

Interactive comment on “The detection of nocturnal N₂O₅ as HNO₃ by alkali- and aqueous-denuder techniques” by G. J. Phillips et al.

Anonymous Referee #1

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This is a short paper that identifies a potentially important artifact in current instrumentation for measurements of gas phase HNO₃. The authors suggest that N₂O₅, which can hydrolyze readily to form soluble nitrate, may appear as nitrate in wet-denuder type instruments that are used to sample HNO₃ from the gas phase. They show two figures of ambient data from a site in Germany during summertime for an in-situ instrument that measures N₂O₅ and a wet denuder sampler that measures HNO₃. The data are consistent with a large interference in the determined HNO₃ from the measured N₂O₅. The authors further note that interpretation of artifact N₂O₅ as HNO₃ on such instruments would potentially skew the understanding of nitrate deposition, since

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N₂O₅ undergoes atmospheric chemical processes other than wet or dry deposition to produce soluble nitrate.

The suggestion that N₂O₅ is large in comparison to HNO₃ and that it may be a significant artifact for these instruments is important and should certainly be published and explored in further detail, as the authors recommend. For this reason, the paper is reasonable for publication in AMT

There are two important issues that the authors should consider before publication. First, the data as presented do not prove that there is an interference in the denuder instrument, but rather that there is plausibly or likely an interference. The N₂O₅ signal, expressed as equivalent nitrogen mass, is always less than the reported HNO₃ and shows temporal peaks during the same time periods. Since N₂O₅ is known to undergo heterogeneous uptake, it is plausible or even likely that a part of the observed signal is indeed from N₂O₅. However, the authors do not present data that would indicate the efficiency of N₂O₅ uptake in the instrument. While it is plausibly or even likely to be unity, the authors should be clear that the analysis provides only an upper limit to the potential interference rather than a measurement of the actual interference. Second, it is somewhat surprising that there is no laboratory data to confirm the findings of the field data. The authors could relatively easily introduce an N₂O₅ standard to both instruments in the absence of HNO₃ (or with a known HNO₃ content) to quantify the effect precisely. While such an analysis is likely beyond the scope of the paper in its current form, the outlines of such experiments should at the very least be included and recommended for future work.

In addition to these general comments, the authors should consider the following more specific comments:

Abstract: the denuders should be sensitive to the sum of HNO₃ + 2N₂O₅, rather than HNO₃ + N₂O₅.

Page 7490. Bottom: Why is N₂O₅ hydrolysis left out of HNO₃ sources? It's much more

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important than NO₃ + DMS.

Page 7491, line 5: “which is”

Page 7495, line 4: Worth noting here that that N₂O₅ is equivalent to 2 NO₃- when sampled into a wet denuder since this was not made clear in the abstract.

Page 7495, line 7: “High correlation” seems a poor description since the time resolution of MARGA is so low. The statement should simply read that N₂O₅ is smaller than, but a significant fraction of, measured nitrate in MARGA. If there is a correlation between CRDS N₂O₅ and MARGA, it should be plotted as a correlation plot. There is ample room for extra figures. What is the coefficient of correlation of such a plot during dark time periods (even selected ones)?

Page 7495, line 12: Statement not substantiated, but the authors could consider the existing literature data for HNO₃ and / or N₂O₅ to make a better case for the seasonality. As just one example, Wood et al. (ACP, 5, 483-491, 2005) show low mixing ratios of N₂O₅ during winter in the San Francisco Bay Area of the U.S. that would not likely constitute a significant interference for a nitrate instrument.

Page 7496, top: The influence of N₂O₅ on nylon filter based systems for HNO₃ measurement seems as though it would be rather easy to test in the laboratory. This suggests an important direction for future work.

Page 7496, lines 18-21: The statement is not quite correct – largest N₂O₅ mixing ratios have been observed in summertime conditions due to the generally faster rate of NO₃ oxidation during warm conditions. Large N₂O₅ mixing ratios may also be observed in winter for the reasons stated, but they do not necessarily exceed summer mixing ratios.

Page 7496, lines 25-27: Here again, N₂O₅ hydrolysis is omitted as a source of HNO₃. As above, the reason for this omission is not clear. The discussion that follows seems to imply that N₂O₅ can only serve as a source for condensed phase NO₃-, which is not the case. Even if N₂O₅ reacts heterogeneously, the resulting inorganic nitrate

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partitions to either the gas or aerosol phase depending on the thermodynamics of the aerosol (or ground) surface.

Page 7497, lines 9-19: The discussion of ClNO₂ and NO_x recycling is useful. However, the discussion does not consider the direct recycling of NO_x by N₂O₅, which may survive in large quantities through to sunrise to recycle NO_x (see, for example, Perner et al., JGR, 90, 3807-3812, 1985; Brown et al. JGR, 108, D94299, 2003)

Page 7497 – 7498, last sentence before conclusions: The authors should consult references from Heitnz et al. JGR, 101, 22891-22910 1996; Geyer et al. Atmos. Environ., 35, 3619-3631, 2001; and Vrekoussis et al., ACP, 7, 315-327, 2007. These references include long term measurements of NO₃ and calculated N₂O₅ that could be used to generate a comparison to inorganic nitrate levels, or to typical values if the latter are not reported directly in these papers. In light of the speculative nature of statements of seasonal dependences earlier in the paper, this would be a very useful comparison.

Page 7498, lines 11-13: It is not clear that this statement is definitive – see comments above. Has the presented data really shown that the measured HNO₃ *is* N₂O₅, or just that it likely comes from N₂O₅?

Page 7498-7499: I agree more strongly with the last part of the sentence (“for many purposes this is unsatisfactory”) than the first part about using daytime only measurements. My subjective recommendation here is that the authors stick to the original point that the potential for N₂O₅ interference should be recognized and quantified through better measurements of all reactive N species, as they state at the end of this paragraph.

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 7489, 2012.

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