RESPONSE TO REVIEWERS

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Point-by-point responses to reviewers are included below. Reviewer comments are in blue. Responses are in black, and text added or altered is quoted in orange. Line numbers are those in the updated tracked changes PDF document.

Responses to Reviewer RC1:

Wei et al. characterize the distribution, seasonality, and speciation of reactive oxidized nitrogen (NO_y*) in the upper troposphere using measurements from research campaigns and commercial flights and compare them to a global model simulation to test our understanding of* NO_y *sources & chemistry. They analyze the similarities and differences in the* NO_y *speciation in different regions and seasons and identify discrepancies between the observations and the model. This study tackles an important topic since the cycling of oxidized nitrogen in the global troposphere affects tropospheric ozone and OH, and thus climate and tropospheric oxidant levels. The paper is very well-written and the conclusions, for the most part, are well supported by the data and analysis presented. Here are some points that need to be clarified further:*

(1) The UT is defined as 8-12 km. This is appropriate for the mid-latitudes. but not the tropics. I understand this might be because the DC8 has a ceiling of 12 km, but this should be clarified.

We now clarify this in Section 2.1:

"The DC-8 research aircraft has sampled ambient air covering the near full extent of the troposphere" (line 150)
"... within a wide pressure range from 180 hPa (~8 km) to the DC8 ceiling of 450 hPa (~12 km). This captures the full vertical extent of the midlatitude upper troposphere, but not the tropics. The tropical tropopause, according to NASA Modern-Era Retrospective analysis for Research and Applications version 2 (MERRA-2) meteorology, extends to ~16 km." (lines 176-179)

(2) Lines 159-185: The authors use NO_2 *calculated from the photochemical steady state instead of the measurements because of interference in the chemiluminescence instrument. The SEAC4RS TD-LIF* NO_2 *measurements may also be biased high (Silvern et al. 2018, Shah et al. 2023) and this could affect the TD-LIF measurements of the sum of PANs, etc. which are*

calculated by subtracting the measured NO_2. Is a correction to TD-LIF measurements of these NOy species needed?

The largest contributor to TD-LIF NO_2 interference is MPN (100% decomposition; Reed et al. (2016)). Shah et al. (2023) estimate a 0-21% NO_2 interference for SEAC^{4}RS TD-LIF NO_2 measurements. If we use 21% as an upper bound, this is ~5 pptv of the median SEAC^{4}RS PSS NO_2; a small contribution (~3%) to the 190 pptv PNs.

We adjust the text to include it in the discussion of Figure 4:
"… from factors such as unmeasured components, positive interference in the NO_y instrument, or a low bias in the TD-LIF PNs …" (Lines 384-385)

We now discuss this in the paper in the context of Figure 4:
"TD-LIF measurements of PNs are calculated from the difference in NO_2 detected with the NO_2 channel and with the PNs channel set to a temperature at which all PNs decompose (Day et al., 2002). A bias in NO_2 could therefore impart a bias in PNs. The largest source of TD-LIF interference is 100% decomposition of MPN (Reed et al., 2016) and MPN during SEAC^{4}RS far exceeds any of the other campaigns. If we use the higher-end interference of 21% from Shah et al. (2023) for SEAC^{4}RS, this equates to ~5 pptv of SEAC^{4}RS PSS NO_2. This is only ~3% of the 190 pptv SEAC^{4}RS PNs." (lines 399-404)

(3) One of the paper's conclusions is that GEOS-Chem underestimates MPN during SEAC^{4}RS. MPN seems to make up an unexpectedly large fraction of the observed NO_y during SEAC^{4}RS, and including it in the sum of the NO_y species degrades the correlation with the total NO_y measurements (Figure 4). This leads me to suspect that the MPN measurements may be biased high. It would be valuable if the authors could dig in a little more to find further support for the MPN measurements, and the conclusion that our understanding of MPN sources is rather poor. They could, for example, look at the ATom data downwind of the southeast US to see if there is a substantial difference between the total NO_y and the sum of the NO_y species. Do other studies show a significant underestimate of VOCs in GEOS-Chem during SEAC^{4}RS?

The ATom measurements are much closer to North Africa (Figure 2 in the main manuscript) than to the southeast US, so would not be suitable for corroborating the large MPN contribution to total NO_y during SEAC^{4}RS. If we instead infer MPN by subtracting the sum of HNO_4 and all PANs measured with the CIMS instrument from the TD-LIF PNs measurement and assume most PANs are measured by the CIMS instrument, MPN declines from 85 to 49 pptv (from 24% to 14% of NO) for SEAC^{4}RS. This is 32 pptv less than the MPN in Figure 5. Even so, MPN still makes a greater relative contribution to total NO_y during SEAC^{4}RS than is inferred for the other campaigns and far more than is simulated with GEOS-Chem.

This is added to Section 3.2:

"The far larger fraction of MPN to total NO_y during SEAC^{4}RS (Figure 5(b)) warrants further investigation. If we instead estimate MPN by subtracting the sum of HNO_4 and all PANs measured with the CIMS instrument from the TD-LIF PNs, making the assumption that CIMS measures most PANs, MPN is 49 pptv and the contribution to NO_y declines from 24% to 14%. This is still at least double the contribution for any other campaign." (Lines 483-486)

And incorporated in the comparison to the model in Section 3.3 to confirm that a substantial model underestimate in MPN still holds:

"The sum of measured and modelled individual NO_y components are not significantly different for SEAC^{4}RS, though the model overestimates HNO_3 by 64 pptv and underestimates MPN by 81 pptv compared to the TD-LIF measurements and by 45 pptv compared to MPN inferred using TD-LIF PNs and CIMS HNO_4 and PANs (Section 3.2)." (Lines 562-565)

The abstract and conclusions are also updated to incorporate this range in MPN contribution and to give the most conservative model bias:

"Methyl peroxy nitrate (MPN) makes an outsized contribution to NO_y (14-24%) over the Southeast US." (Lines 21-22)
"A model underestimate in MPN of at least ~50 pptv (13-fold) over the Southeast US" (Lines 25-26)
"The relative contribution of most other components is similar across all campaigns, except for MPN that is 15-24% of NO_y for SEAC^{4}RS over the Southeast US and much less (2-7%) for all other campaigns, though MPN measurements are rare and susceptible to biases." (Lines 605-607)

The potential underestimate in modelled VOCs measured during SEAC^{4}RS is confirmed by a persistent low model bias calculated by Chen et al. (2019b) for free tropospheric VOCs of ~60%. We now include this in Section 3.3:

"Chen et al. (2019a) estimated that the GEOS-Chem underestimate in free tropospheric VOCs during SEAC^{4}RS is on average ~60%, but exceeds a factor of 2 for many of the VOCs assessed." (Lines 567-568)

(4) Lines 54 – 75: I presume nighttime NO_y chemistry in the UT is slow enough to be ignored, but it would be good to describe it briefly and state why it is not important, if that is the case.

We now describe the dominant nighttime chemistry, acknowledge its importance and the severe lack of detailed measurements to aid our understanding:

"Nighttime NO_y chemistry is also important, but aircraft campaign measurements of the nocturnal upper troposphere are mostly of total NO_y from commercial aircraft campaigns. The nighttime chemistry not in Figure 1 includes NO reaction with OH forming nitrous acid (HONO) that accumulates in the absence of photolysis, as well as NO_2 reaction with O_3 to form the nitrate radical (NO_3) that further reacts with NO_2 to produce N_2O_5, a precursor of aerosol nitrate (pNO_3) (Bradshaw et al., 2000)." (p. 2 lines 90-92; p. 3 lines 100-101)

(5) Lines 365- 372: The paragraph discusses the minor NO_y species not included in the analysis, but it does not discuss particulate nitrates (organic & inorganic). Shouldn't these aerosol species be included in NO_y, even if they are minor in the UT?

We discuss the potential contribution of pNO3 to the upper troposphere NO_y budget in the context of Figure 4 that, for 100% sampling efficiency, 4% of total NO_y:

"Chemiluminescence NO_y instruments also measure pNO_3, but with uncertain sampling efficiencies (Bourgeois et al., 2022). For 100% efficiency and using the Aerosol Mass Spectrometer (AMS) measurements of submicron (< 1 μm) pNO_3, the contribution is at most 1% of NO_y for ARCTAS for a median pNO_3 of ~0.01 μg m^{-3} (~4 pptv), ~4% for SEAC^{4}RS for pNO_3 of ~0.04 μg m^{-3} (~14 pptv), ~4% for KORUS-AQ for pNO_3 ~0.07 μg m^{-3} (~25 pptv), and <2% for ATom for pNO_3 <0.01 μg m^{-3} (~4 pptv)." (lines 393-397)

And again in the context of Figure 5:

"pNO_3, absent in Figure 5 due to the uncertain sampling efficiency of the chemiluminescence instrument, is at most 4% for SEAC^{4}RS and for KORUS-AQ (Section 3.1), comparable to the contribution from PPN." (lines 479-481)

(6) I suggest that NO_y be called "reactive oxidized nitrogen" instead of "reactive nitrogen," which includes reduced nitrogen (NH3, etc.). And also that in this work NO_y does not include N_2O.

Thank you for the suggestion. We have replaced all instances of "reactive nitrogen" with "reactive oxidized nitrogen".

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