Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-730

Anonymous Referee #2

Referee comment on "The formation and mitigation of nitrate pollution: comparison between urban and suburban environments" by Suxia Yang et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-730-RC2, 2021

General comments

Yang *et al.* analyze data from several sites in the Pearl River Delta to assess mechanisms for the production of nitrate aerosol, an increasingly important component of $PM_{2.5}$ pollution in China. The analysis shows that the contribution of photochemical and dark mechanisms varies by site and depends on both the chemistry and the dynamics of the planetary boundary layer. It further shows that NO_x reductions are unlikely to improve nitrate pollution despite being the major precursor due to the dependence of NO_x oxidation rates on NO_x itself. Reductions in VOCs, by contrast, are effective at all sites in both NO_x and O_3 reductions.

The paper is well written, easy to follow and well organized. It is of substantial interest to the readership of ACP. I recommend publication following attention to the specific comments below.

Specific comments

Line 53: Nitrate reductions can be site specific, but the same is true for ozone and for the same reasons as detailed later in the manuscript. Can identify this effect here.

Line 71-74: Nitrate photolysis to produce HONO remains uncertain. References that also place limits on this process should be included.

Romer, P.S., *Constraints on Aerosol Nitrate Photolysis as a Potential Source of HONO and NOx.* Environmental Science & Technology, 2018. **52**(23): p. 13738-13746.

Lines 81-84: Aerosol pH is also an important process that should be identified and referenced for HNO_3partitioning. See for example:

Guo, H., *Effectiveness of ammonia reduction on control of fine particle nitrate.* Atmos. Chem. Phys., 2018. **18**(16): p. 12241-12256.

Lawal, A.S., *Linked Response of Aerosol Acidity and Ammonia to SO2 and NOx Emissions Reductions in the United States.* Environmental Science & Technology, 2018. **52**(17): p. 9861-9873.

Nenes, A., *Aerosol pH and liquid water content determine when particulate matter is sensitive to ammonia and nitrate availability.* Atmos. Chem. Phys., 2020. **20**(5): p. 3249-3258.

Franchin, A., *Airborne and ground-based observations of ammonium-nitrate-dominated aerosols in a shallow boundary layer during intense winter pollution episodes in northern Utah.* Atmos. Chem. Phys., 2018. **18**(23): p. 17259-17276.

Line 87: Can also reference McDuffie 2018b for the variation of $ClNO_2$ yields.

McDuffie, E.E., *$ClNO_2$ Yields From Aircraft Measurements During the 2015 WINTER Campaign and Critical Evaluation of the Current Parameterization.* Journal of Geophysical Research: Atmospheres, 2018. **123**(22): p. 12,994-13,015.

Line 95: Also suggest earlier references from California, e.g.

Brown, S.G., *Wintertime Vertical Variations in Particulate Matter (PM) and Precursor Concentrations in the San Joaquin Valley during the California Regional Coarse PM/Fine PM Air Quality Study.* Journal of the Air & Waste Management Association, 2006. **56**(9): p. 1267-1277.

Chow, J.C., , *PM2.5 chemical composition and spatiotemporal variability during the California Regional PM10/PM2.5 Air Quality Study (CRPAQS).* Journal of Geophysical Research: Atmospheres, 2006. **111**(D10): p. n/a-n/a.

Line 190-191: There is a reference to integrity and temporal coverage of the measurements as a limitation on the data, without much explanation. More detail on which instruments were functioning at which times could be given in the introduction to

this section or the SI.

Line 216: How was the dilution rate determined? This is an important parameter that is normally fit to achieve agreement with observations in box modeling approaches. The 24 hour inverse rate constant appears to be rather an arbitrary guess.

Line 264-265: Explain why this approach is meaningless.

Lines 271-273: Large N_2O_5 mixing ratios were present elsewhere in the time series in S3 but do not appear to be associated with poor representation of nitrate in S2. Is this explanation consistent with the data?

Line 289-294: Suggest comparing this result to that of the Franchin paper above, which shows the same effect but more dramatically for aircraft data in northern Utah, USA.

Line 309-311: Meaning of this sentence is not clear. Is the morning increase in nitrate being attributed to photochemical NO_2 oxidation in the residual layer, or does the word "might" here indicate uncertainty? If the former, the later discussion of nighttime accumulation of nitrate would appear to conflict with this statement.

Line 316: A sustained level of nearly 2 ppbv of NO in excess O_3 at 488 m implies very rapid mixing with surface NO emissions. Is this likely to be the case, and if so, would it be consistent with an analysis of an isolated residual layer? More likely might be that the NO instrument zero is not well characterized, and that NO was in fact zero at this altitude. If so, the reaction of NO_3 + NO would present no limit for nighttime chemistry at 488 m.

Line 336: The instrument descriptions indicate that NH_3 was measured. Was there excess gas phase NH_3as implied by the ion balance in Figure S5?

Line 351-353: The effect of periodic large N_2O_5 and $ClNO_2$ is more likely due to vertical than horizontal transport – so these concentrations may be associated with the overlying residual layer.

Line 430: The model of residual and boundary layer mechanisms for nitrate production is certainly more complete than most similar analyses. However, horizontal transport in the residual layer, especially as part of nocturnal jets, has been invoked in some analyses of winter nitrate production in the California central valley (see Brown and Chow references above). Some comment in this section about the differences in horizontal transport would be useful, even if it is not possible to quantitatively analyze this effect for the data in this study. The assumption here is that the residual layer and the nocturnal boundary layer originate at the same location, which is not necessarily the case. As noted later in the paper, this is one of the limitations of box modeling.

Line 445-446: The NO_x sensitivity at Heshan looks neutral or near peak – that is O_3 and nitrate would stay approximately constant for an initial NO_x reduction. Also, could define what is meant by "initial' here – just an infinitesimal increment, or a fixed number such as 5 or 10%.

Supplement, lines 135-138: The sensitivity to the $ClNO_2$ yield is explored, but not the N_2O_5 uptake coefficient. Can the authors comment on the sensitivity to this parameter? Importantly, there may be almost no sensitivity here if the system is limited by the reaction of $NO_2 + O_3$. If so, the N_2O_5 uptake coefficient would need to be reduced substantially before the heterogeneous reaction becomes important or rate limiting. Can the authors comment on these aspects of the model sensitivity?

Technical corrections

Line 43: replace "are" with "is an"

Line 62: hygroscopic properties

Line 231: particle rather than particles

Line 365-367: Check sentence grammar

Line 399-400: Check meaning – what is "nitrate of nitrate"