



The detection of nocturnal N_2O_5 as HNO_3 by alkali- and aqueous-denuder techniques

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Received: 19 September 2012 – Published in Atmos. Meas. Tech. Discuss.: 15 October 2012

Revised: 22 January 2013 – Accepted: 29 January 2013 – Published: 5 February 2013

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 $\text{HNO}_3 + 2\text{N}_2\text{O}_5$. 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 and 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

ecosystem 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, the heterogeneous hydrolysis of N_2O_5 , the thermodynamic repartitioning of particle-phase nitrate, and the reaction of the nitrate radical, NO_3 , with dimethyl sulphide (DMS) (Yvon et al., 1996) and a number 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 is 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 HNO_3 /particle nitrate and, therefore, it is possible that its role was considered interchangeable with HNO_3 . 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 N₂O₅ production, its fate, and its temporal occurrence differ markedly from HNO₃.

N₂O₅ is formed via a number of steps beginning with the reaction of NO₂ with O₃:



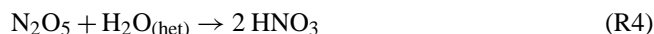
In the daytime NO₃ is rapidly photolysed reforming NO or NO₂, or reacts with NO to reform NO₂. However, during the night, when photolysis frequencies are low, and NO is removed by reaction with O₃, NO₃ can react with NO₂ to form N₂O₅, which is in thermal equilibrium with its precursors:



With the equilibrium given by

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

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 NO₃, e.g. via reaction with biogenic VOCs, or 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 the 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 (CAST-NET) (<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 (Monitor for Aerosols and Gases in Ambient Air, Metrohm Applikon BV, Netherlands) 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 MARGA-type systems and used for the evaluation of models and the investigation of gas-particle partitioning of nitrate have been reported by a number of authors (Aan de Brugh et al., 2012; Twigg et al., 2011; 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 southwestern 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 spectrometer (CRDS) system for the measurement of N₂O₅, 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 a larger study of the nocturnal chemistry of NO₃ and N₂O₅.

2.1 N₂O₅ by off-axis cavity ring-down spectroscopy

The N₂O₅ system is a two-channel off-axis cavity ring-down system (OA-CRDS) which detects the NO₃ radical in one channel and the sum of N₂O₅ and NO₃ 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 N₂O₅ 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 Metrohm Applikon BV, 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 m³ h⁻¹, through a short, < 25 cm length of high density polyethylene (HDPE) tube, through 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 online every hour using ion chromatography. The detection system is continuously calibrated by the use of an internal standard of LiBr. In addition, before starting the ambient measurements standard solutions were injected to check the retention times and the analytical system. The MARGA system measures very reactive analytes and therefore care must be taken with the inlet systems as significant losses of gases such as HNO₃ can occur. Our inlet system including cyclone were cleaned after approximately 2 weeks of operation.

3 Results and discussion

3.1 Co-located MARGA HNO₃ and OA-CRDS N₂O₅

The time series of gas-phase HNO₃ detected as NO₃⁻, referred to subsequently as the nitrate anion, 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 a distinct similarity to the N₂O₅ series and on certain days, e.g. 16/17 August, the nocturnal MARGA signal is dominated, > 90%, by signal most

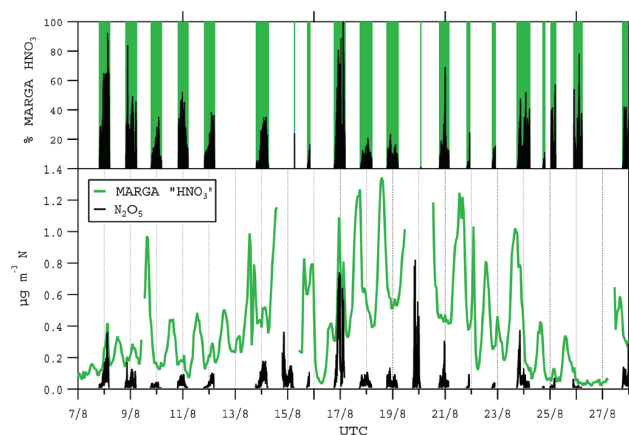


Fig. 1. Bottom panel: time series of N₂O₅ measured by CRDS and “HNO₃” measured by MARGA during August 2012 from the Taunus observatory, Kleiner Feldberg, Germany. Top panel: nocturnal contribution of measured N₂O₅ to the MARGA HNO₃ signal and the calculated remaining contribution of HNO₃ when data was measured concurrently. There was no N₂O₅ data available on the night of the 13 August and partial data available on the nights of the 14/22/23 August.

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 Celsius. Even in these summer conditions, the average campaign contribution of N₂O₅ to the nocturnal MARGA HNO₃ signal is 17% assuming a detection efficiency of 1 for N₂O₅ and each N₂O₅ molecule captured resulting in 2 NO₃⁻ ions detected. It is possible that in colder regions during winter, with longer nights and lower NO₃ loss rates, that a large N₂O₅ mixing ratio relative to HNO₃ will be encountered.

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 (Flechard 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 pack techniques. We are uncertain as to whether systems which use nylon filters, e.g. CASTNET (Bytnerowicz et al., 2001), to

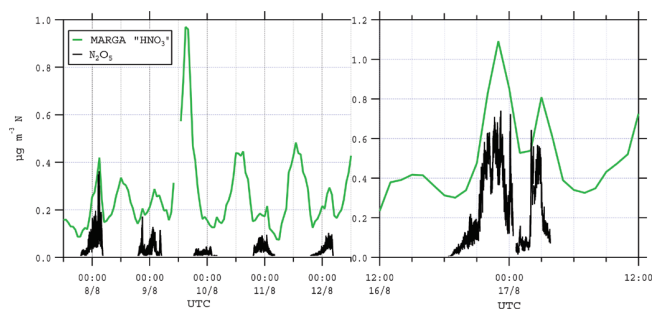


Fig. 2. Expanded time series of the effect of N₂O₅ on the detection of HNO₃ by an aqueous denuder technique. Left panel: 7 August to 12 August 2012. Right panel: 16 to 17 August 2012.

remove HNO₃ for analysis are likely to suffer from N₂O₅ 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 N₂O₅ hydrolysis on the filter surface.

3.3 Ambient measurements of N₂O₅

N₂O₅ 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 NO₃ and N₂O₅ 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 N₂O₅ 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 N₂O₅ 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 NO₃ 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. It is possible that during the cold, long, polluted northern hemisphere night, with relatively high concentrations of NO_x and O₃ and low concentrations of BVOCs, that N₂O₅ makes up a significant proportion of Σ (HNO₃ + 2N₂O₅).

3.4 The likely significance of the detection of N₂O₅ as HNO₃

The chemical processes which control the formation and loss of N₂O₅ and HNO₃ are not the same and therefore analytical techniques reporting N₂O₅ as HNO₃ are systematically incorrect. HNO₃ will be produced in the presence of NO₂ in periods, usually the daytime, with sufficient OH radical concentrations and, to lesser extent owing to the lower reactivity, at night via NO₃ reactions with VOCs. The resulting HNO₃

may partition into the aerosol phase or be lost via dry and wet deposition. Further chemical 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 HNO₃/NO₃⁻ and additionally lost via dry and wet deposition. Although daytime deposition velocities have been assumed to be similar (Zhang et al., 2012) and turbulence limited, N₂O₅ being present only at night, will be lost to dry deposition in addition to losses on aqueous aerosol surfaces; 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. 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. In addition to the recycling of NO_x via ClNO₂, N₂O₅ may itself recycle NO_x. The rapid photolysis of NO₃ at sunrise will drive the thermolysis equilibrium towards the formation of NO_x. Measurements of HNO₃ which are sensitive to N₂O₅ will therefore, during periods of significant mixing ratios of N₂O₅, over-estimate the concentrations of HNO₃ and over-estimate the contribution of HNO₃ to the total nitrate deposition.

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 N₂O₅ and HNO₃ to the total concentration of NO_y. It is therefore important that the response of the various nitric acid sampling systems to dinitrogen pentoxide is quantified and published.

4 Conclusions

Aqueous denuders are very likely sensitive to N₂O₅ in addition to HNO₃, and it is likely that alkaline denuders are at least partially sensitive to N₂O₅. The main question remaining is to what extent are HNO₃ datasets using these techniques affected. The detection of the sum of N₂O₅ + HNO₃ as HNO₃ in systems using alkaline or aqueous denuder acid gas removal may result in the misrepresentation of seasonal and geographic pattern of the contribution of HNO₃ to gas-phase oxidised nitrogen deposition. The detection of N₂O₅ is a systematic error and it is possible that in some cases, in high time-resolution datasets, a large proportion of the HNO₃ signal is due to the detection of N₂O₅. Data presented here show that a significant portion of nighttime HNO₃ measured via an aqueous annular denuder system is N₂O₅. 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 N₂O₅. The campaign average of nocturnal N₂O₅ contribution was 17%, of the HNO₃ signal. Previous modelling work by Riemer et al. (2003) found that the inclusion of N₂O₅ heterogeneous processes in chemical transport models “causes remarkable changes in the nocturnal concentrations of nitrogen containing species” illustrating the importance of N₂O₅ in the anthropogenic nitrogen cycle. In addition, the confusion of attempting to compare model output of HNO₃ 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 HNO₃ concentrations sometimes fail to agree with measurement data when model performance seems to be good for other forms of reactive N, such as NO₂ and NH₃ (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 N₂O₅ detection, possible in addition to possible artefacts arising from newly observed molecules such as ClNO₂.

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. It is also important that the sensitivity to the N₂O₅ is determined in all denuder-type systems before datasets of HNO₃ are published.

Acknowledgements. We thank H. Bingemer and the staff and department of Geophysics of the Johann Wolfgang Goethe-University, Frankfurt am Main for logistical support and the use of the Taunus Observatory. We also thank Johannes Schneider of the Max Planck Institute for Chemistry for the logistical aspects of the INUIT-TO campaign.

The service charges for this open access publication have been covered by the Max Planck Society.

Edited by: P. Herckes

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