

Interactive comment on “Daytime HONO, NO₂ and aerosol distributions from MAX-DOAS observations in Melbourne” by Robert G. Ryan et al.

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AUTHOR RESPONSES IN BLUE ITALIC TEXT

1. This paper reports measurements of HONO, NO₂ and aerosol using a MAX-DOAS instrument in the city of Melbourne, Australia. It shows enhanced levels of HONO, often peaking in the middle of the day, which would not typically be expected. The authors postulate a ground based photoactivated source of HONO, using evidence based on the dependence of high HONO levels since rainfall, combined with the observed diurnal profiles. It is an interesting paper with potentially significant results in terms of the effect of HONO as an OH source and hence on atmospheric oxidizing capacity. It

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is well written with good, easy to see figures. However, it suffers from the fact that no concurrent other measurements were made, making a full analysis of the effect of HONO on the chemical processes happening difficult. Hence many of the conclusions drawn are based on a bit of speculation which is not ideal. However, the data is of such interest (especially as it contains vertical profiles of HONO) that I do believe it should be published subject to some extra analysis. I realise there is no way to go back and back the extra measurements required but I think there are things that could be done to improve the analysis and conclusions.

We thank the reviewer for their suggestions that lead to improvements of the reactive nitrogen chemistry and exploitation of vertical information provided by the MAX-DOAS, significantly improving the manuscript.

2. One of the great advantages of the MAX-DOAS measurement is that it gives a vertical profile of HONO. Often, measurements are only made at the ground and as HONO is so short lived and postulated sources are often surface based, it is possible that the effect of HONO as an OH source in the entire boundary layer is overestimated. Here, the authors calculate $P(\text{OH})$ from HONO and ozone photolysis and show that in the daytime, OH from HONO is an order of magnitude more than from ozone. However could they do this for the entire vertical profile measurements and hence provide a comparison between the two sources of OH for the entire boundary layer? This would provide an interesting contrast to just looking at the surface data.

In order to compare the OH radical production throughout the troposphere, we have accessed ozone-sonde data collected at the Broadmeadows site which provides temperature, relative humidity and ozone mixing ratio profiles throughout the troposphere (and stratosphere). Using the TUV model, photolysis rates $J(\text{HONO})$ and $J(\text{O}^1\text{D})$ were calculated as a function of height through the troposphere. Hence equations 3 and 4 in the manuscript could be used to calculate the OH production rates $P(\text{OH})$ in ppb h^{-1} throughout the troposphere, which are shown in a new figure (now Fig. 9).

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It should be noted that in the course of these calculations a mistake was found in the original surface $P(\text{OH})$ calculation and therefore (previously) Fig. 11(e) has been updated. The wrong ozone mixing ratios were used in calculating $P(\text{OH}, \text{O}^1\text{D})$ meaning that this was underestimated. Accordingly, using the HONO diurnal cycle from 7th March and the appropriate ozone mixing ratios taken from the average EPA values (peaking at 27 ppb) around the city of Melbourne, the OH production due to HONO exceeded that due to ozone by a factor of 4 rather than a factor of 10. The highlighting of the OH production source due to HONO in the abstract of the manuscript has also been changed from reporting a source "up to ten times stronger" to "up to four times stronger".

HONO has previously been observed to be the dominant primary OH production mechanism in urban areas (e.g. Ren et al. (2003); Elshorbany et al. (2009)) using in situ measurements and modelling of surface mixing ratios. Given that the MAX-DOAS technique provides vertical profiles of HONO, the calculation of vertical OH production profiles due to HONO photolysis is possible. With co-located ozone sonde measurements at the Broadmeadows site, primary OH production has been compared across the lowest 8 km of the troposphere in Fig. 9(b). Ozone sonde data has been averaged across all measurements (17 midday measurements, approximately weekly) during the MAX-DOAS measurement period (21 December 2016 to 7th April 2017). This is compared with the average midday HONO profile from the 33 days with peak HONO greater than 0.2 ppb in the lowest retrieval layer. It was assumed that there were no HONO sources above the MAX-DOAS top retrieval height (4 km). HONO Fig. 9(b) shows that while OH production is dominated close to the ground by HONO photolysis, ozone photolysis is dominant above 1 km and will therefore be the dominant OH radical source throughout the whole troposphere. This demonstrates that considering only surface values can give a distorted picture of the relative importance of different radical sources, and highlights the ability of the MAX-DOAS technique to provide important vertically resolved information on tropospheric oxidation chemistry."

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3. The authors should also make some comment about other radical sources and how these may compare to the primary OH production from HONO and ozone photolysis (even if they have to estimate what concentration of other species may be).

We have added brief comments on the OH chemistry in response to this comment and point 5 (below). However, in this work we have restricted our study focus to the reactive nitrogen cycle and hence feel that discussion of other radical sources (i.e. VOCs) falls outside the scope of the present paper. Addressing this question with sufficient detail would require emissions data and/or in situ measurements for VOCs, among other species, which are currently lacking for Melbourne. However, given the ability of the MAX-DOAS to measure both ozone and formaldehyde, a key VOC oxidation product, we aim to address this question in future work with an extended MAX-DOAS dataset.

4. I think showing correlation between HONO and NO₂ at different altitudes as well as just at the ground (as in figure 12), would provide some information as to a potential HONO source. Presumably the correlation should get less with increasing height if the HONO source is some form of ground based NO₂ conversion.

This is an interesting idea which was partially explored in the manuscript (previously at Page 13, lines 30-35) when considering the relationship between the retrieved total column and surface values for HONO and NO₂. Here it was found (now using improved regression analysis following comments from Reviewer 2) that the correlation between surface mixing ratio and total column was stronger for HONO than for NO₂ potentially indicating that the HONO source was more likely dominated by the surface than NO₂.

To extend this to the discussion of potential HONO sources as the Reviewer suggests, the correlation between NO₂ and HONO mixing ratios in different retrieval layers was calculated and does indeed decrease with increasing altitude (the table appears in the Supplementary Information Document). However, the interpretation of this finding is not straightforward. While this could indicate conversion of NO₂ at the ground level is contributing to the observed HONO, the same result could equally be interpreted as

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being due to the strong vertical HONO gradient due to its shorter lifetime. Furthermore, comparison of correlations at different altitudes from the MAX-DOAS retrieval is complicated by the fact that except for the total column and the lowest retrieval layer, the sensitivity of the retrieval to the measurements (see averaging kernels) is different for NO₂ and HONO. Furthermore, the work conducted to address point 6 below suggest that NO₂ ground conversion cannot bridge the missing daytime HONO source gap, and this point has been added to the discussion.

In the text of the manuscript, the question has been addressed at (previously) Page 18, lines 19-20, which previously read: "Even if reaction R5 cannot explain the observed HONO levels, the strong correlation of 0.81 between HONO and NO₂ surface concentrations (fig. 12) suggests that NO₂ is implicated in some other way."

Updated text: "The strong correlation coefficient of 0.81 between HONO and NO₂ mixing ratios in the lowest retrieval layer (Fig. 10) suggests that NO₂ may implicated in the daytime HONO production. The correlation coefficient decreases with increasing altitude (see Table S3 in the Supplementary Information) which could indicate that conversion of NO₂ at the ground level is contributing to the observed HONO. However, caution should be taken in interpreting this result since the shorter lifetime and hence expected stronger vertical gradient of HONO compared to NO₂ would also lead to a decreasing correlation with altitude. Furthermore, given that the PSS calculation includes the strong NO₂ ground conversion rate in Lee et al. (2016) and still cannot replicate the average HONO diurnal profile, photolytic ground NO₂ conversion cannot be the dominant daytime HONO producer in Melbourne."

5. It is a shame there are no NO measurements to allow a steady state and thus a 'missing' HONO concentration to be calculated. However, the authors could make some broad estimate of NO based on their NO₂ measurement and at least a rough estimate of OH concentration and calculate steady state HONO. I think this is important to show how the daytime HONO observed cannot be explained by standard chemistry.

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The resulting HONO PSS state concentration is similar in magnitude and diurnal shape to other literature examples , e.g. in London (Lee et al., 2016). A plot of the HONO PSS along with the average observed HONO concentration is now included in the manuscript (part of figure 9), and details of the HONO PSS calculation and result form an updated introduction to Section 3.5 "Possible daytime HONO sources".

6. Some attempt should also be made to calculate the source of HONO from other postulated mechanisms (e.g. surface NO₂ conversion, soil based emission) to give some idea as to whether these mechanisms can produce the daytime HONO observed. Again, it is difficult to do this without some of the supporting data, however estimates could be made based on measurements in other cities in the literature.

Michoud et al., 2014 and Lee et al., 2016 provide useful parameterisations for many different HONO sources including direct HONO emission from traffic, conversion of HNO₃, aerosol-mediated NO₂ to HONO conversion and ground-mediated NO₂ to HONO conversion.

- Calculating the expected aerosol-mediated conversion of NO₂ requires measurements of aerosol surface area (not available). In addition, as discussed at (previously) page 18, lines 1-6 the observed correlation is low between aerosols and HONO suggesting that aerosol-mediated processes cannot explain the observed HONO.*
- Neither HNO₃ nor nitrate was measured at Broadmeadows and is very difficult to estimate without appropriate emission factors.*
- Again, without appropriate emission factors for NO_x, calculating the HONO due to traffic is very difficult however the diurnal cycle of the HONO/NO₂ ratio, which is always > 1%, strongly suggests that traffic emissions cannot explain the observed HONO.*

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- *Photoactivated daytime ground conversion of NO₂ is discussed in Lee et al., (2016), and the parameterization therein has been used to estimate the contribution of NO₂ ground conversion in Melbourne. The result now appears in Fig. 9 along with the calculated HONO PSS concentration demonstrating that the PSS + maximal NO₂ ground conversion rate in Lee et al., (2016) cannot explain the observed daytime HONO.*
- *Direct quantification of the soil emission contribution to the observed HONO is impossible without more information on local soil properties ? this is being followed up and will be the subject of further work. However, the contribution can be estimated from (previously) Fig. 13 which shows how the HONO diurnal cycle varies with soil moisture. Since original submission of the manuscript, soil water content percentage (% SWC) has been located through the Australian Bureau of Meteorology which has enabled this figure to be remade using bin values comparable with the literature, rather than the previous arbitrary rainfall index. Comparison along these lines and in response to Reviewer 2 have been added to the Discussion section. In an attempt to show that the missing HONO budget may be closed by soil based emissions, literature values for HONO and NO fluxes have been added to the HONO PSS rate calculation and plotted alongside the observed missing daytime HONO production rate. This now appears in figure 9.*

7. It would be useful to have a table of HONO and NO₂ levels from the literature from other cities round the world. Whilst there is some mention of comparisons in the text it would be clearer if this was brought together in tabular form to allow for easy comparison.

To address this and a similar comment from Reviewer 2, a table of urban HONO and NO₂ measurements reported in the literature has been included in a Supplementary Information document and referenced in the manuscript.

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