

**The detection of
nocturnal N₂O₅ as
HNO₃**

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**The detection of nocturnal N₂O₅ as HNO₃
by alkali- and aqueous-denuder
techniques**

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Abstract

The almost total anthropogenic control of the nitrogen cycle has led to wide ranging trans-national and national efforts to quantify the effects of reactive nitrogen on the environment. A number of monitoring techniques have been developed for the measurement of nitric acid and subsequent estimation of nitrogen deposition within large networks and for process studies on shorter measurement campaigns. We discuss the likelihood that many of these techniques are sensitive to another important gas-phase component of oxidized nitrogen; dinitrogen pentoxide (N_2O_5). We present measurements using a MARGA wet annular denuder device alongside measurements of N_2O_5 with a discussion of evidence from the laboratory and the field which suggests that alkali- and aqueous-denuder measurements are sensitive to the sum of $\text{HNO}_3 + \text{N}_2\text{O}_5$. Nocturnal data from these denuder devices should be treated with care before using HNO_3 concentrations derived from these data. This is a systematic error which is highly dependent on ambient conditions and is likely to cause systematic misinterpretation of datasets in periods where N_2O_5 is significant proportion of NO_y . It is also likely that deposition estimates of HNO_3 via data obtained with these methods is compromised to greater or lesser extents depending on the season and environment of the sampling location.

1 Introduction

Nitric acid (HNO_3) is an important fraction of gas-phase oxidised nitrogen and has been monitored and measured for a number of years as part of national and trans-national government sponsored efforts to understand the important issue of eco-system acidification and transboundary air pollution (Sutton et al., 2011). HNO_3 can be considered to be the end-point for the gas-phase chemical processing of NO_x ($\text{NO}_2 + \text{NO}$) via the reaction of NO_2 with the hydroxyl radical (OH) in the troposphere and the reaction of the nitrate radical, NO_3 , with dimethyl sulphide (DMS) (Yvon et al., 1996) and a number

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of VOC species (Finlayson-Pitts and Pitts, 1997). HNO_3 is efficiently deposited on surfaces (Huebert and Robert, 1985) or can partition into the particulate phase in the presence of alkaline dust, sea salt or excess ammonia (Wexler and Seinfeld, 1992). However, not all NO_x is lost from the atmosphere via formation of HNO_3 .

Dinitrogen pentoxide (N_2O_5) is an important fraction of oxidised nitrogen which frequently relegated as a minor player with respect to its contribution to N deposition. Methodological descriptions of monitoring techniques for HNO_3 rarely mention N_2O_5 (e.g. Tang et al., 2009; Bytnerowicz et al., 2001; Markovic et al., 2012; Dong et al., 2012; Thomas et al., 2009) and do not consider the possibility that it may cause measurement interferences despite its ubiquity and reactivity. This may be for a number of reasons, including the technical challenges in its detection and, in the main, nocturnal occurrence. It is also true that, until relatively recently, the vast majority of N_2O_5 was thought to end up as nitrate and, therefore, it is possible that its role was considered trivial. This may be true for wet and dry deposition; however, these are not sufficient reasons for its neglect when considering the mechanisms at work within the environmental nitrogen cycle for, as we shall see, the mechanisms of N_2O_5 production, its fate, and its temporal occurrence differ markedly from HNO_3 .

N_2O_5 is formed via a number of steps beginning with the reaction of NO_2 with O_3 :



In the daytime NO_3 is rapidly photolysed reforming NO or NO_2 , or reacts with NO to reform NO_2 . However, during the night, when photolysis frequencies are low and NO has been removed by reaction with O_3 , NO_3 can react with NO_2 to form N_2O_5 which is in thermal equilibrium with its precursors:



With the equilibrium given by,

$$[\text{N}_2\text{O}_5] = K_{\text{eq}}[\text{NO}_3][\text{NO}_2] \quad (1)$$

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K_{eq} is strongly dependent on temperature, varying with $\sim \exp^{(11000/T)}$ with cold conditions favouring the formation of N₂O₅. At an NO₂ mixing ratio of 1 ppbv and temperature of 270 K the ratio of N₂O₅ to NO₃ is about 300 : 1 which drops to a ratio of approximately 1 : 1 at a temperature of 295 K (Brown and Stutz, 2012). Losses of N₂O₅ can be divided into direct and indirect losses. Indirect losses are processes resulting in the loss of precursor species, e.g. reactions of NO₃ with biogenic VOCs, or reaction with NO, which drive the equilibrium (1) to the right. Direct losses of N₂O₅ are mainly heterogeneous hydrolysis on particles (Brown and Stutz, 2012) and other surfaces, or the reaction with aqueous particle chloride (Finlayson-Pitts et al., 1989), the total uptake efficiency depending strongly on the particle composition (Bertram et al., 2009; Chang et al., 2011):



ClNO₂ is photolysed in the morning following production, reforming NO_x in addition to Cl radical. Ambient measurements of the formation of ClNO₂ are relatively recent and scarce. However, they show the importance of the chloride channel of the heterogeneous loss of N₂O₅ in the marine (Osthoff et al., 2008; Riedel et al., 2012), continental North American (Thornton et al., 2010; Mielke et al., 2011), and Western European environments (Phillips et al., 2012).

A number of studies and monitoring networks have used data derived from denuder sampling techniques for both the estimation of acid deposition and the investigation of gas-particle dynamics of nitrogen in the atmosphere. In North America, the Clean Air Status and Trends Network (CASTNET) (<http://epa.gov/castnet/javaweb/index.html>) measures nitric acid data by both nylon filter packs (Bytnerowicz et al., 2001) and, more recently, is assessing the performance of the MARGA system for the measurement of fluxes and concentrations reactive gases and aerosols (Cowen et

al., 2011). In Asia, the Acid Deposition and Monitoring Network in East Asia (EANET) (<http://www.eanet.cc/index.html>) uses denuder methods to monitor nitric acid concentrations and estimate acid deposition. In the UK, the United Kingdom Eutrophying and Acidifying Pollutants (UKEAP) network uses monthly alkaline-denuder samplers to measure concentrations of nitric acid and estimate acid deposition. Across Europe as a whole, the NitroEurope project (Sutton et al., 2011) and European Monitoring and Evaluation Programme (EMEP) under the Convention of Long-range Transboundary Air Pollution use network of filter-pack systems and denuders in addition to a number of intensive monitoring periods (Aas et al., 2012) using higher time-resolution techniques to estimate acid deposition and study the processes controlling nitrogen chemistry and dynamics in the atmosphere. Data from these programs is freely available.

Denuder methods for the detection of nitric acid using the higher time resolution rotating annular denuder type measurements are becoming more common. Recent datasets obtained with the GRAEGOR/MARGA and used for the evaluation of models and the investigation of gas-to-particle partitioning of nitrate have been reported by a number of authors (Aan de Brugh et al., 2012; Aas et al., 2012; Makkonen et al., 2012; Schaap et al., 2011). The hourly time resolution of these datasets has a number of advantages over the monthly and weekly data available from monitoring networks, allowing researchers to investigate in more detail the chemistry and dynamics of nitrogen in the lower atmosphere.

2 Methods

We present data measured during August 2012 from the Taunus Observatory, Kleiner Feldberg, to the NW of Frankfurt, Germany. The Taunus Observatory is situated at the summit of the Kleiner Feldberg, 825 m above sea-level, just north of the heavily populated Rhein-Main area of South-western Germany. The site has been described in detail by Handisides (2001). A MARGA 1S annular denuder system was deployed on top of the observatory roof, approximately 3 m from a cavity ring-down absorption

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spectrometer (CRDS) system for the measurement of N_2O_5 previously deployed at this location in both 2008 and 2011 (Crowley et al., 2010b; Phillips et al., 2012). The instruments were deployed as part of larger study of the heterogeneous chemistry of N_2O_5 .

2.1 N_2O_5 by off-axis cavity ring-down spectroscopy

The N_2O_5 system is a two-channel off-axis cavity ring-down system (OA-CRDS) which detects NO_3 radical in one channel and the sum of N_2O_5 and NO_3 via thermal dissociation in the second channel. The instrument has been deployed on a number of previous occasions and is described in detail by (Crowley et al., 2010b). The concentration of N_2O_5 is calculated by subtraction and total uncertainty is estimated at 15 %.

2.2 Monitor for Aerosols and Gases in Ambient Air (MARGA)

The MARGA system is a commercialised version of the GRAEGOR analyser developed by ECN, Netherlands (Thomas et al., 2009; ten Brink et al., 2009) and produced by Applikon Analytical BV, the Netherlands. The methodology and instrument description is contained in references above and so a brief description of the method follows. The MARGA was operated as per the manufacturer instructions as it would usually be operated in the field. The air sample was drawn, at $1\text{ m}^3\text{ h}^{-1}$, through a short, $< 25\text{ cm}$ length of high density polyethylene (HDPE) tube, through a Teflon coated PM10 cut-off cyclone into a wet rotating denuder (WRD). The WRD consists of two concentric glass tubes wetted with IC grade water. The gases are efficiently denuded in the WRD, but the low mobility of particles prevents them from diffusing to the walls of the WRD. The air sample then enters the steam-jet aerosol collector (SJAC) where the water soluble particle fraction is condensed using steam and collected. The samples from both the WRD and SJAC are analysed on-line every hour using ion chromatography. Standard additions are made to determine the retention times of the analytes and to calibrate the analytical system.

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3 Results and discussion

3.1 Co-located MARGA HNO₃ and OA-CRDS N₂O₅

The time series of gas-phase HNO₃ detected as NO₃⁻ in the ion chromatograph and N₂O₅, both as N-equivalent mass, are plotted in Fig. 1, bottom panel. N₂O₅ mixing ratios were variable with peak concentrations of approximately 800 pptv. The nocturnal portion of the MARGA time series exhibits clear portions, see Fig. 2, with high correlation to the N₂O₅ series and on certain days, e.g. 16/17 August, the nocturnal MARGA signal is dominated, > 90%, by signal most likely arising from the hydrolysis of N₂O₅ in the denuder. This short series of data was obtained in the high summer with nocturnal temperatures ranging between 15 and 25 °C. Even in these summer conditions the average campaign contribution of N₂O₅ to the nocturnal MARGA HNO₃ signal is 17%. We expect the contribution to be higher in colder regions during the winter, with longer nights and lower NO₃ losses, both resulting in large N₂O₅ mixing ratios relative to HNO₃.

3.2 Alkaline denuder and filter methods

The absorption of constituents of ambient air by denuding technology followed by determination of the nitrate anion concentration is a frequent method for the determination of ambient HNO₃ concentrations. For example, the Nitro Europe (NEU) monitoring network using the DELTA denuder system (Tang et al., 2009) to determine monthly HNO₃ concentrations from which deposition maps are developed and against which dispersion models are tested (Flecharde et al., 2011). The acid gases are denuded by passing ambient air through alkali coated glass tubes and subsequently tested for nitrate anion by ion chromatography. The efficient removal of N₂O₅ (and NO₃) is likely to occur on the surface of alkali-coated denuder tubes resulting in the detection of two NO₃⁻ for every N₂O₅ sampled (Crowley et al., 2010a). It is therefore likely that a similar sensitivity to ambient N₂O₅ will be observed in datasets using denuder and filter

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pack techniques. We are uncertain as to whether systems which use nylon filters, e.g. CASTNET (Bytnerowicz et al., 2001), to remove HNO_3 for analysis are likely to suffer from N_2O_5 detection artefacts in ambient conditions, though we expect that this would be favoured at high relative humidity resulting in the presence of water leading to N_2O_5 hydrolysis on the filter surface.

3.3 Ambient measurements of N_2O_5

N_2O_5 is not a commonly measured trace gas owing to the technically difficult nature of its detection Brown and Stutz (2012) present a comprehensive review of the current state of knowledge with respect to NO_3 and N_2O_5 in the atmosphere. Ambient point measurements are usually achieved via absorption spectroscopy such as cavity ring-down spectroscopy (CRDS) (Schuster et al., 2009; Simpson, 2003; Brown et al., 2001). Mixing ratios of N_2O_5 are highly variable (e.g. Matsumoto et al., 2005; Ayers and Simpson, 2006; Osthoff et al., 2006; Brown et al., 2003, 2007). In regions with high concentrations of NO or VOCs, the steady-state concentration of N_2O_5 can be below the detection limit, e.g. < 1 pptv, of current analytical instrumentation (e.g. Rinne et al., 2012). However, in situations with long NO_3 lifetimes and low particle surface areas, atmospheric mixing fractions can exceed several ppbv (e.g. Phillips et al., 2012) tying up a significant proportion of NO_x . In general, large N_2O_5 mixing ratios are likely to be favoured in Northern Hemisphere winter owing to the longer nights, colder temperatures and high NO_2 mixing ratios along with lower emission rates of NO_3 scavengers such as terpenes.

3.4 The likely significance of the detection of N_2O_5 as HNO_3

The chemical processes which control the formation and loss of N_2O_5 and HNO_3 are not the same and therefore analytical techniques reporting N_2O_5 as HNO_3 are systematically incorrect. HNO_3 will be produced in the presence of NO_2 in periods, usually the daytime, with sufficient OH radical concentrations and, to lesser extent owing to the lower reactivity, at night via NO_3 reactions with VOCs. The resulting HNO_3 may partition into the aerosol phase or be lost via dry and wet deposition. Further chemical

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transformations do not occur in atmospherically relevant timescales. Conversely N₂O₅ is produced via Reaction (R2) which, owing to the rapid photolysis of the nitrate radical, only occurs with sufficient rate during periods of low sunlight, i.e. the night. N₂O₅ losses are, to some extent, similar to HNO₃. N₂O₅ is lost into the aqueous particle phase via hydrolysis producing NO₃⁻ and additionally lost via dry and wet deposition. Although daytime deposition velocities can be assumed to be similar (Zhang et al., 2012) and turbulence limited, N₂O₅ being present only at night, will be lost to dry deposition less favourably than to aqueous aerosol surface; the final deposition rate via hydrolysis being mediated via the losses of particle NO₃⁻. In addition, there is a second chemical pathway open to N₂O₅; N₂O₅ can react on the surface of Cl⁻ containing aqueous particles, e.g. aged sea salt or NH₄Cl, and produce ClNO₂ and HNO₃. ClNO₂ is not soluble and will leave the aqueous particle system. The nighttime losses of ClNO₂ are negligible and result in the survival of NO_x in an unreactive form until the morning. At daybreak ClNO₂ is photolysed, liberating an active chlorine radical and NO₂. The presence of this loss pathway for N₂O₅ will prolong the atmospheric lifetime of NO_y, and consequently the atmospheric transport distance, as it cycles back via the HO_x-NO_x chemical cycles. Measurements of HNO₃ that are sensitive to N₂O₅ will therefore, during periods of significant mixing ratios of N₂O₅, will over estimate the concentrations of HNO₃ and also the deposition of nitrate estimated from those measurements.

The consequences of the detection of N₂O₅ as an artefact within analytical systems are also dependent on the use to which the data is put, and the characteristics of the dataset. For example if, in high time resolution data, the diurnal pattern of HNO₃ concentration can be observed, then interpretations and comparison with models should not be affected during daylight hours or periods where NO₃ lifetimes are short. However, when weekly or monthly integrated concentrations of HNO₃ are measured and data is analysed on a seasonal basis, then some periods during the year may be affected to greater extents than others, for example in regions with low BVOC emissions and longer periods of darkness. We are not aware of long-term seasonal datasets

reporting the simultaneous contribution of N_2O_5 and HNO_3 to the total concentration of NO_y .

4 Conclusions

Aqueous denuders are sensitive to N_2O_5 in addition to HNO_3 and it is likely that alkaline denuders are at least partially sensitive to N_2O_5 . The main question remaining is to what extent are HNO_3 datasets using these techniques affected. The detection of the sum of $\text{N}_2\text{O}_5 + \text{HNO}_3$ as HNO_3 in systems using alkaline or aqueous denuder acid gas removal will likely result in the misrepresentation of seasonal and geographic pattern of gas-phase oxidised nitrogen deposition. The detection of N_2O_5 is a systematic error and it is possible that in some cases, in high time-resolution datasets, a large proportion of the HNO_3 signal is due to the detection of N_2O_5 . Data presented here show that a significant portion of nighttime HNO_3 measured via an aqueous annular denuder system is N_2O_5 . The warm-temperature summertime during which these measurements were obtained may be a lower limit of the effect as higher VOCs and warmer temperatures both militate against the formation of N_2O_5 . The campaign average of nocturnal N_2O_5 contribution was 17%, of the HNO_3 signal. Previous modelling work by (Riemer et al., 2003) found that the inclusion of N_2O_5 heterogeneous processes in chemical transport models “causes remarkable changes in the nocturnal concentrations of nitrogen containing species” illustrating the importance of N_2O_5 in the anthropogenic nitrogen cycle. In addition, the confusion of attempting to compare model output of HNO_3 with measures which are essentially the sum of two separate chemical entities with differing lifetimes and environmental fates may be partly the reason why modelled surface HNO_3 concentrations sometimes fail to agree with measurement data when model performance seems to be good for other forms of reactive N, such as NO_2 and NH_3 (Fowler et al., 2012). The standard network detection systems which use alkali and/or aqueous denuder systems should be tested for the effect of erroneous N_2O_5 detection, possible in addition to possible artefacts arising from newly observed molecules such as ClNO_2 . Owing to the fast photolysis of NO_3 , it would be possible to eliminate the

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contribution of the artefact N₂O₅ by using a daytime-only sampling methodology, although for many purposes this is unsatisfactory. Measurements of N₂O₅ should be made with a wide seasonal and geographical reach to assess the extent of monitoring bias and also to help validate the difficult task of modelling the contribution of NO₃ and N₂O₅ to the NO_y budget. It is also important that the chloride production channel of heterogeneous N₂O₅ loss should be correctly included in models assessing reactive N deposition and chemical transport of reactive nitrogen. The uncertainties associated with this process are still relatively large and consequently more work is needed to ascertain its importance, both with respect to the nitrogen cycle, but also for the effect of chlorine activation on atmospheric radical cycling in the troposphere.

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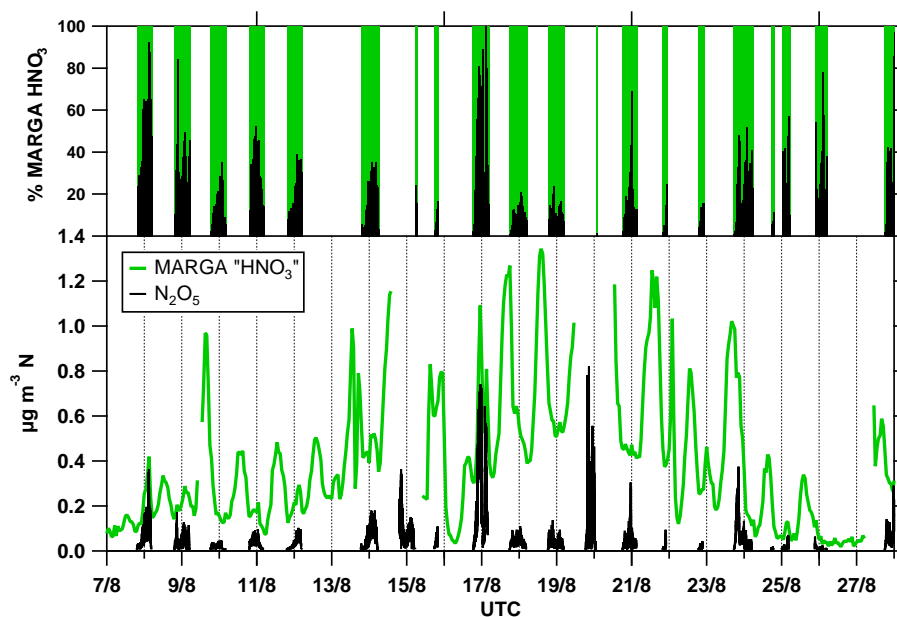


Fig. 1. Bottom panel: time series of N_2O_5 measured by CRDS and HNO_3 measured by MARGA during August 2012 from the Taunus observatory, Kleiner Feldberg, Germany. Top panel: nocturnal contribution of measured N_2O_5 to the MARGA HNO_3 signal and the calculated remaining contribution of HNO_3 when data was measured concurrently. There was no N_2O_5 data available on the nights of 13 and 27 August and partial data available on the nights of 16/22/23 August.

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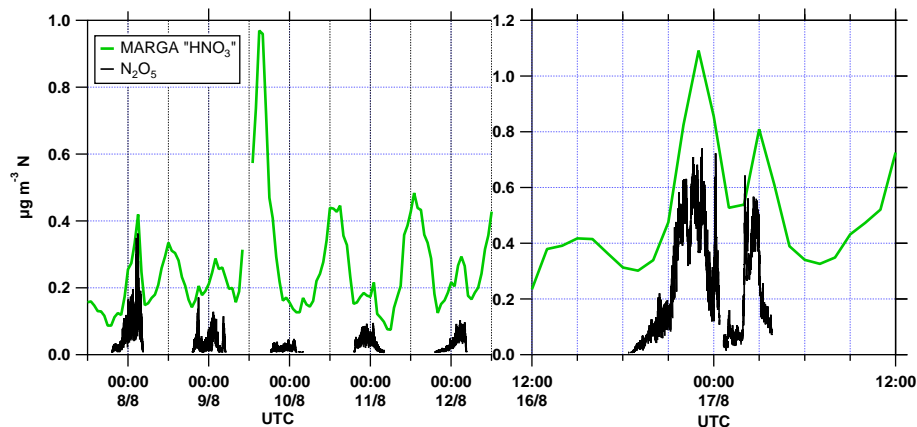


Fig. 2. Expanded time series of the effect of N_2O_5 on the detection of HNO_3 by an aqueous denuder technique. Left panel: 7 August to 12 August 2012. Right panel: 16 August to 17 August 2012.

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