RESPONSE TO REVIEWERS

Ms. Ref. No.: egusphere-2024-3388, doi:10.5194/egusphere-2024-3388

Journal: Atmos. Chem. Phys.

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".

References:

Bourgeois, I., Peischl, J., Neuman, J. A., Brown, S. S., Allen, H. M., Campuzano-Jost, P., Coggon, M. M., DiGangi, J. P., Diskin, G. S., Gilman, J. B., et al.: Comparison of airborne measurements of NO, NO_2, HONO, NO_y, and CO during FIREX-AQ, Atmos. Meas. Tech., 15, 4901-4930, doi:10.5194/amt-15-4901-2022, 2022.

Bradshaw, J., Davis, D., Grodzinsky, G., Smyth, S., Newell, R., Sandholm, S., and Liu, S.: Observed distributions of nitrogen oxides in the remote free troposphere from the NASA Global Tropospheric Experiment Programs, Rev. Geophys., 38, 61-116, doi:10.1029/1999rg900015, 2000.

Chen, X., Millet, D. B., Singh, H. B., Wisthaler, A., Apel, E. C., Atlas, E. L., Blake, D. R., Bourgeois, I., Brown, S. S., Crounse, J. D., et al.: On the sources and sinks of atmospheric VOCs: An integrated analysis of recent aircraft campaigns over North America, Atmos. Chem. Phys., 19, 9097-9123, doi:10.5194/acp-19-9097-2019, 2019a.

Chen, X., Millet, D. B., Singh, H. B., Wisthaler, A., Apel, E. C., Atlas, E. L., Blake, D. R., Bourgeois, I., Brown, S. S., Crounse, J. D., et al.: On the sources and sinks of atmospheric VOCs: an integrated analysis of recent aircraft campaigns over North America, Atmos. Chem. Phys., 19, 9097-9123, doi:10.5194/acp-19-9097-2019, 2019b.

Day, D. A., Wooldridge, P. J., Dillon, M. B., Thornton, J. A., and Cohen, R. C.: A thermal dissociation laser-induced fluorescence instrument for in situ detection of NO_2, peroxy nitrates, alkyl nitrates, and HNO_3, J. Geophys. Res.: Atmos., 107, doi:10.1029/2001jd000779, 2002.

Reed, C., Evans, M. J., Di Carlo, P., Lee, J. D., and Carpenter, L. J.: Interferences in photolytic NO_2 measurements: explanation for an apparent missing oxidant?, Atmos. Chem. Phys., 16, 4707-4724, doi:10.5194/acp-16-4707-2016, 2016.

Shah, V., Jacob, D. J., Dang, R., Lamsal, L. N., Strode, S. A., Steenrod, S. D., Boersma, K. F., Eastham, S. D., Fritz, T. M., Thompson, C., et al.: Nitrogen oxides in the free troposphere: implications for tropospheric oxidants and the interpretation of satellite NO_2 measurements, Atmos. Chem. Phys., 23, 1227-1257, doi:10.5194/acp-23-1227-2023, 2023.

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Response to Reviewer RC2:

Wei et al. use different aircraft measurements combined with a global model simulation to characterise upper tropospheric NOy and assess our understanding of the processes governing it. The manuscript is generally well written and easy to follow. The topic is important and timely, affecting for example tropospheric oxidation capacity and ozone formation.

Below, I have listed certain areas where I would still like to see more detail, followed by a list of minor comments.

1. The comparison between the IAGOS and DC-8 flights. There is a rather large difference in NOy levels between the two, which is explained to result from differences in flight altitudes (lines 241-242). As the comparison of these two flight measurements forms a core part of the manuscript, I would like to see more detailed comparisons here, like altitude profiles of NOy from the two types of measurements. Do they match up?

We now include a supplementary figure (Figure S1; pasted below) showing the seasonal mean vertical profiles of collocated DC-8 and IAGOS NO_y and we discuss the features in this figure in the text to support the distinct altitude ranges sampled by DC-8 and IAGOS and consistency in NO_y for the few instances that sampling is vertically collocated.

"The two campaigns sample distinct altitude ranges of the upper portion of the upper troposphere centred at ~240 hPa (~10 km) for IAGOS and a wider vertical extent of the lower portion of the upper troposphere centred at ~360 hPa (~1.5 km below IAGOS) for DC-8 (Figure S1). There is a general pattern of a steep increase in NO_y with altitude, with the exception of IAGOS layers located near 300 hPa in March-May and September-November (Figure S1). Average NO_y is similar between the two campaigns for the rare instances that DC-8 and IAGOS sample the same pressure layers (Figure S1)." (lines 316-322)

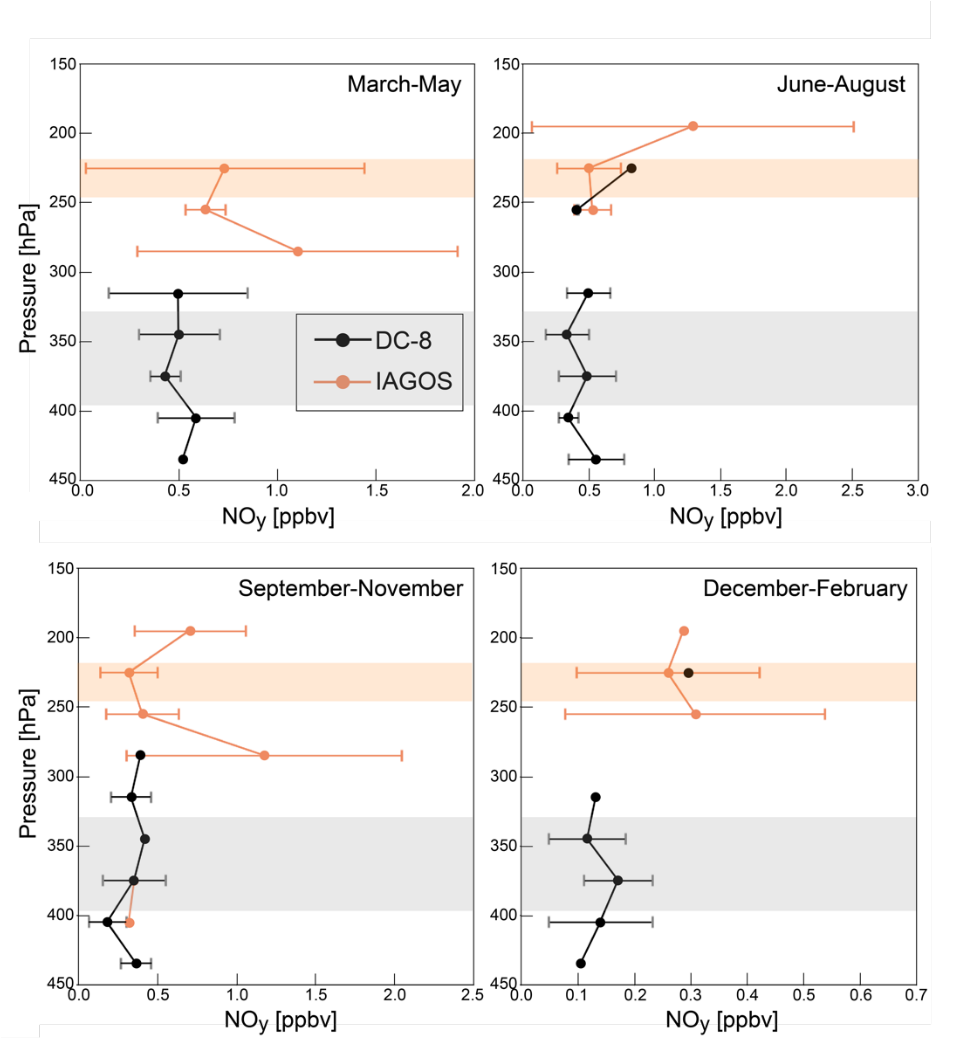

Figure S1: Comparison of seasonal mean vertical profiles of total reactive nitrogen (NO$_y$) from spatially collocated DC-8 and IAGOS aircraft observations. Symbols are means from averaging upper troposphere (450-180 hPa) observations into 30 hPa bins. Lines are standard deviations. Shading indicates the typical vertical sampling range (pressure standard deviation) of DC8 (grey) and IAGOS (orange). Pressure range selection and screening for stratospheric influence and plumes are detailed in the main manuscript.

2. SEAC^{4}RS stands out from the other campaigns in Figs. 4 and 5. These differences are expected to arise from the high contribution of MPN to NOy in that campaign. Especially the poor correlation seen in Fig. 4 leads me to suspect there may be something wrong with these measurements, or then that MPN would not be properly reflected in the NOy measurements. Could you analyse further, whether these MPN measurements are indeed high and correct, or may there be some interference in them?

Further analysis assessing a potential high bias in MPN is detailed in the first part of the response to reviewer # 1, Comment (3). Even with this smaller MPN concentration, the conclusion that the model substantially underestimates MPN still holds.

3. Altitude definitions: upper troposphere is here defined as 8-12 km in altitude. However, tropopause may be kilometers higher in the tropics: can you justify the choice of altitude range further?

This is addressed in response to Reviewer #1, Comment (1).

Minor comments:
Abstract, lines 23-24: fractional/percentage values of the over/underestimation would be useful here

Added as 10-90% for PPN and 31-65% for NO_2. (lines 23-24)

Line 54, Fig. 1: can you provide references justifying these are the main species & reactions?

To better represent the key studies that have informed dominance of NO_y components and the reactions in Figure 1, we have edited the text and cited these studies as below:

"Chemical cycling of dominant daytime NO_y components, informed by past review and measurement compilation studies of the free troposphere (Emmons et al., 1997; Bradshaw et al., 2000), is illustrated in Figure 1." (lines 73-74).

Lines 61-63: add ref for the photolysis vs thermal decomposition
Huey (2007) added. (Line 82)

Lines 65-68: add refs
Schultz et al. (1999) added for NO_x reservoir compound transport and subsidence. (Lines 88-87)

Text edited to clarify that existing citations substantiate slow loss processes in the upper troposphere:

"Loss processes in the dry upper troposphere are slow and dominated by subsidence, resulting in long NO_y lifetimes of 10-20 days (Logan, 1983; Prather and Jacob, 1997). Similarly, NO_x

has a lifetime of about a week compared to less than a day in the boundary layer (<2 km) (Jaeglé et al., 1998).” (Lines 87-89)

Lines 76-78: add ref

We have edited the text, so that the citations appear before the sentence starting “These studies have either focused on ...”. For completeness, we have also added other relevant citations. The updated text reads as:

“Modelling studies evaluating best understanding of NO_y in the upper troposphere routinely identify stark discrepancies between observed and modelled total NO_y, NO_x, and the ratio of NO-to-NO_2 in the upper layers of the troposphere (Jaeglé et al., 1998; Talbot et al., 1999; Bertram et al., 2007; Hudman et al., 2007; Liang et al., 2011; Nault et al., 2015; Huntrieser et al., 2016; Travis et al., 2016; Fisher et al., 2018; Silvern et al., 2018; Lee et al., 2022; Cohen et al., 2023). These studies have either focused on a few NO_y components, or a single aircraft campaign.” (Lines 107-112)

Line 104: add ref

Singh et al. (2006) added. (Line 155)

Lines 105-107: mention that the exact definitions for screening will follow

Thank you for the suggestion. We rather decided to delete “... and that have limited influence from stratospheric air”, as this data screening aspect was not a factor in eliminating INTEX-NA and DC3. (Line 156)

Line 126: would times relative to sunrise and sunset be more appropriate? You screen for jNO2 as well, but this leads to different representation of high- and low latitudes (as mentioned on lines 139-140). I'm not requesting you to redo all the analyses, but preferably comment on if this has an effect on the results

We do already use the reported solar zenith angle (SZA) values to confirm that are time range and jNO_2 filter removes data with large SZA (sunrise/sunset). (Line 201). Given this, we do not expect any effect on our results if we instead used SZA.

Line 127: full vertical extent. But this does not include full vertical extent, esp. in tropics

This text has been updated to address the similar Reviewer #1, Comment (1).

Screening criteria: how much data do these criteria exclude? In other words, how typical are the sought-for background conditions?

We now state provide these statistics and the main cause for data loss:

"The proportion of observations at 450-180 hPa is 42-50% for ATom and 16-37% for the other campaigns. After applying all other data screening, 20% of all data are retained for ATom and 7-11% for the other campaigns." (Lines 202-203).

Lines 135-136: refs for these screening criteria

These are already provided as Hudman et al. (2007) and as Shah et al. (2023). (Lines 196-198)

Line 137: what does approximately zero mean?

Zero within the range of uncertainty of the instrument.

Line 149: ref talks about TD-CIMS specifically

Thank you for pointing this out. We have replaced the Slusher et al. (2004) reference with Huey (2007). (Line 212)

Lines 151-153: ref

This information is obtained directly from the dataset.

Line 154: ref for TD-LIF

Day et al. (2002) added. (Line 217)

Eq. 1, also in the text: NO and NO2 should be in square brackets

These are intentionally not in square brackets, as the units are distinct (pptv) from the compounds in squares brackets (molecules/cm^3).

Line 181: how is HO2 measured?

HO_2 is measured using a laser induced fluorescence.

Line 184, RO2 relatively insignificant: I could not easily find this in the reference. Is it so?

Shah et al. (2023) state that it makes a small contribution in the free troposphere, so we have reworded our text to more closely match theirs:

"... but we ignore this reaction as it is relatively insignificant throughout the free troposphere (Shah et al., 2023)." (Lines 248-249).

Line 202: are O3, CO and jNO2 also measured on the commercial aircraft?

O_3 and CO are, as is now made clear in the text:

"... and daytime filtering as is applied to DC-8 data (Sect. 2.1) using IAGOS O_3 and CO measurements." (Line 273).

There are no jNO_2 measurements, but there is no need to include this filtering step, as none of the coincident flights extend to the high latitudes. Now also stated in the text:

"There are no NO_2 photolysis frequency measurements, but the requirement for spatial coincidence with ATom excludes polar twilight and night measurements at high latitudes." (Lines 274-275)

Line 222: do you mean below-cloud?

Yes. Corrected (Line 293).

Lines 242-243: ref or show data

Data are now shown in response to your Comment 1.

Fig. 3 b: is panel b needed?

Yes. The panel helps illustrate the size of seasonal variability in total NO_y. Despite large differences in absolute concentrations of DC8 and IAGOS NO_y, both exhibit relatively similar seasonal changes, whereas the model (state of knowledge) seasonal shifts in NO_y are too modest.

Lines 261-266: would it be easier to read if common measurements were listed, and then campaign-wise which compounds were included?

We now summarise this information in a new Table 1 (pasted below) for greater clarity and refer to the table in the Figure 1 caption and in the text (Line 350).

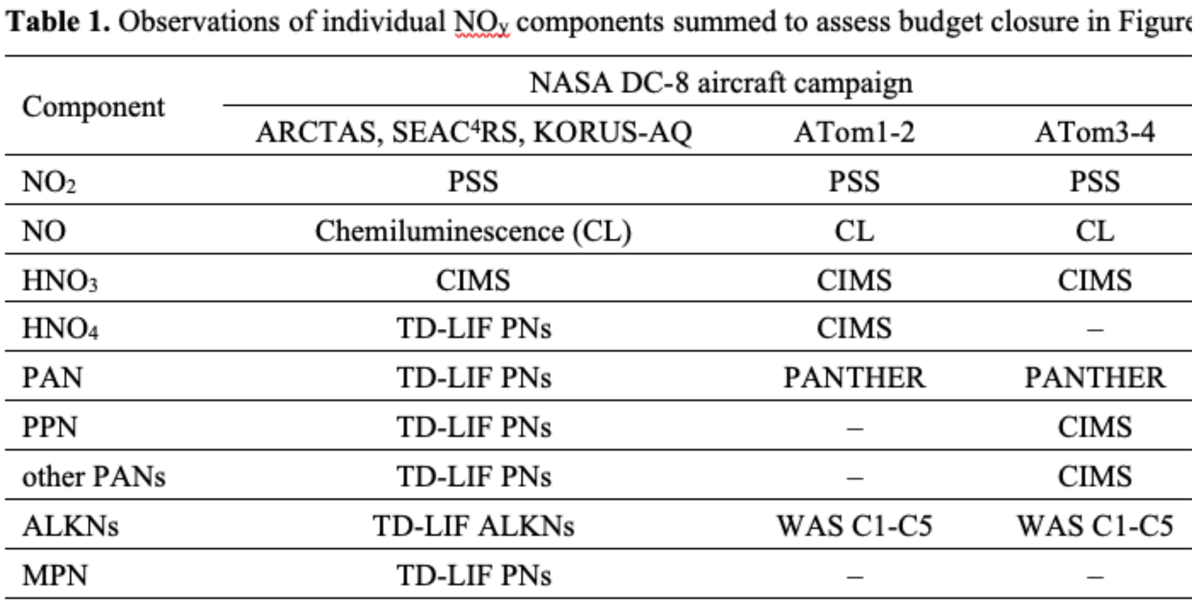

Table 1. Observations of individual NO_y components summed to assess budget closure in Figure

Component	NASA DC-8 aircraft campaign		
	ARCTAS, SEAC^{4}RS, KORUS-AQ	ATom1-2	ATom3-4
NO_2	PSS	PSS	PSS
NO	Chemiluminescence (CL)	CL	CL
HNO_3	CIMS	CIMS	CIMS
HNO_4	TD-LIF PNs	CIMS	–
PAN	TD-LIF PNs	PANTHER	PANTHER
PPN	TD-LIF PNs	–	CIMS
other PANs	TD-LIF PNs	–	CIMS
ALKNs	TD-LIF ALKNs	WAS C1-C5	WAS C1-C5
MPN	TD-LIF PNs	–	–

Lines 294-296: does including the HCN observations improve the agreement?

At the risk of over-interpreting a rough estimate of HCN interference, we now state that the HCN interference estimates are consistent with the unaccounted NO_y in Figure 4:

"These lower-end interference estimates are similar in size to the percent missing NO_y (13% for ARCTAS, 3% for SEAC^{4}RS, 8% for KORUS-AQ, 1-22% for ATom)." (Lines 390-391)

Section 3.2: includes long and complicated section on inferred concentrations, should this rather be in the methods section?

We prefer to keep it in this section, as the inference requires knowledge of the median values of the measured NO_y components presented in Figure 5.

We now state in the methods Section 2.1 that inference is needed for quantities not measured:

"The NO_y components not measured during specific campaigns are inferred. These include HNO_4 for KORUS-AQ, and ATom-3-4, PPN for ATom-1-2, and MPN for ARCTAS, ATom-1-4 and KORUS-AQ. The approaches used to infer these values differs, informed by the results, so a detailed description of this inference is in Section 3.2." (Lines 251-254)

And in Section 3.2, we adjust the text of the 2 paragraphs to accommodate this pre-introduction to inference in the methods section and to focus paragraph 1 on HNO4 and PPN and paragraph 2 on MPN:

Lines 425-442:
"Inferred DC-8 HNO_4 and PPN in Figure 5 use ATom-1 HNO_4 and ATom-4 PPN for combined ATom-1 and -4 components, and, similarly, ATom-2 HNO_4 and ATom-3 PPN for combined ATom-2 and -3. KORUS-AQ HNO_4 is estimated to be 37 pptv by multiplying the SEAC^{4}RS median fraction of HNO_4 (HNO_4/NO_y = 0.06) by the KORUS-AQ median NO_y. SEAC^{4}RS is used, as HNO_4 is thermally unstable (Ryerson et al., 2000) and so varies with temperature. Mean upper troposphere ambient temperatures for KORUS-AQ (252 K) are more consistent with SEAC^{4}RS (246 K) than the other campaigns (238 K for ARCTAS, 238K-241 K for ATom).

The inferred ~10 pptv ARCTAS MPN is from the estimate by Browne et al. (2011). KORUS-AQ MPN is estimated by bounding a potential range from two approaches. The first is the median value of the difference between TD-LIF total PNs and the sum of all individual CIMs PANs and our inferred HNO_4 of 37 pptv, yielding MPN = 75 pptv. This likely overestimates MPN, as the CIMS instrument does not measure an exhaustive suite of PANs. Lee et al. (2022) estimated with a box model and KORUS-AQ measurements that unmeasured PANs account for ~20% of total PNs during KORUS-AQ, though this is for air masses impacted by petrochemical and other anthropogenic VOCs and NO_x emissions. Accounting for these unmeasured PANs yields a lower-bound KORUS-AQ MPN of 8 pptv. The MPN that we infer then for KORUS-AQ is 42 pptv, the midpoint of 8 and 75 pptv, accounting for 7% of KORUS-AQ NO_y. As the GEOS-Chem model MPN is consistent with DC-8 inferred MPN during ARCTAS, we multiply the GEOS-Chem ATom MPN fractions (MPN/NO_y ~0.01 for ATom-1 and -4 and ~0.02 for ATom-2 and -3) by ATom DC-8 NO_y to infer ATom MPN of < 6 pptv."

We have also rewritten the first half of the ALKNs paragraph to focus it on the results in Figure 5, rather than the challenges of inferring >C5 ALKNs during ATom:

"Only the C1-C5 ALKNs are shown in Figure 5 for ATom. The remote measurements of total ALKNs available from ARCTAS that would be most suitable to assess the likely contribution of longer chain (>C5) ALKNs are on median 5 pptv less than the ATom C1-C5 ALKNs measurements. The total ARCTAS total ALKNs measurements are also very noisy, as indicated by a range of -113 pptv to ~333 pptv. The range in ARCTAS WAS C1-C5 measurements, by comparison, is 8-29 pptv. Contributions of >C5 ALKNs to total ALKNs for SEAC^{4}RS (~50%) and KORUS-AQ (~60%), representative of the continental upper troposphere, suggest that >C5 ALKNs in remote regions are <50% of total ALKNs or <12 pptv (median of C1-C5 ALKNs for ATom1-4)." (p. 12 lines 443-447; p.13 lines 461-463)

Line 359: coincidence of the individual to total NOy? What about disregarding ALKN as they make a relatively small fraction of NOy to achieve higher southern hemisphere coverage?

Indeed, this approach could have been adopted instead, but as we do already include a paragraph dedicated to the southern hemisphere (Lines 488-493) that covers the relative contribution of the dominant component PAN, and the seasonality in total NO_y that we find to be generally consistent with the northern hemisphere biased findings.

Lines 366-368: ref for negligible contribution

These are already provided following the initial opening sentence of the paragraph. Following that sentence, we elaborate that NO_3 and HONO have very short lifetimes, as both rapidly photolyze.

Line 370: check the reference. For 100 ppt NO the lifetime is 15 seconds, so for the max average NO campaign (SEAC4RS) it is close to a minute. Noontime clear sky photolysis lifetime is around 6 s, longer off-noon and at high latitudes. Not saying that NO3 would be significant, but that people often underestimate NO3 daytime lifetimes

Thank you for pointing out this issue. We have amended the text:

NO_3 has a lifetime of a few seconds during the day, due to efficient photolysis (Brown and Stutz, 2012). (Lines 497-498)

Lines 371-372: how much shorter?

We now state this in terms of the 50% faster photolysis rates expected for HONO from knowledge of the wavelength at which is photolyzes and the increase in actinic flux and hence photolysis frequencies with altitude at this wavelength:

Photolysis of HONO would be further enhanced (by ~50% at 390 nm) in the upper troposphere where photolysis frequencies are enhanced (Hofzumahaus et al., 2002; Reed et al., 2016). (p. 13, line 499; p. 14, lines 514-515)

Lines 391-392: ref, or is this your result?

Our result. This is clarified in updated text added to address Reviewer #1, Comment (5). To accommodate that update, we amend the text in these lines too:

"These are on median, ~0.01 μg m^{-3} during ARCTAS, ~0.07 μg m^{-3} during KORUS-AQ, ~0.04 μg m^{-3} during $SEAC^4RS$ and <0.01 μg m^{-3} during ATom (Section 3.1)." (Lines 533-534)

Line 417: ref

Text slightly modified to clarify that this is our analysis of the data:

"The model high bias in HNO_3 could be because of a factor of 2 overestimate in our modelled H_2O_2 compared to observed H_2O_2 for $SEAC^4RS$." (Lines 569-580)

Lines 460-461: was this mentioned in the results section?

Yes. In Section 3.1, we discuss the role of lightning in affecting seasonality of total NO_y measured by IAGOS and DC8. (Lines 310-311)

Line 490: maybe cite all sources here again.

Done. (Lines 651-653)

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Characterization of reactive oxidized nitrogen in the global upper troposphere using recent and historic commercial and research aircraft campaigns and GEOS-Chem

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Abstract. Reactive oxidized nitrogen (NO_y) in the upper troposphere (UT) influences global climate, air quality, and tropospheric oxidants, but this is informed by limited knowledge of the relative contribution of individual NO_y components in this undersampled layer. Here we use sporadic NASA DC-8 aircraft campaign observations, after screening for plumes and stratospheric influence, to characterise UT NO_y composition and evaluate current knowledge of UT NO_y as simulated with the GEOS-Chem model. Use of DC-8 data follows confirmation that these intermittent data reproduce NO_y seasonality from routine commercial aircraft observations (2003-2019), supporting use of DC-8 data to characterize UT NO_y. We find that peroxyacetyl nitrate (PAN) dominates UT NO_y (30-64% of NO_y), followed by nitrogen oxides ($NO_x \equiv NO + NO_2$) (6-18%), peroxynitric acid (HNO_4) (6-13%), and nitric acid (HNO_3) (7-11%). Methyl peroxy nitrate (MPN) makes an outsized contribution to NO_y (14-24%) over the Southeast US relative to the other regions sampled (2-7%). GEOS-Chem, sampled along DC-8 flights, exhibits much weaker seasonality than DC-8, underestimating summer and spring NO_y and overestimating winter and autumn NO_y. The model consistently overestimates peroxypropionyl nitrate (PPN) by ~10-16 pptv or 10%-90% and underestimates NO_2 by 6-36 pptv or 31%-65% as the model is missing PPN photolysis. A model underestimate in MPN of at least ~50 pptv (13-fold) over the Southeast US results from uncertainties in processes that sustain MPN production as air ages. Our findings highlight that greater understanding of UT NO_y is critically needed to determine its role in the nitrogen cycle, air pollution, climate, and abundance of oxidants.

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1 Introduction

Reactive oxidized nitrogen (NO_y) in the upper troposphere impacts global climate, surface air quality and the oxidizing capacity of the whole troposphere (Mickley et al., 1999; Bradshaw et al., 2000; Dahlmann et al., 2011; Worden et al., 2011). NO_y is an important climate driver because tropospheric ozone (O_3) production is limited by the availability of NO_y, particularly in the upper troposphere where the radiative forcing efficiency of O_3 peaks (Dahlmann et al., 2011; Worden et al., 2011; Rap et al., 2015). Influence on tropospheric O_3 production also affects abundance of the main atmospheric oxidant, the hydroxyl radical (OH), thus altering the lifetimes of the longer-lived greenhouse gas methane and the air pollutants carbon monoxide (CO) and volatile organic compounds (VOCs) (Murray et al., 2013; Seltzer et al., 2015).

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Knowledge of dominant daytime NO_y compounds, sources, chemistry, fate, and persistence in the upper troposphere has been largely informed by observations and models used as part of research and commercial aircraft campaigns (Boersma et al., 2011; Marais et al., 2018; Silvern et al., 2018; Travis et al., 2016; 2020). Instruments onboard research aircraft that sample the upper troposphere, in particular the recently retired NASA DC-8 platform, have undergone substantial development to directly measure and derive estimates of a large suite of upper tropospheric NO_y compounds. These include nitrogen oxides ($NO_x \equiv NO + NO_2$), peroxyacetyl nitrate (PAN) and other prominent PAN-type compounds, nitric acid (HNO_3), peroxynitric acid (HNO_4), alkylnitrates (ALKNs) and, more recently, methyl peroxy nitrate (MPN).

These aircraft campaigns have confirmed that sources of NO_y to the upper troposphere are dominated by lightning NO_x emissions (Levy II et al., 1999; Gressent et al., 2014; 2016; Marais et al., 2018), causing a seasonal maximum in NO_y in summer months and a minimum in winter in parts of the world such as the northern midlatitudes where there is large seasonal variability in lightning activity (Blakeslee et al., 2014; Stratmann et al., 2016). Other NO_y source contributors include NO_x emissions from cruising altitude aircraft (Brasseur et al., 1996), stratospheric downwelling of air masses laden with HNO_3 and NO_2 that also promote prompt formation of PANs on mixing with cold upper tropospheric air (Levy II et al., 1980; Jacob et al., 2010; Liang et al., 2011), deep convective uplift of surface pollution (Ehhalt et al., 1992; Jaeglé et al., 1998; Bertram et al., 2007), and aged air masses initially very photochemically active that accumulate MPN (Nault et al., 2015).

Chemical cycling of dominant daytime NO_y components, informed by past review and measurement compilation studies of the free troposphere (Emmons et al., 1997; Bradshaw et al., 2000), is illustrated in Figure 1. During the day, NO and NO_2 are in photostationary steady state, as NO oxidation, mostly by O_3, is balanced by NO_2 photolysis. NO_x also reacts to form reservoir compounds. For NO_2, these include HNO_3 from reaction with OH, PANs from reaction with peroxy acyl radicals (RC(O)OO), HNO_4 from reaction with the hydroperoxyl radical (HO_2), and MPN from reaction with the methyl peroxy radical (CH_3O_2). PANs in the upper troposphere are typically dominated by PAN followed by peroxypropionyl nitrate (PPN) (Singh, 1987; Roberts, 1990; 1998; 2002). For NO, reservoir compounds include ALKNs from reaction with non-acyl peroxy radicals (RO_2). Recycling of reservoir compounds back to NO_x is dominated by photolysis, as thermally labile peroxy nitrates (PNs) including PANs, HNO_4 and MPN are stable against decomposition in the cold upper troposphere (Huey, 2007). This recycling along with NO_y sources to the upper troposphere sustains upper tropospheric NO_x concentrations at ~30 pptv over the remote ocean and ~100 pptv over polluted landmasses (Marais et al., 2018; 2021; Shah et al., 2023). Stable NO_x reservoir compounds are transported long distances before subsiding and decomposing on warming, thus supplying other parts of the world with oxidants (HO_x) and O_3 precursors (NO_x and peroxy radicals) (Schultz et al., 1999). Loss processes in the dry upper troposphere are slow and dominated by subsidence, resulting in long NO_y lifetimes of 10-20 days (Logan, 1983; Prather and Jacob, 1997). Similarly, NO_x has a lifetime of about a week compared to less than a day in the boundary layer (<2 km) (Jaeglé et al., 1998).

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

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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).

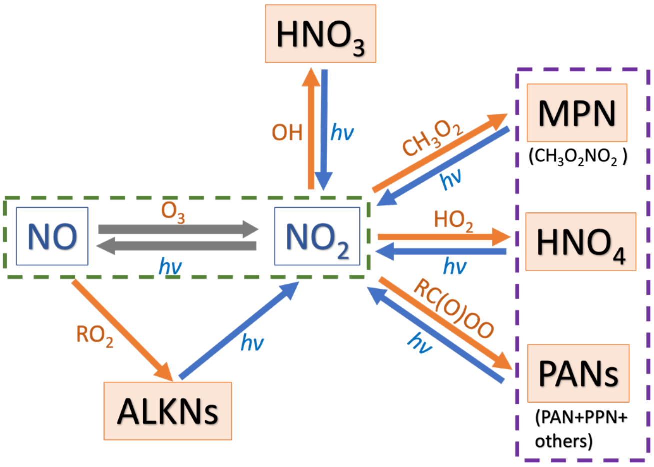

Figure 1: Dominant daytime reactive oxidized gas-phase nitrogen components and reaction pathways in the upper troposphere. Arrow colours distinguish formation (orange) and photolytic (hv) decomposition (blue) of reservoir compounds. Dashed boxes indicate compounds of the NO_x family (green) and classed as peroxy nitrates (purple). "R" in RC(O)OO and RO_2 represents an alkyl group.

Modelling studies evaluating best understanding of NO_y in the upper troposphere routinely identify stark discrepancies between observed and modelled total NO_y, NO_x, and the ratio of NO-to-NO_2 in the upper layers of the troposphere (Jaeglé et al., 1998; Talbot et al., 1999; Bertram et al., 2007; Hudman et al., 2007; Liang et al., 2011; Nault et al., 2015; Huntrieser et al., 2016; Travis et al., 2016; Fisher et al., 2018; Silvern et al., 2018; Lee et al., 2022; Cohen et al., 2023). These studies have either focused on a few NO_y components, or a single aircraft campaign. A more holistic investigation of all NO_y components is needed, as is advocated by Murray et al. (2021), to reduce uncertainties in knowledge of the current, past, and potential future abundances of tropospheric oxidants. Past studies have also documented the challenges examining measurements made in the upper troposphere. These include screening for stratospheric influence, determining the height of the chemical tropopause, and selecting observations and campaigns that are climatologically representative of a standard atmosphere (Weinheimer et al., 1994; Fuelberg et al., 2000; Bertram et al., 2007; Barth et al., 2015; Huntrieser et al., 2016). Instruments measuring NO_2 are also susceptible to interference from decomposition of the least thermally stable NO_x reservoir compounds, HNO_4 and MPN, that are abundant in the cold upper troposphere (Ryerson et al., 2000; Shah et al., 2023). NO_y from these same instruments can also be biased by decomposition of non-NO_y fixed nitrogen compounds prevalent in the upper troposphere, such as hydrogen cyanide (HCN) (Bradshaw et al., 1998).

Here we use NASA DC-8 research and IAGOS commercial aircraft campaign measurements, each spanning more than a decade, to characterize global NO_y seasonality and composition in the upper troposphere. This follows careful campaign and data selection to isolate observations sampling the upper troposphere under standard

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conditions for broad assessment of consistent NO_y seasonality between DC-8 and routine commercial aircraft campaign observations. We go on to use the DC-8 data to critique contemporary understanding of upper tropospheric NO_y as simulated by the GEOS-Chem model.

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2 Materials and methods

2.1 Research aircraft observations of total and components of NO_y

The DC-8 research aircraft has sampled ambient air covering the near full extent of the troposphere since its maiden campaign in 1985 (Culter, 2009). Many of the initial campaigns included instruments that measured a subset of the NO_y components shown in Figure 1, typically continuous measurements of total NO_y, NO, HNO_3, PAN and PPN, and whole air sampler (WAS) collection and laboratory detection of C1-C5 ALKNs (Singh et al., 1999). Since 2004, DC-8 campaigns have included continuous measurements of HNO_4, other PAN-type species and total PNs (Singh et al., 2006). Given this, we only consider DC-8 campaigns with a relatively consistent suite of instruments that mostly sampled well-mixed air representative of a climatologically standard atmosphere. These criteria eliminate the summer 2004 Intercontinental Chemical Transport Experiment-North America (INTEX-NA) campaign (Singh et al., 2006; Singh et al., 2009) that is the only DC-8 campaign since 2004 to not include a NO_x and NO_y chemiluminescence analyzer, and the summer 2012 Deep Convective Clouds and Chemistry (DC3) campaign that targeted convective thunderstorms influenced by fresh surface pollution and lightning NO_x emissions (Barth et al., 2015).

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The DC-8 campaigns we use are the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) over the Arctic and sub-Arctic in spring and summer 2008 (Jacob et al., 2010), the Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC^{4}RS) over the Southeast US in late summer and early autumn 2013 (Toon et al., 2016), the Korea-United States Air Quality (KORUS-AQ) over South Korea in late spring and early summer 2016 (Crawford et al., 2021), and the Atmospheric Tomography Mission (ATom) that included 4 sub-campaigns along the same flight path from pole to pole over the Atlantic and Pacific Oceans in all 4 seasons from 2016 to 2018 (Thompson et al., 2021). ATom sub-campaigns are ATom-1 in July-August, ATom-2 in January-February, ATom-3 in September-October and ATom-4 in April-May. The data for these campaigns are from NASA data portals for each campaign downloaded as merged 1-minute files for ARCTAS (NASA, 2009), SEAC^{4}RS (NASA, 2015) and KORUS-AQ (NASA, 2017) and as two separate merged files for ATom with the WAS C1-C5 ALKNs data at variable time intervals of 40 s, 1 min and 2 min and without the WAS C1-C5 ALKNs data at 1-minute resolution (NASA, 2021).

Figure 2 shows the global sampling extent of the upper troposphere by NASA DC-8 after applying filtering criteria to the data to isolate observations representative of photochemical steady-state conditions. For this, we select daytime (08h30-15h30 local solar time or LST) observations 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. We separate the stratosphere from the troposphere with a tropopause definition that can be applied to all datasets. We remove data with observed O_3

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concentrations above thresholds that represent the location of the chemical tropopause (Zahn et al., 2002). The thresholds we use are a single year-round value for the tropics (20°N to 20°S) of 100 ppbv (Dameris, 2015) and seasonally varying values everywhere else calculated using the day-of-year dependent O_3 tropopause equation derived by Zahn et al. (2002) from the inverse relationship between O_3 and CO observations from commercial aircraft campaigns. These are 120 ppbv in spring, 103 ppbv in summer, 74 ppbv in autumn, and 91 ppbv in winter. We also screen for stratospheric intrusions (identified as observations with O_3/CO > 1.25 mol mol^{-1}) (Hudman et al., 2007), fresh NO_x emissions (NO_y/NO < 3 mol mol^{-1}), fresh convection (large (> 10 nm diameter) condensation nuclei > 10^4 cm^{-3}), biomass burning plumes (CO > 200 ppbv and acetonitrile > 200 pptv) (Shah et al., 2023), as well as instances where NO_2 photolysis frequencies are approximately zero. The latter removes high latitude ATom measurements obtained at 08h30-15h30 LST under dark conditions during polar twilight or polar night. The data that are retained correspond to solar zenith angles ≤ 80° in polar regions, and ≤ 60° at other latitudes. The proportion of observations at 450-180 hPa is 42-50% for ATom and 16-37% for the other campaigns. After applying all other data screening, 20% of all data are retained for ATom and 7-11% for the other campaigns.

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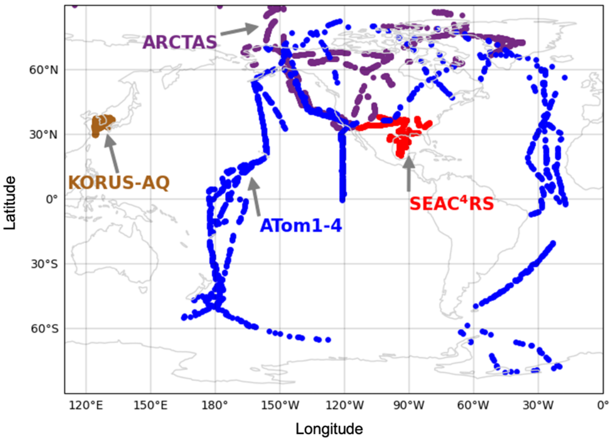

Figure 2: Extent of NASA DC-8 sampling of the upper troposphere under standard, steady-state conditions. Colours distinguish ARCTAS (plum), SEAC^{4}RS (red), KORUS-AQ (brown), and ATom (blue). ATom points are the 1-minute resolution data.

The DC-8 instruments measuring NO_y components (Figure 1) that are common to all campaigns include a chemiluminescence instrument measuring NO, NO_2, and total NO_y (Ryerson et al., 2000; Pollack et al., 2010; Bourgeois et al., 2022), a chemical ionization mass spectrometer (CIMS) measuring HNO_3 (Crounse et al., 2006), a CIMS measuring HNO_4, PAN, PPN, and other PANs (Huey, 2007), and a Whole Air Sampler (WAS) collecting samples analysed in the laboratory using gas chromatography with flame ionization and atomic emission to detect C1-C5 ALKNs (Blake et al., 2003). The other PANs measured with the CIMS include peroxyacryloyl nitrate (APAN), peroxyisobutyryl nitrate (PiBN), peroxybutyryl nitrate (PBN), and peroxybenzoyl nitrate (PBZN). Other instruments deployed for select campaigns are Thermal-Dissociation Laser Induced Fluorescence (TD-LIF) measuring NO_2, total PNs and total ALKNs (ARCTAS, KORUS-AQ, SEAC^{4}RS) (Day et al., 2002) and the PAN

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and Trace Hydrohalocarbon ExpeRiment (PANTHER) instrument measuring PAN (ATom). There are also TD-LIF methyl peroxy nitrate (MPN) measurements reported in the SEAC^{4}RS dataset and derived for ARCTAS by Browne et al. (2011).

Concentrations of NO_2 in the upper troposphere are close to chemiluminescence instrument uncertainty (Pollack et al., 2010; Bourgeois et al., 2022) and the measurements include interference from decomposition of NO_x reservoir compounds in the instrument inlet. The Reed et al. (2016b) temperature-dependent inlet temperature decomposition profiles of individual NO_x reservoir compounds for an instrument similar to that operated on the DC-8 suggests interference of 80-100% MPN and 15-45% HNO_4 for the typical inlet temperature range of the DC-8 chemiluminescence instrument of 20-30°C (Bourgeois et al., 2022). For the campaigns that measured HNO_4 and derived or measured MPN, this amounts to 13-27 pptv for ARCTAS and 71-92 pptv for SEAC^{4}RS. Given this, we instead calculate NO_2 using the NO-NO_2 photochemical steady state (PSS) approximation, as is now standard (Travis et al., 2016; Shah et al., 2023; Horner et al., 2024). Conversion of NO to NO_2, mostly (75%) due to oxidation by O_3 in the upper troposphere (Silvern et al., 2018), is balanced by NO_2 photolysis back to NO:

$$\mathrm{NO} \xrightarrow{\mathrm{O_3/HO_2/BrO}} \mathrm{NO_2} \qquad \text{(R1)}$$

$$\mathrm{NO_2} \xrightarrow{\mathrm{h\nu}} \mathrm{NO} \qquad \text{(R2).}$$

As NO_x is in steady state for the daylight observations we isolate, NO_2 can be calculated as follows:

$$\mathrm{NO_2} = \mathrm{NO} \times \left(\frac{k_1[\mathrm{O_3}]+k_2[\mathrm{HO_2}]+k_3[\mathrm{BrO}]}{j_{\mathrm{NO_2}}}\right) \qquad \text{(1).}$$

Compounds in square brackets are in molecules cm^{-3}. NO and NO_2 are in pptv. Terms not introduced yet include the NO_2 photolysis frequency, $j_{\mathrm{NO_2}}$, in s^{-1}, bromine monoxide (BrO), and rate constants of NO oxidation (R1) (k_{1-3}), in cm^3 molecule^{-1} s^{-1}. Temperature-dependent values of k_{1-3} are those recommended by the Jet Propulsion Laboratory (JPL) (Burkholder, 2020), calculated using DC-8 ambient temperature measurements. NO, [O_3], and $j_{\mathrm{NO_2}}$ are from the DC-8 measurements and [HO_2] is from the DC-8 measurements for all campaigns, except SEAC^{4}RS when it was not measured. We use GEOS-Chem (detailed in Sect. 2.3) simulated [HO_2] to estimate SEAC^{4}RS PSS NO_2. [BrO] is from GEOS-Chem for all campaigns. NO is also converted to NO_2 by organic peroxy radicals (RO_2), but we ignore this reaction as it is relatively insignificant throughout the free troposphere (Shah et al., 2023).

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The NO_y components not measured during specific campaigns are inferred. These include HNO_4 for KORUS-AQ, and ATom-3-4, PPN for ATom-1-2, and MPN for ARCTAS, ATom-1-4 and KORUS-AQ. The approaches used to infer these values differs, informed by the results, so a detailed description of this inference is in Section 3.2.

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2.2 Commercial aircraft observations of total NO_y

We use routine observations of upper tropospheric total NO_y from instruments on commercial long-haul passenger aircraft to determine if the intermittency and brevity of DC-8 campaign observations are representative of climatological conditions. The In-service Aircraft for a Global Observing System (IAGOS) European research infrastructure (Boulanger et al., 2018) provides routine in situ measurements of NO_y (Petzold et al., 2015). These are available from two IAGOS programmes: the Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft (MOZAIC) (Marenco et al., 1998) from 2001 to 2005 (Volz-Thomas et al., 2005) and the Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container (CARIBIC) since December 2004 (Brenninkmeijer et al., 2007; Stratmann et al., 2016).

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We consider the MOZAIC and CARIBIC observations together (collectively named IAGOS), as both programmes employed a chemiluminescence instrument with the same NO_y detection technique (Volz-Thomas et al., 2005; Brenninkmeijer et al., 2007). Direct intercomparison of NO_y is not possible, as there is no overlap in MOZAIC and CARIBIC NO_y. Data from 2003 to 2019 are used; 2003-2005 for MOZAIC and 2005-2019 for CARIBIC. We isolate daytime, upper tropospheric observations by applying the same O_3 tropopause, stratospheric O_3 intrusion, and daytime filtering as is applied to DC-8 data (Sect. 2.1) using IAGOS O_3 and CO measurements. There are no NO_2 photolysis frequency measurements, but the requirement for spatial coincidence with ATom excludes polar twilight and night measurements at high latitudes. We do not screen for observations impacted by fresh emissions, vertical convection or biomass burning plumes, due to unavailability of concurrent measurements of suitable chemical tracers in the IAGOS data. As we consider 17 years of IAGOS data, we assume that the influence of these is dampened in the long-term median of NO_y. Both the IAGOS and DC-8 data are gridded to the same 2° latitude × 2.5° longitude grid.

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2.3 The GEOS-Chem Model

We use the GEOS-Chem global 3D chemical transport model version 13.0.2 (https://doi.org/10.5281/zenodo.4681204; last accessed May 2021) to represent contemporary understanding of upper tropospheric NO_y for comparison to DC-8. The model is driven with consistent MERRA-2 assimilated meteorology at 2° × 2.5° (latitude × longitude) over 47 vertical layers from the surface of the Earth to 0.01 hPa. The model emissions local to the upper troposphere include cruising altitude aircraft from the Aviation Emissions Inventory Code (AEIC) (Stettler et al., 2011) and lightning emissions as described in Murray et al. (2012). Surface emissions of NO_x and VOCs precursors of ALKNs and PNs are from the anthropogenic Community Emissions Data System (CEDS) inventory of Hoesly et al. (2018), the Model of Emissions of Gases and Aerosols from Nature (MEGAN) biogenic VOCs inventory version 2.1 (Guenther et al., 2012), the soil NO_x emission inventory of Hudman et al. (2012), and the Global Fire Emissions Database version 4 with small fires (GFED4s) for open burning of biomass (Giglio et al., 2013). Wet deposition of gas-phase HNO_3, the terminal sink for NO_y subsiding from the upper troposphere, includes in-cloud (rainout) and below-cloud (washout) scavenging as detailed in Amos et al. (2012) and enhanced scavenging as described by Luo et al. (2020).

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We sample the model at the same time and location as the DC-8 observations using the ObsPack diagnostic (https://www.esrl.noaa.gov/gmd/ccgg/obspack/; last accessed 23 October 2021) following a minimum 10-month spin-up preceding each campaign to initialize chemistry and large-scale circulation throughout the troposphere.

Modelled components of NO_y include NO, NO_2, HNO_3, HNO_4, PAN, PPN, peroxymethacroyl nitrate (MPAN), MPN, and ALKNs.

3 Results and Discussion

3.1 DC-8 campaign NO_y seasonality and budget closure

Figure 3 compares seasonality in UT NO_y from IAGOS and DC-8. Most of the overlap is with ATom along the North Atlantic flight corridor in all seasons, ARCTAS over the Canadian Arctic and Greenland in March-May (MAM) and June-August (JJA), and SEAC^{4}RS over the Southeast US in September-November (SON). IAGOS NO_y exhibits similar peaks in spring (563 pptv) and summer (565 pptv), due to intensive seasonal lightning in the northern hemisphere (Stratmann et al., 2016). Decline in this source decreases NO_y in autumn to 365 pptv and NO_y further decreases in winter to an annual minimum of 284 pptv.

DC-8 NO_y seasonality is similar to that of IAGOS, though the magnitude of DC-8 NO_y is consistently on average ~130 pptv (range of 80 pptv in SON to 170 pptv in DJF) less than IAGOS NO_y in all seasons. The ~130 pptv greater IAGOS NO_y likely results mostly from differences in sampling altitudes. The two campaigns sample distinct altitude ranges of the upper portion of the upper troposphere centred at ~240 hPa (~10 km) for IAGOS and a wider vertical extent of the lower portion of the upper troposphere centred at ~360 hPa (~1.5 km below IAGOS) for DC-8 (Figure S1). There is a general pattern of a steep increase in NO_y with altitude, with the exception of IAGOS layers located near 300 hPa in March-May and September-November (Figure S1). Average NO_y is similar between the two campaigns for the rare instances that DC-8 and IAGOS sample the same pressure layers (Figure S1). Another minor factor may be IAGOS NO_y instrument interference from HCN. The IAGOS chemiluminescence instruments use a hydrogen (H_2) reagent to convert oxygenated nitrogen compounds to NO, whereas DC-8 uses CO, a compound not permitted on commercial aircraft (Bradshaw et al., 1998; Volz-Thomas et al., 2005; Thomas et al., 2015). The H_2 reagent converts anywhere from 2 to 20% of HCN to NO_y (Weinheimer, 2006). HCN ambient concentrations typically seasonally vary from ~200 to 300 pptv in the upper troposphere, amounting to an interference of 4-60 pptv (Li et al., 2003; Le Breton et al., 2013).

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Deleted: that of IAGOS at ~360 hPa. According to the DC-8 measurements, NO_y is ~100 pptv more at 240 hPa (IAGOS mean altitude) than at 360 hPa (DC-8 mean altitude) as shown in the vertical profile of northern hemisphere upper tropospheric NO_y in Figure 3 (c). NO_y level approaching tropopause is higher than the rest layers of upper troposphere.

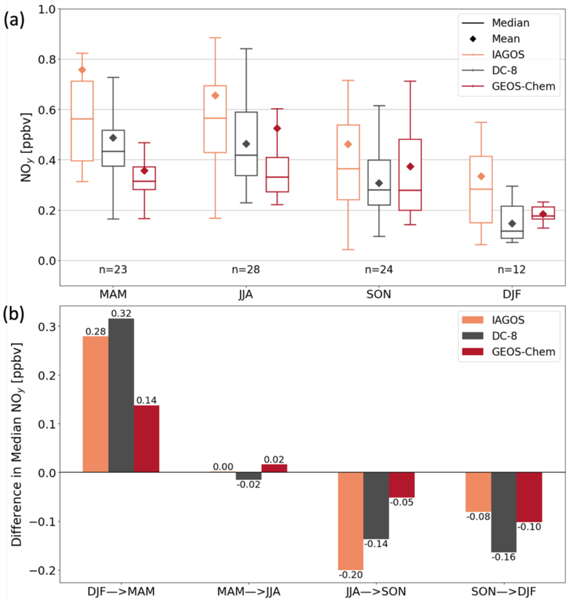

Figure 3: Seasonality of northern hemisphere upper tropospheric NO$_y$. Panels show seasonal means and medians (a) and seasonal transitions (b) of collocated gridded 2° × 2.5° NO$_y$ from IAGOS (orange), DC-8 (grey), and GEOS-Chem (red). Data in (a) are medians (lines), 25th and 75th percentiles (boxes) and means (diamonds). Inset text in (a) gives the number (n) of overlapping grid cells. Seasonality in (b) is the change in median NO$_y$ in (a) from one season to the next.

Figure 4 shows the relationship between the sum of individual NO$_y$ components and total NO$_y$ for each DC-8 campaign. We use these scatterplots to determine whether most NO$_y$ components are measured in each campaign, given our intention to use DC-8 to assess contemporary understanding of upper tropospheric NO$_y$. The instruments and individual components of NO$_y$ summed to compare to total NO$_y$ are listed in Table 1. The measured components include NO; PSS NO$_2$ (Equation (1)); HNO$_3$; PAN measured as PAN for all ATom sub-campaigns and as part of total PNs for ARCTAS, SEAC^{4}RS and KORUS-AQ; HNO$_4$ measured as HNO$_4$ for ATom-1 and -2 and as part of total PNs for ARCTAS, SEAC^{4}RS and KORUS-AQ; C1-C5 ALKNs for all AToms; total ALKNs for SEAC^{4}RS, KORUS-AQ, and ARCTAS; PPN and other PANs for all except ATom-1 and -2; and MPN as part of total PNs for ARCTAS, SEAC^{4}RS and KORUS-AQ. The evaluation in Figure 4 is biased toward the northern hemisphere, as the low time resolution sampling of the WAS C1-C5 ALKNs during ATom leads to loss of data in the southern hemisphere (Figure 2) to achieve coincidence of DC-8 total and individual components of NO$_y$.

Table 1. Observations of individual NO_y components summed to assess budget closure in Figure 4

Component	NASA DC-8 aircraft campaign		
	ARCTAS, SEAC^{4}RS, KORUS-AQ	ATom1-2	ATom3-4
NO_2	PSS	PSS	PSS
NO	Chemiluminescence (CL)	CL	CL
HNO_3	CIMS	CIMS	CIMS
HNO_4	TD-LIF PNs	CIMS	–
PAN	TD-LIF PNs	PANTHER	PANTHER
PPN	TD-LIF PNs	–	CIMS
other PANs	TD-LIF PNs	–	CIMS
ALKNs	TD-LIF ALKNs	WAS C1-C5	WAS C1-C5
MPN	TD-LIF PNs	–	–

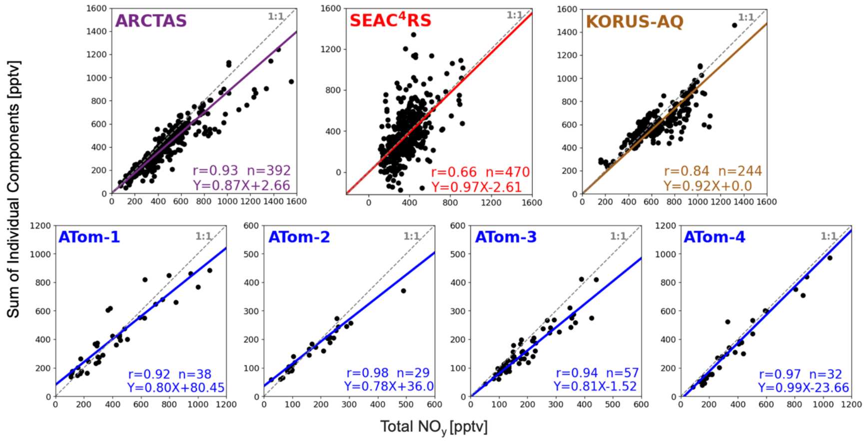

Figure 4: Proportion of reactive oxidized nitrogen components measured during each campaign. Individual points compare the coincident sum of individual NO_y components (Table 1) to measured total NO_y during NASA DC-8 campaigns. Individual NO_y components used in the figure are detailed in the text. Dashed grey lines are the 1:1 relationship. Coloured lines and inset equations are the Theil-Sen regression fit to the observations. Other inset values are the Pearson's correlation coefficient (r) and number of points (n). Axis ranges differ in each panel.

Total measured NO_y and the sum of individual NO_y components are strongly correlated ($r > 0.8$) for all campaigns, except SEAC^{4}RS ($r = 0.66$). The weaker correlation for SEAC^{4}RS is from the large contribution of MPN to total PNs measured by the TD-LIF instrument. If instead we replace TD-LIF PNs with the sum of CIMS PANs and HNO_4, the correlation with total measured NO_y increases to $r = 0.91$, but the regression slope decreases from 0.97 in Figure 4 to 0.82, as MPN is ~20% of SEAC^{4}RS NO_y. The large contribution of MPN to total NO_y during SEAC^{4}RS is from aged air initially influenced by lightning, biomass burning and deep convective uplift of surface pollution with large amounts of VOCs and NO_x. These large amounts of VOCs and NO_x cause very active photochemistry that enhances abundance of the MPN precursor, CH_3O_2 (Browne et al., 2011; Nault et al., 2015).

The regression slopes in Figure 4 indicate that most NO$_y$ components are measured during each campaign, ranging from 0.78 for ATom-2 (78% of individual NO$_y$ components measured) to 0.99 for ATom-4 (99% measured). The slopes suggest that between 1-22% of NO$_y$ originates from factors such as unmeasured components, positive interference in the NO$_y$ instrument, or low bias in the TD-LIF PNs. Bradshaw et al. (1998) estimated a temperature-dependent interference from HCN of 8-15% for chemiluminescence instruments that, like those deployed on DC-8 campaigns, use a CO reagent. We estimate a lower-end (8%) interference for mean ambient upper troposphere temperatures measured along the flight paths in Figure 2. Using DC-8 HCN observations, this amounts to ~53 ppt or 12% of NO$_y$ for ARCTAS, ~19 pptv or 5% of NO$_y$ for SEAC^{4}RS, ~40 pptv or 6% NO$_y$ for KORUS-AQ, and ~17 pptv or 6% NO$_y$ for ATom 1-4. These lower-end interference estimates are similar in size to the percent unaccounted NO$_y$ (13% for ARCTAS, 3% for SEAC^{4}RS, 8% for KORUS-AQ, 1-22% for ATom).

Chemiluminescence NO$_y$ instruments also measure pNO$_3$, but with uncertain sampling efficiencies (Bourgeois et al., 2022). For 100% sampling efficiency and using the Aerosol Mass Spectrometer (AMS) measurements of submicron (< 1 µm) pNO$_3$, we estimate a pNO$_3$ contribution that 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).

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% thermal decomposition of MPN (Reed et al., 2016b) and MPN during SEAC^{4}RS far exceeds any of the other campaigns. If we use the higher-end MPN 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.

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3.2 Upper tropospheric NO$_y$ composition

Figure 5 provides a breakdown of the absolute and relative contributions of individual NO$_y$ components to total NO$_y$. ATom-1 and -4 are combined, as these sub-campaigns have a very similar range in NO$_y$ (Figure 4) and in median total and individual components of NO$_y$, as the sampled seasons (spring and summer) have very similar NO$_y$ (Figure 3). Similarly, ATom-2 and -3 (autumn and winter) are combined. Campaigns are further grouped into remote (ARCTAS, ATom) and continental (SEAC^{4}RS, KORUS-AQ), as local influence from continental sources like anthropogenic emissions and intense lightning leads to a greater relative contribution of NO$_x$ and lesser contribution of PAN for the continental upper troposphere and vice versa for the remote upper troposphere.

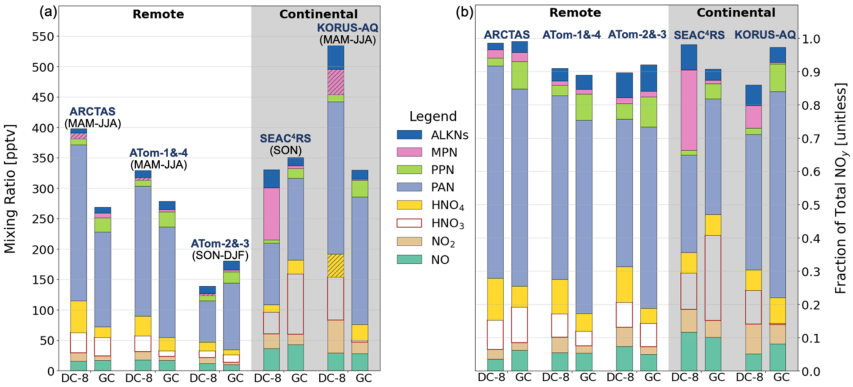

Figure 5: NO$_y$ composition in the upper troposphere along DC-8 flight tracks. Bars are median values of absolute (a) and relative (b) individual NO$_y$ components observed and inferred from the observations during DC-8 campaigns and simulated by GEOS-Chem (GC). Seasons sampled are given above each bar (a) and the grey shading distinguishes sampling in the remote (no shading) and continental (shaded) upper troposphere. Hatchings in (a) indicate inferred concentrations (see text for details). Bar components from bottom to top are NO, NO$_2$, HNO$_3$, HNO$_4$, PAN, PPN, MPN, and ALKNs.

Inferred DC-8 HNO$_4$ and PPN in Figure 5 use ATom-1 HNO$_4$ and ATom-4 PPN for combined ATom-1 and -4 components, and, similarly, ATom-2 HNO$_4$ and ATom-3 PPN for combined ATom-2 and -3. KORUS-AQ HNO$_4$ is estimated to be 37 pptv by multiplying the SEAC^{4}RS median fraction of HNO$_4$ (HNO$_4$/NO$_y$ = 0.06) by the KORUS-AQ median NO$_y$. SEAC^{4}RS is used, as HNO$_4$ is thermally unstable (Ryerson et al., 2000) and so varies with temperature. Mean upper troposphere ambient temperatures for KORUS-AQ (252 K) are more consistent with SEAC^{4}RS (246 K) than the other campaigns (238 K for ARCTAS, 238K-241 K for ATom).

The inferred ~10 pptv ARCTAS MPN is from the estimate by Browne et al. (2011). KORUS-AQ MPN is estimated by bounding a potential range from two approaches. The first is the median value of the difference between TD-LIF total PNs and the sum of all individual CIMs PANs and our inferred HNO$_4$ of 37 pptv, yielding MPN = 75 pptv. This likely overestimates MPN, as the CIMS instrument does not measure an exhaustive suite of PANs. Lee et al. (2022) estimated with a box model and KORUS-AQ measurements that unmeasured PANs account for ~20% of total PNs during KORUS-AQ, though this is for air masses impacted by petrochemical and other anthropogenic VOCs and NO$_x$ emissions. Accounting for these unmeasured PANs yields a lower-bound KORUS-AQ MPN of 8 pptv. The MPN that we infer then for KORUS-AQ is 42 pptv, the midpoint of 8 and 75 pptv, accounting for 7% of KORUS-AQ NO$_y$. As the GEOS-Chem model MPN is consistent with DC-8 inferred MPN during ARCTAS, we multiply the GEOS-Chem ATom MPN fractions (MPN/NO$_y$ ~0.01 for ATom-1 and -4 and ~0.02 for ATom-2 and -3) by ATom DC-8 NO$_y$ to infer ATom MPN of < 6 pptv.

Only the C1-C5 ALKNs are shown in Figure 5 for ATom. The remote measurements of total ALKNs available from ARCTAS that would be most suitable to assess the likely contribution of longer chain (>C5) ALKNs are on median 5 pptv less than the ATom C1-C5 ALKNs measurements. The ARCTAS total ALKNs measurements are also very noisy, as indicated by a range of -113 pptv to ~333 pptv. The range in ARCTAS WAS C1-C5

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measurements, by comparison, is 8-29 pptv. Contributions of >C5 ALKNs to total ALKNs for SEAC^{4}RS (~50%) and KORUS-AQ (~60%), representative of the continental upper troposphere, suggest that >C5 ALKNs in remote regions are <50% of total ALKNs or <12 pptv (median of C1-C5 ALKNs for ATom1-4). According to the measurements, remote region C1-C5 ALKNs are dominated by methyl nitrate (C1 ALKN), accounting for 40% of ATom C1-C5 ALKNs and 49% for ARCTAS. Second is isopropyl nitrate (C3 ALKN), making up 17% of ATom C1-C5 ALKNs and 25% for ARCTAS. The >C3 ALKNs dominate ALKNs in the continental upper troposphere, accounting for 92% of total ALKNs for SEAC^{4}RS and 71% for KORUS-AQ. These we estimate as the difference between TD-LIF total ALKNs and the sum of WAS C1-C3 ALKNs.

The sum of KORUS-AQ NO_y components total 531 pptv, >130 pptv more than SEAC^{4}RS, ARCTAS, and ATom-1 and -4 that are within a narrow range of 330-400 pptv. Minimum NO_y are for the remote autumn and winter measurements from ATom-2 and -3 at 141 pptv. Despite the wide range in absolute total and components of NO_y, the relative contribution of many individual NO_y components is consistent across all campaigns. These include NO (7 ± 3%; mean ± 1σ standard deviation), NO_2 (6 ± 2%), HNO_3 (9 ± 2%), HNO_4 (9 ± 3%), PPN (3 ± 1%), and ALKNs (5 ± 3%). PAN, the dominant NO_y component in all campaigns, is least consistent, ranging from 30-41% for the continental upper troposphere to 44-64% for the remote upper troposphere. The HNO_4 fraction (10-13%) in the remote upper troposphere is more than the continental upper troposphere (~6%), due to colder temperatures for ATom and ARCTAS. MPN is uniquely prominent during SEAC^{4}RS, accounting for 24% of NO_y compared to 2-7% inferred for all other campaigns. 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 KORUS-AQ (Section 3.1), comparable to the contribution from PPN.

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.

The NO_y composition information in Figure 5 has a northern hemisphere sampling bias to achieve coincidence. ATom observations south of the Equator exhibit a similar seasonal pattern to the northern hemisphere: summer > spring > autumn > winter NO_y, except that the southern hemisphere spring and summer NO_y differ by ~90 pptv, whereas there is near-negligible difference for the northern hemisphere (Figure 3). As with the northern hemisphere, PAN accounts for most southern hemisphere NO_y, ranging from ~32% for ATom-1 (July-August) to ~42% for ATom-2 (January-February).

Nighttime dominant NO_y compounds N_2O_5, NO_3, and HONO are not included in Figure 5, as these have near-negligible daytime abundances. Of these, there are only measurements of N_2O_5, limited to ATom-3 and -4, that represent ~0.1% of upper tropospheric NO_y along the daytime ATom flight tracks in Figure 2. NO_3 has a lifetime of a few seconds during the day, due to efficient photolysis (Brown and Stutz, 2012). HONO also rapidly photolyzes with a near-surface lifetime of 15 min (Sörgel et al., 2011). Photolysis of HONO would be further

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3.3 Contemporary understanding of UT NO$_y$

GEOS-Chem northern hemisphere upper troposphere NO$_y$ is compared to the observations in Figures 3 and 5. In Figure 3, GEOS-Chem median NO$_y$ is less than DC-8 in summer and spring by ~103 pptv, similar to DC-8 in autumn, and greater than DC-8 in winter by ~60 pptv. As a result of these differences in absolute NO$_y$, the model underestimates the IAGOS and DC-8 seasonal shifts in NO$_y$ from winter to spring and from summer to autumn.

The sum of the GEOS-Chem fractional contributions of NO$_y$ components in Figure 5(b) that do not sum to 1 are because the model NO$_y$ budget also includes components not measured during DC-8, such as MPAN and halogenated ALKNs. Consistent across all campaigns is model underestimate in NO$_2$ and overestimate in PPN. The model version we use does not include photolysis of PPN, even though this is known to occur (Harwood et al., 2003). PPN photolysis rather than thermal decomposition is the dominant loss pathway of PPN in the cold upper troposphere. PPN photolysis is scheduled for inclusion in a later model version (version 14.5) than is used here (Horner et al., 2024). Inclusion of PPN photolysis would liberate up to ~16 pptv NO$_2$, resolving the 10-16 pptv model underestimate in NO$_2$. Other studies have addressed model biases in NO$_2$ by including photolysis of pNO$_3$ forming HONO that rapidly photolyses to NO$_x$ (Shah et al., 2023; Horner et al., 2024). pNO$_3$ concentrations are too small in the upper troposphere for this to be a substantial NO$_2$ source. These are on median, ~0.01 μg m^{-3} during ARCTAS, ~0.07 μg m^{-3} during KORUS-AQ, ~0.04 μg m^{-3} during SEAC^{4}RS and <0.01 μg m^{-3} during ATom (Section 3.1).

The model exhibits significant campaign-specific biases in total NO$_y$ for ARCTAS (129 pptv underestimate), KORUS-AQ (205 pptv underestimate), ATom-1 and -4 (51 pptv underestimate) and ATom-2 and -3 (42 pptv overestimate). The model underestimate in ARCTAS NO$_y$ is due mostly to a ~100 pptv low bias in PAN and, to a lesser extent, a 35 pptv underestimate in HNO$_4$. The model bias for ATom-2 and -3 is due almost entirely to PAN. For KORUS-AQ, all NO$_y$ components except PPN are underestimated, indicative of an overall underestimate in NO$_y$ sources to the upper troposphere over this region. The ATom-1 and -4 underestimate in NO$_y$ is due mostly to a low model bias in PAN and HNO$_3$. Overall, the model underestimates the contrast in upper tropospheric NO$_y$ between the remote and continental upper troposphere.

GEOS-Chem simulates individual C1-C3 ALKNs, but most >C3 ALKNs are included as a lumped species. There are other >C3 ALKNs represented individually in the model, such as those formed from isoprene oxidation (Fisher et al., 2016), but abundances of these are near-negligible in the upper troposphere. DC-8 C1 ALKN is only 4% of ALKNs for SEAC^{4}RS and 11% for KORUS-AQ, whereas in the model these are a much greater component of ALKNs: 40% for SEAC^{4}RS and 29% for KORUS-AQ. Modelled >C3 ALKNs are a far smaller portion of total ALKNs (29% for SEAC^{4}RS and 23% for KORUS-AQ) than the observations (Sect. 3.2). Modelled C1 ALKN concentrations are consistently less than the observed values by ~2 pptv for ARCTAS and ~1 pptv for ATom.

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Modelled C3 ALKN is ~1 pptv less than the observations for ARCTAS, but ~1 pptv more than the observations for ATom.

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). The model low bias in MPN suggests that the model underestimates influence of NO_x and reactive VOCs sources on aged air over source regions with a mix of emissions from fires and lightning, and deep convective injection of surface pollution. Chen et al. (2019) 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. The model high bias in HNO_3 could be because of a factor of 2 overestimate in our modelled H_2O_2 compared to observed H_2O_2 for SEAC^{4}RS. An overestimate in H_2O_2 indicates a model overestimate in HO_2 that promotes formation of HNO_3 and that would also account for the ~10 pptv overestimate in modelled HNO_4. Modelled HO_2 is used to calculate PSS NO_2 for SEAC^{4}RS (Equation (1), Sect. 2.1), but this only imparts a small high bias (~1.7 pptv) in SEAC^{4}RS PSS NO_2. Model bias in H_2O_2 for ARCTAS (>100 pptv) may also be the cause for the model underestimate in ARCTAS HNO_4 of ~35 pptv.

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Modelled KORUS-AQ HNO_3, ALKNs, and MPN are all biased low. The low biases in these NO_y components may be because of a general underestimate in NO_y sources over South Korea where there are large anthropogenic NO_x and VOCs sources that are represented in the model with a global inventory (CEDs) that may not suitably account for local emissions (Travis et al., 2024). Lightning NO_x emissions could also be underestimated in the heavily parameterized inventory in GEOS-Chem (Murray et al., 2012; Marais et al., 2018), but this is a challenging NO_x source to evaluate over locations that include other prominent sources of NO_x.

The model biases identified in this work hinder accurate determination of the radiative effect of tropospheric ozone for short-term climate impact assessments, the oxidative capacity of the troposphere for quantifying the lifetime and persistence of the greenhouse gas methane, tropospheric column densities of NO_2 from space-based UV-visible instruments that are retrieved with modelled vertical profiles of NO_2, NO_x emissions by comparing modelled and observed oxidized nitrate wet deposition fluxes that depend on the abundance of soluble HNO_3, and harm of nitrogen deposition to vulnerable habitats.

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4 Conclusions

We used NASA DC-8 aircraft measurement data from the ARCTAS, SEAC^{4}RS, KORUS-AQ, and ATom campaigns to characterize reactive oxidized nitrogen (NO_y) in the global upper troposphere. This followed confirmation from comparison to routine total NO_y measurements from the IAGOS commercial aircraft campaign that DC-8 has the same seasonality of peak NO_y in summer and spring and minimum NO_y in winter in the northern hemisphere. Consistency supports use of DC-8 campaign data to characterise NO_y under standard daytime conditions.

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We also confirm that most (78-99%) NO_y components were measured during DC-8 campaigns. These include nitrogen oxides (NO_x), and inorganic (HNO_3 and HNO_4), and organic (PANs, MPN, and alkyl nitrates) reservoirs of NO_x. PAN is the dominant NO_y component for all campaigns (30-64%), followed by NO_x (6-18%), HNO_4 (6-13%) and HNO_3 (7-11%). 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.

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The GEOS-Chem model is sampled along the DC-8 flight tracks to assess the state of knowledge of upper tropospheric NO_y. Consistent model biases for all campaigns include an overestimate in PPN and underestimate in NO_2. The model lacks PPN photolysis that would address the PPN model bias and mostly resolve the NO_2 bias. In the continental upper troposphere, the model underestimates total NO_y for KORUS-AQ, but reproduces total NO_y for SEAC^{4}RS, though with too much HNO_3 and too little MPN. Over remote regions, the model biases are less severe, and are likely related to the weak seasonal variability in total NO_y in comparison to DC-8 and IAGOS. A possible cause of this is errors in model representation of maritime lightning NO_x emissions that influence NO_y abundance in spring and summer.

Our results underscore the need for sustained measurements of upper tropospheric reactive oxidized nitrogen for further refinement of knowledge of upper tropospheric NO_y sources, advection, and chemical processing. This is crucial for advancing our understanding of the global nitrogen cycle and its broader environmental impacts.

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Author Contributions

Study concept by EAM and NW. NW led the data analysis and simulated GEOS-Chem. The manuscript is initiated by NW and co-written by EAM. GL aided in data analysis, RGR in the use of ObsPack, and BS in the use of IAGOS NO_y observations. All authors reviewed and edited the manuscript.

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Competing interests

The authors declare that they have no conflict of interest.

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supported by AERIS. IAGOS-CARIBIC data are also available from the IAGOS-CARIBIC team (see http://www.caribic-atmospheric.com)

Data and Software Availability

All data and software used in this study are from publicly accessible repositories: Zenodo for GEOS-Chem (The International GEOS-Chem User Community, 2021), the AERIS data service for IAGOS (Boulanger et al., 2018), and NASA data archives for ARCTAS (NASA, 2009), SEAC^{4}RS (NASA, 2015), KORUS-AQ (NASA, 2017), and ATom (NASA, 2021).

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