

The goal of this work is to improve our understanding of NO<sub>x</sub> in the free troposphere, and implications for atmospheric oxidation and interpretation of satellite NO<sub>2</sub>. Overall, this paper looks at how well four atmospheric chemistry models simulate background NO<sub>x</sub> leveraging observations from three aircraft campaigns. The authors show that observed ozone is consistent with steady state calculations using observed NO, and it is likely that upper tropospheric NO<sub>2</sub> measurements have interferences from thermal decomposition of NO<sub>x</sub> reservoirs at cold temperatures. The authors find that lightning and aircraft emissions are the main contributors to the free tropospheric contribution of NO<sub>2</sub> to the total column but differ in their seasonality. The model underestimates NO (and the NO<sub>2</sub> column) during the ATom campaign over the remote oceans, which the authors suggest is due to missing photolysis of particulate nitrate.

This paper could be a useful contribution to the field and to those trying to use NO<sub>2</sub> satellite information combined with models to infer emissions. I recommend the authors make the following minor revisions before publication in ACP.

### **Major Comments**

One concern is that this paper is relied on for evidence of particulate nitrate photolysis “Andersen, S. T., Carpenter, L. J., Reed, C., Lee, J. D., Chance, R., Sherwen, T., Vaughan, A. R., Bloss, W. J., Sommariva, R., Nott, G., Neves, L., Read, K., Heard, D. E., Seakins, P. W., Whalley, L. K., Boustead, Fleming, L. T., Stone, D., and Fomba, K. W.: Extensive field evidence for the release of HONO from the photolysis of nitrate aerosols, *Sci. Adv.* (in review), 2022.” but it is not yet available. As photolysis of particulate nitrate is currently poorly constrained, it appears that this paper with help support the inclusion of this pathway in models.

The authors need to better defend the solution of particulate nitrate photolysis, and not underestimated transport of NO<sub>x</sub> in alkyl or peroxy nitrates, or direct NO emissions from the ocean, particularly since the authors discuss that underestimated MPN and alkyl nitrates in the model suggests missing chemistry.

The authors should also be clearer about their recommendations for how NO<sub>2</sub> observations should be treated in the future. Should they be ignored in favor of PSS, or should measurements focus on the improvements made during Bradshaw et al., 1999?

Finally, the authors should discuss recommendations for observing emissions trends given the importance of the free tropospheric contribution to columns, for example by only looking at regions with column amounts over a certain threshold. They haven’t quantified for us how important the free tropospheric background is to the column over cities and whether an approach removing columns with a significant background contribution could help to clarify trends in surface NO<sub>x</sub> emissions.

### **Minor comments**

Line 129 – This statement is confusing “Silvern et al. (2018) showed that using the observed NO<sub>2</sub> vertical profile from SEAC<sup>4</sup>RS in the NASA NO<sub>2</sub> column retrieval for the OMI satellite instrument decreases the retrieved NO<sub>2</sub> columns over the southeastern US by 30%, suggesting

the possibility of a systematic bias in the NO<sub>2</sub> column retrievals.” You have just told us that NO<sub>2</sub> measurements have interferences, so likely the observed profile is biased, not the retrieval. Please clarify.

In Bradshaw et al., 1999, observations matched photostationary steady state, using a “a highly modified photofragmentation two-photon laser-induced fluorescence (PF-TP-LIF) instrument.” Could you explain how these modifications differ from current LIF techniques and provide some guidance on whether the modifications from Bradshaw et al., 1999 should be employed in the future to better measure NO<sub>2</sub>?

Similarly, can you explain why the MPN corrections in the SEAC4RS LIF observations were insufficient?

Line 248 – How do you justify that sea salt is internally mixed with sulfate/ammonium/nitrate in the fine mode?

Line 390 – Please clarify. Is this ‘unheated’ channel the one you are saying still has a measurement bias, presumably because the channel is still warmer than ambient temperatures due to being on the inside of the aircraft?

Line 410 – I am curious if your simulations with photolysis of particulate nitrate produced appreciable during SEAC4RS/DC3 as SENEX observations showed HONO outside of direct sources was negligible (< 15 ppt)

<https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1002/2016JD025197>.

Line 430 – How does this finding change the conclusion of Travis et al., 2016 that the model NO<sub>2</sub> columns were inconsistent with other constraints on emissions?

Line 435 – Does it really make sense to discuss a ‘global background of NO<sub>2</sub>’ given its short lifetime of only hours? Also, “background” is sometimes used to mean non-anthropogenic. Possibly consider different terminology.

Fisher et al., 2018 (<https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2018JD029046>) suggest that the underestimated NO could be direct emissions from seawater. Discuss whether this is a possible alternative to photolysis of particulate nitrate.

Line 474 – As you are also simulating HNO<sub>3</sub> and PAN, it would be more consistent to compare your own simulations to HNO<sub>3</sub> and PAN, and then you could avoid a citation to a presentation (Zhai et al., 2022) rather than peer-reviewed literature. The authors should also show comparisons with observed particulate nitrate and show whether photolysis improves or degrades that simulation.

Line 474 – How do you know there is no overestimate of NO<sub>x</sub> sinks? You haven’t shown us this. Or do you just mean NO<sub>2</sub> + OH is not overestimated which is why you cite Travis et al., 2022 for OH?

Line 476 – Also Henderson et al., 2012 - <https://acp.copernicus.org/articles/12/653/2012/> and Seltzer et al., 2015 <https://acp.copernicus.org/articles/15/5973/2015/acp-15-5973-2015.pdf>.

Line 585 – Can you discuss again the biases in your GEOS-Chem simulation of PAN in the context of this discussion? Is PAN underestimated in the MBL?

Line 620 – This conclusion is without addressing model underestimates of OH reactivity. Please discuss how you would expect model ozone to change if OH reactivity was increased in the model.

Line 694 – Why would estimating free tropospheric concentrations in February be beneficial? What would be the application for such an estimate?

Line 718 – What are the differences in the reaction rates for  $\text{NO} + \text{O}_3$  and  $\text{NO}_2 + \text{OH} + \text{M}$  in GMI vs. GEOS-Chem?

Figure 1 – Is there a reason to put NO on the same scale as  $\text{NO}_2$ ? It would be easier to see the discussed NO biases if the scale was reduced.

Line 732 – Is there a reason this decrease would impact only the free troposphere and not the boundary layer?

Line 765 – I assume then that the higher spatial resolution of TEMPO will allow for a better examination of trends in emissions moving forward as it will be less sensitive to FT background. Also, why haven't studies only focused over urban regions to look at trends?

Line 776 – Can you clarify exactly what needs to be done for future  $\text{NO}_2$  measurements? Reconsider the amount of MPN that might interfere? Make the modifications described in Bradshaw et al., 1999?

Line 784 – This again makes me curious about peroxy nitrates (PAN etc) as well, and whether the model underestimates  $\text{NO}_x$  transport that could be part of the underestimate in ATom NO. You say on line 299 that PAN is small, but also the perturbation in NO needed is small.

Line 805 – But again, how would you expect the ozone response to change if OH reactivity was increased?

Line 813 – Is there any reason to suggest focusing analysis of  $\text{NO}_x$  trends/emissions on regions where the  $\text{NO}_x$  column is high enough to have low uncertainty from the large free tropospheric background?