In the study of Weyland et al. remote airborne passive DOAS measurements of nitrous acid (HONO) - an important source of the OH radical - are presented. The observations show higher concentrations in the boundary layer (BL), which decrease towards the free troposphere (FT), but again increase in the tropical upper troposphere (UT). All HONO concentrations exceed expected values by know gas phase sources and sinks, which is explained by particle nitrate photolysis in the lower atmosphere, while new HONO gas phase sources are proposed to explain excess HONO at lower temperatures in the UT.

Caused by its high importance for the oxidation capacity of the atmosphere and by the limited data on vertical gradients, especially at higher altitudes, the study is of high importance and should be published after my concerns (especially major concern 3) have been considered.

We are grateful to the reviewer for the constructive comments, which we reply to below.

Mayor concerns:

First, I have to apologize that I am no expert in the passive DOAS technique used in the present study and thus my review will only focus on the sources/sinks/mechanisms/etc. of nitrous acid. I recommend that also an expert in the used experimental technique should review the present study. I thus also apologize for questions to the DOAS approach used, which may be trivial for the experts...

We appreciate these concerns, since most readers may not be experts in DOAS either.

1) Gradients in the BL:

In Fig. 5 and 6 the vertical gradients of HONO are presented. While the observed decreasing HONO levels from the BL to the FT are expected (decreasing precursors like NO_x, nitrate) and are also qualitatively described by the models (Fig. 6), there are very unusual positive vertical gradients below 3 km (CAFE) and ca. 1 km (EMeRGe), for which the concentrations are decreasing towards the ground, see Fig. 5. Here all former gradient studies in the BL show continuously decreasing HONO levels from the main source region (ground: heterogeneous and direct emission sources) to higher altitude, which is in contrast to the present results, cf. all gradient studies e.g. on high towers, but also ground based MAX-DOAS data, the latter of which cover partially the same altitude range (ground to a few km altitude) as studied here. I am also missing these MAX-DOAS gradient results (e.g. Hendrick et al., 2014 (see reference list); Garcia-Nieto et al., Sci Total Environ, 643 (2018) 957-966; Ryan et al., 2018 (see reference list); Wang et al., 2019 (see reference list); Wang et al., AMT, 13 (2020) 5087-5116; He et al., Sci. Total Environ, 858 (2023) 159703; Xing et al., Sci Total Environ, 915 (2024) 169159) both, in the introduction, but also in the discussion sections.

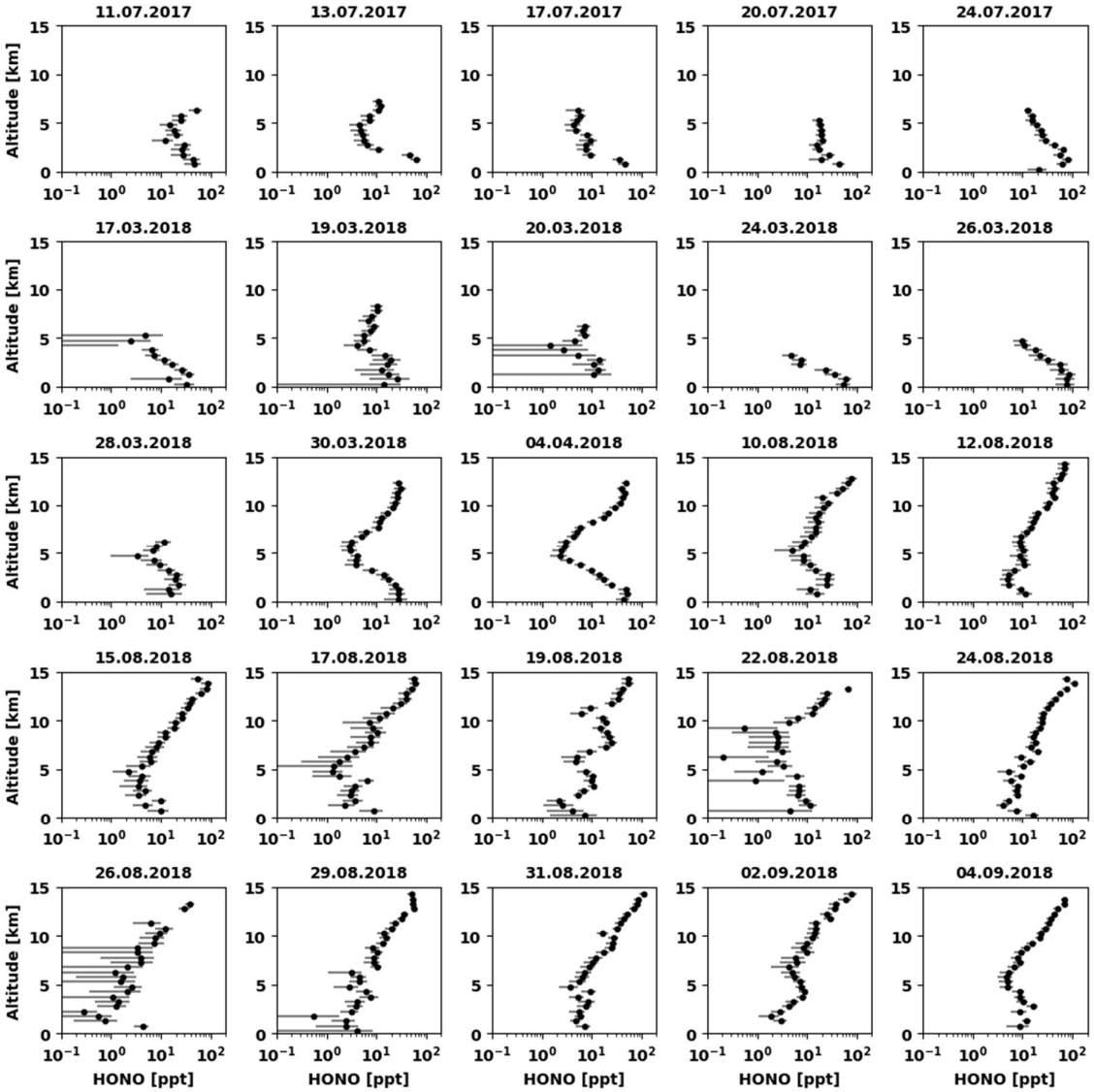
Interestingly, positive gradients below 1 km are also predicted by the EMAC model at lower altitude (see e.g. Fig. 6b), which is also hard to understand. Since NO levels should maximize near to the ground (source region of NO_x from soils/combustion...), also modelled HONO

should decrease with height, even when considering only gas phase reactions R1 to R3 in the models.

Also, in Figure 2 the “representative HONO profiles” (blue lines) are very unrealistic at <1 km altitude (decreasing to zero towards the ground…?), which is again in contrast to all previous observations.

Can you explain these unusual observations/predictions in the BL? Could the data retrieval be a reason, e.g. by using an invalid a priori profile (see Fig. 2)?

The data below 3 km altitude generally show quite a bit of variability due to heterogeneous conditions and, for CAFE-Africa, data are quite sparse since they were collected primarily during ascents and descents of the aircraft. Therefore, we argue that concluding on inverse vertical gradients in the lower troposphere is quite uncertain and stretches the information content of the dataset. Horizontal variability close to the ground (seen by a fast-moving aircraft) might map into apparent gradients with height.



Altitude profiles of HONO VMRs for each of the 25 flights of the EMeRGe and CAFE-Africa missions analyzed in this study in black, with error bars. Note the logarithmic x-axes. VMRs are binned by 500-meter altitude ranges.

As evidenced by the above figure (logarithmic altitude profiles of HONO VMRs for each of the 25 scientific flights analyzed), negative gradients in the BL are not a general feature of the data, rather they are an artefact of the averaging and from specific instances of some flights where the operative variable may not be the altitude at all.

Specifically in the context of Figure 2: the minimum reported altitude is several hundred meters above sea level, but the profiles are plotted on an altitude grid which reaches the ground.

2) Increasing HONO levels in the UT:

In the present study very high HONO levels (up to 150 ppt) and positive HONO gradients were observed in the UT (see Fig. 5). The HONO levels also result in extremely high production rates of HONO/OH of up to 1.6 ppb/h (!) in UT, see line 489. These production rates are also very unusual and would be similar to urban ground level observations (close to the main source region, with precursor levels orders of magnitude higher compared to the UT…)? While also in the study by Heue et al., 2014 high HONO levels were observed in the UT (but on average only 37 ppt, the 160 ppt shown by the yellow bar in Fig. 5 were obtained only under some extreme assumptions), these were observations from thunderstorms, for which high levels of OH and NO are formed in the flash path and where the HONO observations were reasonably well explained by the gas phase reaction R1 (NO+OH). In contrast, in the present study the high levels seem to be a general feature of the UT, which cannot generally be explained by lightning (see short photolytic lifetime of HONO, many observations will be outside of thunderstorms).

However, before proposing any new HONO source reactions, as done in the present study, the experimental data should be checked again. Here the a priori profiles assumed seem to have a strong impact on the calculated HONO levels (see Fig. 2 for lower altitude). For the data retrieval, the authors assumed zero HONO levels in the stratosphere (see line 125-126), which may not be the case. Caused by high stratospheric ozone levels, high actinic flux and low pressure (less quenching of $O(^1D)$), high OH levels may result. Since there is also NO in the stratosphere, this may also lead to significant HONO levels by the gas phase source reaction R1 in the overlaying stratosphere. If there is also light absorption by this stratospheric HONO, the upper tropospheric HONO will be overestimated with the zero stratospheric HONO assumed in the a priori profile.

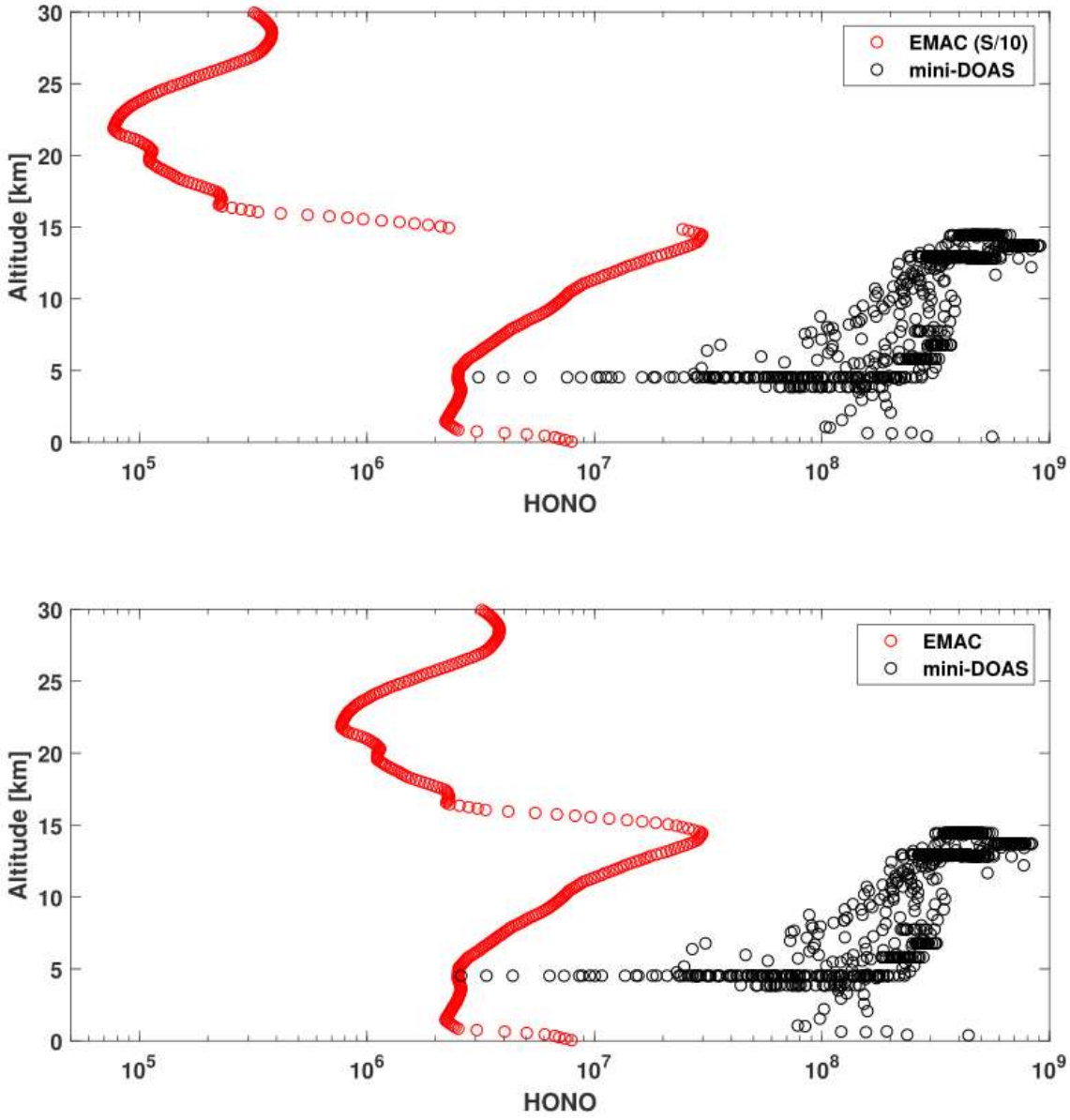
By ignoring potential HONO absorption in the overlaying atmosphere, could that be a reason for the increasing HONO in the upper troposphere (see "C-shape profile")? But again, I am not familiar with the experimental technique used, and I recommend that this issue is also reviewed by an expert.

At the end, the proposed HONO source strength in the UT looks very unrealistic to me.

These are very insightful questions. To clarify, the models predict – and the a priori profiles include – HONO above the maximum flight altitude; it is only the HONO reference SCD which is fixed to zero, since the stratospheric column is <1% of the total SCD anyway. While more stratospheric HONO may be present than the models predict, the scaling method compensates for such a case by construction, as does the line-of-sight sensitivity of limb spectroscopy. Stratospheric HONO in the a priori profiles does little to affect the resultant HONO VMRs, since the slanted light-path through the stratosphere is not long relative to the

line-of-sight path and the influence of scattered photons from the below the aircraft (see e.g. Kluge et al. (2000)). If the HONO absorption seen in the dSCDs were primarily due to overhead (stratospheric) absorption, the SCDs would be modulated in large part by the solar zenith angle of the sun. Moreover, including overhead HONO absorption into the reference SCD of the HONO retrieval only strictly increases the resultant HONO VMRs at all altitudes, which is why it is set to zero instead; these HONO VMRs are retrieved under conservative assumptions.

Consider the following figure: if the a priori HONO is adjusted to underpredict stratospheric HONO by an order of magnitude, the resultant HONO is consequently biased high (since less absorption can be attributed to 'overhead' and therefore divided out by the alpha factors). However, this does not change the general trend, nor that the retrievals far exceed model predictions in the troposphere. We also have no reason to suspect that the models underpredict HONO in the stratosphere to such a degree. A factor of two underprediction of stratospheric HONO meanwhile, only changes the HONO VMRs by some 5% on average.



For a sample flight, HONO concentration altitude profiles predicted by EMAC in red, and inferred from the scaling method in black. In the upper panel, a priori HONO concentrations above the maximum flight altitude have been reduced by an order of magnitude, and the resultant HONO retrieved with the scaling method is modulated accordingly.

3) Correlation studies:

The authors try to identify potential source reactions by correlating the measured HONO levels against different precursors/measures (e.g. NO_2, HNO_3, radiation), which is too simple, although also often applied in other studies. The HONO levels are not representative for any production term (P(HONO)), which the authors are looking for. E.g. at low actinic flux (morning/evening/clouds), HONO may be much higher compared to high actinic flux conditions (noon) although the formation rates - e.g. by any NO_2 dark conversion source (e.g. R5), may be the same! Thus, simple correlations using only HONO concentrations are often misleading. For example, during nighttime ground HONO perfectly correlates with Radon, but they have no chemical link (this is an "auto-correlation" the authors also mentioned, which is triggered by the variation of the vertical mixing/BLH...). Or observed nighttime correlations of HONO (or HONO/NO_2) with RH in the BL are artificial (decreasing temperature = increasing RH but also lead to a more stable atmosphere => higher S(ground)/V => faster heterogeneous formation...).

Since OH/J(HONO)/NO/[HONO] data are available (to calculate the PSS, [HONO]excess and P(HONO)excess), please correlate P(HONO)excess (= the "missing" source) against different expected precursors/measures, e.g.:

-NO_2

-NO_2*J(NO_2)

-HNO_3/nitrate

-HNO_3/nitrate*J(HNO_3)

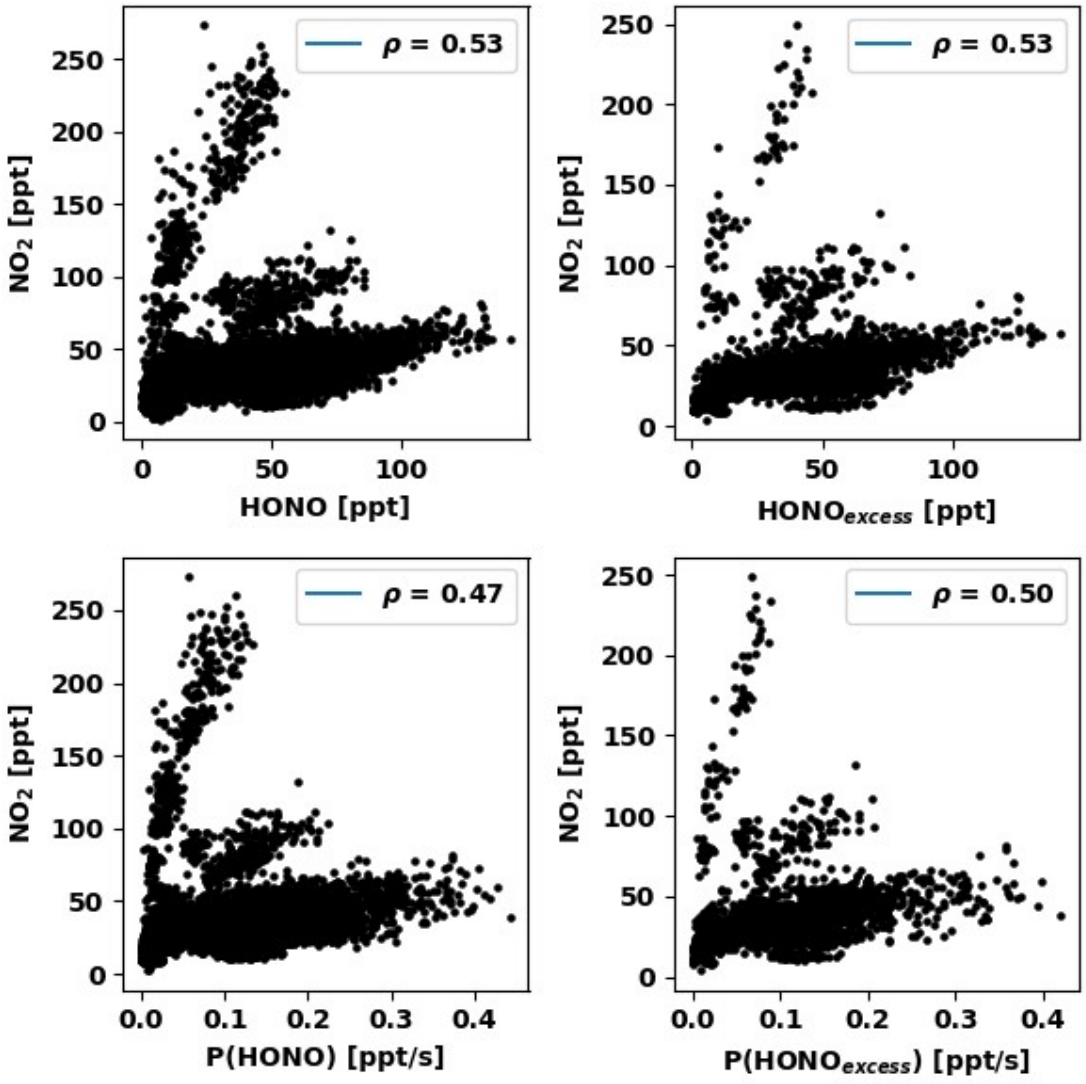
-S(particle)/V

-S(particle)/V*NO_2

-S(particle)/V*NO_2*J(NO_2)

-...

Please note that OH data are only available in the CAFE-Africa data; no instrument measured OH during either EMeRGe mission. As such, excess HONO can only be determined relative to model data (which has a much worse temporal resolution) for the EMeRGe missions, where this concern is most relevant (in the polluted lower troposphere). Determining the correlations relative to excess HONO during CAFE-Africa, where $[HONO]_{PSS}$ can be calculated from in situ measurements, yields nearly identical coefficients (see the following figure). This is hardly surprising, since the measured HONO is often an order of magnitude larger than $[HONO]_{PSS}$ or indeed model predictions. Otherwise, determining the correlations between proposed HONO formation mechanisms (products of the reactants) and P(HONO) is rarely quantitatively different than a correlation with HONO VMRs. This is because the measurements take place exclusively during daylight and there is not much variance in the measured photolysis frequencies.



NO_2 VMRs as a function of HONO, $HONO_{excess}$, P(HONO), and $P(HONO_{excess})$ for all data from the CAFE-Africa mission. The correlation coefficient between the two quantities is given in the legend.

By way of example, the above figure shows the correlation between NO_2 and either HONO, $HONO_{excess}$, P(HONO) or $P(HONO_{excess})$, from the CAFE-Africa data where such calculations are possible. For the EMeRGe data, the $HONO_{excess}$ and $P(HONO_{excess})$ cannot be determined -- P(HONO) can be determined but is hardly different from the correlation with HONO VMRs. In the case of the CAFE-Africa data, determining $HONO_{excess}$ or $P(HONO_{excess})$ also sacrifices some data resolution, since the HORUS instrument has a time resolution of some 40 seconds, compared to the UV spectral integration times of 20 seconds. We do not consider the minor difference in coefficients worth this loss of resolution. The figure shows that correlations among all four variants are largely identical and thus can be used interchangeably.

4) Definition of the EF (eq. (2) and (3)):

The EF to describe HONO formation by the nitrate photolysis should be better defined. In Eq. (2) only HONO formation from nitrate photolysis is considered ($J(NO_3^-=>HONO)$, but not the total photolysis frequency of particle nitrate ($J(NO_3^-)$) as specified, which in reality will also lead to NO_x formation (main product channel of the nitrate photolysis). I.e. if only considering the total loss of nitrate, as written here, the EF would be in reality (with HONO and NO_x formation...) even higher! Define here that only the HONO channel is considered for nitrate photolysis... Or define and use also the HONO-yield besides the total $J(NO_3^-)$... Also, in Eq. (3) only the HONO levels exceeding the PSS (eq. 1) should be considered, i.e. [HONO]excess... Otherwise the EF is overestimated.

These issues get visible e.g. in Fig. 7, for which the grey data (very small EFs around 1 using gas phase HNO_3 data as nitrate...) seems to indicate that besides gas phase photolysis of HNO_3 no other source would be necessary to explain all HONO formation at flight height... I.e. this would imply: “mission accomplished, all HONO sources identified...”. However, as the quantum yield for HONO formation by HNO_3(g) photolysis is <<1 (the main channel is NO_2+OH), equation (2) should be more precisely defined (s. above, it should be $J(NO_3^-=>HONO)$). Since HNO_3 photolysis in the gas phase will not mainly lead to HONO, the EF for the grey data should be much higher! E.g. if a quantum yield of HONO formation by HNO_3-photolysis of 0.01 is assumed (HNO_3+hn=>HONO+O), the EFs should be 100x higher than those shown in the figure, i.e. there is still an unexplained HONO source... Also, in lines 387-389, it is not the low photolysis frequency of HNO_3, but the very low quantum yield for HONO formation during gas phase photolysis, for which NO_2 is the main product! If HNO_3 photolysis were a pure HONO source, the observations could be well explained even when using the low photolysis frequency of HNO_3(g), see grey data in Fig. 7.

The caveat for $J(NO_3^-$ -> HONO) has been added; the assumption made by Andersen et al. (2023) (and the same assumption made here) is that the photolysis of particulate nitrate only leads to HONO. The intent of this assumption is to determine which EFs would be necessary to produce the measured HONO *at least*. The EFs may indeed be higher than what is reported here: they are conservative estimates. The text has been updated to reflect this.

We have also added a clarification for the reader that HNO_3 photolysis does not predominantly yield HONO. The addition of HNO_3 data into figure 7 serves only to highlight the possibility that there may be more particulate nitrate in these airmasses than measured by the C-ToF-AMS instrument (requiring in turn lower EFs), not to suggest that the photolysis of gaseous nitric acid may explain HONO production.

Specific concerns:

The following concerns are listed in the order they appear in the manuscript.

Line 3-4:

It should be “for example” (and not “as well as”) and delete “particulate”, as a) nitrate photolysis is also a heterogeneous process (“as well as”) and b) takes place on particles and on ground surfaces (for near ground observations nitrate photolysis on ground surfaces will be even more important, see e.g. doi: https://doi.org/10.1029/2003GL018620 or doi: https://doi.org/10.1038/ngeo1164).

In addition, the most important “heterogeneous formation mechanisms” are also photochemical reactions, e.g. NO_2+org+hn... Thus, write this sentence more generally.

The line has been changed to “several photochemical and heterogeneous formation mechanisms, including the photolysis of nitrate”.

Line 17, Perner and Platt (1979):

The first detection of HONO in the atmosphere was by Nash, 1974 (https://doi.org/10.3402/tellusa.v26i1-2.9768), see “Since its discovery…”.

We cited Perner and Platt rather as a source for the claim that the sources and sinks of nitrous acid have been a matter of debate, but have added a citation to Nash in the same sentence.

Line 20-21:

HONO is not only the most important OH source for polluted conditions, but also in remote regions, see many studies under polar conditions, where also “production of OH from the photolysis of HONO may outpace OH production from the reaction of $O(^1D)$ with H_2O“, see e.g. doi: https://doi.org/10.1029/2011JD016643 .

We have added the reference.

Line 38:

Delete again “particulate” as especially for “near-surface measurements” also photolysis of nitrate on ground surfaces gets more important than particle nitrate photolysis, see references above (concern line 3-4).

‘Particulate’ has been removed.

Line 43, Ma et al (2013b):

The first reference Ma et al., should be (2013a).

Regarding this and several other comments to the same effect: the labelling of some papers as (a) or (b) is done automatically by the style file recommended by Copernicus according to the position of the reference within the bibliography, not the order of appearance within the manuscript itself and is wholly outside the authors' control.

Line 44-47:

For the topic of this section ("heterogeneous reactions involving NO_x on macroscopic surfaces") the used references are partially not suitable. Delete the references on nitrate photolysis here (Scharko et al. (2014), Wang et al. (2015), Laufs and Kleffmann (2016), Benedict et al. (2017), Ye et al. (2017)) as this is explained in the next paragraph. You may also shift those references to this section and may add here some others on heterogeneous NO_2 reactions.

We have removed some references to avoid ambiguity; those references are still included elsewhere where appropriate.

Lin 50-51:

The soil production of HONO should be described more generally, e.g. "by soil bacterial processes", as nitrite/HONO is also formed from ammonia oxidation (not only nitrate reduction).

The description has been changed accordingly.

Line 51, Song et al. (2023b):

The first reference Song et al. should be (2023a).

See the reply to the comment on Line 43.

Line 53, Ma et al. (2013a):

The second reference Ma et al., should be (2013b).

See the reply to the comment on Line 43.

Line 59:

Delete "inorganic", as most photosensitized NO_2 mechanisms are "organic", e.g. on polyaromatic species, like polyphenols, humic acid, etc., see Stemmler et al., George et al..

'Inorganic' has been erased; now says "ground heterogeneous chemistry".

Paragraph, line 62-70:

I am missing all ground MAX-DOAS studies, which also measure HONO up to some km altitude. The strong negative gradients observed in all these MAX-DOAS studies agree well with all gradient studies on high towers but are in contradiction to those shown in the present study, see major concerns.

See our reply above to the major concern.

Lines 75-77:

This is reasonable only if dense wildfire plumes are excluded. Here HONO can be transported over longer distances/altitudes, caused by the lower photolysis frequencies in/below dense plumes and by strong convective vertical transport during wildfires.

We can be sure that the telescopes were not looking into dense wildfire plumes with the help of the images taken by the IDS uEYE digital camera mounted into the instrument which also looks in the starboard direction relative to the direction of flight, along the horizon, and captures images of the sky every second.

Line 106, Nussbaumer et al. (2021b):

The first reference Nussbaumer et al. should be (2021a)

See the reply to the comment on Line 43.

Line 115-118:

Just as a comment, I agree to the used reference by Stutz et al. (2000). There are several former studies which confirm these cross sections, which are also the generally accepted values in the community.

We concur.

Line 307:

You may add "see Fig. 6" behind the brackets, as the statement is confirmed in Fig. 6.

Yes, but it is also confirmed in figure 5, and figure 6 is not introduced until line 320.

Line 311:

These "some tens of ppts within the MBL" are in contrast to the max few ppts observed near to sea level, e.g. on Cape Verde island (same region as CAFE), see e.g. Fig. 3a in Crilley et al. (2021) (https://doi.org/10.5194/acp-21-18213-2021, between <1 and 3 ppt…). Do you have any explanation for the much higher levels in the BL, also with respect to the expected negative vertical gradients, seen in all gradient studies, i.e. at a few hundred meters altitude (lower altitudes range of the present study) HONO levels should be even lower than these few ppts?

This is not the first study to observe some tens of ppts of HONO within the MBL (see 10.1126/sciadv.add6266).

Crilley et al. (2021) measured HONO at CVAO in November/December, the CAFE-Africa data presented here were measured in August/September. Otherwise, Crilley et al. (2021) did not measure particulate nitrate; our suggestion is that the HONO we measure comes in large part from this particulate nitrate, the presence of which may not be constant with season.

Line 316:

Add “and a Zeppelin” behind “aircraft”.

‘and a Zeppelin’ has been added.

Fig. 5:

In the legend, it should be Ye et al., (2016a). In addition, please also check the BLH, which is typically between 1-2 km during daytime, but not at 3 km as shown here?

We draw the MBL height at 3 km altitude only for better comparison with Andersen et al. (2023), not as a strict measure of the mixing layer height.

Line 336-338:

If wrong assumptions are used only in the evaluation of HONO, this conclusion is not justified. E.g. stratospheric HCHO levels may be indeed close to zero, while HONO levels not ... I.e. there could be some non-considered light absorption by HONO in stratospheric air, leading to an overestimation of HONO at flight height, see major concern...

But I agree (below lines 339-340), reactions R1 to R3 may be not sufficient to explain atmospheric HONO levels... However, I expect that these additional HONO sources, for which particle nitrate photolysis is yet the main proposed source at higher altitude is decreasing with altitude (see gradients in particle nitrate...).

See our reply above to the major concern.

Line 398-401:

In dense biomass plumes (“…influenced by biomass burning…“) the actinic flux may be much lower than measured outside of the plume and considered in a model. If J(HONO) is lower, HONO levels during daytime may be also higher than expected by the model.

The averaging kernel of the mini-DOAS retrievals are dozens of square kilometers in the horizontal plane (not accounting for the vertical FOV). It is true that flying outside a plume while looking towards one would induce a local variability not represented by in situ measurements or models, however this alone cannot explain the ubiquitous detection of HONO in the troposphere. For examples of how the instrument may probe biomass burning plumes, see Kluge et al. (2020).

Line 407-409:

Neither d[HONO]/dt(total) - what is written here - nor the concentration (see below) should be used, but d[HONO]/dt(excess), i.e. the missing P(HONO) to explain HONO exceeding the PSS, see major concerns.

See our reply above to the major concern.

Line 409-410:

I cannot follow this statement. Which “auto-correlation” do you mean? If HONO is formed by any dark source (e.g. by reaction (5)), P(HONO)excess would be constant (although the excess HONO over the PSS would vary during daytime, with a minimum at noon...) and not correlating with J(HONO) - certainly, only if soot/organics and NO_2 levels (see reaction (5)) are constant... In contrast, only if HONO is formed by any photochemical source (e.g. particle nitrate photolysis), P(HONO)excess would correlate with J(HNO_3)*[nitrate]... Because of the different diurnal shapes of J(HONO) and J(HNO_3), the correlation of P(HONO) excess would be higher with J(HNO_3) compared to J(HONO) in this case... When calculating P(HONO)excess, J(HONO) is already considered and there is no “auto-correlation”... See major concern, do not use simple HONO levels.

For example, any products which include J(HONO) or J(NO_2) will necessarily show strong correlations since J(HONO) ~ J(NO_2). Worth emphasizing is that we use Spearman’s rank correlation coefficient (since the relationship between HONO and the reactants may not be linear). Unfortunately, this also means that any monotonic association between variables will necessarily correlate.

Line 416-417:

In polluted air, almost all pollutants will increase compared to background air (see “auto-correlation”). That is why simple correlations of concentrations can lead to artificial conclusions, s. major concerns.

We concur. The correlations are between volume mixing ratios, but even still we cannot avoid that polluted air contains many types of pollutants simultaneously; these are field measurements after all.

Line 418-419:

First, better use P(HONO) extra against NO_2, see above... Second, if the excess HONO is formed e.g. by particle nitrate photolysis (the most probable source at higher altitudes), its correlation with [NO_2] would be much weaker compared to [nitrate] (and even better with [nitrate]*J(nitrate)…), see different lifetimes of NO_2/HNO_3/nitrate...

As above, correlating a product which contains J(HONO) with a product which contains J(NO_2) will be strongly correlated in any case as the photolysis frequencies are functions of the same measurements of actinic flux. J(HONO) ~ J(NO_2)

Line 420-422:

Please reanalyze the correlations by using P(HONO)extra, see above... Trace gas levels will correlate by definition, see HONO and Radon, but that is meaningless. In contrast, a correlation of (P(HONO)excess with any precursor of 0.7 would be great for field data!

See our reply above to the major concern.

Line 424-425:

Photolysis of nitro-phenols is not a main proposed HONO source, see Bejan et al. (2007) and certainly not at the higher altitudes studied here, caused by the expected low levels of nitrophenols.

Here we mention the mechanism only because it was proposed in the literature and exclude it because no instrument was present to measure nitro-phenols (or proxies thereof); we did not expect to identify nitro-phenol photolysis as a major source of HONO in the free troposphere.

Line 426-428:

This is certainly a weak point, because OH data is necessary to calculate the PSS and P(HONO)extra. Thus, I would only concentrate on the CAFE data in the present study.

Concentrating on the CAFE-Africa data would exclude an entire dataset of lower tropospheric HONO measurements and the associated in situ measurements of many proposed precursors to HONO formation.

Line 434:

It is trivial that HONO will correlate e.g. with HCHO (both are high/low in polluted/clean air masses...), see highest correlation during the EMeRGe campaigns, but they most probably have no chemical link... Do not use the HONO mixing ratios, see above...

This is why we emphasize that the correlations between HONO observations and the product of reactants of some mechanism should be stronger than the correlations which may come 'for free' in polluted air.

Lines 439:

Please reformulate after reasonable correlations (using P(HONO)extra...)) have been formed...

Unfortunately, no better correlations are forthcoming as we do not have in situ OH data during either EMeRGe mission.

Lines 449-454:

HONO formation by NO_2 conversion on particles is typically of low importance, as the uptake kinetics of NO_2 on any particle surface and the particle S/V ratios are much too low to explain any significant HONO formation compared to ground surface NO_2 conversion or nitrate photolysis. During nighttime/daytime values of gamma(NO_2) are only as high as some times $10^{-6}/10^{-5}$ were measured on any realistic surface. Also, the exception NO_2+soot (here gamma values up to 10^{-1} were reported) cannot explain any significant HONO formation, as the uptake kinetics quickly slow down by passivation of the soot surface. And even for any photo enhanced NO_2+soot reaction (see footnote V in Table A1) gamma values $<10^{-6}$ were observed in Monge et al. (2010), which are also too low. For the photocatalytic conversion of NO_2 on

dust/TiO_2 the low TiO_2 photocatalyst content in dust (only a few %) has to be considered, for which gamma values also only in the range 10^{-5} are expected and measured, see e.g. doi:10.1029/2007GL032006 (only for pure TiO_2 it could reach 10^{-4}). These values, together with the low S(particle)/V cannot explain any significant HONO formation.

In contrast, most studies which propose a particle NO_2 conversion source use simple correlation analysis as done here (see correlation of HONO and Radon...). From these studies, values of gamma(NO_2)SS of typically >10^{-4} were inferred, which have never been observed in any realistic lab study on any realistic surface... Also, all model studies which use realistic uptake kinetics show a minor contribution by NO_2+particles.

In this context, we can only correlate the available measurements and not those desired in a study designed for HONO. We agree that correlation is not causation, but we are not correlating diurnal cycles of unrelated quantities. We also conclude that most of the correlations are unimpressive and do not identify a definitive HONO formation mechanism using this analysis; the correlations shown here are not provided as compelling evidence for a specific NO_2 + particle conversion mechanism.

Line 450:

First reference Zheng et al. should be (2020a)...

See the reply to the comment on Line 43.

Line 458-459:

For HONO formation on soot neither the mass nor the number is a suitable measure, but the surface area. If SMPS data is available take the S/V ratio.

Unfortunately, only mass and number are available from the SP2 instrument.

Line 472:

Second reference Zheng et al. should be (2020b)...

See the reply to the comment on Line 43.

Line 483-486:

Please revalue this statement with the reanalyzed correlations, see above.

See the reply to the comment on line 439.

Line 490-492:

Exactly! As HONO strongly decreases with altitude (see e.g. all MAX-DOAS studies), P(HONO) should be much lower in the FT compared to polluted near ground conditions (see cited references)! I.e., these references prove that there is no agreement.

Our measurements at low altitudes may not compare well with ground-based measurements, as they (our measurements) are biased by their occurrence during ascents and descents of the aircraft near airports. Otherwise, there is a sparse history of airborne HONO detection with simultaneous measurements of photolysis frequencies.

Line 601:

The second reference Nussbaumer et al. should be (2021b)

See the reply to the comment on Line 43.

Table A1:

General:

- Please use consistent numbering of all reactions, here and throughout the text:

E.g. Here reaction no. 1 is similar to R1 in the text, while the others are different. This is confusing. Name them here also by (RX, RY, ...)

The reactions in the body of the manuscript are referred to as RX, the mechanisms in the table (in the appendix) are referred to as mechanisms to avoid confusion.

- In addition, some of the reactions are not up to date and/or may be deleted for simplicity, e.g.:

- Reaction 3 was excluded by Ye et al., see also footnote (iii);

If we exclude reaction 3 entirely because of Ye et al. (2015), a reader unfamiliar with Ye et al. (2015) could reasonably ask why it was not included.

- Reaction 4 was a multiphoton excitation process at high photon flux density of the laser used in Li et al., which will not happen at solar actinic fluxes, see also footnote (iv);

See the reply to the comment on reaction 6 below.

- In addition to the deactivation issue of reaction 5, even for any photo enhancement of NO_2+soot (see footnote (v)) the observed uptake coefficients (Monge et al.) are too low ($<10^{-6}$) to be of importance. However, reaction 5 is not only limited to soot as specified here, but was observed on many organic substrates, like polyphenols, PAHs, organic grime, etc. see e.g. studies by Markus Ammann's and Christian George's groups... Thus, another reaction NO2+organic(het.) may be a more general ground surface nighttime source of HONO;

We agree, but nighttime is of no relevance here since the instrument analyzes scattered skylight.

- The shown mechanism of reaction (6) is not possible, as uptake coefficients of N_2O_4(g) (see second reaction (6)) of larger than one are necessary to explain NO_2 experiments/field observations at low ppb levels of NO_2 (= sub ppq levels of N_2O_4(g)...). This reaction works well

at the high ppm levels used in Finlayson-Pitts et al., but not at low atmospheric ppb levels. Observed uptake coefficients of NO_2 on water, humid Teflon surfaces, etc. are typically $<10^{-7}$ at ppb levels, which cannot explain HONO formation in the atmosphere. Since HONO formation by NO_2 better follows <1. order kinetics (see increasing $HONO/NO_x$ with decreasing NOx levels in the atmosphere, see also decreasing HONO yields with increasing NO_2 in lab studies), reaction (v) on organics (not soot, but e.g. organic grime, see above) is a better candidate for nighttime HONO formation, also because of the much higher uptake coefficients for NO_2+org. in lab studies (in the 10^{-6} range) compared to NO_2+H_2O.

We thought it would be valuable to check that mechanisms which *should not* work do not erroneously correlate well with the measured HONO.

- Reaction 7 is the photocatalytic reaction of NO_2 on photocatalysts like TiO_2 (often Anatase) which shows a much faster uptake kinetics than 10^{-8}, observed for silica particles (see footnote vii). The reaction of NO2+silica is better represented by reaction 6, but definitely not by reaction 7. For the photocatalytic reaction on TiO_2, NO_2 uptake coefficients of up to some 10^{-4} were observed (see e.g. https://doi.org/10.1039/B609005B or see Dyson et al. in the reference list), which decrease to values of 10^{-5} to 10^{-6} at low % content of TiO_2 in dust (see e.g. https://doi.org/10.1029/2007GL032006). For strong dust events this could be a candidate for HONO formation at flight height, e.g. during CAFE.

Unfortunately, for the CAFE-Africa mission the only proxy for dust events are aerosol mass or volume measurements.

- Reaction 8 is indeed slow for pure HNO_3 adsorbed on clean surfaces, but may get important in the presence of organics/photosensitizers, see e.g. https://doi.org/10.1038/s41598-018-37973-x, https://doi.org/10.1029/2022GL098035.

We agree.

Specific Table A1:

Reaction (6): delete the “J.” in the reference Finlayson-Pitts et al. (2003).

‘J.’ has been deleted.

Footnote (iv): The reference Crowley (2018) is missing in the reference list?

Dillon and Crowley (2018) is in the reference list.

Footnote (viii): The second reference Song et al. should be (2023b).

See the reply to the comment on Line 43.

Figure A3:

Not [HONO] but P(HONO)excess calculated from [HONO] exceeding the PSS should be considered, see major concern. If NO/OH/J(HONO) data are available...

Hydroxyl was only measured during the CAFE-Africa mission. Therefore, this calculation could be made for CAFE-Africa (see above), but then comparison to EMeRGe data, where this calculation is not possible, compares dissimilar quantities. Unfortunately, the correlation analysis of the EMeRGe data is also the more interesting of the two, given the predominantly lower tropospheric character of the measurement altitudes.

References:

General comments on the reference format style:

- besides the volume, also the issue should be listed, e.g. Acker et al: 33(2) and many others;

- for some references besides the normal http:// address / doi-number also an "_eprint" address is listed (e.g. Acker et al., Alicke et al., ...), which is unusual? Please follow the recommended reference style and if this is indeed recommended by the journal, it is missing for many other references (e.g. Akimoto et al., Alvarez, ...);

- also, for most references the "publisher" is listed besides the journal's name, which is also unusual. If indeed recommended, this information is missing for many other references (Acker et al., Alicke et al., Alvarez, Bogumil et al., ...), unify;

- please subscript all numbers in chemical formulas, e.g. Acker et al., the "2" in "HNO2". Only for a few references the chemical formula are correctly written, e.g. Dillon et al., Dorich et al., Hendrick et al., Hrdina et al., Marno et al., ... ;

- for some references the http-links are not working, although the dois are correct? See Bogumil et al., Huang et al., Jacob et al., Kleffmann et al. 2003, Li, X. et al., 2012, Ma et al., 2013a, Mark et al., Reisinger, Weger et al.;

-delete blanks: Cheng et al: e1601 530, George et al.: NO 2, Jiang et al.: 12 115–12 131, Finlayson-Pitts et al.: NO 2, Kalberer et al: 13 825–13 832, Kluge et al., 2020: 12 363–12 389, Laufs and Kleffmann: HNO 3, Lu et al.: 114 002, Mao et al.: e2021GL095 740, Martins-Costa et al.: 20 937–20 941, Nussbaumer et al., 2023: 12 651–12 669, Sullivan et al.: HNO 3 and 30 537–30 539, Romer et al.: 13 738–13 746, Rotermund et al.: 15 375–15 407, Ryan et al.: 13 969–13 985, Scharko et al.: 11 991–12 001, Schulz et al.: 14 979–15 001, Song et al., 2023b: 15 733–15 747, Stutz et al., 2000: 14 585–14 592, Tao et al.,: 11 729–11 746, Thalman et al.:

O 2 –O 2, 15 371–15 381, Wang et al., 2025: 121 094, Wang et al., 2020: 10 807–10 829, Weger et al.: 17 545–17 572, Xu et al.: 10 557–10 570, Zhang et al., 2021: 15 809–15 826, Zhu et al., 2019: 13 067–13 078, Zhu et al., 2003: 10 667–10 677.

The eprint and publisher information was imported erroneously and has been removed. Blanks have been removed, subscripts added, and missing page numbers added. Blanks in five-digit numbers, however, are part of the typesetting, not the information provided in the citations and cannot be removed. Otherwise, the broken DOI links are an artefact of the manuscript article type: the line numbers are read as part of the hyperlink where there is a line break; this should not be a problem upon publication. All the specific comments which follow are otherwise addressed.

Specific comments references:

Acker et al.: paper no. L02809 is missing;

Alicke et al.: paper no. 8247 is missing, delete PHO 3–1–PHO3–17;

Alvarez: paper no. A183 is missing, delete “number: 0”;

Amedro et al: it should be “OH+NO_2”, delete “OH & thinsp; + & thinsp;NO2” (LaTeX used….?);

Bejan et al.: Abd El Aal, Y.;

Order the two Butkovskaya references chronologically (first 2005 and then 2007...);

Chatfield: doi number is missing: https://doi.org/10.1029/94GL02659;

Crowley et al. (2025): Please list all authors, see e.g. Andres Hernandez et al., where also more than 10 authors are listed... Unify style… The doi number is missing: https://doi.org/10.1039/D5EA00006H ;

Deutschmann et al.: Puķīte is not correctly written;

Dörisch et al: m/z 62;

George et al.: Add missing authors (more than 10 also in other references…); add Doi number: https://doi.org/10.5194/acp-23-7799-2023;

Graham et al.: add Doi number: https://doi.org/10.1016/0009-2614(77)80387-4;

Heue et al.: Brenninkmeijer, C. A. M.;

Horvath et al.: doi missing: https://doi.org/10.1002/kin.550200903;

Finlayson-Pitts et al.: Finlayson-Pitts, B. J., Wingen, L. M., Sumner, A. L., and Ramazan K. A.;

Kleffmann et al. (2005): paper no. L05818 is missing;

Kritten: add “Dissertation, Ruperto Carola University of Heidelberg, Germany”;

Lammel and Cape: 361-369;

Ma et al. (2013b): (2008-2011), delete "(2008 & ndash ; 2011)" ;

Ndour et al., paper no. is missing: L05812;

Sullivan et al: Sullivan, M.N., Chu, L. T., and shift this reference down to “S”;

Oswald et al.: Andreae, M. O., Meixner, F. X.;

Platt et al.: Pitts Jr,. J. N.;

Rothman et al.: Champion, J.-P., Flaud, J.-M., Mandin, J.-Y.;

Serdyuchenko et al.: ...cross-section - Part 2...; delete: "& n dash"

Singh et al: Crilley, L. R., Pope, F. D., and Bloss, W. J.;

Song et al.: article no. 30 is missing;

Zhang et al: the paper no. L15820 is missing;

Zhou et al. (2003): paper no. 2217 is missing;

Ziereis et al.: the paper no. L05115 is missing.

General comments:

HONO is a significant source of OH radicals in the atmosphere. Elucidating the formation mechanisms of HONO is vital to understanding the OH budget. This paper presents airborne remote sensing measurements of HONO in various environments. The possible formation mechanisms of HONO in the PBL, FT, and UT are discussed. This work has important implications for atmospheric chemistry. This manuscript is well written, and ACP is an appropriate venue. I would recommend publishing the paper after the following comments are addressed.

We are grateful to the reviewer for the positive and constructive evaluation of our work. Our reactions to the comments which are helpful in improving the manuscript are described below.

Specific comments:

Lines 74-75: Would HONO emissions from nighttime biomass burning contribute to the airborne observations, e.g. free troposphere?

Given HONO's atmospheric lifetime against photolysis of only ~10 minutes and the measurements exclusive daytime occurrence as well as the distance to any biomass burning HONO source, we consider this unlikely.

HONO retrievals: It seems that the model results were used to generate a priori profiles of the target gases. As shown in Figure 6, the models cannot capture the high mixing ratios of HONO in the UT. That said, the modeled shape of HONO is different from the observation. Would this inconsistency introduce uncertainties to the retrievals of HONO?

The relative shapes of the predicted (a priori) and inferred HONO concentration profiles are largely in agreement and differ only in magnitude, see the updated figure 6. While the models do not predict much HONO in the UT, they also don't predict much HONO in the LT, and the relative distribution of HONO in the troposphere is similar. As such, the influence on the scaling method via the alpha factors is minor – most HONO absorption in the limb should come from the line of sight (rather than from overhead or from multiple scattering) regardless (for details see Kluge et al. (2000)).

Table 2: The uncertainties of OH, HO_2, and HNO_3 should be given, as these values are critical to the [HONO]pss calculation.

The uncertainties of several measurements including OH, NO, & J have been added as they are necessary for the $[HONO]_{PSS}$ calculation. Some of the uncertainties in other instruments have not been quantified -- these are, however, not critical.

Figure 3: The symbols are messed up. Can the authors tune the size of the symbols to see if it is easy to read?

We reduced the marker sizes for better visibility. The size of the legend has also been reduced.

Figure 6: It is difficult to tell the model and observation discrepancies at different heights because of the overlap of many data points. Can the authors average the vertical profiles of both the model and observations every 500 m or so to make the comparison clearer?

The VMRs retrieved by the mini-DOAS and predicted by the models have now been binned by altitude at 500m increments in figures 6, A1, and A2. Furthermore, the altitude profiles of the means have been plotted on a logarithmic scale such that it is easier to see the discrepancies between measurements and model predictions.

Lines 362-365: Is there any observational criteria to assume it was an unpolluted MBL?

The distance from the west coast of the African continent in relation to horizontal and vertical transport times and the photochemical lifetimes of NO_x (and indeed as evidenced by NO_x VMRs measured by the instruments aboard HALO) excludes considerable anthropogenic pollution sources. Specifically, when considering HONO formation, the NO_2 concentrations are most important for heterogeneous HONO formation mechanisms other than the photolysis of nitrate. In fact, according to the measured NO_x concentrations, 'low-NOx' is a better qualification, and the text has been updated accordingly.

Section 4.3: Correlation analysis between HONO and a specific parameter provided very limited information on the mechanisms, as also noted by Reviewer 1. The authors should perform more analysis following the suggestions.

See also our answer to reviewer 1. The correlation analysis is also performed between HONO and the products of reactants from the various proposed formation mechanisms. The alternatives proposed by reviewer 1 do not account for the lack of in situ OH data during the EMeRGe missions – i.e. for much of the dataset, HONOexcess and $P(HONO_{excess})$ cannot be determined. Otherwise, correlations with the HONO production term P(HONO) instead of HONO VMRs are qualitatively quite similar ($\rho \pm 0.03$), as indicated in the figure in the response to reviewer 1.

Lines 463-465: It is unclear how aerosol water content was obtained. Is it calculated by using a thermodynamic model, e.g. E-AIM or ISORROPIA?

We used relative humidity as a proxy for aerosol water content since there was no instrumentation to observe it directly and our modelling attempts using ISORROPIA yielded non-physical results due to unconstrained boundary conditions, i.e. the type and amount of cations needed to balance the budget of measured anions in the sub-micron aerosol. The manuscript states this in L473.

The manuscript by Weyland et al. presents vertically resolved measurements of HONO using differential optical absorption spectroscopy (DOAS) throughout the troposphere using data from three field campaigns (i.e., EMeRGe-EU, EMeRGe-Asia, and CAFE-Africa). Data includes air masses that are either aged background air or have been influenced by biomass burning or anthropogenic emissions. The authors show that measured HONO throughout the troposphere exceeds that which would be expected from gas-phase chemistry (Fig 6) using two atmospheric chemistry models (EMAC and MECO(n)). The authors suggest numerous possible mechanisms that could possibly account for the excess HONO (Section 4).

There are merits to the article (e.g., HONO dataset) that would be of interest to readers of ACP. However, the inclusion of some highly speculative and inconclusive sections (particularly 4.2-4.4) require substantial revision or removal before publication.

We thank the reviewer for the positive and constructive evaluation of our work; our point-by-point replies to the reviewer's comments are given below.

MAJOR COMMENTS

I suggest that the authors consider converting this paper into a Measurement Report. The authors present an extensive dataset of vertically resolved mixing ratios of HONO throughout the troposphere that is useful given the limited availability of such measurements. This dataset is useful for those studying the overall oxidative capacity of the atmosphere. The model runs using EMAC and MECO(n) are also helpful in showing that known gas-phase chemistry alone cannot account for all the HONO. However, at this time, I find Sections 4.2 - 4.4 to be too highly speculative to be included in a research article:

As the reviewer correctly points out, our manuscript includes a unique dataset, respective model runs, extensive posterior analysis of the data and a discussion of potential implications. All these components are original research contributions by a community-spanning group of laboratories aimed at deciphering an unknown physico-chemical process.

We disagree however that sections 4.2 to 4.4 are 'too highly speculative' since:

1. The observations reported in section 4.2 largely corroborate the findings of Andersen et al. (2023) on the amount of HONO in the unpolluted marine boundary layer around Cape Verde and the evidence which supports their suggestion that these are primarily caused by nitrate photolysis.
2. In section 4.3, we demonstrate by comparison of our HONO measurements with modelled data for the EMeRGe missions that in addition to gas-phase formation, other HONO formation mechanism(s) must act to explain measured HONO in the lower to mid troposphere. We are aware that the correlation analysis informed by the simultaneously measured gas and aerosol parameters (or proxies thereof) from onboard the aircraft (see Table 2) do not provide convincing evidence that any of the thus far proposed HONO formation mechanisms listed in Table A1 may make a sizable contribution to the inferred excess HONO. Noteworthy however, is that since some of

the proposed HONO formation processes listed in Table A1 may act in parallel with different contributions as a function of location and time, a correlation analysis is probably too simple to unravel the possible causes for the inferred excess HONO.

3. We agree that – since the process of HONO formation in the upper troposphere (section 4.4) is largely unknown-- parts of the discussion tend to be speculative. Nonetheless, we argue that it is a genuine feature of a research article to put its findings into the context of previous hypotheses put forward by the community.

In that regard, the discussion in sections 4.2—4.4 is a valuable guide for the reader to evaluate potential follow-up research directions. Therefore, we argue that our manuscript is a suitable research article for ACP, not a measurement report.

- Section 4.2: If this were to remain in the manuscript, I would have expected the authors to have included particulate nitrate photolysis in their model runs to show how much this impacts HONO mixing ratios in the MBL during CAFE-Africa. The authors have already inferred enhancement factors (EFs) for the photolysis frequency of particulate nitrate relative to that of gaseous nitric acid (Fig 7), but the manuscript is missing is a model run that actually shows what impact this has on HONO mixing ratios.

There are papers which attempt to close the HONO measurement – model gap; the aim of this paper is to explore proposed HONO formation mechanisms using the coincident measurements available from the HALO aircraft. A study showing the impact of nitrate photolysis on modelled HONO (https://acp.copernicus.org/articles/25/16945/2025/) demonstrates that nitrate photolysis alone does not yet account for the gap between measured and modeled HONO.

- Section 4.3: Correlations are presented, but overall, the section is inconclusive (Lines 483-484). I realize some of these factors are beyond the authors' control (e.g., lack of data), but there remains a great deal of uncertainty. Also, if I look at the subplot showing mechanisms for EMeRGe-EU and specifically the black bars, Mechanisms 3-13 all have a ρ(HONO) around 0.75. Are the correlations truly showing which mechanisms are relevant?

Indeed, this section highlights that more precise measurements and instrumentation would be necessary to investigate this subject further. We would argue that the insufficiency of the employed instrumentation to precisely determine HONO formation mechanisms is itself worth publishing and that dedicated research missions with instruments and analysis methods are necessary to resolve the conundrum of atmospheric HONO formation.

- Section 4.4: This section is probably the most speculative of the three. There are no reported measurements of HOONO in the atmosphere (Line 526) and very little kinetics work has been done in the scientific literature at the necessary temperatures and conditions (Line 625). The whole narrative for this section is reminiscent of what might be included in a funding proposal as opposed to a research article.

We concur in part. However, HOONO has been proposed to exist in the UT (Amedro et al., 2020) and there are abundant studies on its chemistry (see the references in the manuscript, L535). While the latter mostly cover warmer temperatures than those present in the UT, our discussion of HOONO as a source of HONO is rooted in these previous findings by others and thus invoking HOONO is not purely speculative.

However, it is correct that uncertainties are large. Therefore, section 4.4 extensively reviews the available information and puts it into the context of our measurement conditions. Thus, we make the reader aware of the potential processes, their uncertainties, and the missing pieces of evidence (to be collected by follow-up studies). We clearly label the HOONO hypothesis as being uncertain and that further research is needed (L719).

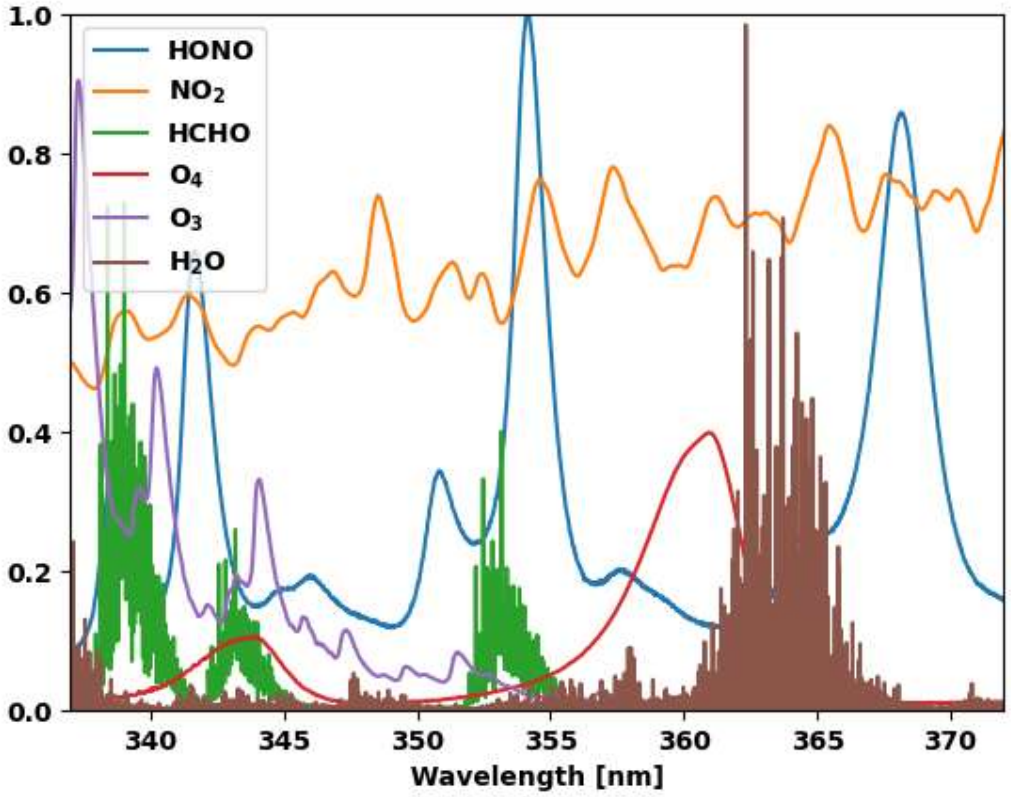
A Measurement Report would still include the HONO dataset and EMAC and MECO(n) model runs but would leave for future study a more in-depth analysis of some of the heterogeneous HONO formation mechanisms or HONO from peroxynitrous acid oxidation.

See our general reply above.

OTHER COMMENTS

- Figure 1: Could the absorption cross-sections for interfering species be plotted as well alongside HONO? Moreover, the black trace is confusing since the authors say it is the "fit including the residual". Generally, the residual is plotted separately from the fit since the residual shows what the fit did not capture from the raw signal.

Species in DOAS don’t generally ‘interfere’; other gases absorb light in the same wavelength range that HONO does, but they have their own unique cross section features, see below. None of the gases which absorb light in this wavelength range share HONO’s three distinct peaks.



A selection of gases which absorb UV light in the wavelength range where HONO dSCDs are retrieved, plotted as a function of wavelength with an arbitrary y-scale.

The caption of Figure 1 has been amended: "The measured OD is plotted as a function of wavelength in black."

- Figure 2: Specify what subplots a, b, c, and d are referring to in the caption.

We now explicitly define the combination of profiles for each panel.

- Figures 3, 4, 5, 6, A1, A2, A3: The figures need to be remade so that data is not being obscured by other data. For example, it is currently impossible to see the range of HCHO in Figure A2 measured by mini-DOAS since the model runs are covering it up. Can binning data in some figures (such as Figs 5, 6, A1, and A2) be considered to make it easier to assess?

This was also mentioned by reviewer 2. Marker sizes of figures 3 and 4 have been reduced. In figures 6, A1, and A2, VMRs are now binned by altitude at 500m increments, as well as plotted on a logarithmic x-scale to make the discrepancies between measurements and model predictions easier to see. Figure 5 was *not* binned by altitude since it is now the only figure in which the variability of HONO within altitudes can still be seen. The font size of figure A3 has been reduced, and data with missing tags removed to reduce clutter.

- Line 147: Reference to Figure 1 does not make sense here.

The text has been amended to make explicit that figure 1 *of the cited paper* is meant, not figure 1 of the manuscript.

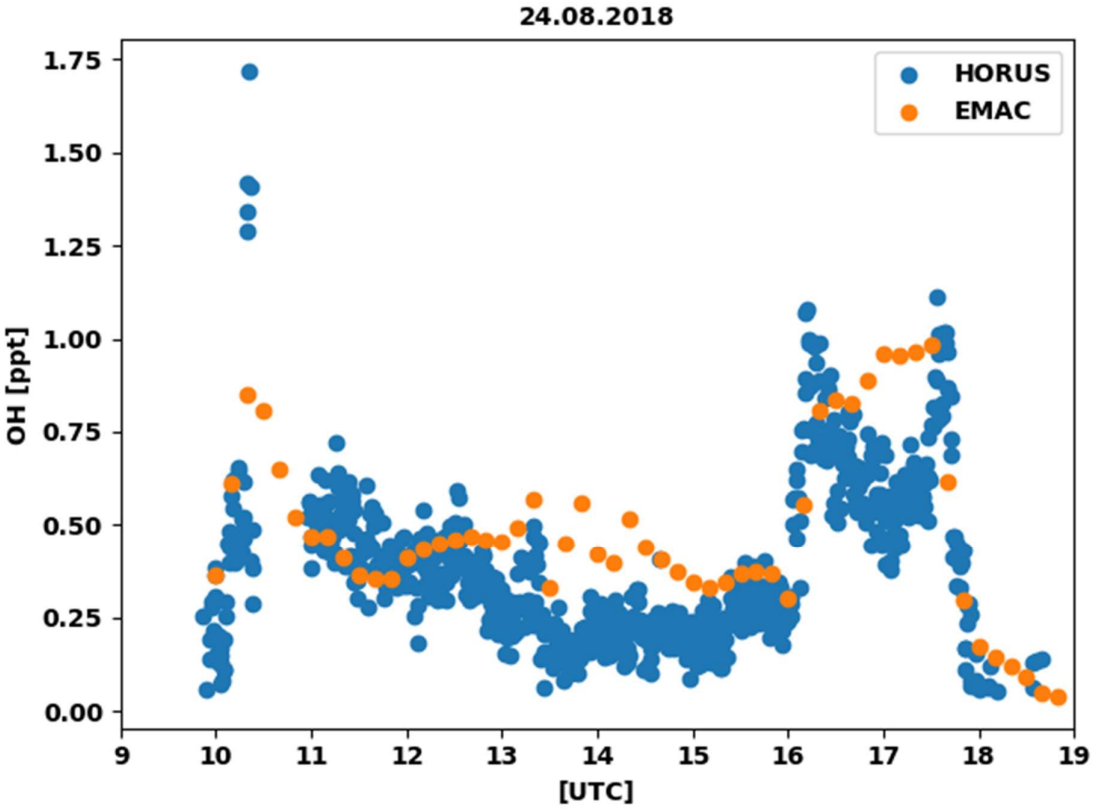
- Line 297-298: While the trend is captured, the magnitude of the mini-DOAS HCHO mixing ratio seems to be consistently higher than the two models in Fig A2, but it is hard to tell given how the data points are being covered up. Does this imply the models are underestimating OH (which impacts HONO as well)?

It is not the particular focus of this study, but the observed HCHO VMRs often exceed the predictions of both the EMAC and MECO(n) models. During EMeRGe, another in situ instrument was available to measure HCHO -- it also measured more than the models predicted (see Andres Hernandez et al. (2022)). Unfortunately, the modeled OH can only be compared with measurements in the case of the CAFE-Africa data, where only EMAC predictions are available, while in situ measurements of HCHO are not available for CAFE-Africa.

- Line 341: It seems that OH was measured for CAFE-Africa? If so, I would like to see OH plotted against OH from EMAC and MECO(n) since that would be informative for showing how well the models are capturing the oxidative capacity of the atmosphere and the OH necessary for HONO production.

Only EMAC OH data is available during CAFE-Africa, however at a temporal resolution $1/40^{th}$ of the in-situ instrument (HORUS, see table 2) which measured OH. Rather, Figure 9 exists to emphasize that using measured OH (and measured NO & measured J_{HONO}) to calculate $[HONO]_{PSS}$ does not explain the excess HONO, i.e. the underestimation of HONO by the models is not driven simply by an underestimation of OH within the models.

As evidenced by the following figure, while the EMAC model's predictions of OH do not match the in-situ observations of the HORUS instrument, the disagreement is variable, hardly a factor of 2, and therefore cannot be invoked to explain the order of magnitude difference between observed and modeled HONO.



For a single flight from the CAFE-Africa mission, a time series of the OH VMRs measured by the HORUS instrument (blue) and predicted by the EMAC model (orange).