

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

Anonymous Referee #2

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This paper presents co-located data on measurements of N₂O₅ and ‘HNO₃’ for an upland site in central Europe, and shows that a significant fraction of ‘HNO₃’ measured using a rotating wet denuder might have originated from sampling N₂O₅. 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 N₂O₅ as ‘HNO₃’ 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.

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dissociation of NH₄NO₃) then clearly there is an issue to be addressed by the use of ‘HNO₃’ data rather than ‘true’ HNO₃ data.

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)

L14: not so much considered as ‘trivial’ as recognised as being included within what is measured as ‘HNO₃’, i.e. its effective composition after dry deposition and reaction with surface water

7492: I4: N₂O₅ also plays an important role as a reservoir for NO₃ radicals; ignoring its presence would lead to overestimation of NO₃ concentration and reactions in the night-time atmosphere, particularly when considering vertical gradients.

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

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.

7495 I3: perhaps describe HNO₃ here as ‘HNO₃’ given the likely inclusion of N₂O₅ in these data. How much HNO₃ was lost in the inlet to the MARGA, particularly on the PM₁₀ cyclone? Was the inlet heated at all? Even PTFE removes HNO₃ 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 N₂O₅ to ‘HNO₃’.

L13: however, in winter ozone concentrations are lower and NO emissions may be greater, so there may be more NO around to destroy NO₃, leading to lower N₂O₅ formation. Some example calculations/quantification would be helpful to develop this line of argument.

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L25: this may not be the largest problem with alkaline denuders, which probably sample HONO with similar efficiency as HNO₃, the HONO being rapidly oxidised to HNO₃ on the denuder by ozone, so that the sample when analysed contains information from HNO₃, HONO (and N₂O₅). In rural areas, HONO concentrations may be similar to those of HNO₃ at night.

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

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

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

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.

L11: why does the sea-salt need to be 'aged'? Does the reaction not occur on fresh sea-salt particles? ClNO₂ 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 ClNO₂ have a role in producing HCl in droplets?

L15: it's not clear how this pathway necessarily leads to a longer atmospheric lifetime for NO_y – the argument is presumably that reaction to ClNO₂ leads to transfer from the condensed phase to the gas phase, thereby preventing loss as nitrate in wet deposition. . .but again, the lifetime of NO_y then presumably reflects the relative importance of wet and dry deposition processes.

L18: why will overestimation of HNO₃ lead to higher deposition estimates if N₂O₅ deposits from the atmosphere to the surface at the same rate as HNO₃, as suggested? Is the rate of deposition of 'HNO₃' different from (HNO₃+N₂O₅)?

7498 L8: see above – it certainly misrepresents the composition of 'HNO₃' but may
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make little difference (if any) to the deposition rates of oxidised N.

L20: and HONO (see above)

Technical comments:

7491 I5: which is frequently

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