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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Daytime HONO, NO_2 and aerosol distributions from MAX-DOAS observations in Melbourne" *by* Robert G. Ryan et al.

Anonymous Referee #2

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This work comprehensively presents an approach for MAX-DOAS retrievals for HONO, NO2, and aerosol vertical distributions in the absence of collocated measurements. The manuscript describes the approach taken to calculate the vertical profiles, clearly presents the underlying assumptions with literature reference for context and tests the potential error in those assumptions through a sensitivity analysis. This analysis allows the Authors to present vertical profiles of the two trace gases and aerosol over the urban area of Melbourne, Australia. Unlike most urban environments, daytime peaks in HONO concentrations were observed that typically have been reported for rural environments. The authors present suggestions as to the potential sources of this observation within the context of several recent findings in the literature. Overall, this

is a solid manuscript, which is quite nearly enough work for two separate publications and will be suitable - with minor revisions suggested below - for publication in Atmospheric Chemistry and Physics. Some lengthy areas and a number of figures could be clarified/removed from the manuscript into a Supporting Information document to increase the focus of the work. Some literature regarding daytime HONO release from soils is absent from the discussion.

There is a single major revision to this work that should be made regarding regressions. It is not clear what regression approach the Authors used, but atmospheric datasets typically require accounting of error in both measures (e.g. (Wu and Yu, 2018)). The authors present a Pearson correlation coefficient in Figure 7 and discuss correlations heavily in their discussion from there on. This suggests that a linear least-squares analysis was used, which assumes error in the ordinate alone. The authors should clarify this and present appropriate regression metrics (e.g. slope and regression coefficient) when discussing correlations. Much of the discussion surrounding these comparisons is qualitative while the wording suggest that quantitative evaluations have been made. Including this quantitative information will strengthen the discussion.

Minor comments throughout the manuscript are as follows:

Reference to figures throughout the manuscript should be capitalized as 'Fig. X' instead of 'fig. x'

Page 3, Lines 30-35: Interferences from clouds, as presented in the discussion, should be included in the drawbacks here.

Page 4, Line 30: repetition of 'and' to be corrected

Page 5, Line 11: differential slant column density is presented here and presumably is the source of the 'dSCD' term used later in the paper. Please define here, if this is correct.

Page 6, Figure 2: Keep the traces in panel c) consistent with the caption. Suggest

switching O3 and HCHO in the caption to be in the same order as the traces.

Page 6: Figure 2 and Table 1 could be moved to a supporting information document to reduce manuscript length.

Page 7: Figure 3 could be moved to a supporting information document to reduce manuscript length. Figure 4 could be easier to interpret if the time axis is consistent with the others in the manuscript. Two hour time intervals here, and in other diurnal plots, would provide the most detail without becoming cluttered. Figure 4 could benefit from being presented with larger panels if the other figures and table are moved to supporting documentation.

Page 8: Section 2.3 is quite long and is detailed for the manuscript, but feels like a lot of detail has also been left out. A suggestion here would be to simplify and condense this section further to improve its clarity (e.g. Equation 1 is not accessible to those not familiar with all of the literature in this section and could be considered superfluous along with many of the details) or some of the details could be moved to supporting documentation and expanded upon in the interests of allowing greater ease of reproduction of this detailed work.

Page 8, Line 14: K presented as a weighting function matrix does not appear in either Equation 1 or Equation 2. Please revise.

Page 9, Lines 9-23: These are results. Suggest relocating to the results and discussion section.

Page 10, Figure 5: There are acronyms (or short-hand notation) being used in the upper row of panels which are not defined in the caption. Please do so. In the bottom row of panels, there are 20 different lines presented in each panel and the values for each are very small in the legend. Are all of these necessary or can half of them be removed without undermining the findings? It would allow all panels in this figure to be increased in size and make it easier to read. Finally, panels (a) and (b) are not labeled

here. Please add these.

Page 10, Line 4: repetition with 'the'

Page 10, Lines 13-14: 'by a bias towards the a priori due to lower measurement sensitivity at these levels' This explanation is unclear. Please consider revising to improve the clarity here.

Page 11, Figure 6: This figure could be moved to a supporting document. The panels are alphabetically labeled, so the text boxes for each can be removed. VCD is not defined in the caption. Also add a note regarding the exponent terms for NO2 and HONO VCD values as they may be easily missed.

Page 11, Line 10: 'the lowest 500m' should be 'in the lowest 500 m'

Page 11, Lines 11-14: Is the 'high sensitivity' instrumental sensitivity or retrieval sensitivity? Use of the word sensitivity here is a bit unclear and the retrieval sensitivity might be more intuitively termed 'potential error' or 'estimation error' or simply 'error'.

What is a 'low error budget'? This wording is not consistent with the rest of this section. Please clarify.

Page 12, Figure 7: From here on forward, the regression analyses should be clearly presented. A useful quantity that would have been obtained in the analysis here is the slope, which gives some indication of the bias that is discussed qualitatively. Such bias is expected given that the in-situ monitors are located at ground level (on top of sources), while the MAX-DOAS is observing more dilution of those sources. In the caption of this figure there is a reference to 'surface concentration' measured by the MAX-DOAS, but isn't the lowest elevation angle somewhere between 100 - 500 m above ground level? This isn't terribly clear and could help bridge these observations with ground observations more easily.

Page 12, Line 9: 2.5 should be a subscript. In addition, wouldn't ceiliometer or LIDAR measurements be more useful in validating the MAX-DOAS aerosol results?

Page 12, Line 17: The technique used by the EPA has not been presented and should be added as supporting instrumentation details in section 2.1. Presumably these are chemiluminescent analyzers with molybdenum converters?

Page 12, Line 19: What is the slope of the comparison? What type of regression was used?

Page 13, Lines 6-9: Add appropriate quantitative regression data here, along with coefficient values that justify selection of wording such as 'correlated strongly'. The direction of the correlation is also important. Was the relationship a positive or negative one in each of these cases? Please provide these quantitative details.

Page 13, Lines 14-17: These ratios have been derived from measurements made at night or from tunnel studies and their applicability to the interpretation of daytime data is questionable. During the day, the longer lifetime of NO2 relative to HONO could result in the observed diurnal pattern of HONO/NO2 by simple boundary layer mixing processes diluting the surface NO2 while the surface HONO source does not change (i.e. it could be independent of NO2, as suggested by the weekend dataset). It may be worthwhile to discuss this further and carry it into the later discussion or to remove HONO/NO2 as a suitable daytime metric entirely.

Page 13, Lines 33-35: Quantitative values for 'correlated strongly'. This is consistent with literature reports of surface processes dominating over aerosol NO2 conversion. Please cite some examples of this.

Page 14, Figure 8: This figure could be moved to the supporting information document. Remove text boxes on each panel. Label each alphabetically. If necessary, clarify what is on each panel in the caption. Reduce the number of labeled ticks on each ordinate axis.

Page 14, Figure 9: Change time axis to two-hour intervals. The date format on top of each column is different from that in Figure 8. Keep date formats consistent throughout

the manuscript and consistent with ACP guidelines. Remove 'conc.' from the HONO and NO2 labels. They are correctly identified as mixing ratios in the caption.

Page 15, Line 7: Delete 'well'

Page 15, Lines 27-28: These daytime values are higher than might be expected given that the measurement is being made through a large volume and from the NO2 intercomparison. This would suggest in-situ HONO measurements might exceed 0.5 ppb. How does the > 0.2 ppb HONO value compare to other reports in urban and rural environments?

Page 15, Lines 32-33: The authors discuss that HONO does not peak in the early morning during their daylight observations. Are there examples of MAX-DOAS observations capable of seeing the previous night's HONO prior to photolysis? What are the vertical resolution differences between these MAX-DOAS measurements and how might that impact the observations (i.e. if the 'surface' bin is deeper than other observations, you'd expect to observe lower levels). Also, are there limitations in the MAX-DOAS measurement near sunrise with the instrumental orientation that could result increase the error in capturing a quantitative absorption signal for HONO at this time?

Page 16, Figure 10: Consider moving this figure to a supporting information document. The discussion does a good job of conveying the information presented here.

Page 16, Lines 1-5: It would improve the discussion to report the daytime maximum mixing ratios observed in these other locations, for context.

Page 17, Figure 11 (and other similar instances): The caption does not describe the panels correctly here. Further, the caption description for the similar panels can be improved by changing the phrase directed for the first panel to the following: 'Diurnal cycle plots for the 1 hourly averages of (a) NO2, (b) HONO, (c) HONO/NO2, and (d) aerosol extinction surface values at Broadmeadows'. The alphabetical indicators for

each panel should be displayed outside the axes throughout this figure.

Page 18, Line 7: The citations here are not in the proper format to present via 'e.g.'. This is also a hanging sentence. Please correct it.

Page 18, Lines 11-18: These ratio values continue to be potentially misleading. Suggest careful revision or even removing this part of the discussion since intensive chemical description of the HONO/NO2 ratio under sunlit conditions has not been well-established.

Page 18, Line 20: 'suggests that NO2 is implicated in some other way'. The weekend data presented here suggests that this may not be true OR that the mechanism is NO2-saturated. See some discussion of this in (Pusede et al., 2015).

Page 19, Figure 13: The data presented here suggest that there is a suppression of HONO daytime surface flux due to increased soil water content. There are a few instances of this hypothesis being tested under laboratory and field conditions that may be worth mentioning here (Donaldson et al., 2013;Donaldson et al., 2014;Oswald et al., 2013;Scharko et al., 2015;Su et al., 2011;Weber et al., 2015). Comparison to the microbial pathways, reversible partitioning, and surface adsorption/dissolution could all enhance the discussion.

Page 19, Lines 1-2: The literature has been clear on the aerosol surface area conversion of NO2 to HONO being a minor daytime production route for some time. Suggest including some references to the literature that have demonstrated the phenomenon here in support of your findings.

Page 20, Line 17: This instance of biocrust discussion should be expanded if there are local biocrusts near the observation site, and generally throughout the Melbourne area. The established literature on this, coupled to anything known about regional biocrust microbial composition, may facilitate a stronger capacity to speak on this potential daytime HONO source instead of speculating.

References

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