

Authors comment: The detection of nocturnal  $N_2O_5$  as  $HNO_3$  by alkali- and aqueous-denuder techniques.

We thank the reviewers for their comments and suggestions.

We would like three important points to be taken from this paper.

First, denuder methods detect  $N_2O_5$  (very probably) with efficiency close to 1. As reviewer one has pointed out, we do not have lab confirmation, but as the process is well known in the lab and the field data is consistent with a high efficiency then we are very confident that this is the case.

Second, the artefact most probably has an effect on the interpretation of data measured using these techniques. The magnitude of the effect is not easily assessed as it will depend on the relative concentrations of  $HNO_3$  and  $N_2O_5$ , which, in turn, depend on numerous other factors such as the lifetime of  $NO_3$  and will vary with levels of biogenic VOCs,  $NO_x$ , and with altitude and season.

Three: Although  $N_2O_5$  is the acid anhydride of  $HNO_3$  it does not behave chemically in an identical manner. As discussed in the paper,  $N_2O_5$  can react with particle chloride and produce  $ClNO_2$  which is photolysed in the morning, reforming  $NO_2$  and activating a halogen radical. So it is incorrect to assume  $N_2O_5$  measured as gas-phase nitrate is lost from the atmosphere by deposition at the same rate as nitric acid especially considering that  $N_2O_5$  is a “nighttime only” trace gas for which rates of turbulent transfer apply even if the surface resistance is (like  $HNO_3$ ) not limiting.

It is incorrect to measure the sum of  $HNO_3 + 2N_2O_5$  and call it  $HNO_3$ . Research should not be operational even if its outputs are used by policymakers.

Reviewer #1:

This is a short paper that identifies a potentially important artifact in current instrumentation for measurements of gas phase  $HNO_3$ . The authors suggest that  $N_2O_5$ , which can hydrolyze readily to form soluble nitrate, may appear as nitrate in wet-denuder type instruments that are used to sample  $HNO_3$  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  $N_2O_5$  and a wet denuder sampler that measures  $HNO_3$ . The data are consistent with a large interference in the determined  $HNO_3$  from the measured  $N_2O_5$ . The authors further note that interpretation of artifact  $N_2O_5$  as  $HNO_3$  on such instruments would potentially skew the understanding of nitrate deposition, since  $N_2O_5$  undergoes atmospheric chemical processes other than wet or dry deposition to produce soluble nitrate.

The suggestion that  $N_2O_5$  is large in comparison to  $HNO_3$  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

We thank the reviewer for their comments and suggestions. We answer each comment below.

General comments.

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  $N_2O_5$  signal, expressed as equivalent nitrogen mass, is always less than the reported  $HNO_3$  and shows temporal peaks during the same time periods. Since

N<sub>2</sub>O<sub>5</sub> is known to undergo heterogeneous uptake, it is plausible or even likely that a part of the observed signal is indeed from N<sub>2</sub>O<sub>5</sub>. However, the authors do not present data that would indicate the efficiency of N<sub>2</sub>O<sub>5</sub> 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 N<sub>2</sub>O<sub>5</sub> standard to both instruments in the absence of HNO<sub>3</sub> (or with a known HNO<sub>3</sub> 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.

We agree with the reviewer that as we do not show the efficiency of detection of N<sub>2</sub>O<sub>5</sub> with wet rotating denuder-IC and therefore this is an upper limit to the detection. However, the reaction of N<sub>2</sub>O<sub>5</sub> on aqueous surfaces is well known and we are confident in assigning the nocturnal increase in gas-phase NO<sub>3</sub><sup>-</sup> to the presence of N<sub>2</sub>O<sub>5</sub>. However, we will make it clear in the text that a detection efficiency of 1 for N<sub>2</sub>O<sub>5</sub> is an upper limit.

We did not complete a laboratory study of the detection efficiency of N<sub>2</sub>O<sub>5</sub> for logistical reasons. The instruments were only operational in the same location during the field study where it was not a trivial matter to setup a source of N<sub>2</sub>O<sub>5</sub> for both instrument to sample. Both instruments had prior commitments during the post campaign period.

Specific comments.

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 HNO<sub>3</sub> + 2N<sub>2</sub>O<sub>5</sub>, rather than HNO<sub>3</sub> + N<sub>2</sub>O<sub>5</sub>.

We agree.

Page 7490. Bottom: Why is N<sub>2</sub>O<sub>5</sub> hydrolysis left out of HNO<sub>3</sub> sources? It's much more important than NO<sub>3</sub> + DMS.

This is an oversight. The reviewer is, of course, correct and we amend the discussion of the chemistry as per R4 and R5.

Page 7491, line 5: "which is"

Corrected.

Page 7495, line 4: Worth noting here that that N<sub>2</sub>O<sub>5</sub> is equivalent to 2 NO<sub>3</sub><sup>-</sup> when sampled into a wet denuder since this was not made clear in the abstract.

We will make this clear.

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 N<sub>2</sub>O<sub>5</sub> is smaller than, but a significant fraction of, measured nitrate in MARGA. If there is a correlation between CRDS N<sub>2</sub>O<sub>5</sub> 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)?

The phrase “high correlation” was used as the variables are obviously correlated. We agree this can be misconstrued as a use of the word in mathematical fashion. We will amend this as the reviewer suggests. The comparison of the time series is enough to see that the variables are remarkable similar in their behaviour.

Page 7495, line 12: Statement not substantiated, but the authors could consider the existing literature data for HNO<sub>3</sub> and / or N<sub>2</sub>O<sub>5</sub> 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 N<sub>2</sub>O<sub>5</sub> during winter in the San Francisco Bay Area of the U.S. that would not likely constitute a significant interference for a nitrate instrument.

The important thing is the relative concentration of nitric acid and dinitrogen pentoxide. Wood et al measured N<sub>2</sub>O<sub>5</sub> but not HNO<sub>3</sub>. The authors estimate that the nighttime production of HNO<sub>3</sub> via N<sub>2</sub>O<sub>5</sub> was 9 times larger than the daytime production via OH and NO<sub>2</sub> and also estimate concentrations of nitric acid. The estimation of nitric acid of 1.4 to 4.1 ppbv was made assuming all NO<sub>3</sub><sup>-</sup> produced goes to the gas phase (an upper limit) and as the paper was published before the first field measurements of ClNO<sub>2</sub> and as a marine-influenced area it is likely that at least part of the estimate of nocturnal nitric acid would be ClNO<sub>2</sub>. After considering these factors we are rapidly in the ballpark of issues for nitric acid measurements which are sensitive to N<sub>2</sub>O<sub>5</sub>. However all of these points are uncertain and we do not feel we advance the discussion much by more speculation. Further measurements need to be made. We will amend the statement to make it more general.

Page 7496, top: The influence of N<sub>2</sub>O<sub>5</sub> on nylon filter based systems for HNO<sub>3</sub> measurement seems as though it would be rather easy to test in the laboratory. This suggests an important direction for future work.

We agree and we state in the conclusions the importance of quantifying possible artefacts in filter-based sampling systems.

Page 7496, lines 18-21: The statement is not quite correct – largest N<sub>2</sub>O<sub>5</sub> mixing ratios have been observed in summertime conditions due to the generally faster rate of NO<sub>3</sub> oxidation during warm conditions. Large N<sub>2</sub>O<sub>5</sub> mixing ratios may also be observed in winter for the reasons stated, but they do not necessarily exceed summer mixing ratios.

We assume the reviewer is referring to the rate of NO<sub>2</sub> + O<sub>3</sub> as NO<sub>3</sub> is already in the highest oxidation state. And then we assume that they are referring to the higher concentrations of O<sub>3</sub> in the summer?? In summer NO<sub>3</sub> is more efficiently reduced by biogenic hydrocarbons and thus the production of N<sub>2</sub>O<sub>5</sub> is reduced. In winter, the ratio of N<sub>2</sub>O<sub>5</sub> to NO<sub>3</sub> will (for a given NO<sub>2</sub> concentration) be larger due to the more favourable equilibrium constant (lower temperature). However, there are too many variables and the only way to categorically tackle this issue to go and make measurements of HNO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>. We will amend the statement to make it less categorical.

Page 7496, lines 25-27: Here again, N<sub>2</sub>O<sub>5</sub> hydrolysis is omitted as a source of HNO<sub>3</sub>. As above, the reason for this omission is not clear. The discussion that follows seems to imply that N<sub>2</sub>O<sub>5</sub> can only serve as a source for condensed phase NO<sub>3</sub><sup>-</sup>, which is not the case. Even if N<sub>2</sub>O<sub>5</sub> reacts

heterogeneously, the resulting inorganic nitrate partitions to either the gas or aerosol phase depending on the thermodynamics of the aerosol (or ground) surface.

We will amend this as for the comment earlier and R4 and R5.

Page 7497, lines 9-19: The discussion of ClNO<sub>2</sub> and NO<sub>x</sub> recycling is useful. However, the discussion does not consider the direct recycling of NO<sub>x</sub> by N<sub>2</sub>O<sub>5</sub>, which may survive in large quantities through to sunrise to recycle NO<sub>x</sub> (see, for example, Perner et al., JGR, 90, 3807-3812, 1985; Brown et al. JGR, 108, D94299, 2003)

We note that (in the boundary layer) the lifetime of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> is generally much shorter than the duration of a night and that a large fraction of NO<sub>x</sub> converted to N<sub>2</sub>O<sub>5</sub> will often not be converted to NO<sub>x</sub> at sunrise. However, we will include this aspect of the chemistry in the discussion.

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 NO<sub>3</sub> and calculated N<sub>2</sub>O<sub>5</sub> 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.

These papers do not contain simultaneous measurements of HNO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, only estimates of N<sub>2</sub>O<sub>5</sub> from NO<sub>3</sub> measurements. The magnitude of the artefact crucially depends on the relative amount of the two different species and we are not convinced that more discussion of it aids our main point.

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 HNO<sub>3</sub> \*is\* N<sub>2</sub>O<sub>5</sub>, or just that it likely comes from N<sub>2</sub>O<sub>5</sub>?

We think that it is very likely that it comes from N<sub>2</sub>O<sub>5</sub>. We will amend the statement.

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 N<sub>2</sub>O<sub>5</sub> interference should be recognized and quantified through better measurements of all reactive N species, as they state at the end of this paragraph.

We agree. We use both reviewers comment to improve the recommendations for future work.

#### Anonymous reviewer #2

This paper presents co-located data on measurements of N<sub>2</sub>O<sub>5</sub> and ‘HNO<sub>3</sub>’ for an upland site in central Europe, and shows that a significant fraction of ‘HNO<sub>3</sub>’ measured using a rotating wet denuder might have originated from sampling N<sub>2</sub>O<sub>5</sub>. The paper is clearly written, but some statements are made without justification (see below). A distinction also needs to be made more clearly about the ‘fitness for purpose’ of different measurement techniques – if an estimate of dry deposition is required (for example) the inclusion of N<sub>2</sub>O<sub>5</sub> as ‘HNO<sub>3</sub>’ is probably irrelevant, given that both molecules would be expected to deposit at rates limited only by turbulence. If, however,

measurements are made to elucidate processes occurring in the atmosphere at short time scales (e.g. dissociation of  $\text{NH}_4\text{NO}_3$ ) then clearly there is an issue to be addressed by the use of 'HNO<sub>3</sub>' data rather than 'true' HNO<sub>3</sub> data.

We thank the reviewer for their comments, suggestions and corrections.

Specific comments

7491 L6: I'm not sure whether it is 'relegated as a minor player', or completely ignored! However, for the purpose of estimating dry deposition, this may be irrelevant (see above)

The extent of irrelevancy is unknown and in addition it is still dangerous to report these measurements as if they are HNO<sub>3</sub> as this makes comparisons with models problematic (see replies to reviewer 1).

L14: not so much considered as 'trivial' as recognised as being included within what is measured as 'HNO<sub>3</sub>', i.e. its effective composition after dry deposition and reaction with surface water

N<sub>2</sub>O<sub>5</sub> is not HNO<sub>3</sub>. Unlike HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub> is not present during the day and does not react like HNO<sub>3</sub>.

7492: I4: N<sub>2</sub>O<sub>5</sub> also plays an important role as a reservoir for NO<sub>3</sub> radicals; ignoring its presence would lead to overestimation of NO<sub>3</sub> concentration and reactions in the night-time atmosphere, particularly when considering vertical gradients.

We agree. NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> mixing ratios are strongly coupled (they are in equilibrium determined by temperature and NO<sub>2</sub> levels) and the loss of either one will impact on the concentration of the other.

7493: I17: are there also datasets from measurements made using URG or other parallel plate denuder systems?

There is a technical report cited in this article by Markovic et al. We are not aware of any other URG datasets.

7494 I19: do the authors mean 'standard solutions' or 'internal standards'? The latter are routinely used in MARGA systems, but the former are not used routinely.

We mean standard solutions. An internal standard was present in every sample. Standard additions were injected in addition.

7495 I3: perhaps describe HNO<sub>3</sub> here as 'HNO<sub>3</sub>' given the likely inclusion of N<sub>2</sub>O<sub>5</sub> in these data. How much HNO<sub>3</sub> was lost in the inlet to the MARGA, particularly on the PM<sub>10</sub> cyclone? Was the inlet heated at all? Even PTFE removes HNO<sub>3</sub> from an air stream, particularly if coated with aerosol particles. How often was the inlet cleaned? This would have the effect in the dataset of overestimating the contribution from N<sub>2</sub>O<sub>5</sub> to 'HNO<sub>3</sub>'.

The inlet system was cleaned on the 20<sup>th</sup> August. We did not measure the losses of reactive gases on the inlet system. We observed the artefact at the beginning of the campaign, throughout the campaign and after inlet cleaning. We observed no evidence to support the statement made regarding a change in the relative losses of HNO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>. As far as we know, losses in these systems are not checked routinely on campaigns other than by coarse comparison with filters, which is inappropriate as both methods may suffer from the N<sub>2</sub>O<sub>5</sub> artefact.

L13: however, in winter ozone concentrations are lower and NO emissions may be greater, so there may be more NO around to destroy NO<sub>3</sub>, leading to lower N<sub>2</sub>O<sub>5</sub> formation. Some example calculations/quantification would be helpful to develop this line of argument.

Apart from in highly polluted air masses or very close to NO emission sources, NO is titrated at night (by O<sub>3</sub>) to NO<sub>2</sub> and will therefore not represent a loss of NO<sub>3</sub>. The shorter lifetimes of NO<sub>3</sub> in summer due to biogenic emissions (e.g. of terpenes) will often (but not always) outweigh the NO effect.

L25: this may not be the largest problem with alkaline denuders, which probably sample HONO with similar efficiency as HNO<sub>3</sub>, the HONO being rapidly oxidised to HNO<sub>3</sub> on the denuder by ozone, so that the sample when analysed contains information from HNO<sub>3</sub>, HONO (and N<sub>2</sub>O<sub>5</sub>). In rural areas, HONO concentrations may be similar those of HNO<sub>3</sub> at night.

We report an artefact due to N<sub>2</sub>O<sub>5</sub> sampling which is based on our measurements of N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub>. As we made no measurements of HONO, we cannot comment on the likelihood of this potential, further artefact when using alkaline denuders.

7496 I6: the same problem would also arise for filters with a high particle loading

We agree.

L20: some quantitative calculations here would be helpful to develop the argument (see above)

We are not sure what the reviewer is referring to. The production and loss terms for N<sub>2</sub>O<sub>5</sub> depend on the particular character of the measurement location. It would be a difficult task to cover all possible combinations of variables and is beyond the scope of this paper.

L25: they are 'systematically incorrect' but may be adequate for purpose if all that is required is an estimate of dry deposition.

This may or may not be true, but again this is the point of the paper. N<sub>2</sub>O<sub>5</sub> is not HNO<sub>3</sub> (they only co-exist at night) and under certain circumstances does not deposit as HNO<sub>3</sub>. In any case measurements using techniques sensitive to both NO<sub>y</sub> species should be reported as the sum and not just HNO<sub>3</sub>.

7497 I8: this generalisation is weak – the relative rate of removal to aerosol surface or to the land surface will depend on turbulence regime, aerosol loading, humidity etc.

We will refer to previous measurements by Crowley et al. where this was the case and make the statement less general.

L11: why does the sea-salt need to be 'aged'? Does the reaction not occur on fresh sea-salt particles? ClNO<sub>2</sub> is not 'soluble' in liquid water, but what is its solubility in droplets with high ionic strength and small radius, where surface energies and solubility reactions become very different from those in the bulk phase of pure water? Does ClNO<sub>2</sub> have a role in producing HCl in droplets?

Laboratory experiments have shown that ClNO<sub>2</sub> is released at 100 % (per N<sub>2</sub>O<sub>5</sub> taken up) if sufficient chloride is available. Only in acidic particles is there some evidence for further transformation to Cl<sub>2</sub>. Our larger MARGA dataset in conjunction with mass spectrometric measurements of ClNO<sub>2</sub> at this site are not consistent with an artefact from ClNO<sub>2</sub> in the measurements of gas-phase or particle-phase chloride.

L15: it's not clear how this pathway necessarily leads to a longer atmospheric lifetime for NO<sub>y</sub> – the argument is presumably that reaction to ClNO<sub>2</sub> leads to transfer from the condensed phase to the gas phase, thereby preventing loss as nitrate in wet deposition: The lifetime of NO<sub>y</sub> presumably reflects the relative importance of wet and dry deposition processes.

NO<sub>x</sub> is reproduced by the production of ClNO<sub>2</sub> via photolysis. We reform a gas-phase species, i.e. NO<sub>2</sub>, with a longer lifetime than HNO<sub>3</sub> with respect to deposition. This increases the lifetime of NO<sub>y</sub>.  
NO<sub>y</sub> = NO<sub>2</sub> + NO + ClNO<sub>2</sub> + N<sub>2</sub>O<sub>5</sub> + HNO<sub>3</sub> etc....

L18: why will overestimation of HNO<sub>3</sub> lead to higher deposition estimates if N<sub>2</sub>O<sub>5</sub> deposits from the atmosphere to the surface at the same rate as HNO<sub>3</sub>, as suggested? Is the rate of deposition of 'HNO<sub>3</sub>' different from (HNO<sub>3</sub>+N<sub>2</sub>O<sub>5</sub>)?

If deposition rates are calculated from a measurement of the sum of HNO<sub>3</sub> + 2N<sub>2</sub>O<sub>5</sub> and it is assumed that it all deposits at the same rate as HNO<sub>3</sub> then the deposition rate will be over-estimated. The N<sub>2</sub>O<sub>5</sub> measured will not necessarily deposit as was pointed out in the discussion of the chemistry. It can reform NO<sub>2</sub> via reaction with particle chloride and at sunrise via NO<sub>3</sub> photolysis. In addition, N<sub>2</sub>O<sub>5</sub> is a nocturnal species and any contribution it makes towards total N deposition occurs in the night where, in general, less turbulence is experienced resulting in decreased relative deposition rates and making model parameterizations more problematic.

7498 L8: see above – it certainly misrepresents the composition of 'HNO<sub>3</sub>' but may make little difference (if any) to the deposition rates of oxidised N.

"May" is the important word here and we refer to the three points at the beginning. Again, N<sub>2</sub>O<sub>5</sub> is not HNO<sub>3</sub> and the misrepresentation of one as the other will have "knock-on" effects in models of chemistry when comparing to measurements. Models will need to compare their output of 2N<sub>2</sub>O<sub>5</sub> + HNO<sub>3</sub> with measurements which "may" have significant effects. We do not know and measurements of HNO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> using specific analytical techniques should be made in a number of locales and seasons for this issue to be clarified.

L20: and HONO (see above)

We didn't measure HONO and so it is beyond the scope of this paper.

Technical comments:

7491 I5: which is frequently

We will amend this.