

Interactive comment on “Secondary formation of nitrated phenols: insights from observations during the Uintah Basin Winter Ozone Study (UBWOS) 2014” by B. Yuan et al.

Anonymous Referee #2

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This manuscript describes some novel measurements of nitrated phenols made in the Uintah Basin late January into early February, 2014. The measurements themselves are novel and indicate a high sensitivity and reasonable specificity for the target species. The measurements are complemented by a fairly simple modeling exercise, which shows that the data can be fitted by a chemical model accompanied by deposition and dilution terms without too much tweaking.

Overall, this is a valuable study, which can be published without too many changes.

The measurements are fairly novel, and perhaps would benefit from a little more discussion. The figures showing mass spectral peak-fitting are central to understanding

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the quality of the data, but are relegated to Supplemental Material. I would like to see them featured more prominently, and with some further discussion. For example, how variable are the other signals shown in Figures S2 (A-D)? What are the proposed identities of some of the other peaks, and do they show similar diurnal profiles? For that matter, when were the shown spectra taken (date, time of day)? A little more information along these lines would help others to assess the reliability and generality of the technique.

On the other hand, quite a lot of space is devoted to the model, which does not really bring a whole lot of insight to the chemistry. Admittedly, it is shown that the modeled diurnal profiles match the measurements quite well, but it is after all “only” a box model, and transport and dilution are treated simplistically. However, the interpretation of the model does not overstep its limits, and the exercise is useful, if only in showing that the measured diurnal profiles are reasonable.

Specific comments: There are a few spots in the manuscript where the grammar needs tightening up. E.g., 28662, line 16. “oxidation. . . with nitration process. . .” 28666, lines 7-20. Repeats discussion of acetic anhydride. Also, it wasn’t totally clear whether you were talking about your own IMR, or comparing to others. 28670, line 10. “inertial” should be “inert” ?

28670, model tests in Fig S3. Was the photolysis to give phenoxy + NO₂ the only channel included? Since this channel reforms NP, you can’t really rule out its occurrence concurrently with HONO production, since as you say it would be a null channel. Since the overall quantum yield is only about 1E-3, there is a lot of room for parallel channels occurring. Admittedly, though, Bejan et al. (2006) point out that photolysis of 2.5 ppm 3-methyl-2-nitrophenol led to <0.14 ppb NO₂, so the channel is probably only small.

28671, lines 17022. What is the rationale for assuming that the interference is only present during the night? How would alternative assumptions affect the conclusions from the model?

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28675. Presumably the reaction of OH with phenol is such a small contributor to NP production because the OH mostly adds to the ring? Maybe a comment would help to clarify this. It is interesting that so many sources of C₆H₅O₂ (and consequently, C₆H₅O) exist. Of the flux through C₆H₅O₂ + NO, only about a third makes NP. Is this because phenoxy radicals cycle back to RO₂ through the O₃ reaction? How does the inclusion of the phenoxy + NO reaction affect the phenoxy and NP budgets around mid day? Interpretation of these figures might be a little easier if the NO₂ and O₃ levels were given somewhere.

28676, line 17. Just to clarify; you mean 100% of nitrated phenols that are actually lost by photolysis (since the overall quantum yield is <1E-3).

Figure 5, caption. Delete "in (b) and (d)".

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