RESPONSE TO REFEREE COMMENTS for

Gonzalez et al., Impact of stratospheric air and surface emissions on tropospheric nitrous oxide during ATom; acp-2021-167:

Reviewer 1

"This paper describes the global distribution of tropospheric N_2O mixing ratios measured during the airborne Atmospheric Tomography (ATom) mission. Much of the paper focuses on the technical aspects of the retrieval method, while the last sections focus on the interpretation of the data, which involves many other co-measured species and complex comparison of profiles and scatterplots. Overall, this is an important dataset that definitely merits publication.

Below are some suggestions to help clarify and improve the presentation:"

We thank the reviewer for their time and providing positive and constructive comments to improve manuscript acp-2021-167. We revised the manuscript accordingly and incorporated all the proposed changes.

***Comment # 1*:**

Abstract, Line 46-47 (and similar statements in the Conclusion). "*This retrieval strategy improved the precision of our N_2O measurements by a factor of 3, enabling us to recover the precision to that of previous missions.*" This sentence is confusing since it doesn't provide a reference point for the factor of 3 (e.g., is this relative to UCATS and PANTHER, to previous QCLS measurement on HIPPO, or something else?). Also, the use of "*recover*" implies, without providing context, that something was lost and needed to be recovered.

Reply: The retrieval strategy described in this work improved the precision of our ATom N_2O measurements by a factor of 3. This factor was calculated based on based on the stdev. of calibration measurements. With this improvement, precision of ATom N_2O data was similar to the precision of previous missions such as HIPPO. The impact of the retrieval strategy on the data is explained in the third paragraph of section 2.2:

"*The Neptune-PCA analysis improved the overall precision by a factor of 4 for CH_4 and a factor of 3 in the case of N_2O with respect to the precision of the original retrievals, as measured by the standard deviation of retrieved mixing ratios during calibrations*".

Other related sentences have been rephrased for clarification. A new sentence has been added in paragraph 2 in section 2.2. The abstract and conclusion has been modified as shown below.

i) Abstract:

"*We introduce a new spectral retrieval method to account for the pressure and temperature sensitivity of the instrument when deployed on aircraft. This retrieval strategy improved the precision of our ATom QCLS N_2O measurements by a factor of 3 (based on the stdev. of calibration measurements)*".

*ii) Section 2.2. paragraph 2***:**

"*We have achieved significant improvement in the precision and accuracy of the ATom QCLS N_2O data using a new method dubbed the "Neptune algorithm", developed by Aerodyne Research, Inc., and that has been further developed and applied to the data sets described here. Using this algorithm, the precision of the retrieved N_2O data measured with the damaged QCLS, was similar to that reported in HIPPO*".

iii) Conclusions:

"*This method improved the precision of our QCLS N_2O measurements (based on the stdev. of calibration measurements) by a factor of 3, allowing us to provide N_2O measurements at the level of precision shown in previous aircraft missions*".

Comment # 2: Introduction. Line 71, "*plus emissions related to human activities such as fertilization, biomass burning*" Please delete fertilization, since this is already covered in the previous sentence about microbial production in soils under cultivation. Fertilizer provides substrate for the microbes to produce N_2O, as opposed to biomass burning and industry, which are abiotic mechanisms.

Reply: We agree with the reviewer and the word "fertilization" has been deleted from that sentence:

"*Most N_2O emissions are attributed to microbial nitrification and denitrification in natural and cultivated soils, freshwaters and oceans, plus emissions related to human activities such as biomass burning and industrial emissions (Butterbach-Bahl et al., 2013; Saikawa et al., 2014; Thompson et al., 2014a; Upstill-Goddard et al., 2017; WMO, 2018).*"

Comment # 3: Line 93. Should last "an" be "and"?

Reply: In this sentence we are enumerating the 3 possible reasons for the bias observed in the models.

Comment # 4: Introduction. Line 84-85. The Valentini source from African rivers seems large. Is this *Tg N_2O* (as written?) or TgN_2O-N?

Reply: The unit is Tg N_2O as written in the text, however, this estimation accounts for both biogenic sources and fires in the African continent. This information has been included in the manuscript for clarification (lines 84-85, second paragraph of the introduction) and the reference to Valentine et al. (2014) has been added to the reference list:

"*N_2O emissions from biogenic sources and fires in Africa are estimated at 3.3 ± 1.3 Tg N_2O yr^{-1} (Valentini et al., 2014).*"

Valentini, R., Arneth, A., Bombelli, A., Castaldi, S., Cazzolla Gatti, R., Chevallier, F., Ciais, P., Grieco, E., Hartmann, J., Henry, M., Houghton, R. A., Jung, M., Kutsch, W. L., Malhi, Y., Mayorga, E., Merbold, L., Murray-Tortarolo, G., Papale, D., Peylin, P., Poulter, B., Ray- mond, P. A., Santini, M., Sitch, S., Vaglio Laurin, G., van der Werf, G. R., Williams, C. A., and Scholes, R. J.: A full greenhouse gases budget of Africa: synthesis, uncertainties, and vulnerabilities, Biogeosciences, 11, 381–407, doi:10.5194/bg-11-381-2014, 2014.

Comment # 5: Introduction. Lines 108-110 "*we present a new retrieval strategy to account for the pressure and temperature dependence of laser-based instruments, specifically for the use of quantum cascade laser spectrometers on aircraft*". Similar to my comments above about lines 46-47, does this imply uncertainties in previous campaigns (HIPPO, ORCAS) where this new strategy was not used? Or did something go wrong specifically during ATom that required the new strategy? Please clarify.

Reply: To perform high quality measurements using quantum cascade laser spectrometers while deployed on aircraft, a proper alignment of the optics is critical. An accident at the beginning of the ATom mission, where the QCLS was dropped to the ground by the shipping company, misaligned the optics of the QCLS. Even though we completely re-aligned the cell between ATom-1 and ATom-2, we observed an increased sensitivity of the optical elements surrounding the cell to the aircraft maneuvers. Pressure and temperature variations during aircraft maneuvers can cause mechanical stress to the optical elements surrounding the cell, by introducing fringes on the spectra or changing the shape of the detected laser intensity profile; thus, introducing noise in the measured spectrum.

As a consequence of this accident, the precision of the QCLS N_2O, estimated as a function of the standard deviation of the mean values of the high and low mixing ratio tanks used for in-flight calibrations, was up to 3 times higher than that in HIPPO. We tried several retrieval strategies to improve QCLS N_2O data from ATom and the Neptune Algorithm provided the best improvement in the precision of the QCLS N_2O in ATom to reach the levels of precision in HIPPO. We described these facts in the first paragraph of section 2.2:

"*The QCLS was damaged during shipping to the deployment site before the start of ATom-1, and the resulting alteration in the optical alignment modified the sensitivity of the instrument to temperature and pressure changes during aircraft maneuvers. This increased sensitivity was observed in all ATom deployments. At a constant altitude, instrumental precision was similar to the precision measured during HIPPO (see Allan-Werle variance analysis in Fig. 2 in Santoni et al. 2014 for HIPPO and Fig. S3 for ATom), but drifts were observed during altitude changes due to the effects of changes in cabin pressure and temperature on the spectral location of interference fringes that arise in the optical path outside the sample cell. In addition, flight altitude changes could mechanically stress the optical elements surrounding the cell, further modulating fringes or changing the shape of the detected laser intensity profile. These spectral artifacts ultimately reduced the accuracy of mixing ratios retrieved from spectral fitting. The spectral artifacts most strongly affected the measurements of CH_4 and N_2O. Several post-processing methods using the TDL-Wintel software were explored to improve the precision and accuracy of ATom QCLS N_2O data, most with little success. Since the measured spectra were all saved, it is possible to re-fit the data with different fit parameters. A limited number of interference fringes may be included in the set of fitting functions. However, none of the previously used full re-fitting strategies significantly improved the data accuracy*".

The precision of QCLS N_2O during ATom is similar to that in HIPPO after retrieving the data with the Neptune Algorithm. It is true that this algorithm could also be applied to previous missions such as HIPPO and ORCAS missions to increase the precision of the retrieved N_2O if it is needed, but that has not been done here.

Comment # 6: Section 2.2 and line 167. Again, it is unclear whether the "significant improvement in the precision and accuracy of the QCLS N_2O data" was necessitated by the damage described in the previous paragraph, or would have been done anyway.

Reply: This is clarified by adding the following sentence in section 2.2:

"*Using this algorithm, the precision of the retrieved N_2O data measured with the damaged QCLS, was similar to that reported in HIPPO*".

Comment # 7: Line 231. Please clarify whether UCATS and PANTHER were also made during ATom.

Reply: We have modified the first sentence of section 3.1 for clarification:

"*Measurements of N_2O on the DC-8 during ATom were obtained by four instruments (i) the Unmanned Aircraft Systems Chromatograph for Atmospheric Trace Species (UCATS, Hintsa et al., 2021), (ii) the PAN and other Trace Hydrohalocarbon ExpeRiment (PANTHER; Moore et al., 2006; Wofsy et al., 2011), (iii) the Programmable Flask Package Whole Air Sampler (PFP; Montzka et al., 2019), and (iv) our 1-Hz QCLS.*"

Comment # 7: Line 237. The term PFP is introduced here without explanation. Was PFP measured on ATom too?

Reply: PFP is introduced in the first paragraph of section 3.1 as one of the four instruments that provided N_2O data during ATom (see answer to comment # 6). We also clarified in the first two sentences of the second paragraph of section 3.1 that the merged files including these measurements, and used here, are ATom merged files:

"*We compared QCLS, PANTHER and UCATS in 10s intervals as provided in the ATom merged file, MER10_DC8_ATom-1.nc, available at the Oak Ridge National Laboratory Distributed Active Archive Center (ORNL-DAAC, Wofsy et al., 2018, https://doi.org/10.3334/ORNLDAAC/1581). The ATom file MER-PFP merged with the PFP sampling interval, also available in this repository, was used to compare QCLS and PFP data.*"

Comment # 8: Line 259, I would suggest a more formal or quantitative adjective than "*great*".

Reply: The word "great" has been replaced by "*excellent*" in the sentence. The quantitative value of this adjective is given in the previous sentence when we established that the difference between PFP and the surface stations is 0.008 ± 0.34 ppb (95% C. I.):

"*In contrast, UCATS and PFP showed 0.27 ± 0.37 and 0.008 ± 0.34 ppb (95% C. I.), low bias with respect to the surface data, respectively (Fig.2B1-2B4). Due to the excellent agreement between PFP and the surface stations and the consistent offset that QCLS shows against PFP and the stations, in the following sections, QCLS N_2O data presented in this publication is corrected by subtracting the offset with respect to the PFP data on-board in each deployment: 1.03 ± 0.13 ppb in AT-2, 1.49 ± 0.19 ppb in AT-3, and 1.18 ± 0.17 ppb in AT-4. The final official archive data file includes a new column where these corrections have been applied (N$_2$O_QCLS_ad)*".

Comment # 9: Line 290. Extra "and" in the sentence?

Reply: The typo has been corrected.

<u>Comment # 10</u>: Line 300-302. This sentence is confusing because Antarctic vortex breakup usually occurs in November or December, not October. Second, what is the basis for claiming maximum STT in the NH is ending in October?

Reply: We agree with the reviewer that the statement in this line is not properly expressed since this is not the message we wanted to deliver. Our data show N_2O depletions throughout the troposphere during mid-October 2017 at high southern latitudes (SH, 50°S-85°S, Fig. 3c) prompted by the enhanced downwelling of the Brewer–Dobson circulation (BDC) in late winter–spring that reinforces the downward transport of stratospheric air depleted in N_2O throughout the free troposphere (1-8 km). The effect of the BDC is also observed at northern hemisphere middle and high latitudes in spring (May, ATom-4, Fig 3e).

We have modified the first paragraph on section 4.1. for clarification:

"We observed the strongest depletions (> 5 ppb) in N_2O mixing ratios at high latitudes and altitudes, consistent with stratospherically influenced air (Fig. 3). Stratosphere-troposphere exchange processes allow stratospheric-depleted N_2O to be distributed throughout the troposphere. The NOAA surface network shows a seasonal minimum of N_2O 2–4 months later than the stratospheric polar vortex break-up season. This seasonal minimum is observed at the surface around May in the southern hemisphere and around July in the northern hemisphere (see Fig. S8 and S9) (cf. Nevison et al., 2011 and references therein. The enhanced downwelling of the Brewer–Dobson circulation (BDC) in late winter–spring, reinforces the downward transport of stratospheric air depleted in N_2O throughout the free troposphere (1-8 km), as observed in October in the southern hemisphere (ATom-3, Fig. 3c and 3f) and in May in the North Atlantic (ATom-4, Fig 3e). The N_2O depletion is likely the result of stratospheric air being moved downwards by the BDC and trapped by the polar vortex, with a more pronounced effect in the southern hemisphere where the polar vortex is stronger. These results support previous work suggesting that downward transport of stratospheric air with low N_2O exerts a strong influence on the variance of tropospheric N_2O mixing ratios (Nevison et al., 2011; Assonov et al, 2013)".

<u>Comment # 11</u>: Lines 303-306. It seems like there are a lot of variables that might affect these percentages. For example, how are they affected by the altitude of the observations? Did each deployment have the same fraction of air sampled at higher altitudes?

Reply: The reviewer is correct about the fact that these percentages could vary as a function of the number observations by altitude and latitude ranges. The stratospheric influence of air depleted in N_2O is observed at different levels depending on the season, as it is described later in the manuscript. There is also no aircraft data in the SH high latitudes in ATom-2. In these lines we only wanted to give an overall estimation of the influence of stratospheric air depleted in N_2O in the tropospheric N_2O by calculating the absolute number of 1 min-observations affected by stratospheric air (i.e., N_2O differences < -0.5 ppb relative to the NOAA MBL background) relative to the total number of 1 min-data for each of the deployments, independently of the altitude range. Due to the confusion and because of the irrelevance of this information, we have deleted it from the manuscript. See reply to Comment # 10.

<u>Comment # 12</u>: Line 310 refers to Figures 3b, e as though they are March/April, but the panels are labeled on the panels as May (?) Similarly, Figures 3c, f are cited as representing Aug/Sep, but are labeled on the panels as October. Is line 310 just speculation or is it based on ATom data measured early on deployments 3 and 4 (lines 106-107 suggest some April and Sep data were collected)?

Reply: The sentence has been modified for clarity as three different figures are mentioned here simultaneously. As it is shown in Figures S8 and S9, bands of depleted N_2O begin to reach the surface in March-April in the Southern Hemisphere with a maximum depletion observed around May, while in the Northern Hemisphere, the maximum depletion is observed around July at the surface. A typo on the referring figures was also corrected. See reply to Comment # 10.

Comment # 13: Line 319. Please clarify that the NH-SH gradient of N_2O is much smaller than that of CO and SF_6. Otherwise, lines 320-321 don't make much sense.

Reply: The suggestion has been included in a new sentence:

"*Overall, the interhemispheric gradient of N_2O is much smaller than that of CO and SF_6 (Fig. 4), but the difference for each species is driven by larger anthropogenic emissions in the northern hemisphere*".

Comment # 14: Line 322-323. Please explain in more detail. What kind of mixing is being described here?

Reply: In the second paragraph of section 4.1, we are describing the correlations between N_2O and other tracers (tracer-to-tracer correlations). The term mixing in this paragraph is referring to the mixing between stratospheric and tropospheric air. These airmass mixing can be quantified using the N_2O as stratospheric tracer as it is rapidly depleted in the stratosphere. Krause et al. (2018) shows that the N_2O-CO correlation plot can be used either to determine the degree of mixing between stratospheric and tropospheric air as well as to determine the different mixing timescales. The sentences related with this concept have been re-written and more details have been added. In addition, subplots in Fig. 4 have been labelled and captions changed accordingly.

"*The impact of stratosphere-to-troposphere transport can be studied by combining information on tracers of stratospheric air such as ozone (O_3 from the NOAA - NO_yO_3; Bourgeois et al., 2020), sulfur hexafluoride (SF_6 from PANTHER), CFC_{12} (from PANTHER) and carbon monoxide (CO from QCLS). These tracers are usually used either because they are strongly produced in the stratosphere (e.g. O_3) or because they are tracers of anthropogenic emissions in the troposphere with a strong stratospheric sink (e.g., CO, SF_6 and CFC_{12}). In addition, meteorological parameters such as potential vorticity (PV), the product of absolute vorticity and thermodynamic stability (PV was generated by GEOS5-FP for ATom) can be used to trace the stratosphere-to-troposphere transport.*

Overall, the interhemispheric gradient of N_2O is much smaller than that of CO and SF_6 (Fig. 4), but the difference for each species is driven by larger anthropogenic emissions in the northern hemisphere. The tracer-tracer correlations shown in Fig. 4 show different patterns. The linear trend between N_2O and O_3 or CFC-12 highlights the role of depletion (N_2O and CFC-12) and production (O_3) in the stratosphere (Fig. 4a1, 4a4). When N_2O is plotted against the anthropogenic tracers, CO and SF_6, two distinct trends are observed. Tropospheric N_2O can be identified as the horizontal band containing high N_2O (> 328 ppb) and variable CO and SF_6, whereas the vertical band with variable N_2O and small changes in CO and SF_6, shows the mixing between tropospheric air and stratospheric air depleted in N_2O (Fig. 4a1–4a3). The N_2O versus CO plot shows an L-shaped (bimodal) curve similar to those typically observed on O_3-CO correlations during events of stratosphere-to-troposphere airmass mixing (Fig. 4a2, Krause et al., 2018). A quasi-vertical line in the N_2O–CO plot (e.g. constant CO) is indicative of a strong impact of stratospheric air, where CO shows the stratospheric equilibrium mixing ratio (Krause et al., 2018). The lower the CO background, the greater the influence of the stratospheric air during the airmass mixing (North Atlantic high latitudes in Fig. 4a2) and vice versa. A strong correlation is also indicative of rapid mixing between the two air masses. During ATom, the strongest impact of stratospheric air was observed in the Pacific mid and high latitudes in February (ATom-2) and in the Atlantic in May (ATom-4, Fig. S11). At the Pacific northern mid and high latitudes (NMHL

> 30º N), we found a consistent linear relationship between N_2O and O_3, with a relatively constant N_2O/O_3 slope (-0.05 to -0.04) during all seasons. Linear correlations between N_2O and CFC-12 highlight the dominant influence of stratospheric air depleted in these two substances in the range of mixing ratios observed at mid and high latitudes (Fig. S11)".

"Figure 4: (a) Correlations between N_2O and O_3 (a1), CO (a2), SF_6 (a3), and CFC-12 (a4) at mid and high latitudes (30 °–85 ° N) during Northern Hemisphere spring (ATom-4). The data are colored as a function of the ocean basin and hemisphere: Pacific North Mid-High Latitudes (Pac-NH, >30 ° N) in red, Pacific South Mid-High Latitudes (Pac-SH, <30 ° S) in dark blue, Atlantic South Mid-High Latitudes (Atl-SH, <30 ° S) in light blue and Atlantic North Mid-High Latitudes (Atl-NH, >30 ° N) in orange. Note that the N_2O and O_3 axes are reversed. (b) Correlations between anomalies in potential vorticity relative to its mean latitudinal distribution in the free troposphere (2–8 km) and anomalies in N_2O (b1, b3) and CFC-12 (b2, b4) as a function of latitude during spring (ATom-4) over the Pacific and Atlantic basins. Mid-latitudes are shown in orange in the SH and clear brown in the NH."

Comment # 15: Paragraph starting on 313. This paragraph could move less abruptly between each species (CO, O_3, SF_6, CFC_{12}). Also, it's not clear why these 4 species were chosen for the Figure 4 scatterplots. Does each one illustrate a specific new point?

Reply: Each of the species was chosen to demonstrate particular behavior. CO, O_3, SF_6 and CFC_{12} are well-known tracers of stratospheric air, either because they are strongly produced in the stratosphere (e.g. O_3) or because they are tracers of anthropogenic emissions in the troposphere (e.g., CO, SF_6 and CFC_{12}). As it is shown in Figure 4, the tracer-tracer correlations of these species relative to N_2O show different patterns and trends. The linear trend of N_2O vs O_3 or CFC-12 emphasizes the main role of stratospheric air on depleting N_2O and CFC-12 and producing O_3; whereas the correlation between N_2O and the anthropogenic tracers CO and SF_6, allows us to distinguish between the range of tropospheric N_2O mixing ratios from those affected by the influence of stratospheric air depleted in N_2O. The content of the paragraph has been re-organized and more details have been added (see reply to comment #14).

Comment # 16: Figure 5. X-axis labels are overlapping and hard to read on N_2O/CH_3CN profile. Perhaps use same scale as N_2O/CH_4 panel.

Reply: We have modified Fig. 5 for a better reading. See answer to comment # 26.

Comment # 17: Line 382. H_2O_2, PAA and CO profiles in Figure 5 are characterized by enhanced values at the surface. In contrast, N_2O is lower at the surface than at 4 km.

Reply: In Fig. 5 the highest CO mixing ratios are observed below 2 km together with the highest mixing ratios of HCN, SO_2, toluene, benzene and propane, indicating the influence of industrial emissions. In this layer, N_2O mixing ratios are similar to MBL levels (NOAA MBL reference is the dashed line in Fig. 5A2) with the exception of the N_2O peak at 2 km following the relative humidity (RH) profile. Between 0 and 2 km H_2O_2 and PAA show an increasing trend with altitude like N_2O. We think the referee is referring to the fact that highest concentrations of PAA and H_2O_2 are observed at 2 km, while N_2O mixing ratios around 4 km seem to be higher than at 2 km. This is related to the contribution of two different airmasses (see PT and RH profile) and different sources dominating the emissions in each layer: Industrial emissions dominate close to the surface and biomass burning events dominate the emissions at higher altitudes. In any case, PAA and H_2O_2 show similar trends to N_2O below 6 km, differing on the rate of increase / decrease in mixing ratios which is modulated by the influencing source at a given altitude.

We have added the following sentence in the first paragraph of section 4.2.1:

"*In this profile, close to the surface, the lowest QCLS N_2O mixing ratios agree with the NOAA MBL N_2O (dashed line in Fig. 5b).*"

Comment # 18: Figure 6. Perhaps point out in second panel that the APO axis is reversed to illustrate the negative correlation to N_2O.

Reply: The suggestion has been included in the caption of Figure 6:

"Figure 6: (a) Vertical profiles of PT and RH and tracers, N_2O, APO, MSA, CH_2Br_2, CH_4, CO_2, CO, HCN, CH_3CN, NO_3^-, NH_4^+, SO_4^{2+}, H_2O_2, PAA ($CH_3C(O)OOH$), SO_2, NO_y, benzene, toluene and propane, corresponding to profile 9 on 1 May 2018. Dotted blue line in plot A2 represents the NOAA-MBL reference (N_2O-MBL) at the latitude of the flight. Dashed red line shows the N_2O-MBL at the origin of the airmasses suggested by the footprints (25 ° S). (b) N_2O - APO correlations between 0 and 4 km possibly describing the latitudinal gradient of N_2O (s represents the slope of the linear fit). (c) Footprint maps tracing surface regions influencing mixing ratios measured at the altitude ranges of 0–2, 2–4, 3–5, 5–7 and 9–11 km, respectively. Blue squares show the sample locations. Values below 3 ppt / $nmol^{-1}$ m^{-2} s^{-1} are not included. Note that the APO axes are reversed to illustrate the negative correlation to N_2O".

Comment # 19: Line 414 influences should be "influenced".

Reply: The typo has been corrected.

Comment # 20: Line 416 "with higher APO and lower N_2O" would be more meaningful written as "with lower APO and higher N2O" since this is a fall profile in which the ocean thermocline would be deepening, ventilating water enhanced in N_2O and depleted in O_2.

Reply: We agree with the referee that the re-phrasing they propose would be more meaningful if we were observing oceanic N_2O emissions. Unfortunately, during ATom we could not observed this important N_2O source as, in those possible scenarios, our N_2O records were dominated by the N_2O latitudinal gradient. In a given profile we could see N_2O mixing ratios differing in more than 1 ppb depending on the latitudinal origin of the airmass (Fig. 6).

Comment # 21: Line 423 contrasts should be "contrast".

Reply: The typo has been corrected.

Comment # 22: Line 426 the decrease of CO_2 seems consistent with the strong biological drawdown of CO2, especially in regions with intensive agriculture, during the spring/summer growing season (e.g., Schuh et al., Global Change Biology (2013) 19, 1424–1439, doi: 10.1111/gcb.12141). It might be interesting to show a CO_2 profile (since so many other species are shown in Fig. 7).

Reply: We agree with the referee that decreasing CO_2 with increasing trends of N_2O mixing ratios could be consistent with the biological drawdown of CO_2 due to agriculture. During ATom, several profiles show decreasing CO_2 with increasing N_2O, with a relatively high Pearson coefficient in the MBL (< 2 km, Table 1):

Table 1. Correlation coefficients (r) between N_2O and several chemical species for those cases where a high negative correlation between N_2O and CO_2 was found ($-0.96 < r < -0.7$)

Profile	H_2O_2 ppt	PAA ppt	OA $\mu g \cdot m^{-3}$	NH_4^+ $\mu g \cdot m^{-3}$	HCN ppt	APO per meg	CO_2 ppm	CO ppb	SO_2 ppt	SO_4^{2} $\mu g \cdot m^{-3}$
20170928 P-1	0.02	0..45	-0.29	-0.78	-0.79	0.86	-0.87	0.75	-0.22	-0.68
20171011 P-1	-0.26	0.86	0.36	-0.75	0.22	0.75	-0.80	0.77	0.34	-0.87
20171011 P8	0.77	0.53	0.30	0.01	0.68	0.81	-0.77	0.82	0.16	0.75
20171019 P-1	0.29	0.94	0.89	0.93	-0.52	0.89	-0.91	0.97	-0.29	0.91
20180424 P-1	-0.23	0.85	0.18	0.19	0.87	0.86	-0.86	-0.86	-0.23	0.43
20180501 P5	NA	NA	-0.33	-0.72	NA	0.73	-0.78	-0.78	NA	-0.46
20180517 P-1	0.66	0.88	0.19	-0.79	0.62	0.80	-0.90	-0.90	0.81	-0.37
20171019 P4	0.87	0.89	0.63	-0.13	0.78	0.02	-0.96	0.96	-0.22	-0.65
20171020 P2	0.83	0.15	0.66	-0.77	0.81	-0.55	-0.81	0.82	0.35	-0.84
20180424 P-1	-0.23	0.85	0.18	0.19	0.87	0.86	-0.86	-0.86	-0.23	0.43
20180519 P11	0.03	0.25	0.84	0.87	0.73	-0.17	-0.81	-0.85	-0.06	0.02
20180521 P-1	0.90	0.85	0.65	0.75	0.81	-0.91	-0.75	0.25	0.68	0.79
20170201 P3	0.77	0.73	0.49	0.43	0.63	-0.43	-0.70	0.25	NA	0.64
20180503 P3	0.95	0.88	-0.6	-0.38	0.37	-0.34	-0.78	0.65	0.11	-0.18

However, as we express in the second last paragraph in the conclusions "*Because agricultural activities do not have unique tracer signatures, we were not able to distinguish contributions from cultivated and natural soils to N_2O emissions from the ATom data. Previous airborne studies have observed these inputs, using flights in agricultural areas (Kort et al, 2008), and at towers in these regions (e.g., Nevison et al, 2017; Miller et al., 2008)*". The CO_2 profiles have been added to each of the study cases (Fig. 5 to 8). In Fig. 7, the decrease in CO_2 around 2 km is also observed by other chemicals species and it seems to be related to a change of airmass (see PT profile), but we could not really isolate events of agriculture emissions of N_2O.

Comment # 23: Lines 430-434. This seems like a very complex mix of influences to disentangle. Is this even possible?

Reply: Because our measurements were taken far from the most active regions and some of the activities (such as agriculture) do not show unique tracer signatures, a distinction of the different sources contributing to N_2O enhancements in a given atmospheric layer of the atmosphere is not possible in most of the scenarios. We expressed this thought in the last paragraph introducing section 4.2 as well as in the conclusions.

i) Last paragraph introducing Section 4.2:

"*In most cases, because we were sampling in the middle of the oceans and not over the source regions, the distinction between the different sources contributing to the observed N_2O enhancements is not possible. We also observe that the impact of the different sources to N_2O mixing ratios is regionally dependent. Here we describe, with some examples, the sources contributing to the major enhancements of N_2O observed during ATom by oceanic regions, although we cannot pinpoint precisely the source processes.*"

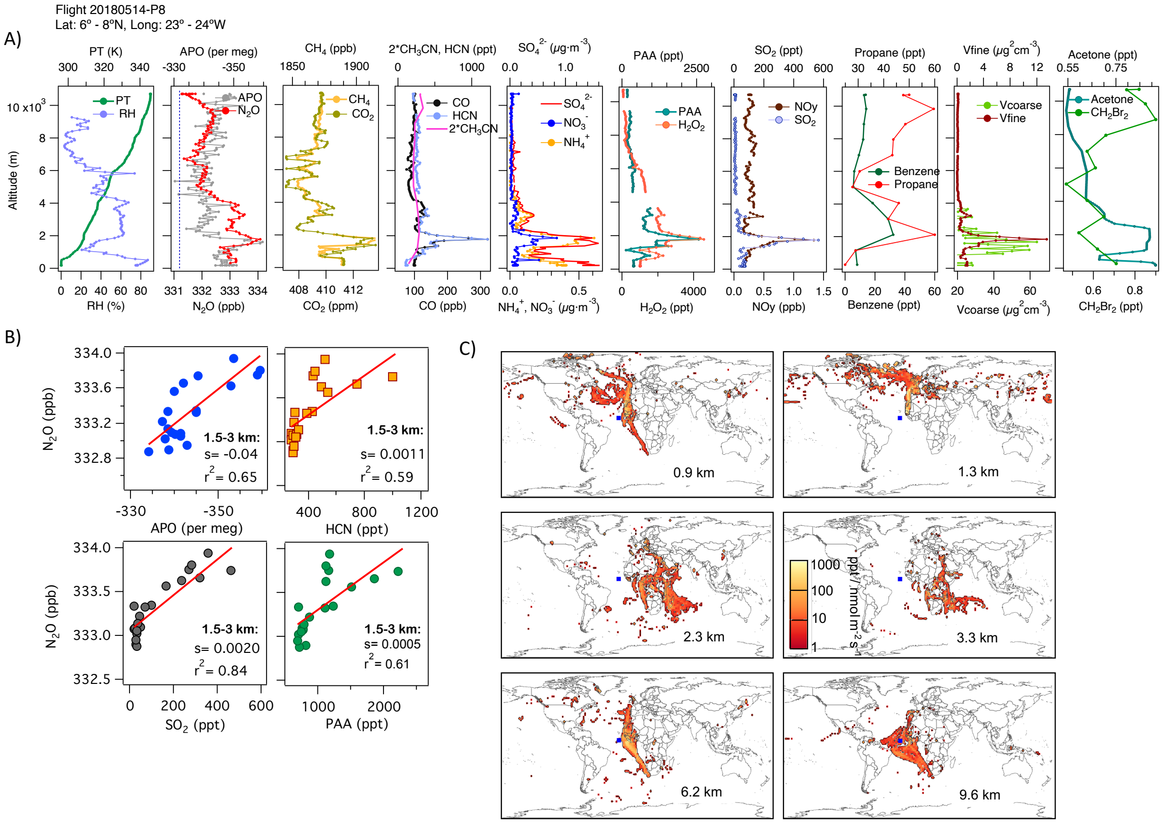
ii) Conclusions:

"*Since H_2O_2 and PAA are products of photochemical pollution, this observation raised the question as to whether significant N_2O may be produced by heterogenous processes involving HONO or NO_x reactions in acidic aerosols close to sources, or in very heavily polluted areas. It is hard to make a definite conclusion based on measurements so far from the most active regions. Studies directed at understanding this question would have to be carried out directly in the polluted areas. Because agricultural activities do not have unique tracer signatures, we were not able to distinguish contributions from cultivated and natural soils to N_2O emissions from the ATom data. Previous airborne studies have observed these inputs, using flights in agricultural areas (Kort et al, 2008), and at towers in these regions (e.g., Nevison et al, 2017; Miller et al., 2008).*

Comment # 24: Line 436-438, why wouldn't this also be an ocean feature, e.g., from upwelling off the coast of Mauritania (as per Ganesan et al. 2020)? The N_2O v. APO slope is similar in sign and magnitude to that shown in Figure 6, except that in the Fig. 6 panel, the APO axis runs normally (negative to less negative), whereas in the Fig. 7 (and Fig. 8) scatterplot, the APO is reversed to run from negative to more negative.

Reply: During discussions with Britton B. Stephens and Eric Morgan, both responsible for APO measurements during ATom, we concluded that the negative correlation between N_2O and APO at 2 km in Fig. 7 most likely represents depletion of APO by industrial combustion, stoichiometrically consistent with the observed increases in CO_2 and CH_4.

Note that APO axes are reverse in the three figures (Figs. 6, 7 and 8), running from left to right from less negative to more negative values, to illustrate the negative correlation to N_2O when an oceanic influence is observed.



<u>Comment # 25</u>: Line 448. Please elaborate "By using a profile specific background." Was an atmospheric transport model used in this exercise?

Reply: Yes. An atmospheric transport model was used to calculate the surface influence. Both reviewers highlighted that this section needed more information. A more detailed explanation on how Fig.9 was designed is now included in the manuscript:

i) We added a new sentence at the end of the second paragraph in section 4.2:

"The footprint can be convolved with a known flux inventory of a non-reactive gas to calculate the expected enhancement/depletion of that gas for each receptor point."

i) We added two new paragraphs at the end of section 4.2.2:

"To understand the origin of the enhancements in N_2O, we calculated the enhancement expected in the atmosphere based on monthly mean estimates of anthropogenic emission from the Emissions Database for Global Atmospheric Research (EDGAR, http://edgar.jrc.ec.europa.eu/). We convolved the calculated surface influence (footprint) with the inventory to calculate the N_2O enhancement expected for each receptor. We also calculated the contribution of each region and source sector to the overall enhancement. This allowed us to quantify the dominant sources for various layers within each profile. Each of the calculated enhancements were then compared to the enhancement in N_2O observed for the profiles. The observed N_2O enhancements were calculated relative to the NOAA MBL reference (Fig 8a, dashed red line) for each 10s observation, with background concentrations chosen for locations close to the origin of the airmass indicated by the surface influence (shown as dashed and dotted lined on the N_2O altitude profiles in Figs 5 – 8). We also included a 0.4 ppb uncertainty for the observed enhancements based on our measurement precision.

In the Atlantic during ATom 2 (Feb 2017; Fig 9), the largest N_2O enhancement is attributed to African agriculture (peaking at 2 ppb at 2 km), with smaller but significant influence from Asia and Europe (0.5 ppb each at 2-4 km, Fig. S14). The observed and modeled N_2O enhancements agree within an order of magnitude for the profile, but the model underestimates the high altitude (4-7 km) N_2O enhancement by <1 ppb and overestimates the lower altitude enhancement (2-4 km) by ~1 ppb. The difference in N_2O enhancement could be due to a strong latitudinal gradient in N_2O across this profile or the timing of emission of N_2O sampled along this single profile compared to a monthly mean estimate from the inventory. Strong correlations between N_2O and HCN ($r^2 = 0.95$), CO and CH_3CN suggest a source of N_2O from burning emissions also contribute to the N_2O enhancement (Fig. 8 and Fig. S12). However, when we convolved the monthly mean fire contributions from the Global Fire Emissions Database (GFED, https://www.globalfiredat.org) with the surface influence footprints (as described above), we find that the wildfire produced N_2O is minimal for this profile (~0.2 ppb), suggesting fires of anthropogenic or urban origin might be the source of that contribution (Figs. 8A–C, 9, S12 and S13)."

<u>Comment # 26</u>: In general, could a common set of species and profiles for Figure 6-8 (or at least Fig 7-8) be chosen and displayed consistently? It would be easier for the reader to compare and contrast the different points being made with each of these multi-paneled figures.

Reply: Figures 5 to 8 and their captions have been modified to consistently show the same chemical species with a similar color code to make easier for the reader to go through them. See below:

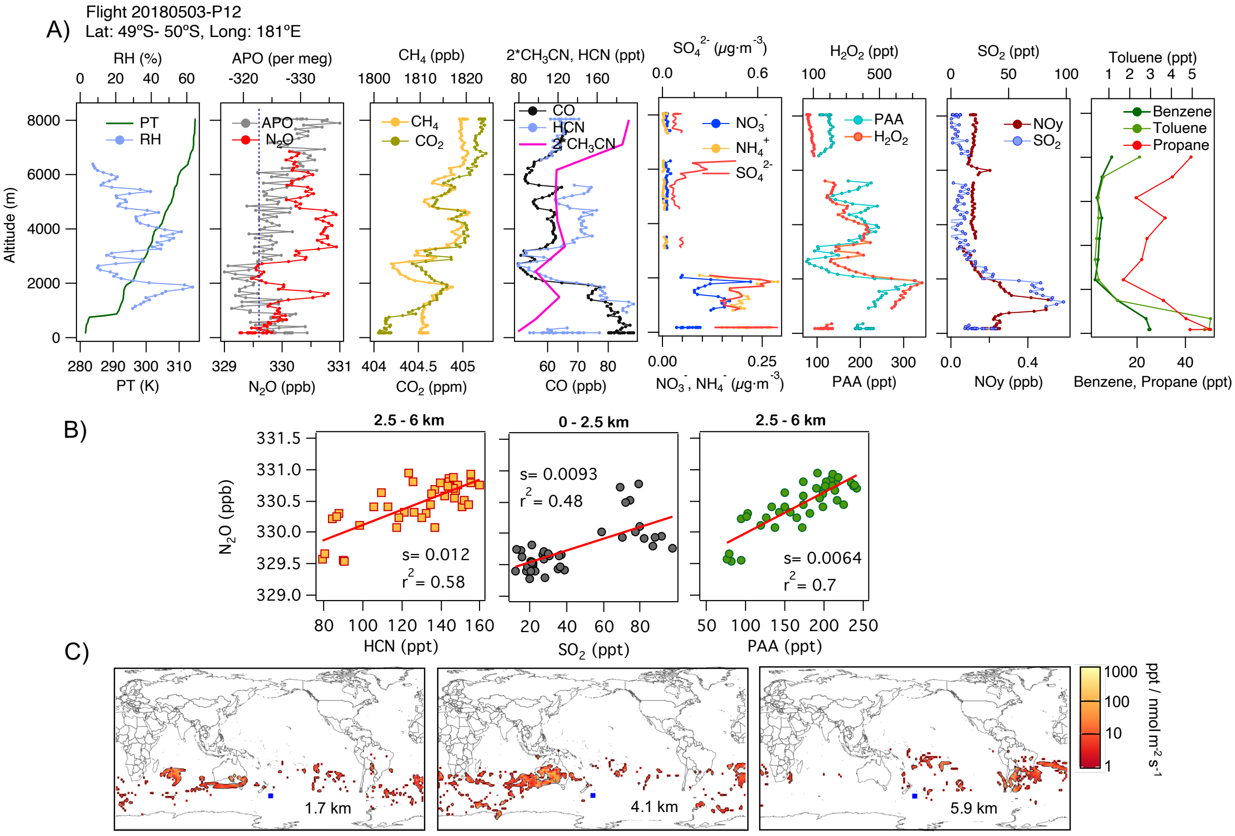


Figure 5: (A) Vertical profiles of Potential Temperature (PT), Relative Humidity (RH), N_2O, APO, CH_4, CO_2, CO, HCN, CH_3CN, NO_3^-, NH_4^+, SO_4^{2+}, H_2O_2, PAA ($CH_3C(O)OOH$), SO_2, NO_y, benzene, toluene and propane from profile 12 on 3 May 2018. Dotted blue line in plot A2 represents the NOAA-MBL reference (N_2O-MBL) at the latitude of the flight. (B) Correlations between N_2O and HCN and PAA for altitudes between 2.5 and 6 km and between N_2O and SO_2 for altitudes between 0 and 2.5 km indicate an admixture of marine, biomass burning, urban sources, and oil and gas industry contributions to N_2O mixing ratios (s represents the slope of the linear fit). (C) Footprint maps tracing surface regions influencing mixing ratios measured at the altitude ranges of 1–2, 2.5–5 and 5–7 km, respectively. Blue squares show the sample locations. Values below 3 ppt / (nmol m^{-2} s^{-1}) are not included. Note that the APO axes are reversed.

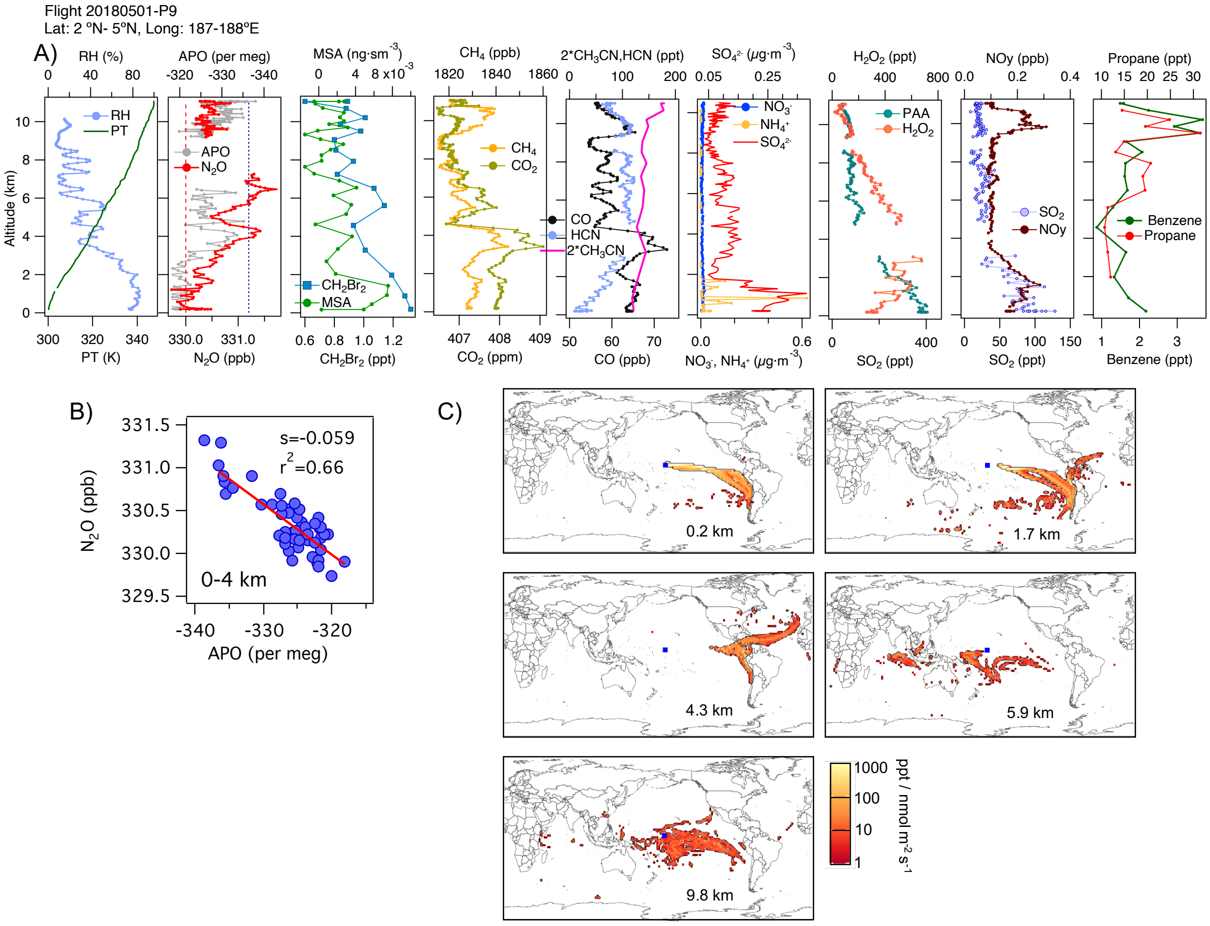


Figure 6: (A) Vertical profiles of PT and RH and tracers, N_2O, APO, MSA, CH_2Br_2, CH_4, CO_2, CO, HCN, CH_3CN, NO_3^-, NH_4^+, SO_4^{2+}, H_2O_2, PAA ($CH_3C(O)OOH$), SO_2, NO_y, benzene, toluene and propane, corresponding to profile 9 on 1 May 2018. Dotted blue line in plot A2 represents the NOAA-MBL reference (N_2O-MBL) at the latitude of the flight. Dashed red line shows the N_2O-MBL at the origin of the airmasses suggested by the footprints (25° S). (B) N_2O - APO correlations between 0 and 4 km possibly describing the latitudinal gradient of N_2O (s represents the slope of the linear fit). (C) Footprint maps tracing surface regions influencing mixing ratios measured at the altitude ranges of 0–2, 2–4, 3–5, 5–7 and 9–11 km, respectively. Blue squares show the sample locations. Values below 3 ppt / nmol^{-1} m^{-2} s^{-1} are not included. Note that the APO axes are reversed to illustrate the negative correlation to N_2O.

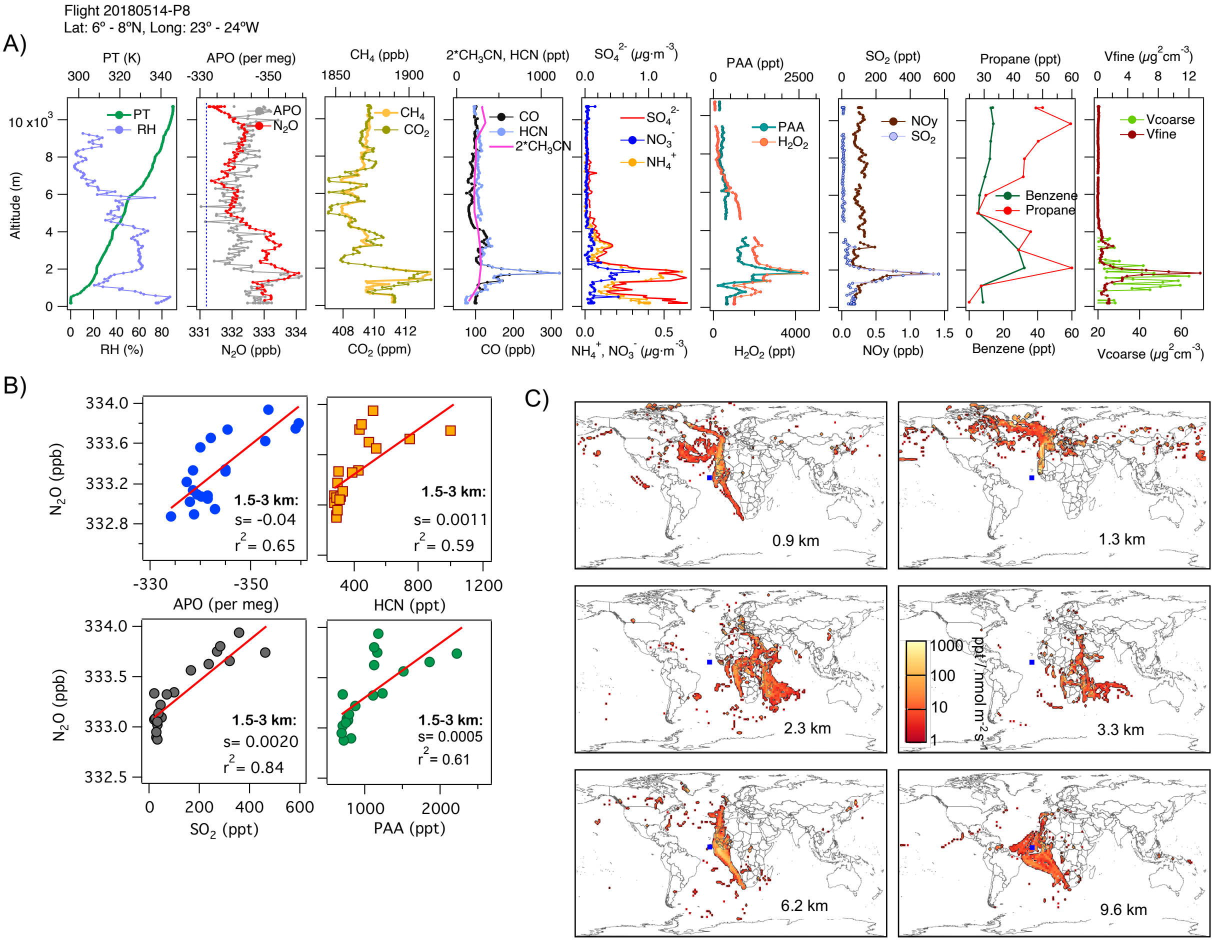


Figure 7: (A) Vertical profiles of PT, RH, and tracers, N_2O, APO, CH_4, CO_2, CO, HCN, CH_3CN, NO_3^-, NH_4^+, SO_4^{2+}, H_2O_2, PAA, SO_2, NO_y, benzene, propane as well as the volume of course and fine particles, corresponding to profile 8 on 14 May 2018. Dotted blue line in plot A2 represents the NOAA-MBL reference (N_2O-MBL) at the latitude of the flight. (B) Correlations between N_2O and APO, HCN, SO_2, and propane between 1 and 3 km show possible contributions from marine upwelling, biomass burning and oil and gas industry, supported by the footprints (s represents the slope of the linear fit). (C) Footprint maps tracing surface regions influencing mixing ratios measured at the altitude ranges of 0–1, 2–4, 4–5, 5–7 and 7–10 km, respectively. Blue square shows the sample point. Values below 3 ppt / nmol m^{-2} s^{-1} are not included. Note that the APO axes are reversed.

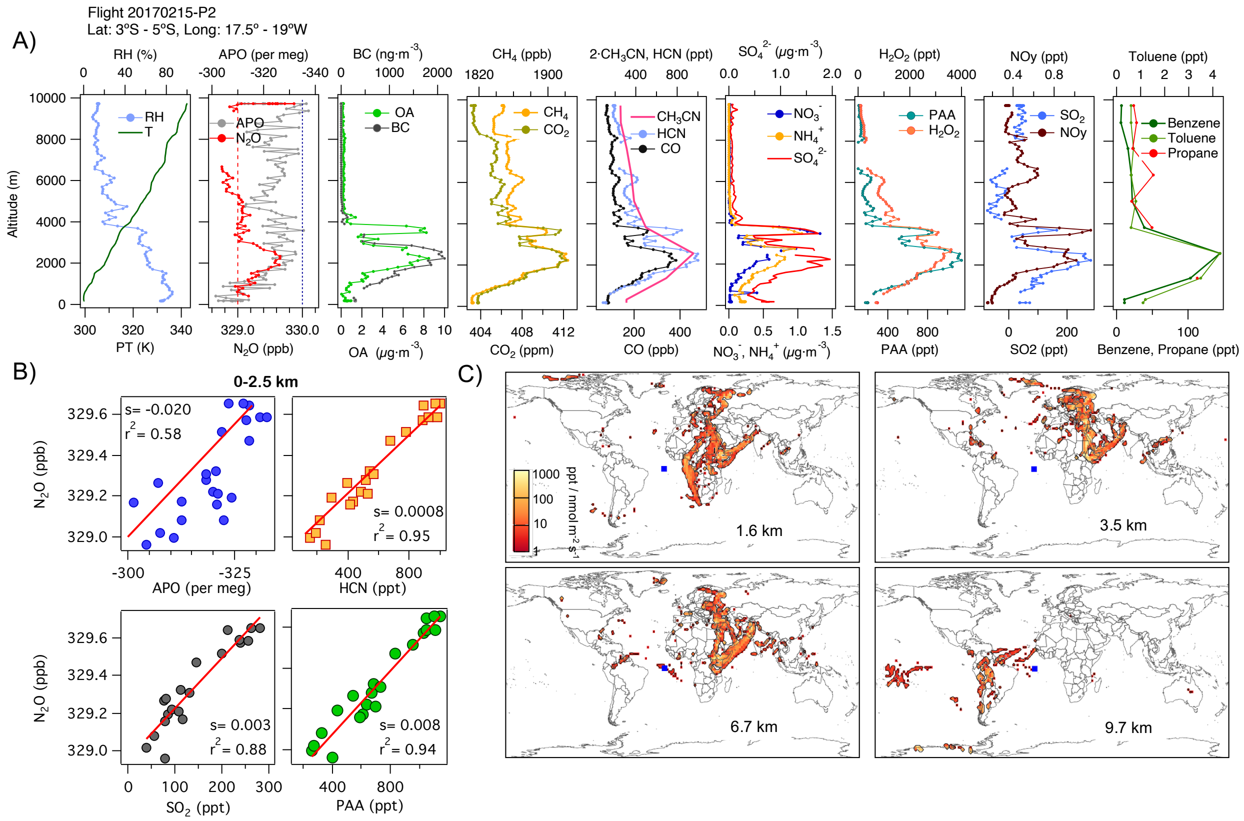


Figure 8: (A) Vertical profiles of PT, RH, and tracers, N_2O, APO, organic aerosols (OA), black carbon (BC), CH_4, CO_2, CO, HCN, CH_3CN, NO_3^-, NH_4^+, SO_4^{2+}, H_2O_2, PAA, SO_2, NO_y, benzene, toluene and propane, corresponding to profile 2 on 15 February 2017. Dotted blue line in plot A2 represents the NOAA-MBL reference (N_2O-MBL) at the latitude of the flight, and red dashed line shows the NOAA-MBL at the origin of the southern airmasses shown by the footprints below 2 km (20°S). (B) Correlations between N_2O and APO, HCN and SO_2, for data observed below 2.5 km, indicate an admixture of marine, biomass burning, urban sources, and oil and gas industry contributions to N_2O mixing ratios (s represents the slope of the linear fit). (C) Footprint maps tracing surface regions influencing mixing ratios measured at the altitude ranges of 0–2, 2–3, 3–4 and 4–7 km, respectively. Blue squares show the sample point. Values below 3 ppt / nmol m^{-2} s^{-1} are not included in the footprint plot. Note that APO axes are reversed.

Reviewer 2

"This manuscript reports results relating to N_2O from a series of flights. The manuscript is well written and presents interesting results, that are useful for the rest of the scientific community. My comments are minor, mainly looking to clarify the presentation".

We thank the reviewer for their time and providing positive and constructive comments concerning manuscript acp-2021-167. We revised the manuscript accordingly and incorporated all the proposed changes.

Comment # 1: Line 40 – I suggest clarifying "is rapidly increasing" by stating "its mixing ratio is rapidly increasing" (or similar phrasing).

Reply: We agree with the reviewer, however, we removed this sentence from the abstract to make it more precise.

Comment # 2: Line 47 and 467 - "factor of 3" relative to what? I know what is meant having read the whole paper, but I think this needs to be explicitly stated in the abstract/ conclusions.

Reply: The retrieval strategy described in this work improved the precision of our ATom N_2O measurements by a factor of 3. This factor was calculated based on the stdev. of calibration measurements. With this improvement, precision of ATom N_2O data was similar to the precision of previous missions such as HIPPO. The impact of the retrieval strategy on the data is explained in the third paragraph of section 2.2:

"*The Neptune-PCA analysis improved the overall precision by a factor of 4 for CH_4 and a factor of 3 in the case of N_2O with respect to the precision of the original retrievals, as measured by the standard deviation of retrieved mixing ratios during calibrations*".

Other related sentences have been rephrased for clarification. A new sentence has been added in paragraph 2 in section 2.2. The abstract and conclusion has been modified as shown below. This issue was also highlighted by Reviewer 1 and changes were made accordingly.

i) Abstract:

"*We introduced a new spectral retrieval method to account for the pressure and temperature sensitivity of the instrument when deployed on aircraft. This retrieval strategy improved the precision of our ATom QCLS N_2O measurements by a factor of 3 (based on the stdev. of calibration measurements)*".

ii) Section 2.2. paragraph 2:

"*We have achieved significant improvement in the precision and accuracy of the ATom QCLS N_2O data using a new method dubbed the "Neptune algorithm", developed by Aerodyne Research, Inc., and that has been further developed and applied to the data sets described here. Using this algorithm, the precision of the retrieved N_2O data measured with the damaged QCLS, was similar to that reported in HIPPO*".

iii) Conclusions:

"*This method improved the precision of our QCLS N_2O measurements (based on the stdev. of calibration measurements) by a factor of 3, allowing us to provide N_2O measurements at the level of precision shown in previous aircraft missions*".

Comment # 3: Line 85 – I was surprised that N_2O emissions from tropical river systems in Africa were so high, so I checked this reference. The bibliography of this manuscript is missing an entry for Valentini 2014, which needs to be added in, I assume it's https://bg.copernicus.org/articles/11/381/2014/. Having skimmed this paper, 3.3 Tg N_2O yr^{-1} seems to come from Table 9, which is total emissions for Africa, of which rivers seem to be a minor contributor. Please check where this number came from, and clarify in the text if necessary.

Reply: The referee is correct. This estimation accounts for both biogenic sources and fires in the African continent. This has been included in the manuscript for clarification (lines 84-85, second paragraph of the introduction) and the reference to Valentine et al. (2014) has been added to the reference list. Reviewer 1 did also refer to this issue. The sentence is rephased as:

"*N_2O emissions from biogenic sources and fires in Africa are estimated at 3.3 ± 1.3 Tg N_2O yr^{-1} (Valentini et al., 2014).*"

Valentini, R., Arneth, A., Bombelli, A., Castaldi, S., Cazzolla Gatti, R., Chevallier, F., Ciais, P., Grieco, E., Hartmann, J., Henry, M., Houghton, R. A., Jung, M., Kutsch, W. L., Malhi, Y., Mayorga, E., Merbold, L., Murray-Tortarolo, G., Papale, D., Peylin, P., Poulter, B., Ray- mond, P. A., Santini, M., Sitch, S., Vaglio Laurin, G., van der Werf, G. R., Williams, C. A., and Scholes, R. J.: A full greenhouse gases budget of Africa: synthesis, uncertainties, and vulnerabilities, Biogeosciences, 11, 381–407, doi:10.5194/bg-11-381-2014, 2014.

Comment # 4: Line 87 – "and the balance from agriculture", I suggest changing "balance" to "rest"?

Reply: The suggestion has been taken into account:

"*According to Tian et al. (2020), anthropogenic sources account for 43% of the global N_2O emissions (7.3 Tg N yr^{-1}), with industry and biomass burning emissions estimated to be 1.6 to 1.9 Tg N yr^{-1} respectively (Syakila and Kroeze, 2011; Tian et al., 2020) and the rest from agriculture*".

Comment # 5: Line 97, 465, 501 - "highly resolved" in what?

Reply: In these lines we are referring to the time resolution of our measurements. QCLS provides 1Hz resolution data. In this work, we have used the ATom merged file, MER10_DC8_ATom-1.nc (ORNL-DAAC, Wofsy et al., 2018, https://doi.org/10.3334/ORNLDAAC/1581), where QCLS data is compiled at 10s-resolution. We have included the time resolution (1 Hz) in these lines for clarification.

Comment # 6: Figure 2 – the figure caption refers to d-g but no plots are labelled d-g.

Reply: We have corrected the typo in the caption as follows:

"*Figure 2: (a) Comparisons between Neptune-corrected QCLS N_2O and (1) UCATS N_2O, (2) PANTHER N_2O, and (3) PFP N_2O for ATom-2 (orange circles), ATom-3 (green stars), and -4 (blue* *squares). We used the 10s averaged merged file to compare QCLS, UCATS and PANTHER data. The PFP flask samples have a longer sampling time (30s to few minutes). The 1:1 line is shown as a dashed line. (b) B) Comparisons between NOAA N_2O surface flask measurements and Neptune-corrected and airborne data from (1) QCLS N_2O, (2) UCATS N_2O, (3) PANTHER N_2O, (4) and PFP N_2O for ATom-2, -3, and -4, similar to A1–A3. The solid line shows the 1:1 relationship + offset. For B1–B4 plots, the airborne data are the mean N_2O values within ± 5° latitude of each surface station and between 1 and 4 km".*

Comment # 7: Line 310 /Figure 3 – the months of the subplots are inconsistent between the figure and the text.

Reply: The sentence has been modified for clarity as three different figures are mentioned here simultaneously. A typo on the referring figures was also corrected. Reviewer 1 also referred to this issue. We have modified the first paragraph on section 4.1. for clarification:

"We observed the strongest depletions (> 5 ppb) in N_2O mixing ratios at high latitudes and altitudes, consistent with stratospherically influenced air (Fig. 3). Stratosphere-troposphere exchange processes allow stratospheric-depleted N_2O to be distributed throughout the troposphere. The NOAA surface network shows a seasonal minimum of N_2O 2–4 months later than the stratospheric polar vortex break-up season. This seasonal minimum is observed at the surface around May in the southern hemisphere and around July in the northern hemisphere (see Fig. S8 and S9) (cf. Nevison et al., 2011 and references therein. The enhanced downwelling of the Brewer–Dobson circulation (BDC) in late winter–spring, reinforces the downward transport of stratospheric air depleted in N_2O throughout the free troposphere (1-8 km), as observed in October in the southern hemisphere (ATom-3, Fig. 3c and 3f) and in May in the North Atlantic (ATom-4, Fig 3e). The N_2O depletion is likely the result of stratospheric air being moved downwards by the BDC and trapped by the polar vortex, with a more pronounced effect in the southern hemisphere where the polar vortex is stronger. These results support previous work suggesting that downward transport of stratospheric air with low N_2O exerts a strong influence on the variance of tropospheric N_2O mixing ratios (Nevison et al., 2011; Assonov et al, 2013)".

Comment # 8: Line 321 / Figure 4 – the text says Fig. 4a-d, but no subplots are labelled c or d. Each subplot needs to be labelled, and that label used consistently in the text, caption, and figure.

Reply: Subplots in Fig. 4 has been labelled and caption modified accordingly. The second paragraph in section 4.1 has been reorganized as follows:

"*The impact of stratosphere-to-troposphere transport can be studied by combining information on tracers of stratospheric air such as ozone (O_3 from the NOAA - NO_yO_3; Bourgeois et al., 2020), sulfur hexafluoride (SF_6 from PANTHER), CFC_{12} (from PANTHER) and carbon monoxide (CO from QCLS). These tracers are usually used either because they are strongly produced in the stratosphere (as O_3) or because they are tracers of anthropogenic emissions in the troposphere with a strong stratospheric sink (e.g., CO, SF_6 and CFC_{12}). In addition, meteorological parameters such as potential vorticity (PV), the product of absolute vorticity and thermodynamic stability (PV was generated by GEOS5-FP for ATom) can be used to trace the stratosphere-to-troposphere transport.*

Overall, the interhemispheric gradient of N2O is much smaller than that of CO and SF6 (Fig. 4), but the difference for each species is driven by larger anthropogenic emissions in the northern hemisphere. The tracer-tracer correlations shown in Fig. 4 show different patterns. The linear trend between N2O and O3 or CFC-12 highlights the role of depletion (N2O and CFC-12) and production (O3) in the stratosphere (Fig. 4a1, 4a4). When N2O is plotted against the anthropogenic tracers, CO and SF6, two distinct trends are observed. Tropospheric N2O can be identified as the horizontal band containing *high N2O (> 328 ppb) and variable CO and SF6, whereas the vertical band with variable N2O and small changes in CO and SF6, shows the mixing between tropospheric air and stratospheric air depleted in N2O (Fig. 4a1–4a3). The N2O versus CO plot shows an L-shape (bimodal) curve similar to those typically observed on O3-CO correlations during events of stratosphere-to-troposphere airmass mixing (Fig. 4a2, Krause et al., 2018). A quasi-vertical line in the N2O–CO plot (e.g. constant CO) is indicative of a strong impact of stratospheric air, where CO shows the stratospheric equilibrium mixing ratio (Krause et al., 2018). The lower the CO background, the greater the influence of the stratospheric air during the airmass mixing (North Atlantic high latitudes in Fig. 4a2) and vice versa. A strong correlation is also indicative of rapid mixing between the two air masses. During ATom, the strongest impact of stratospheric air was observed in the Pacific mid and high latitudes in February (ATom-2) and in the Atlantic in May (ATom-4, Fig. S11). At the Pacific northern mid and high latitudes (NMHL > 30^o N), we found a consistent linear relationship between N2O and O3, with a relatively constant N2O/O3 slope (-0.05 to -0.04) during all seasons. Linear correlations between N2O and CFC-12 highlight the dominant influence of stratospheric air depleted in these two substances in the range of mixing ratios observed at mid and high latitudes (Fig. S11).*

"Figure 4: (a) Correlations between N_2O and O_3 (a1), CO (a2), SF_6 (a3), and CFC-12 (a4) at mid and high latitudes (30°–85° N) during Northern Hemisphere spring (ATom-4). The data are colored as a function of the ocean basin and hemisphere: Pacific North Mid-High Latitudes (Pac-NH, >30°N) in red, Pacific South Mid-High Latitudes (Pac-SH, <30°S) in dark blue, Atlantic South Mid-High Latitudes (Atl-SH, <30°S) in light blue and Atlantic North Mid-High Latitudes (Atl-NH, >30°N) in orange. Note that the N_2O and O_3 axes are reversed. (b) Correlations between anomalies in potential vorticity relative to its mean latitudinal distribution in the free troposphere (2–8 km) and anomalies in N_2O (b1, b3) and CFC-12 (b2, b4) as a function of latitude during spring (ATom-4) over the Pacific and Atlantic basins. Mid-latitudes are shown in orange in the SH and clear brown in the NH."

Comment # 9: Line 448 - I'm unclear how EDGAR has been used to create a profile, some extra explanation is needed here.

Reply: Both reviewers highlighted that this section needed more information. A more detailed explanation on how Fig.9 was designed is now included in the manuscript.

i) A sentence was added at the end of the second paragraph in section 4.2:

"The footprint can be convolved with a known flux inventory of a non-reactive gas to calculate the expected enhancement/depletion of that gas for each receptor point."

i) Two new paragraphs were added at the end of section 4.2.2:

"To understand the origin of the enhancements in N_2O, we calculated the enhancement expected in the atmosphere based on monthly mean estimates of anthropogenic emission from the Emissions Database for Global Atmospheric Research (EDGAR, http://edgar.jrc.ec.europa.eu/). We convolved the calculated surface influence (footprint) with the inventory to calculate the N_2O enhancement expected for each receptor. We also calculated the contribution of each region and source sector to the overall enhancement. This allowed us to quantify the dominant sources for various layers within each profile. Each of the calculated enhancements were then compared to the enhancement in N_2O observed for the profiles. The observed N_2O enhancements were calculated relative to the NOAA MBL reference (Fig 8a, dashed red line) for each 10s observation, with background concentrations chosen for locations close to the origin of the airmass indicated by the surface influence (shown as dashed and dotted lined on the N_2O altitude profiles in Figs 5 – 8). We also included a 0.4 ppb uncertainty for the observed enhancements based on our measurement precision.

In the Atlantic during ATom 2 (Feb 2017; Fig 9), the largest N_2O *enhancement is attributed to African agriculture (peaking at 2 ppb at 2 km), with smaller but significant influence from Asia and Europe (0.5 ppb each at 2-4 km, Fig. S14). The observed and modeled* N_2O *enhancements agree within an order of magnitude for the profile, but the model underestimates the high altitude (4-7 km)* N_2O *enhancement by <1 ppb and overestimates the lower altitude enhancement (2-4 km) by ~1 ppb. The difference in* N_2O *enhancement could be due to a strong latitudinal gradient in* N_2O *across this profile or the timing of emission of* N_2O *sampled along this single profile compared to a monthly mean estimate from the inventory. Strong correlations between* N_2O *and HCN (*$r^2 = 0.95$*), CO and* CH_3CN *suggest a source of* N_2O *from burning emissions also contribute to the* N_2O *enhancement (Fig. 8 and Fig. S12). However, when we convolved the monthly mean fire contributions from the Global Fire Emissions Database (GFED, https://www.globalfiredat.org) with the surface influence footprints (as described above), we find that the wildfire produced* N_2O *is minimal for this profile (~0.2 ppb), suggesting fires of anthropogenic or urban origin might be the source of that contribution (Figs. 8A–C, 9, S12 and S13)".*

Reviewer 3

"This study develops a N_2O retrieval algorithm for the QCLS airborne instrument that reduces the sensitivity of the measurement to temperature and pressure changes in the aircraft cabin. The performance of the QCLS retrieval of N_2O is evaluated using three additional N_2O instruments during the ATom mission. Anomalies in measured N_2O with respect to background mixing ratios are described. The authors demonstrated how anthropogenic and natural sources of these anomalies can be identified using the suite of chemical tracers collected during ATom. Overall, the paper is well-written and the author thoroughly characterize a useful dataset. The comments below are minors and are for clarity in the discussion.".

We thank the reviewer for their time and providing positive and constructive comments concerning manuscript acp-2021-167. We revised the manuscript accordingly and incorporated all the proposed changes.

Comment # 1: Lines 46 – 47: The wording of this sentence is confusing. Did the new retrieval strategy improve measurements by a factor of 3 with respect to previous deployments of the instrument or was a spectra collected during previous missions reanalyzed with improved precision? Please reword to clarify.

Reply: An accident at the beginning of the ATom mission, where the QCLS was dropped to the ground by the shipping company, misaligned the optics of the QCLS. Even though we completely re-aligned the cell between ATom-1 and ATom-2, we observed an increased sensitivity of the optical elements surrounding the cell to the aircraft maneuvers. As a consequence of this accident, the precision of the QCLS N_2O, estimated as a function of the standard deviation of the mean values of the high and low mixing ratio tanks used for in-flight calibrations, was up to 3 times higher than that in the previous mission HIPPO. We tried several retrieval strategies to improve QCLS N_2O data from ATom and the Neptune Algorithm was the one capable to improve the precision of the QCLS N_2O in ATom to reach the levels of precision in HIPPO. We described these facts in the first paragraph of section 2.2:

The retrieval strategy described in this work improved the precision of our ATom N_2O measurements by a factor of 3. This factor was calculated based on the stdev. of calibration measurements. With this improvement, precision of ATom N_2O data was similar to the precision of previous missions such as HIPPO. The impact of the retrieval strategy on the data is explained in the third paragraph of section 2.2:

"*The Neptune-PCA analysis improved the overall precision by a factor of 4 for CH_4 and a factor of 3 in the case of N_2O with respect to the precision of the original retrievals, as measured by the standard deviation of retrieved mixing ratios during calibrations*".

Other related sentences have been rephrased for clarification. A new sentence has been added in paragraph 2 in section 2.2. The abstract and conclusion has been modified as shown below. This issue was also highlighted by Reviewer 1 and changes were made accordingly.

i) Abstract:

"*We introduced a new spectral retrieval method to account for the pressure and temperature sensitivity of the instrument when deployed on aircraft. This retrieval strategy improved the precision of our ATom QCLS N_2O measurements by a factor of 3 (based on the stdev. of calibration measurements)*".

ii) Section 2.2. paragraph 2:

"*We have achieved significant improvement in the precision and accuracy of the ATom QCLS N_2O data using a new method dubbed the "Neptune algorithm", developed by Aerodyne Research, Inc., and that has been further developed and applied to the data sets described here. Using this algorithm, the precision of the retrieved N_2O data measured with the damaged QCLS, was similar to that reported in HIPPO*".

iii) Conclusions:

"*This method improved the precision of our QCLS N_2O measurements (based on the stdev. of calibration measurements) by a factor of 3, allowing us to provide N_2O measurements at the level of precision shown in previous aircraft missions*".

Comment # 2: Line 76: The list of emission estimates in this paragraph is difficult to process. Could they be summarized more concisely? Also, are there conclusions from the ATom analysis that could be discussed in the context of these studies?

Reply: We have organized the sentences and added a few comments in the second paragraph of the introduction for an easier reading as shown below.

"*Much effort has been made to reduce the uncertainties in the individual components of the N_2O global budget (e.g., Tian et al., 2012, 2020; Xiang et al., 2013; Thompson et al., 2014a, b; Ganesan et al., 2020; Yang et al., 2020). Recent estimates of global total N_2O emission to the atmosphere from bottom-up and top-down methods average 17 Tg N yr^{-1} (12.2–23.5 from bottom-up analysis, and 15.9–17.7 Tg N yr^{-1} from top-down approaches, Tian et al., 2020). The most recent estimates of the global ocean emission of N_2O range between 2.5 and 4.3 Tg N yr^{-1}(~ 20% of total emissions), with the tropics, upwelling coastal areas and subpolar regions as the major contributors to these fluxes (Yang et al., 2020; Tian et al., 2020). However, the magnitude of marine N_2O emissions is subject to large uncertainty, due to spatial and temporal heterogeneity (Nevison et al., 1995, 2005; Ganesan et al., 2020; Yang et al., 2020). According to Tian et al. (2020), anthropogenic sources account for ~43% of the global N_2O emissions (7.3 Tg N yr^{-1}), with industry and biomass burning emissions estimated to be 1.6 to 1.9 Tg N yr^{-1} respectively (Syakila and Kroeze, 2011; Tian et al., 2020) and the rest from agriculture. N_2O emissions from biogenic sources and fires in Africa are estimated at 3.3 ± 1.3 Tg N_2O yr^{-1} (Valentini et al., 2014). Agricultural N_2O emission estimates (up to ~37%) range between 2.5 and 5.8 Tg N yr^{-1}, and between 4.9 and 6.5 Tg N yr^{-1} in the case of natural soils (Kort et al., 2008; 2010; Syakila and Kroeze, 2011; Tian et al., 2020). Recent estimates of N_2O emissions from fertilized tropical and subtropical agricultural systems are 3 ± 5 kg N ha^{-1} y^{-1} (Albanito et al., 2017). Most of these estimates are derived from short-term local-scale in-situ measurements and are difficult to extrapolate with confidence to large regions or to the globe*".

As we describe along the study, because we were sampling in the middle of the oceans and not over the source regions, the distinction between the different sources contributing to the observed N_2O enhancement was not possible. However, on Feb 2017, flying over the Atlantic, we measured a strong N_2O signal from the African continent that we attributed to African agriculture (peaking at 2 ppb at 2 km), with smaller but significant influence from Asia and Europe (0.5 ppb each at 2-4 km). The observed and modeled N_2O enhancements (using the EDGAR inventory) agree within an order of magnitude for the profile, but the model underestimates the high altitude (4-7 km) N_2O enhancement by <1 ppb and overestimates the lower altitude enhancement (2-4 km) by ~1 ppb. The difference in N_2O enhancement could be due to a strong latitudinal gradient in N_2O across this profile or the timing of emission of N_2O sampled along this single profile compared to a monthly mean estimate from the inventory. Strong correlations between N_2O and HCN ($r^2 = 0.95$), CO and CH_3CN suggested a source of N_2O from burning emissions also contribute to the N_2O enhancement. However, when we convolved the monthly mean fire contributions from the Global Fire Emissions Database (GFED, https://www.globalfiredat.org) with the surface influence footprints, we find that the wildfire produced

N_2O is minimal for this profile (~0.2 ppb), suggesting fires of anthropogenic or urban origin might be the source of that contribution.

<u>Comment # 3:</u> Line 154: missing coma before "and"

Reply: The typo has been corrected.

Comment # 4: Line 184: "…with respect to the precision of the original retrievals…": please clarify if this is with respect to the original ATom-1 retrievals with the damaged instrument or to all QCLS retrievals during ATom. Overall, the discussion of the calibration improvement and damage to the instrument before ATom-1 seems to be mixed together in this section. Did the damage impact the later ATom missions too?

Reply: In this sentence we are referring to the raw data, retrieved by the TDL-Wintel instrument's software, before applying any possible correction (i.e. the Neptune retrieval). The damage before ATom-1 impacted all ATom missions. After ATom-1 the instrument was re-aligned. However, after this re-alignment, an increased temperature and pressure dependance was observed in all deployments that affected the precision of the instrument. To reduce this dependance, and therefore, improve precision, we designed the Neptune retrieval that was then applied to all missions (ATom-2 to ATom-4). We could not retrieve CH_4/N_2O ATom-1 data because light levels were too low for the CH_4/N_2O laser due to the damage-induced misalignment. We explained this in the third paragraph on section 2.2:

"The laser path of the CH_4/N_2O laser was realigned between ATom-1 and -2 and the Neptune retrieval was applied to CH_4 and N_2O measurements corresponding to the ATom-2, -3 and -4 deployments. Mixing ratios of CH_4 and N_2O could not be retrieved during ATom-1 because light levels were too low for the CH_4/N_2O laser due to the damage-induced misalignment."

We have included an additional sentence in the first paragraph of section 2.2 for clarification:

"This increased sensitivity was observed in all ATom deployments".

Comment # 5: Line 250: What do you mean by "common sampling locations"? Are these locations representative of the atmospheric background and typically not influenced by anthropogenic emissions? Also, Table S.3 shows median mixing ratios of N_2O measured during ATom, not information about the surface stations as indicated in the text.

Reply: If during a flight, a surface station was encountered within a latitude grid of ± 5 degrees, that station was used in the study. For that particular case, a mean value of N_2O within that latitude grid and between 1 to 4 km altitude of QCLS was compared with the mean N_2O at the station located within +/- 5 days of the flight (due to the non-daily frequency of flask samples). We have modified the two first paragraphs in section 3.2 for clarification as shown below.

The reviewer is right that the information about the surface stations was missing. We have now included this information in Table S.3.

"We evaluate the traceability of lower-troposphere N_2O mixing ratios by ATom by comparing the four airborne instruments with the surface measurements of N_2O from the NOAA flask sampling network. If during a flight, a surface station was encountered within a latitude range of 5 degrees north and south with respect to the flight track, that surface station was used in the study.

A mean value of N_2O within that latitude grid of +/- 5 degrees and between 1 to 4 km altitude of instrument was compared with the mean N_2O at the surface station observed between +/- 5 days relative to the flight (due to the non-daily frequency of flask samples). We chose the altitude range between 1 to 4 km to agree with the low free troposphere conditions that characterized most of the selected ground stations. Information about the surface stations used here is shown in Table of S.3 of the Supplement".

Comment # 6: Line 257: Missing "to" in "with respect [to] surface data".

Reply: The typo has been corrected.

Comment # 7: Line 300: Figure 3f is missing in the figure reference. Strong depletion in N_2O mixing ratios at southern high latitudes are seen in both Figures 3c and 3f.

Reply: The reference to Figure 3f has been included.

Comment # 8: Line 300 - 302: How does transport in the northern high latitudes impact the low mixing ratios of N_2O in the southern high latitudes? Perhaps this is a typo.

Reply: We agree with the referee that this paragraph was written in a confusing way since that is not the message we wanted to deliver. In this section we are describing in parallel the downward transport of stratospheric air depleted in N_2O due to the polar vortex break up in the both, southern and the northern, hemispheres and their impact in the following seasons. The first paragraph of section 4.1 has been modified for clarification as it was also suggested by referees 1 and 2.

"We observed the strongest depletions (> 5 ppb) in N_2O mixing ratios at high latitudes and altitudes, consistent with stratospherically influenced air (Fig. 3). Stratosphere-troposphere exchange processes allow stratospheric-depleted N_2O to be distributed throughout the troposphere. The NOAA surface network shows a seasonal minimum of N_2O 2–4 months later than the stratospheric polar vortex break-up season. This seasonal minimum is observed at the surface around May in the southern hemisphere and around July in the northern hemisphere (see Fig. S8 and S9) (cf. Nevison et al., 2011 and references therein. The enhanced downwelling of the Brewer–Dobson circulation (BDC) in late winter–spring, reinforces the downward transport of stratospheric air depleted in N_2O throughout the free troposphere (1-8 km), as observed in October in the southern hemisphere (ATom-3, Fig. 3c and 3f) and in May in the North Atlantic (ATom-4, Fig 3e). The N_2O depletion is likely the result of stratospheric air being moved downwards by the BDC and trapped by the polar vortex, with a more pronounced effect in the southern hemisphere where the polar vortex is stronger. These results support previous work suggesting that downward transport of stratospheric air with low N_2O exerts a strong influence on the variance of tropospheric N_2O mixing ratios (Nevison et al., 2011; Assonov et al, 2013)".

Comment # 9: Line 303 - 306: please clarify how these percentages are calculated. It does not look like 55% of all observation shown in Figure 3c are depleted in N_2O. Are these percentages calculated for specific latitude ranges?

Reply: In these lines, we estimate the influence of stratospheric air depleted in N_2O in the tropospheric N_2O at high latitudes (> 60° N or <-60° S). We calculate the absolute number of 1min-observations affected by stratospheric air (i.e., N_2O difference < -0.5 ppb relative to the NOAA MBL background) relative to the total number of 1min-data at these high latitudes for each deployment, independently of the altitude range. Due to the confusion and because of the irrelevance of this information for the purpose of the study, we have deleted it from the manuscript.

<u>Comment # 10</u>: Line 310: In Figure 3b and 3e, depleted N_2O is seen in the Northern Hemisphere in March-April, not Southern Hemisphere.

Reply: We agree with the reviewer. We have modified the first paragraph in section 4.1 for clarification. See reply to Comment # 8.

<u>Comment # 11</u>: Lines 322 – 223: As written, it is not clear what is meant by "N_2O-CO mixing lines" an "straight mixing lines". Does this refer to the L-shaped curve, discussed earlier in the paragraph? Are there examples of different mixing timescales shown in Figure 3 that can be used to demonstrated this concept?

In section 4.1, we are describing the correlations between N_2O and other tracers (tracer-to-tracer correlations). The term mixing in this paragraph is referring to the mixing between stratospheric and tropospheric air. These airmass mixing can be quantified using the N_2O as stratospheric tracer as it is rapidly depleted in the stratosphere. Krause et al. (2018) shows that the N_2O-CO correlation plot can be used either to determine the degree of mixing between stratospheric and tropospheric air as well as to determine the different mixing timescales. Unfortunately, during ATom, the time period between flights was too long to properly quantify the timescale mixing the reviewer is pointing to. During ATom, we can only observe the degree of mixing between the two airmasses. Therefore, the sentences related with this concept have been re-written and more details have been added. In addition, subplots in Fig. 4 have been labelled and captions changed accordingly.

"*The impact of stratosphere-to-troposphere transport can be studied by combining information on tracers of stratospheric air such as ozone (O_3 from the NOAA - NO_yO_3; Bourgeois et al., 2020), sulfur hexafluoride (SF_6 from PANTHER), CFC_{12} (from PANTHER) and carbon monoxide (CO from QCLS). These tracers are usually used either because they are strongly produced in the stratosphere (as O_3) or because they are tracers of anthropogenic emissions in the troposphere with a strong stratospheric sink (e.g., CO, SF_6 and CFC_{12}). In addition, meteorological parameters such as potential vorticity (PV), the product of absolute vorticity and thermodynamic stability (PV was generated by GEOS5-FP for ATom) can be used to trace the stratosphere-to-troposphere transport.*

Overall, the interhemispheric gradient of N_2O is much smaller than that of CO and SF_6 (Fig. 4), but the difference for each species is driven by larger anthropogenic emissions in the northern hemisphere. The tracer-tracer correlations shown in Fig. 4 show different patterns. The linear trend between N_2O and O_3 or CFC-12 highlights the role of depletion (N_2O and CFC-12) and production (O_3) in the stratosphere (Fig. 4a1, 4a4). When N_2O is plotted against the anthropogenic tracers, CO and SF_6, two distinct trends are observed. Tropospheric N_2O can be identified as the horizontal band containing high N_2O (> 328 ppb) and variable CO and SF_6, whereas the vertical band with variable N_2O and small changes in CO and SF_6, shows the mixing between tropospheric air and stratospheric air depleted in N_2O (Fig. 4a1–4a3). The N_2O versus CO plot shows an L-shaped (bimodal) curve similar to those typically observed on O_3-CO correlations during events of stratosphere-to-troposphere airmass mixing (Fig. 4a2, Krause et al., 2018). A quasi-vertical line in the N_2O–CO plot (e.g. constant CO) is indicative of a strong impact of stratospheric air, where CO shows the stratospheric equilibrium mixing ratio (Krause et al., 2018). The lower the CO background, the greater the influence of the stratospheric air during the airmass mixing (North Atlantic high latitudes in Fig. 4a2) and vice versa. A strong correlation is also indicative of rapid mixing between the two air masses. During ATom, the strongest *impact of stratospheric air was observed in the Pacific mid and high latitudes in February (ATom-2) and in the Atlantic in May (ATom-4, Fig. S11). At the Pacific northern mid and high latitudes (NMHL > 30° N), we found a consistent linear relationship between N_2O and O_3, with a relatively constant N_2O/O_3 slope (-0.05 to -0.04) during all seasons. Linear correlations between N_2O and CFC-12 highlight the dominant influence of stratospheric air depleted in these two substances in the range of mixing ratios observed at mid and high latitudes (Fig. S11)*".

"Figure 4: (a) Correlations between N_2O and O_3 (a1), CO (a2), SF_6 (a3), and CFC-12 (a4) at mid and high latitudes (30°–85° N) during Northern Hemisphere spring (ATom-4). The data are colored as a function of the ocean basin and hemisphere: Pacific North Mid-High Latitudes (Pac-NH, >30° N) in red, Pacific South Mid-High Latitudes (Pac-SH, <30° S) in dark blue, Atlantic South Mid-High Latitudes (Atl-SH, <30° S) in light blue and Atlantic North Mid-High Latitudes (Atl-NH, >30° N) in orange. Note that the N_2O and O_3 axes are reversed. (b) Correlations between anomalies in potential vorticity relative to its mean latitudinal distribution in the free troposphere (2–8 km) and anomalies in N_2O (b1, b3) and CFC-12 (b2, b4) as a function of latitude during spring (ATom-4) over the Pacific and Atlantic basins. Mid-latitudes are shown in orange in the SH and clear brown in the NH."

Comment # 12: Line 388: please specify which short-lived trace gases (and their atmospheric lifetimes) were used in this analysis.

Reply: Overall, the short-lived species used in this study were the PM1 aerosols NO_3^-, NH_4^+ and SO_4^{2+}, PAA, H_2O_2 when there were available. The lifetime for these species ranges between hours (PAA and H_2O_2) to a few days (PM1 particles). We had added this information in the referred sentence as it is shown below:

"*The relatively low mixing ratios of short-lived trace gases (PAA, H_2O_2 and PM1 aerosols with lifetimes ranging from hours to a few days), and the surface influence based on the back trajectories (Fig. S13a), indicate that most of these profiles sampled significantly aged air masses transported for extended periods over the South Pacific*".

Comment # 13: Line 436: The APO axis is flipped in the N_2O-APO correlation panels between Figure 6 and 7, which makes them difficult to compare. Are the N_2O-APO correlations different between the two figures or does the presence of CO_2 and CH_4 indicate a different source for similar correlations observed during two profiles?

Reply: The APO axis is reversed in all figures to better appreciate the possible correlation between the two species. As we stated in the manuscript, enhanced N_2O with depleted APO can indicate marine N_2O emissions from areas with strong upwelling. However, APO is also sensitive to pollution such as biomass burning and fossil fuel combustion as it is shown in Figure 7 in correlation with CO_2 and CH_4 enhancements. In addition, because both N_2O and APO have ocean land-gradients resulting from many influences, correlations can result simply from sampling air transported from different latitudes as it is shown in Figure 6.

Comment # 14: Please state in the caption of Figure 9 that the observe enhancement in N_2O is based on the profile shown in Figure 8.

Reply: We have included this statement in Figure 9.

Comment # 15: Line 452: It would be helpful to show the profiles for N_2O enhancements due to European and Asian EDGAR emissions in Figure 9 to demonstrate this point.

Reply: These profiles are shown in the supporting in formation in Figure S14. However, it is true that by mistake this figure was not mentioned in the manuscript and we have now included it in the discussion. First sentence of the 5th paragraph in section 4.2.2:

"In the Atlantic during ATom 2 (Feb 2017; Fig 9), the largest N_2O enhancement is attributed to African agriculture (peaking at 2 ppb at 2 km), with smaller but significant influence from Asia and Europe (0.5 ppb each at 2-4 km, Fig. S14)".

Comment # 16: Line 461: How does Figure S11 support an anthropogenic origin to the N_2O enhancements seen in Figure 8?

Reply: We thank the reviewer for finding this typo. We are referring there to Figures S12 and S13. We have corrected this typo.

Comment # 17: Overall, Figures 5 – 8 contain a lot of information that can be difficult to digest. Having panels consistent between the figures, as suggested by another reviewer, would help. It would also be helpful to explain in the text why information contained in one figure is different from previously shown figures or why altitude ranges discussed in the text do not match with the correlation coefficient panels shown in figures.

Reply: We initially decided to include in the examples, those chemical species relevant for describing the contribution and / or impact of a specific source in the N_2O profile. However, we agree with the reviewer that there is a lot of information in these figures, making them difficult to digest. Therefore, Figures 5 to 8 and their captions have been modified to consistently show the same chemical species with a similar color code to make it easier for the reader to go through them. See new figures in the reply to comment # 26 from reviewer 1. We have also corrected the text to consistently match the discussed altitude ranges with the correlation coefficient panels shown in the Figures.