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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The changing role of organic nitrates in the removal and transport of NO_x" *by* P. S. Romer Present et al.

Anonymous Referee #1

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This work investigates the changing fate of atmospheric nitrogen oxides (NOx), with a focus on the increasing importance of the role of organic nitrates. The authors develop a framework by which the fate of NOx can be interpreted using the ratio of contributions to the hydroxyl radical loss rate from nitrogen dioxide and volatile organic hydrocarbons (VOC). The method is then demonstrated using observations from 13 separate field studies, predominantly in the US, dating back over the previous 20 years. The authors then use the framework to investigate the changing role of organic nitrates in the continental US, and the implications for air quality policy. This results in some interesting and important conclusions about the future of NOx chemistry in the US. This is an interesting approach to the study of the non-linear sensitivities of atmospheric NOx chemistry and provides another way by which to explore the importance and im-

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Discussion paper

pacts of high and low NOx chemical regimes. The approach will also likely prove to be a useful tool for assessing model organic nitrates and responses to changing emissions. The paper is well written and represents a valuable contribution to the literature. I recommend publication after the following comments have been addressed.

Comments:

1) Figure 2 is a very powerful and novel presentation of historical field observations, and warrants more discussion. The authors use of a fit function of the same form as eqn. 4 is convenient for the purposes of this study, but it would be useful to the reader to know the form of a best fit function to the observational data. The delay seen in the shift from inorganic to organic nitrate dominated NOx loss, as NO2R/VOCR decreases, compared with the best fit line and that predicted by the authors using a fixed VOC speciation (gray line in Fig. 2a) is interesting. This discrepancy occurs at the transition between the high and low NOx regimes identified, i.e. inorganic vs organic nitrate production dominated, and is thus the most important region to understand. It is suggested by the authors that this discrepancy is likely due a change in the effective branding ratio fo organic nitrate production (page 5 line 28), however this needs to be supported. Could it not also be due to a change in the reactivity of the VOC mixture, and therefore VOCR, or changes in fNO? The authors should discuss further the observational trends shown in Fig. 2, and the possible explanations for the discrepancy with the simple fit shown in the red line and with the calculated gray line in Fig. 2a. The authors should also comment on the implications of this discrepancy for the conclusions of the paper.

2) It would be very useful to the reader to understand how the high and low NOx regimes identified in this work differ from the traditional high to low NOx definition used for describing ozone production regimes (e.g. Jaeglé et al. 1999; Thornton et al. 2002). An important parameter in the traditional conceptual model of high and low NOx chemistry is if the dominant peroxy radical reaction partner is NO or another peroxy radical (i.e. the author defined fNO). In Appendix A the authors have already

calculated radical production and loss, and could use this to estimate fNO for each set of observations. It would be helpful for the reader if these values were shown, possibly on Fig. 2a, so the two definitions of high and low NOx chemistries could be compared.

3) Although the assumptions made in the calculations in Appendix A are commonly used, it is also frequently the case that incomplete measurement suites result in discrepancies with observations. As the authors have radical measurements for some of the field data, comparisons with calculated values for these studies would provide a gauge of the uncertainty in the calculations. The authors should also provide an estimate to which this uncertainty impacts the conclusions of the paper.

4) This work focuses on the daytime production of organic vs inorganic nitrates. Perring et al. (2013), however, estimate that the nocturnal production of organic nitrates, via nitrate radical reactions with alkenes and phenols, could account for as much as 50% of regional production. As NOx and VOC emissions change is the importance of this nocturnal pathway to organic nitrate production also likely to change? A recent analysis by Edwards et al. (2017) presented a similar relationship to that shown here, relating nocturnal organic vs inorganic nitrate formation to the ratio of NOx to VOC, and also predicted a transition from inorganic to organic nitrate dominance. The authors should discuss the role of nocturnal organic nitrate production and how this is accounted for and impacts on the conclusions of this work.

References: Jaeglé et al. J. Geophys. Res., 26, 29, 3081-3084, 1999.; Thornton et al. J. Geophys. Res., 107, 12, 4146, 2002.; Perring et al., Chem. Rev., 113, 8, 5848-5870, 2013.; Edwards et al. Nat. Geosci., 10, 7, 490-495, 2017.

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