

Total Peroxy Nitrates (Σ PNs) in the atmosphere: the Thermal Dissociation-Laser Induced Fluorescence (TD-LIF) technique and comparisons to speciated PAN measurements

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Abstract. Peroxyacetyl nitrate (PAN) and its chemical analogues are increasingly being quantified in the ambient atmosphere by thermal dissociation (TD) followed by detection of either the peroxyacyl radical or the NO_2 product. Here we present details of the technique developed at University of California, Berkeley which detects the sum of all peroxy nitrates (Σ PNs) via laser-induced fluorescence (LIF) of the NO_2 product. We review the various deployments and compare the Berkeley Σ PNs measurements with the sums of PAN and its homologue species detected individually by other instruments. The observed TD-LIF Σ PNs usually agree to within 10% with the summed individual species, thus arguing against the presence of significant concentrations of unmeasured PAN-type compounds in the atmosphere, as suggested by some photochemical mechanisms. Examples of poorer agreement are attributed to a sampling inlet design that is shown to be inappropriate for high NO_x conditions. Interferences to the TD-LIF measurements are described along with strategies to minimize their effects.

1 Introduction

Peroxy nitrates (molecules of the form RO_2NO_2 , or PNs) are formed in the atmosphere from the association reaction of peroxy radicals (HO_2 , RO_2) with NO_2 , and can act as temporary reservoirs for NO_x ($=\text{NO}+\text{NO}_2$) resulting in the transport of NO_x far from source regions (e.g., Hudman, et al., 2004; Parrish, et al., 2004, 2009; Zhang, et al., 2008). PNs can be divided into two classes depending on the nature of the RO_2 group: peroxy acyl nitrates (denoted here as PANs, also called acyl peroxy nitrates or peroxy-carboxylic nitric anhydrides) where RO_2 is $\text{R}'\text{C}(\text{O})\text{OO}$, and non-acyl peroxy nitrates where RO_2 does not terminate with a peroxy-carboxylic group or is HO_2 . PANs have thermal stabilities characteristic of the $\text{RC}(\text{O})\text{OO}-\text{NO}_2$ bond, essentially independent of the nature of the R group (Roberts & Bertman, 1992), that lead to lifetimes of minutes to hours in the lower troposphere ($T > 287 \text{ K}$) and months in the upper troposphere ($T < 263 \text{ K}$). Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) are the most abundant, with PAN being generally 75 to 90 % of observed individual species (Roberts, 1990; Roberts et al., 1998; Roberts, et al., 2002). Non-acyl PNs have markedly shorter thermal lifetimes and have significant concentrations only in the colder regions of the atmosphere (Murphy et al., 2004; Roberts, 2007; Kim et al., 2007; Salawitch, et al., 2002; Browne, et al., 2010).



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Aldehyde oxidization and ketone photolysis are the typical precursors of PANs. These carbonyls are often secondary oxidation products (e.g., Singh, 1987, 2003), and relationships between concentrations of the generally observed PANs and the parent primary hydrocarbons have been explored (Roberts, et al., 2001; Roberts et al., 1998; Romero, et al., 2005; Cleary, et al., 2007; LaFranchi, et al., 2009). Photochemical oxidation mechanisms suggest that many other PNs may be formed in the atmosphere (Horowitz, et al., 1998; Bowman, et al., 2003; Cleary, et al., 2007). For example, a simple box model run using the isoprene oxidation sub-mechanism from the Master Chemical Mechanism (<http://mcm.leeds.ac.uk/MCM/>) (Saunders, et al., 2003) with isoprene and NO_x both at ppbv levels generates species other than PAN, PPN, and MPAN (methacryloyl peroxy-nitrate) that can be as much as 40% of the PANs total. These other PAN species are mostly oxygenated, primarily $\text{HOCH}_2\text{C}(\text{O})\text{OONO}_2$ for the isoprene case, whose formation reactions in the mechanism are stated to be “provisional”. Theoretical structure and rate calculations (Méreau, et al., 2001) do predict the precursor association reaction $\text{HOCH}_2\text{CO} + \text{O}_2 + \text{M} \rightarrow \text{HOCH}_2\text{C}(\text{O})\text{OO} + \text{M}$ to be much faster ($1.5 \times 10^7 \text{ s}^{-1}$ vs. $3 \times 10^4 \text{ s}^{-1}$ at 1 atm.) than the decomposition pathway $\text{HOCH}_2\text{CO} \rightarrow \text{CH}_2\text{OH} + \text{CO}$. Conversely, decomposition is predicted to be much more rapid for the case of $\text{HC}(\text{O})\text{CO}$, in agreement with the experiments of Orlando and Tyndall (2001).

There are a variety of aldehydes which have been measured for which the corresponding PAN has not yet been detected in the atmosphere (McClenny et al., 1998; Wedel, et al., 1998; Grossman, et al., 2003). For example, significant levels of nonanal have been measured in air impacted by biogenic emissions (Yokouchi, et al., 1990; Bowman, et al., 2003). Bowman, et al. (2003) complemented those measurements with laboratory studies of the peroxy-nonanyl nitrate yield to suggest that the higher molecular weight PANs could compose a significant fraction of the overall organic nitrogen. Additionally, Lewis, et al. (2000) suggested that a substantial amount of chemically stable, physically volatile, C_9 - C_{11} oxygenated compounds are present in urban atmospheres (see also Cicciolli & Mannozi, 2007). These would also be predicted to be precursors to PAN-like molecules.

It must be noted, however, that with the heavier aldehydes the reaction with OH becomes less likely to extract the aldehydic hydrogen to form the peroxyacyl radical. In the case of nonanal the likelihood is estimated to be around 50%, rather than $\sim 100\%$ for acetaldehyde (Tyndall, et al., 2002) and 95 & 90% for C_3 & C_4 aldehydes (Bowman, et al., 2003). And finally, not all aldehydes are necessarily parents of PANs at all. For example, using the EUPHORE outdoor simulation chamber, Carrasco, et al. (2006) studied the fate of 2-hydroxy-2-methylpropanal (HMP, $\text{HOC}(\text{CH}_3)_2\text{C}(\text{O})\text{H}$), a photo-oxidation product of 2-methyl-3-buten-2-ol (MBO), and observed a 100% apparent yield for acetone production following reaction with OH, whether NO_x was present

or not, apparently indicating the corresponding PAN is not formed. This result agrees with Méreau, et al. (2001) prediction that decomposition should dominate over O_2 addition for the $\text{HOC}(\text{CH}_3)_2\text{CO}$ radical, but disagrees with the MCM prediction of the PAN analog $\text{HOC}(\text{CH}_3)_2\text{C}(\text{O})\text{OONO}_2$ being formed.

The importance of NO_3 to the fate of isoprene has recently been recognized (Horowitz et al., 2007; Brown, et al., 2009; Perring, et al., 2009a; Rollins, et al., 2009). The primary product of that reaction is the aldehyde $\text{CH}_2(\text{ONO}_2)\text{C}(\text{CH}_3)\text{CHCHO}$. Because NO_3 will also abstract aldehydic hydrogens, the nighttime NO_3 reactions with isoprene and other biogenic hydrocarbons could potentially lead to the formation of PANs. The reaction rates for the abstraction step, however, are likely too slow (see e.g., D’Anna et al., 2001; Cabañas et al., 2003) for this to be important.

Although PAN was first identified and measured in the atmosphere by long path infrared absorbance spectroscopy, and PAN in the upper troposphere has been observed by satellite using infrared emission spectra (Glatthor, et al., 2007), most measurements of PANs have used gas chromatography, typically with electron capture detection (GC/ECD) (Stephens, 1969; Roberts, 2007). While the GC/ECD is a sensitive and reliable method for measuring C_2 - C_4 PANs, the response to larger PANs is known to be lower, probably due to some combination of thermal loss during the longer elution times and a decline in the ECD signal with increasing size of the R-group (Flocke, et al., 2005).

A number of measurement techniques based on the ready thermal dissociation of PANs to yield NO_2 and peroxy radicals have been reported. Blanchard, et al. (1990) used thermal dissociation followed by luminol detection of the NO_2 product after the GC column. Later work (Blanchard, et al., 1993) added the chemical amplification of NO to NO_2 by peroxy radicals in the presence of CO. Nikitas, et al. (1997) used Luminol II solutions and omitted the separation column and considered PAN to be the NO_2 difference between an unheated sample stream and one that had been directed through a thermal converter. The NO_2 thermolysis product has also been detected by LIF (Day et al., 2002; Di Carlo et al., 2008), photolysis/chemiluminescence (Alaghmand, et al., 2008), and by cavity ring down spectroscopy (Paul, et al., 2009). Thermal dissociation-chemical ionization mass spectrometric (TD-CIMS) techniques measuring the peroxyacyl radical product have been implemented for field measurements in the past few years (Slusher et al., 2004), including for eddy covariance fluxes (Turnipseed, et al., 2006; Wolfe, et al., 2008).

The TD-LIF technique doesn’t directly measure individual PN species, but rather the sum of all species that yield NO_2 within a certain range of heating conditions: total PNs (or Σ PNs) is the difference between the NO_2 signal from a heated inlet and that from an unheated inlet. This would include not only PANs, but also N_2O_5 , ClONO_2 , BrONO_2 ,

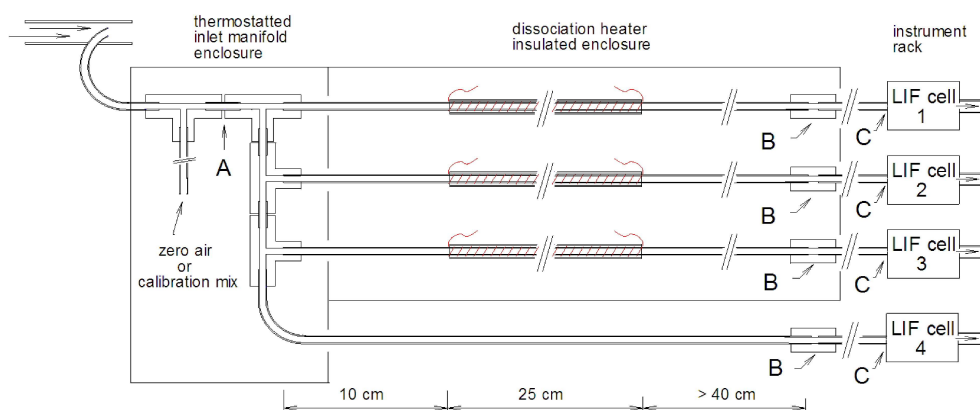


Fig. 1. Schematic of the sampling system. Different instrument configurations have had pressure reduction at points A, B, or C.

HO_2NO_2 , $\text{CH}_3\text{O}_2\text{NO}_2$, etc., if present in the atmosphere and if transmitted through the inlet tubing to the heater (Fig. 1).

Here we compare ambient and chamber TD-LIF measurements of Σ PNs to summed individual species (Σ PANs) from distinct independent methods. The measurements occurred over a span of eight years and include several variations in configurations of TD-LIF sampling inlets and a variety of speciated PANs detection techniques. We explore the agreement under this large range of ambient conditions and assess possible interferences to TD-LIF measurements. We also use the comparison to assess the potential presence of other PN species in the atmosphere that have not been reported using current techniques.

2 The TD-LIF technique for the determination of Σ PNs

2.1 Instrument construction and operation

The Berkeley instrument detects species that contain –O–NO₂ groups by thermal dissociation (TD) followed by laser-induced fluorescence (LIF) of the NO₂ product, was first described by Day, et al. (2002). Over the last decade, a number of sampling and detection variations have been implemented. Figure 1 depicts the general scheme for sampling and dissociation plumbing for an instrument that measures molecules of the form RONO₂ (the sum of alkyl nitrates, or Σ ANs) and HNO₃ in addition to NO₂ and Σ PNs. The design minimizes the amount of plumbing between the inlet tip and the dissociation heaters to minimize wall interactions, which is particularly important for the detection of HNO₃. The PFA Teflon inlet manifold region is thermostatted to 50–80 °C to minimize HNO₃ sticking to the walls (Neuman, et al., 2000) without dissociating PNs. The dissociation heaters are 1/4" (6.35 mm) o.d. quartz tubing wrapped with Nichrome wire and sheathed with larger diameter quartz tubes. Typically heater #1 would be set for HNO₃ dissociation (550–650 °C), #2 for Σ ANs (350–400 °C), #3 for Σ PNs (150–200 °C), and #4 for NO₂ (unheated, <40 °C). Flow rates are 1–2 SLPM

through each. For ground site measurements we use a small blower to pull air past a rearward hooked tube to exclude very large particles and other debris.

The LIF cells are operated at pressures <5 hPa in order to extend the NO₂ fluorescence lifetime beyond 100 ns for the time-gated LIF technique (Thornton, et al., 2000), and the constriction to reduce the pressure may be inserted in a number of places (A, B, C in Fig. 1) between the tip and cells. The different locations for the constriction trade off factors such as sensitivity and susceptibility to interferences versus instrument size and power consumption. When sampling through long lines (1/4" o.d. PFA Teflon) from tower mounted inlets/heaters, stainless steel pinholes were originally placed just after the gas stream re-cools, at the quartz to Teflon tube junctions (points B in Fig. 1) (Day, et al., 2002; Murphy, et al., 2004; Rosen, et al., 2004; Cleary, 2005). Compared to placing the orifice just prior to the detection cells (points C in Fig. 1), this gives much quicker gas transit times as well as much reduced potential for interfering chemical reactions. During most aircraft deployments (and some ground campaigns with short towers), jet expansions have been employed to cool the gas and increase the fraction of NO₂ molecules in the low rotational states being probed and thereby increase the detection sensitivity (Cleary, 2002). In this case the pressure reduction is at the expansion nozzle inside the LIF cell (points C). Most recently, a system with a glass orifice before the heaters (point A) has been implemented in order to reduce interferences caused by high levels of NO_x and O₃, as discussed below.

Dedicating one LIF detection cell for each of the four sample lines as depicted in Fig. 1 is the most straightforward and has the most complete temporal coverage. For lower weight, cost, and power, some deployments have employed 3-way Teflon valves to rapidly switch the sample streams of four heaters to a pair of cells (Murphy, et al., 2006; Bertram, et al., 2007; Perring, et al., 2009b). Alternatively, two inlet heaters may be used with temperature cycling, but at the expense of temporal data coverage (e.g., Rosen, et al., 2004).

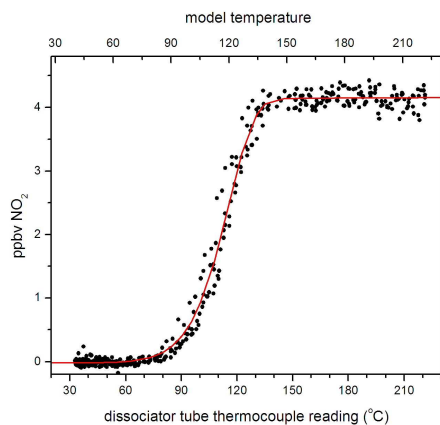


Fig. 2. Kinetic model and laboratory measurement of NO_2 dissociation product versus temperature for PAN.

We model the chemical evolution of PAN, peroxyacyl (PA) radicals, NO , NO_2 , and O_3 in air from the inlet tip to the LIF cell as a plug flow reactor with a prescribed temperature profile. For our 3.6 mm i.d. quartz tubes we use a 7.5 cm temperature transition region from ambient to the set point, 17 cm at the dissociation temperature set point, then 23 cm to cool back to ambient temperature, followed by transit through ambient temperature Teflon tubing to the LIF NO_2 measurement cell. The flow rate is set at 2 SLPM, and the rate constants are the same as in Day, et al. (2002). No attempt is made to measure the true air temperature inside the heated quartz tubes, instead external thermocouples are used and the characteristic dissociation temperatures for individual tubes are determined by temperature scans with reference compounds (i.e. PAN, $n\text{-C}_3\text{H}_7\text{ONO}_2$, and HNO_3). Figure 2 presents a temperature scan from PAN synthesized in the laboratory carried in zero air at 1 atmosphere. Results from the kinetic model are also shown.

Figure 3 shows the results of simulations for atmospheric trace species that yield NO_2 upon thermal dissociation under these conditions, with pressure reduction at point B. Rate constants were added for ClNO_2 (Baulch, et al., 1981; Knauth and Martin, 1978), BrONO_2 (Orlando & Tyndall, 1996), ClONO_2 (Anderson & Fahey, 1990), and CH_3OONO_2 (Zabel, et al., 1989). The dissociation temperatures of these species have not been experimentally verified for this instrument, but it has been reported that nitril chloride (ClNO_2) requires a higher temperature for dissociation than that normally used for measurement of PANs (Osthoff, et al., 2008). The Σ PNs heater temperature is chosen to completely dissociate PAN and related species but to have interferences of less than 1% from the next higher class by thermal stability (Σ ANs). When the pressure reduction is before the heater (point A in Fig. 1), the shorter residence times require higher temperatures: for a 2 SLPM flow we calculate a +45 °C difference for a heater at 0.2 atm versus

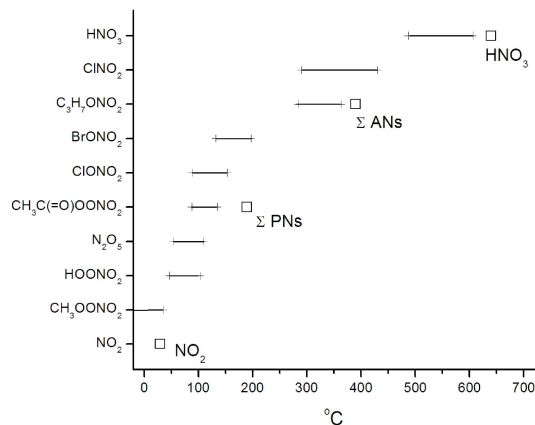


Fig. 3. Modeled 5 to 95% dissociation temperature ranges (plusses) and typical TD-LIF setpoints (squares).

one at 1 atm. This change is small enough that a single set point may be used in airborne applications without active inlet pressure control.

2.2 Calibration

Instruments that detect PAN specifically are generally calibrated either with the vapor diffusing from laboratory-synthesized PAN dissolved in a low vapor pressure hydrocarbon solvent, or by PAN synthesized in the gas phase on demand. Both systems are secondary calibrations by reference to an NO or NO_2 standard. In the gas phase synthesis method, an excess of peroxyacetyl radicals is created by photolyzing acetone at 285 nm, which is combined with a known amount of NO or NO_2 (e.g. Roberts, et al., 2002). Generally, 93% or more is converted to PAN, however if the mercury lamp's phosphor coating is damaged the 254 nm Hg line will photolyze PAN effectively. In addition, self reactions of the excess peroxy radicals result in high concentrations of peroxides and other byproducts which interfere with some detection schemes. The diffusion source is usually calibrated by catalytic conversion of its output to NO followed by ozone chemiluminescence detection, coupled either to the assumption that NO_y impurities (typically CH_3ONO_2 , NO_2 , and HNO_3) are negligible or are directly measured.

The TD-LIF technique takes advantage of the quantitative yield of NO_2 from PAN thermal decomposition. As such, the calibration doesn't require a PAN standard but uses certified standard NO_2 in N_2 mixtures, typically 5 or 10 ppbv. Just prior to each calibration the regulator and plumbing are purged by briefly opening a vented solenoid valve next to the mass flow controller. The standard is diluted with zero air to 0–20 ppbv in 2 to 4 steps, and the inlet is overflowed with the mixture at the tip and prior to the split between channels such that each sees the same calibration gas, as shown in Fig. 1. Comparisons of the NO_2 measured by LIF and photolysis/chemiluminescence have shown agreement to better

than 5% (Thornton, et al., 2003; Fuchs, et al., 2009). To ensure good channel-to-channel precision for the subtractions, calibrations are performed every few hours during ground site measurements. For airborne campaigns these calibrations are made more frequently and initiated in response to changing ambient pressure.

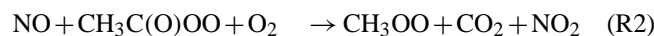
2.3 Instrument performance

Two different types of lasers have been used in the Berkeley LIF instruments. The pulsed dye laser system has been described previously (Thornton, et al., 2000). This laser provides 100–200 mW at 8 kHz repetition rate and is tuned on and off of a molecular rovibronic line at 17086.5 cm^{-1} (585.1 nm). Alternatively, small and efficient diode lasers in the 405–410 nm region have been used to take advantage of the larger NO_2 absorption cross-section ($\sigma \approx 6 \times 10^{-19} \text{ cm}^{-2}$ at 408 nm vs. $\approx 1 \times 10^{-19}$ at 585.1 nm). The disadvantages of the diodes thus far have been lower power ($< 40 \text{ mW}$) and a sharply restricted tuning range (0.3 cm^{-1} vs. 6 cm^{-1}). Additionally, time-gated fluorescence detection is effected by turning the diode current on and off, which further reduces the average excitation power. We have used both external cavity tunable diodes (Toptica model DL-100) and modules without wavelength tuning (Power Technology Inc., IQ series).

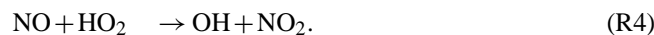
The signal-to-noise ratio (SNR) of an individual NO_2 measurement is determined by the photon count rate per ppbv NO_2 and the background count rate. The dye laser system has a slope (S) of $60 \text{ counts s}^{-1} \text{ ppbv}^{-1}$ with 20 counts s^{-1} background (B) at 120 mW laser power. Cell versus cell relative slopes are within 1%. With 10 s of averaging, photon counting statistics gives an uncertainty for a NO_2 measurement of $\sigma_{\text{NO}_2} = [\sqrt{(2B/t)}/S] \approx 35 \text{ pptv}$, for a detection limit of 70 pptv at $\text{SNR}=2$. Also for 10 s averaging, $\sigma_{\text{NO}_2} = 5\text{--}10 \text{ pptv}$ for the dye laser/jet expansion system (depending on flight altitude), and $\approx 50 \text{ pptv}$ for the 408 nm diode laser systems. For the Σ PNs subtraction difference, the SNR is $(C_2 - C_1) / \sqrt{(\sigma_{C_2}^2 + \sigma_{C_1}^2)}$, where C_2 and C_1 are the concentrations for the heated and unheated channels. This ratio degrades as the ambient $[\text{NO}_2]$ becomes large compared to the net $[\Sigma\text{PNs}]$.

2.4 Accuracy

Factors affecting the accuracy of TD-LIF measurements have been discussed by Day, et al. (2002) and Rosen, et al. (2004). The effect of the $\text{NO} + \text{O}_3$ reaction on photoconversion/chemiluminescence measurements of NO_2 has been discussed by Ryerson, et al. (2000). Here the interference due to Reaction 1 below is generally less than 1% of the NO converted to NO_2 by O_3 . The much faster rate for $\text{NO} + \text{RO}_2$ (Reaction 2, with RO_2 written specifically as $\text{CH}_3\text{C}(\text{O})\text{OO}$ from PAN dissociation) converts less than 5% of NO .



At very high NO concentrations (100 s to 1000 s of ppbv), up to 4 NO_2 molecules for each PAN could in principle be generated by including the further reactions:



The chemical amplification scheme mentioned earlier (Blanchard, et al., 1993) exploits this by adding percent levels of CO to recycle OH to HO_2 via the reaction $\text{CO} + \text{OH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{HO}_2$. Ambient concentrations of CO are much too small to yield detectable amplification.

Elevated concentrations of NO_2 , in addition to lowering the signal-to-noise ratio of the subtraction difference, accelerate the recombination kinetics of the PNs after the heated section leading to the underestimation of Σ PNs, also on the order of 5% or less under typical conditions. The extent of the interferences varies with both residence time and number density, both of which are affected by the choice of the pressure reduction point.

Figure 4 shows the results of simulations for a system initialized with 5 ppbv NO_2 , 1 ppbv NO , 2 ppbv PAN, and 60 ppbv O_3 and with 6.5 m of Teflon tubing between the heated quartz inlet tube and the NO_2 LIF detection cell. The high NO_x level used here was chosen to be representative of conditions encountered during the Boulder, 2005 campaign discussed below. The NO_2 , NO and PAN concentrations are unchanged by the transit through the $50 \text{ }^\circ\text{C}$ inlet tip (0–.05 s), then the PAN is completely dissociated to NO_2 and PA in the $180 \text{ }^\circ\text{C}$ heated zone (.05–.15 s). Ideally there would be no $\text{NO}_2 + \text{PA} \rightarrow \text{PAN}$ recombination or $\text{NO} + \text{PA} \rightarrow \text{NO}_2$ conversion during the cooling and transit to the LIF cell ($>.15 \text{ s}$), however these effects are evident in the atmospheric pressure case shown in the middle frame. In this simulation there is significant loss of NO_2 signal to PAN recombination (-28%) and also gain of NO_2 signal from NO oxidation ($+10\%$). Early pressure reduction reduces both number density of the reactants and the transit time between the inlet tip and the LIF cell, resulting in lowering the interfering NO_2 reactions to less than 3% in this example.

Wall loss rates of the PA radical are the key adjustable parameters in the model. Results from laboratory characterizations of various concentrations of PAN, NO , NO_2 , and H_2O with pressure reduction at points B, were used to tune the wall loss rates (γ) for the PA radicals to the quartz heater and Teflon transit tubing. The combination of $\gamma = .3$ for loss to quartz and $\gamma = .2$ for Teflon best fit the data. The elevated temperatures should minimize the influence of relative humidity variations and condensable organic species in the sampled air; however the γ will likely vary some between individual quartz tubing pieces and with environmental exposure.

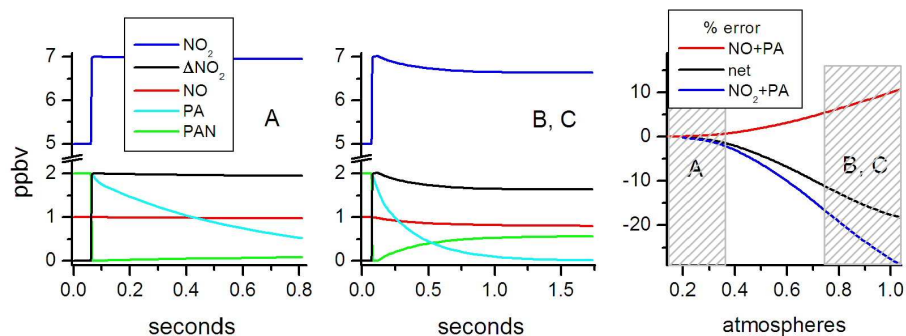


Fig. 4. Modeled evolution from inlet tip to LIF cell for systems with pressure reduction at the tip (position A, left frame) or after the heater (position B or C, middle frame). The PAN signal is the difference between the final NO₂ and the ambient initial NO₂ (5 ppbv), i.e. PAN signal = Δ NO₂ \approx 2 ppbv. The right frame shows the final percent errors versus the pressure in the heater.

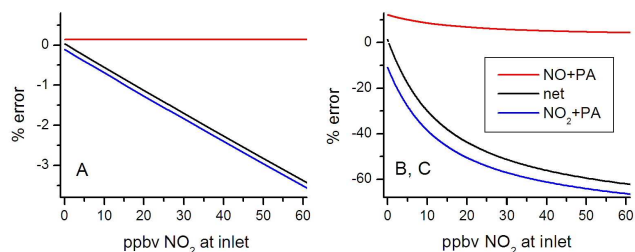


Fig. 5. Modeled final concentrations at the LIF cell with the pressure drop at point A (on left) or points B, C (on right) as a function of [NO₂] at constant 1 ppbv NO and 60 ppbv O₃. Note the factor of 20 difference in scale.

Figures 5 and 6 demonstrate the effect of increasing NO₂ and NO concentrations on the Σ PNs signal, under the same conditions as for Fig. 4. These are somewhat extreme cases because either [NO] or [NO₂] is fixed and so the [NO]/[NO₂] ratio covers a very wide range. In Fig. 5 the extra Σ PNs signal (Δ NO₂) at low NO₂ is from NO oxidation. Very large NO concentrations coincident with 60 ppbv of O₃ could produce a large amount of NO₂ in the atmospheric pressure inlet (Fig. 6), a scenario that is unrealistic in the atmosphere.

Overall, model calculations indicate that when the dissociation occurs at 1 atmosphere pressure NO+PA and NO₂+PA reactions may require correction terms as large as 30% in the PAN measurement when NO and NO₂ are higher than 3 and 4 ppbv, respectively. The terms have opposite signs and the degree of cancellation will depend on the NO₂/NO ratio. With the pressure drop before the dissociation (point A) the effects should be negligible even at high NO and NO₂ levels. These results are used to interpret the comparisons described below.

2.5 Data treatment

For routine application to large datasets taken with atmospheric pressure dissociation, a parameterization for the corrections was derived. Positive interference to NO₂ from the

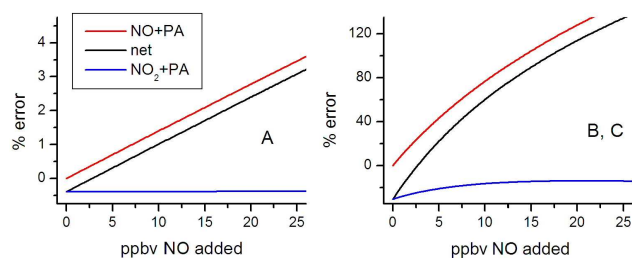


Fig. 6. As in Fig. 5, but as a function of [NO] at the inlet tip with 5 ppbv NO₂ and 60 ppbv O₃.

reaction of NO with O₃ between the inlet tip and the cells has been found to be small for nearly all conditions encountered, and would not affect the difference as it would be the very nearly the same for both the heated and unheated channels. Positive interference from the NO+PA \rightarrow NO₂ reaction is parameterized as $k_{\text{NO+PA}}(T)[\text{PA}][\text{NO}]\tau$, where τ and T are the characteristic time (typically <0.1 s) and effective average temperature (typically 323 K) for the heater to cell transit that best reproduces the results from the laboratory experiments and detailed model. This incorporates the heater temperature profile, PA loss coefficients, etc., into two parameters. Negative interference from the NO₂+PA \rightarrow PAN recombination is taken as $k_{\text{NO}_2+\text{PA}}(M,T)[\text{PA}][\text{NO}_2]\tau$, where M is from the measured pressure in the tubing and τ and T are the same as above. The uncorrected [Σ PNs] measurement is used as an initial approximation for [PA]. An iterative procedure where the corrected [Σ PNs] value used to refine the initial [PA] was explored in early work, but it was determined that points where this would lead to significant additional changes should be discarded as unreliable.

In general, the correction terms for both effects have been small ($<5\%$) for non-urban environments (NO_x < 3 ppbv). For airborne deployments in particular both of the terms have been insignificant except during brief transits of fresh combustion plumes at low altitudes. We have retained the jet expansion (at point C) in this case for the factor of ten or higher

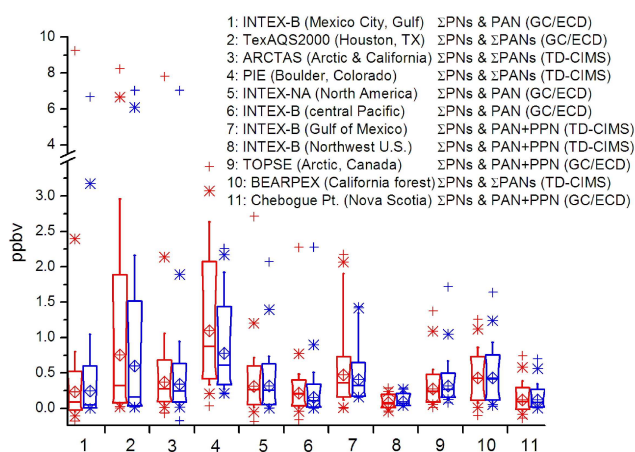


Fig. 7. Statistical overview of campaigns with comparison opportunities. Boxes delineate 10 to 90 percentiles, whiskers extend 5 to 95%, * are 1 and 99%, and + are minima and maxima. Lines through the boxes depict the medians and diamonds are the means. Red (left in the pairs) are TD-LIF Σ PNs and blue (right) are PAN or summed individual species, as available.

gain in sensitivity when used with the tunable dye laser. On the other hand, for recent surface site deployments where high NO_x values were anticipated (i.e. Mexico City, SAPHIR chamber) we have placed the pressure reduction orifice before (point A) the heated section instead of after (point B or C).

3 Field and chamber measurements overview

Table 1 lists 14 deployments with TD-LIF participation from 2000 through 2008, and Fig. 7 presents a statistical overview of the range of concentrations encountered during the campaigns with comparison opportunities. These have been aboard aircraft, at ground sites, and in controlled atmosphere chambers. The conditions have ranged from clean remote where PAN is often the dominant NO_y component, to heavily urban impacted where NO and NO_2 largely exceed other NO_y species.

For the comparisons, careful alignments of the time-bases of datasets are performed before making correlation plots. A weighted total least squares algorithm (Krystek & Anton, 2007) was used, with $1/(15\%+.005 \text{ ppbv})$ and $1/(15\%+.05 \text{ ppbv})$ used as generic weights for the GC/ECD (or TD-CIMS) data and the TD-LIF data, respectively when the values were not stated in the dataset. The results are shown in Table 2 and Fig. 8. Also shown are histograms indicating whether the $\Sigma\text{PNs}+\text{NO}_2$ signal was dominated by NO_2 (values close to 0) or ΣPNs (values close to 1).

3.1 Airborne measurements

The airborne deployments have all utilized the same instrument with the pressure reduction point after the heater and near to or inside of the LIF cell (point C in Fig. 1). For the TOPSE mission (Atlas, et al., 2003) on the NSF/NCAR C-130 aircraft we used an instrument with one channel dedicated to measuring NO_2 and the other to ΣPNs . The instrument occupied one standard “high” rack having 2 bays for 19” panel mounted equipment (44 cm instrument width), each 127 cm tall and 64 cm deep. Total weight was approximately 270 kg and power consumption was about 2 kW. The inlet was machined from PFA Teflon following the design of Ryerson, et al. (1999). Pinholes just prior to each LIF cell gave pressures of 1–5 hPa over the 0–8 km altitude range, with a flow rate of 2 liters per minute per channel at sea level. For this campaign the uncertainty and accuracy for the ΣPNs measurement was estimated to be $\pm 28 \text{ pptv}$ and 15%. The individual species PAN and PPN were measured by the NCAR GC/ECD where one column measured only PAN at $\sim 2.5 \text{ min}$ intervals, while the other measured PAN and PPN but on a $\sim 5 \text{ min}$ cycle (Flocke, et al., 2005). Both GC channels had 2–3 s sampling times. For the TOPSE data the additional interpolation of PAN from both GC channels was described by Thornton (2002). Overall, the measured ΣPNs were consistent with the sum of the individual PAN and PPN measurements with the addition of the calculated HO_2NO_2 (Murphy, et al., 2004).

For the NASA INTEX-NA (Intercontinental Chemical Transport Experiment-North America, 1 July–15 August 2004, www.espo.nasa.gov/intex-na/) campaign (Singh, et al., 2006) using the DC-8 aircraft, the TD-LIF instrument was largely the same as for TOPSE, but with the addition of molecular jet expansions in the NO_2 LIF detection cells and locating additional heaters for alkyl nitrate and nitric acid channels externally in a window-panel mounted probe. The ΣPNs and NO_2 sample stream was drawn from a separate, unheated, probe. The DC-8 payload also included PAN measurements by the NASA Ames GC/ECD (Singh and Salas, 1983) and peroxyxynitric acid by CIMS (Kim, et al., 2007).

For the INTEX-B campaign on the NASA DC8 (www.espo.nasa.gov/intex-b/ (Singh, et al., 2009)), the TD-LIF instrument was the same except for modifications to the inlet system designed to sample HNO_3 more effectively. The inlet manifold and heater assembly depicted in Fig. 1 was adapted to mount on the interior face of a window-panel and sampled from a high speed flow directed from outside the aircraft boundary layer. The external probe was the same as described by Crouse, et al. (2006). The March phase of the campaign was based in Houston, Texas and focused on outflow from Mexico City and the evolution of plumes over the Gulf of Mexico. The April–May phase was based from Honolulu, Hawaii then Anchorage, Alaska and characterized air coming across the Pacific. The NASA Ames GC/ECD instrument also measured PAN on the DC-8,

Table 1. Measurement campaigns with TD-LIF participation

campaign	location	year	months	platform	comparison opportunities	inlet type
TOPSE	Canada/Arctic	2000	February–May	NCAR/NSF C130	GC/ECD PAN & PPN, NO _y	B
INTEX-NA	Eastern US	2004	June–August	NASA DC-8	GC/ECD PAN	C
INTEX-B	Mexico & Pacific	2006	March–May	NASA DC-8	GC/ECD PAN	C
TC ⁴	Costa Rica	2007	July–August	NASA DC-8		C
ARCTAS	Arctic, California	2008	April–July	NASA DC-8	TD-CIMS PANs	C
TexAQS	Houston, TX	2000	July–August	ground site	GC/ECD PANs, NO _y	B
Blodgett	Sierras, CA	2000–2005	all months	ground site		B
CATSUP	Granite Bay, CA	2001	August–September	ground site		B
Big Hill	Sierras, CA	2003	all months	ground site		C
Chebogue Pt.	Nova Scotia	2004	July–August	ground site	GC/ECD PANs	C
PIE	Boulder, CO	2005	June–July	ground site	multiple methods, PANs	C
MILAGRO	Mexico City	2006	March	ground site		A
BEARPEX	Sierras, CA	2007	August–October	ground site	TD-CIMS PANs	A
NO ₃ /N ₂ O ₅	Jülich, Germany	2007	June	SAPHIR chamber	N ₂ O ₅ by multiple methods	A

Table 2. Σ PNs versus speciated PANs comparisons table

opportunity	weighting %, ppbv ¹	species in sum	slope vs. Σ PNs	intercept ppbv	R ²	NO ₂ ppbv min., median, max.	notes
TOPSE		PAN+PPN	1.04 ± .06	.002 ± .020	.77	.00, .013, .08	vs. GC/ECD
INTEX-NA		PAN+PPN+PBN+PBzN+MPAN +MoPAN+APAN	1.06 ± .09	−.030 ± .025	.88	.02, .06, .59	vs. WP-3D TD-CIMS, comparison flight
INTEX-NA		PAN	1.03 ± .01	.005 ± .003	.80	.00, .05, 6.9	vs. DC-8 GC/ECD, full mission
INTEX-B ²		PAN	1.33 ± .02	.037 ± .012	.60	.00, .03, .53	vs. DC-8 GC/ECD
INTEX-B ³	20, .005	PAN+PPN	0.66 ± .02	.13 ± .02	.87	.05, .12, .63	vs. C-130 TD-CIMS
INTEX-B ⁴	20, .005	PAN+PPN	0.93 ± .06	.042 ± .007	.77	.00, .02, .13	vs. C-130 TD-CIMS
ARCTAS		PAN+PPN+PiBN+APAN+PNA	0.97 ± .093	.004 ± .270	.96	.00, .02, .59	vs. TD-CIMS PANs & PNA
ARCTAS		PAN+PPN+PiBN+APAN	0.92 ± .090	.010 ± .240	.94	.00, .02, .59	without PNA (HO ₂ NO ₂)
ARCTAS		PAN+PPN	0.90 ± .089	.022 ± .230	.94	.00, .02, .59	without PNA, PiBN, APAN
TexAQS		PAN+PPN+PiBN+MPAN	0.91 ± .17	.024 ± .88	.91	.80, 7.7, 88	vs. GC/ECD
Chebogue Pt.		PAN+PPN	0.90 ± .02	.005 ± .004	.72	.00, .50, 2.4	vs. GC/ECD
PIE 6/30-7/1		PAN+PPN	0.66 ± .08	−.04 ± .07	.84	.00, 2.3, 44	ambient sampling
BEARPEX	21, .003	PAN+PPN+MPAN	1.08 ± .02	−.04 ± .01	.75	.00, .73, 28	vs. U. Wash. TD-CIMS, 2007
N ₂ O ₅ , Jülich		N ₂ O ₅	1.02 ± .06	−.36 ± .05	.87	1.5, 3.2, 7.5	SAPHIR chamber runs

¹ For the TOPSE dataset Σ PNs were weighted by 1/(15% of measurement + .028 ppbv), otherwise Σ PNs were weighted by 1/(15% of measurement + .05 ppbv). Σ PAN_{*i*} were weighted by 1/(15% of measurement + .005 ppbv) except when stated numbers were available, as given above.

² Gulf of Mexico and Central Pacific phases, March and April–May, 2007.

³ Intercomparison over Gulf of Mexico, 19 March 2007.

⁴ Intercomparison over northwest US, 15 May 2007.

however, the agreement was not as good as during INTEX-NA. We also participated in the 19th March and the 15th May in-flight intercomparison exercises with the NCAR/NSF C-130 which was based in Veracruz, Mexico then Seattle, Washington. The C-130 payload included a TD-CIMS PANs instrument (Flocke, et al., in preparation). The DC-8 TD-LIF 19th March data correlates much better with the C-130 TD-CIMS PAN+PPN than with the DC-8 GC/ECD, however the slope is significantly different from one to one. The excellent agreement between the two aircraft NO₂, etc., measurements

suggests that both aircraft were indeed sampling the same air masses. For the 15th May comparison, the DC-8 Σ PNs also correlated well with the TD-CIMS PAN+PPN, however the ambient concentrations were quite low.

As a part of the Third International Polar Year research effort, measurements were made using the NASA DC-8 aircraft as a part of its ARCTAS 2008 mission (www.espo.nasa.gov/arctas/). The first phase was based in Fairbanks, Alaska, in April and concentrated on long range transport of anthropogenic and biomass burning pollution to the Arctic,

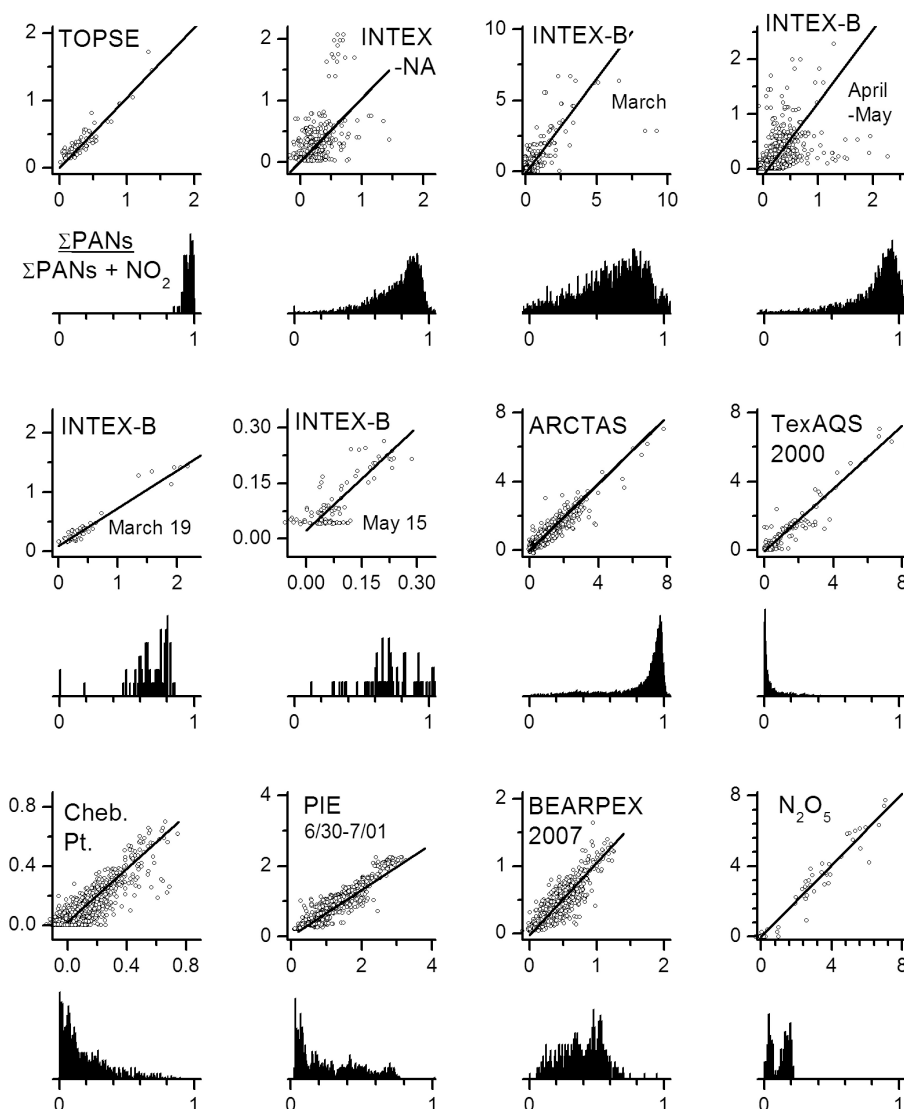


Fig. 8. Speciated Σ PANs (ppbv) vs. TD-LIF Σ PNs (ppbv) scatterplots with fitted lines. Below each are histograms of the Σ PNs fractions of the Σ PNs+NO₂ sums.

as well as chemical and aerosol composition and processes. An intermediate phase was based in southern California during June in conjunction with the California Air Resources Board to characterize ozone, particulate matter, and greenhouse gas sources and chemistry. The final phase was based in Alberta, Canada in July to sample fresh and aged boreal forest fire emissions. The TD-LIF instrument was essentially unmodified since INTEX-B. A TD-CIMS (Slusher, et al., 2004) measured the individual species. PAN and PPN, also PiBN (isobutryl peroxyxynitrate) and APAN (acryloyl peroxyxynitrate) were reported for most flights. Peroxynitric acid (PNA), HO₂NO₂, was measured by a different CIMS (Crouse, et al., 2006). No inlet chemistry corrections were applied to the TD-LIF Σ PNs data, instead the few points having NO >5 ppbv were rejected. Figure 9 presents data

from the final flight, in which conditions ranged from clean background to heavily impacted by biomass burning. The correlation was very good for this flight, and the entire campaign, as shown in Fig. 8. During the Arctic flights HO₂NO₂ was often well above the detection limit and was included in the full dataset correlation. As indicated in Table 2, omitting HO₂NO₂ would drop the slope from .97 to .92 and lower the R² from .96 to .94. The correlation plots are not sufficiently different to include in Fig. 8, but the fitted parameters are included in Table 2.

3.2 Ground site and chamber measurements

During the TexAQS 2000 campaign an extensive suite of ground-site measurements were made from 15 August to 15 September at LaPorte, Texas. The site was about 40 km

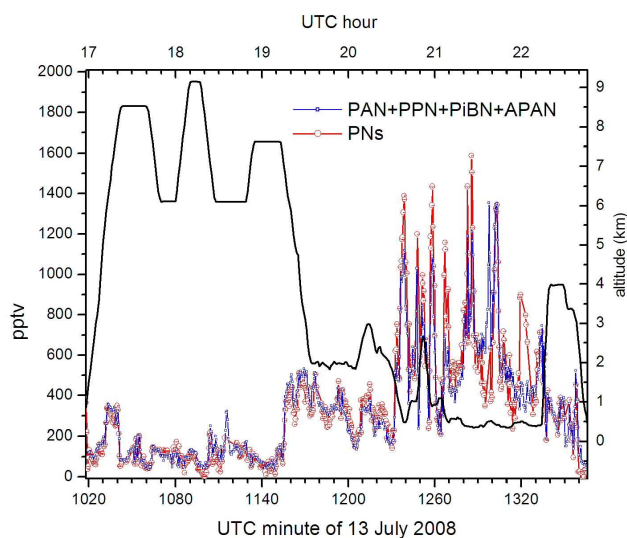


Fig. 9. TD-LIF Σ PNs (red) and sum of speciated PANs (blue) from the TD-CIMS instrument for the ARCTAS flight from Cold Lake, Canada to Los Angeles, California. Forest fire plumes were encountered beginning at about minute 1230.

southeast of Houston and about 20 km from the shipping channel where a large number of petrochemical plants are located (see e.g., Rosen et al., 2004, and references therein). The same two-channel instrument as for the airborne deployments was used here. The inlet block used in the TOPSE campaign was followed by two heated tubes modified to reach higher temperatures to enable Σ ANs and HNO_3 measurements in addition to NO_2 and Σ PNs. The pressure reducing pinholes were placed after the heated dissociation tubes (points B in Fig. 1). The inlet was mounted on a 10 m scaffolding tower, approximately 2 m below the inlet for the NOAA GC/ECD instrument (Roberts, et al., 2001). The inlet temperatures were programmed to sequentially sample HNO_3 , Σ ANs, and Σ PNs with NO_2 . NO_2 and Σ PNs were measured together for 40 min during each 5 h cycle. Because of the high NO_2 levels (occasionally up to 100 ppbv), the two-channel difference had relatively high noise. In addition, artifacts from NO to NO_2 oxidation, as well as PANs recombination in the inlet tubing were not negligible ($\pm 15\%$), but corrected for as described above. The GC/ECD instrument sampled the individual compounds PAN, PPN, PiBN, MPAN for approx. 3 min on 15 min intervals. The uncertainty was reported at ± 0.005 ppbv + 15% for PAN, and slightly larger for the others.

During the summer of 2004, PAN and PPN were measured by GC/ECD at the Chebogue Point, Nova Scotia ground site as part of the overall ITCT ICARTT campaign (Roberts, et al., 2002; Millet et al., 2006) along with Σ PNs. This deployment used the compact TD-LIF instrument with the small blue diode laser described earlier. The inlet heaters were all mounted at the sampling point on the tower and the pressure reduction was at the instrument on the ground (point

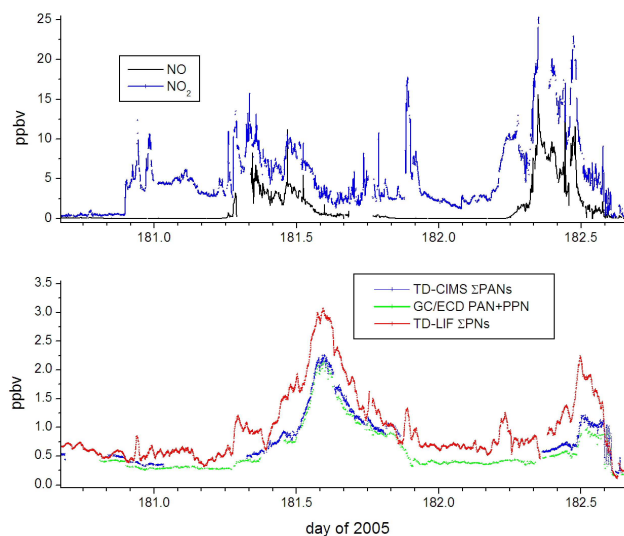


Fig. 10. PAN Intercomparison Exercise ambient sampling period: 30 June–1 July 2005, Boulder, Colorado.

C). Under these low NO_x conditions, the correlation between PAN+PPN and Σ PNs was good here despite the low concentrations of Σ PNs relative to NO_2 (Fig. 8).

The first international PAN Intercomparison Exercise (PIE, <http://acd.ucar.edu/~ffl/PIE2005.html>) was conducted on the Enchanted Mesa overlooking Boulder, Colorado during June and July of 2005 (Tyndall, et al., 2005). Depending on the wind direction, air arrived from the Rocky Mountains or from the heavily traveled highway corridor leading into Boulder. Instruments included five GC/ECDs (gas chromatograph/electron capture detector), TD-CIMS (thermal dissociation-chemical ionization mass spec.), GC/PDD (pulse discharge detector), GC/NICI-MS (negative ion CIMS), and TD-LIF. These were housed in five trailers (one having the standard sources and the reference GC/ECD instrument) which sampled from a common Teflon manifold having 12 to 20 SLPM flow. The instruments sampled ambient air, or were challenged with synthetic PAN (or PPN or isopropyl nitrate) standards at various humidities. Supporting measurements included NO_2 , Σ ANs, and HNO_3 from the TD-LIF, NO and O_3 and basic meteorology for the early part of the exercise by NOAA. The TD-LIF instrument was the same as flown in INTEX-NA, but required longer sample lines to reach the inlet heaters mounted atop the trailer at the manifold connection. Because the pressure reduction in that instrument occurs at the LIF cell instead of at the inlet, the unanticipated high levels of NO_x in the ambient air at this location lead to interferences from the $\text{NO}_2 + \text{PA} \rightarrow \text{PAN}$ recombination and the $\text{NO} + \text{PA} \rightarrow \text{NO}_2 + \text{other products}$ reaction that were more severe than those of TexAQS 2000 study.

Figure 10 shows the results from ambient air sampled during a multi-day period that was variously impacted by fresh vehicle emissions. The temperature ranged from 15 °C at night to 28 °C during the day, the relative humidity 80 to 25%, and the winds were light and variable. The TD-LIF Σ PNs were greater than the sum of the speciated PANs as expected, however the deviations during the most polluted episodes were larger than usual. The correction terms calculated using the available NO, NO₂ and O₃ data were applied to the Σ PNs data were insufficient to bring the Σ PNs data into agreement with the other instruments. As shown in Fig. 11, the Σ PNs/ Σ PANs ratio grows when NO exceeds 1 or 2 ppbv, but the correction doesn't remove all of the NO dependence. Agreement could be achieved by choosing different parameters for these corrections; however the size of the terms needed would be larger than from the laboratory characterization. While it is possible that the extra signal had contributions from unspiciated PANs or other molecules that yield NO₂ when heated to the same temperature range, overall we conclude that this inlet configuration (no pressure reduction until point C) is not suited for surface sites with NO and NO₂ levels over a few ppbv.

BEARPEX-2007 (Biosphere Effects on Aerosol and Photochemistry EXperiment, www.ocf.berkeley.edu/~bearpex/, (Cohen, et al., 2010; LaFranchi, et al., 2009)) was conducted between late August and early October, 2007 at a Ponderosa pine plantation in the Sierra Nevada foothills, a few hours downwind of the Sacramento, California urban area. The same 408 nm diode laser based TD-LIF instrument as had been first deployed at Chebogue Point was interfaced to an inlet system that multiplexed 4 inlets each at 3 heights to 2 LIF cells in order to measure the concentrations and vertical gradients of NO₂, Σ PNs, Σ ANs, and HNO₃. The University of Washington TD-CIMS measurement of PAN, PPN, and MPAN has been described by Wolfe, et al. (2008). Bouvier-Brown, et al. (2009) provides details of the large concentrations of monoterpenes (daytime average of 722 pptv), methylbutenol (459 pptv), isoprene (132 pptv), and other BVOCs during this experiment. LaFranchi, et al. (2009) demonstrated that BVOC oxidation plays a significant role in the PANs budget at this site. The good agreement between Σ PANs and Σ PNs argues against existence of large amounts of unspiciated PANs (e.g. HOCH₂C(O)OONO₂) predicted by BVOC oxidation mechanisms.

The 2007 NO₃/N₂O₅ intercomparison at the SAPHIR chamber in Jülich, Germany (Apodaca, et al., 2010) did not involve PANs. Nevertheless, a couple of items are of interest here. In addition to an instrument that detected N₂O₅ via TD-LIF of the NO₃ radical, we also provided supporting measurements of NO₂, Σ PNs, Σ ANs, and HNO₃ with the small diode-laser based NO₂ TD-LIF instrument. As predicted in Fig. 3, we observed N₂O₅ to be quantitatively converted to NO₂ in our heated inlet. Also, a point not illustrated here but relevant to the PANs budget in the ambient atmosphere is that significant quantities of PAN-type compounds were not

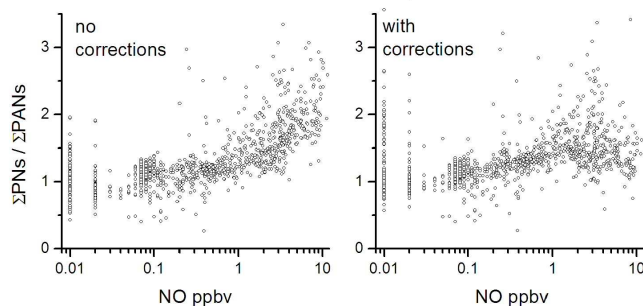


Fig. 11. Data ratios from Fig. 10 plotted against [NO], before and after applying corrections.

produced during the oxidation of isoprene, limonene, or β -pinene by NO₃ during the intercomparison (Fry, et al., 2009; Rollins, et al., 2009).

4 Discussion and conclusions

We find good overall agreement between the TD-LIF measurement of Σ PNs and measurements of individual PN species over a wide variety of environmental conditions. Only 3 experiments have a slope indicating differences larger than 10% (Table 2). One of these is PIE where we believe most of the ambient sampled data occurred at too high (NO_x) for that inlet configuration. As a result we have discontinued use of that inlet design except for remote locations. The ARCTAS and BEARPEX campaigns sampled over a wide range of conditions from clean remote tropospheric to those heavily impacted by urban sources, by isoprene and other forest emissions and by biomass burning.

In some environments PN species other than PANs can become significant. We have shown that N₂O₅ and HO₂NO₂ are measured as PNs by our instrument. It seems probable that CH₃O₂NO₂ is also detected, but that is never expected to be above a few 10s of pptvs, and only then in the coldest regions of the upper troposphere (Murphy et al., 2004; Browne, et al., 2010). Previous inlet systems had not been designed to put CH₃O₂NO₂ unambiguously into the PNs channel versus the unheated NO₂ channel, but that would require little modification to ensure that CH₃O₂NO₂ dissociates only in the PNs channel. Other species such as ClONO₂ or BrONO₂ would also be expected to largely dissociate in the PNs heater, but we do not have data on whether they would survive the Teflon inlet plumbing to reach the heater.

The results argue that the sum of any unmeasured PN species contributes less than 10% to the Σ PNs budget on average. Even for specific cases where aldehyde and other sources of potential unmeasured individual PAN species are large (the forest site) we find that Σ PNs and the sum of individual species agree to within 8%. Chamber data and ambient observations also suggest that significant PNs are not formed by nighttime NO₃/N₂O₅ oxidation of biogenic volatile organic compounds.

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