Interactive comment on “The detection of nocturnal N$_2$O$_5$ as HNO$_3$ 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...
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
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
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 NOx recycling is useful. However, the discussion does not consider the direct recycling of NOx by N2O5, which may survive in large quantities through to sunrise to recycle NOx (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.