis in our methods section:

"There are also many uncertainties with regard to both observations and model representation of dry deposition. Estimates of dry deposition velocities must be made to determine dry deposition fluxes at observation sites. This is typically done by using a multi-layer model (Finkelstein et al.,

2000; Meyers et al., 1998), which calculates deposition velocity as a function of chemical composition, meteorology, and vegetation. Limitations to this method include the lack of meteorological measurements co-located with observation sites, requiring the use of a chemical transport model to estimate deposition velocities. These velocities are uncertain, and different velocity estimation methods can result in fluxes that differ by ~1.6x (Schwede and Lear, 2014). A recent study also shows a high bias in GEOS-Chem for nitrate dry deposition that persists throughout seasons and across multidecadal timeframes (Dutta and Heald, 2023), largely due to a model overestimate of dry deposition velocity of HNO_3. The uncertainty inherent to the dry deposition observations, the limitations of the observations, and the known bias in GEOS-Chem makes dry deposition a more uncertain comparator for NO_x trends than wet deposition. Excluding dry deposition may lead to some bias in capturing anthropogenic trends, as dry deposition tends to be more influenced by urban sources, but seasonal variations, annual trends, and geographic distributions are similar to those found in wet deposition (Dutta and Heald, 2023)."

- The phrase "Trends between dry deposition and wet deposition are similar" should include a citation or be removed. Related to my comments on Section 3.3. below, which suggest expanded consideration of NO_x product composition, the phase of NO_x products also relates to their rate of dry or wet deposition. This could merit discussion depending on the extent to which this phase composition has shifted over the timeframe considered.

We have cited Dutta and Heald (2023) (DOI: 10.1029/2023JD039610) here as a reference for the similarities between wet, dry, and wet + dry deposition trends (see response point directly above).

We appreciate the Reviewer's comments on the phase of NO_x products and the potential impacts on wet and dry deposition. There is no trend in wet/dry composition over time (Silvern et al., 2019), and so we do not expect the NO_x product composition to impact our results over time. We expand further on the comments to Section 3.3 below.

- Lines 167-168: I don't believe that this is correct. For one, the Jaeglé reference is not on an annual basis. More influential is that neither study compares against dry deposition measurements but rather infers a role for dry deposition based on comparisons against measured concentrations. It is important to clarify this point for readers to understand what would be needed for a better understanding of this process (specifically, dry deposition measurements).

We have clarified this to state that the major limitations for dry deposition comparisons are limited measurements and a lack of understanding of dry deposition (see amended text under first bullet point). We have also removed the discussion about the Jaegle reference.

Section 3.3. As mentioned in the "General comments," I disagree that the magnitude of biases and trends in NWD are directly equivalent to NO_x emissions and trends as implied here, at least over the USA. The relationship between NWD and NO_x emissions has likely changed over the timeframe of study, which is in some way indicated by the authors' demonstration that the

sensitivity of nitrate to NO_x has changed over time. However, this finding is not applied for interpretation of the relationship between NWD and NO_x emissions.

I believe that more thought should be given to the change in NO_x lifetime and phase composition over the data record. If anything, the decreased sensitivity of NWD to NOx emissions seems to imply a shorter lifetime over time, differing from the references included in the introduction. Could it be that the lifetime has decreased in less polluted areas? Also, the lifetime of aerosol nitrate is much longer than NO_x, so that a change in NO_x chemical fate to gas v. aerosol over time could affect the distance that NO_x ultimately travels. In other words, I am wondering to what extent NO_x contributes to wet nitrate deposition in the gas (e.g. HNO_3) or aerosol phase, and how has this changed over the timeframe considered? What is the role for a growing influence of organic nitrate? How do the lifetimes of the principal end products differ, and how has that changed over time? If the authors prefer not to add these aspects to the analysis, I feel that the quantitative conclusions should be significantly softened.

The analysis over Europe differs by bringing in a sensitivity simulation that specifically quantifies how the bias changes when NO_x emissions are halved, which is a more appropriate approach. A similar simulation could be developed for the US toward addressing my concern here, but I believe that the analyses suggested above related to lifetime and phase composition could help to inform the process basis for underlying changes in the NWD-NO_x relationship (otherwise, the authors may consider suggesting this as a path for future work).

We appreciate the Reviewer's insightful comments about the NO_x-to-NWD relationship. To address these concerns, we have performed three one-year time-slice sensitivity simulations over the CONUS. In these simulations, we decrease anthropogenic NO_x emissions from CEDS by 50%, paralleling the analysis we performed over Europe. The table below summarizes those results:

% Anthropogenic NOx Reduction	Year	% NWD Reduction	Relative Change
	1985	45	0.9
50	2000	44	0.88
	2015	41	0.82

Here, we do indeed see that the sensitivity of NWD to anthropogenic NOx emissions decreases over time. This could be due to the increased importance of background emissions such as soil NOx in determining NWD magnitudes and trends, or it could be due to a change in NOx lifetimes, as the Reviewer suggested, or a combination. However, we do not think the change in lifetime is the primary driver behind this change in sensitivity. Laughner and Cohen (2019) (DOI: 10.1126/science.aax6832) investigated the impact of NO_x lifetimes on long-term trends in NO_x emissions over the CONUS and concluded that a change in NO_x lifetimes was not sufficient to fully explain NO_x trends, especially the post-2010 flattening. They suggest that it is more likely that the increasing contribution of background NO_x is primarily responsible for these trends, although lifetime does play an important role in improving agreement between predicted and observed NO_2 columns. We address these concerns in Section 3.3 and in the Introduction:

Introduction, starting Line 43: "Recent observations have shown increases in NO_x lifetimes of a few hours since 2006 (Laughner and Cohen, 2019), which may increase the distance NO_x travels before it eventually deposits. However, the small increase in lifetimes is not expected to substantially impact wet deposition since deposition processes such as rainout occur on longer timescales (e.g., days). This suggests that NWD measurements can be used over long timeframes to track NO_x emissions trends, despite potential changes in NO_x lifetime over decades."

Section 3.3, Line 499: "The sensitivity of NWD to anthropogenic NO_x emissions decreases from 1980-2017, and thus the relationship between anthropogenic NO_x and NWD is not strictly 1:1, although NWD is most sensitive to changes in anthropogenic NO_x emissions. This change in sensitivity can be attributed to the increasingly large role of background NO_x emissions to total NO_x, and changes in NO_x lifetime. It is more likely that these changes are better explained by the increasing prevalence of background NO_x, as a previous investigation of NO_x lifetime changes since the 2000s found that changes in lifetime alone cannot fully explain NO_x trends (Laughner and Cohen, 2019). Changes in NO_x lifetime impact NO_x product composition and phase, and future analyses should investigate the role of a changing NO_x lifetime on products such as nitric acid, nitrate aerosol, and organic nitrates."