Quantification of peroxynitric acid and peroxyacyl nitrates using an ethane-based thermal dissociation peroxy radical chemical amplification cavity ring-down spectrometer

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Abstract. Peroxy and peroxyacyl nitrates (PNs and PANs) are important trace gas constituents of the troposphere which are challenging to quantify by differential thermal dissociation with NO₂ detection in polluted (i.e., high-NOₓ) environments. In this paper, a thermal dissociation peroxy radical chemical amplification cavity ring-down spectrometer (TD-PERCA-CRDS) for sensitive and selective quantification of total peroxynitrates (ΣPN = ΣRO₂NO₂) and of total peroxyacyl nitrates (ΣPAN = ΣRC(O)O₂NO₂) is described. The instrument features multiple detection channels to monitor the NO₂ background and the ROₓ (= HO₂ + RO₂ + ΣRO₂) radicals generated by TD of ΣPN and/or ΣPAN. Chemical amplification is achieved through the addition of 0.6 ppm NO and 1.6 % C₂H₆ to the inlet. The instrument’s performance was evaluated using peroxynitric acid (PNA) and peroxyacetic or peroxypropionic nitric anhydride (PAN or PPN) as representative examples of ΣPN and ΣPAN, respectively, whose abundances were verified by iodide chemical ionization mass spectrometry (CIMS). The amplification factor or chain length increases with temperature up to 69 ± 5 and decreases with analyte concentration and relative humidity (RH). At inlet temperatures above 120 and 250 °C, respectively, PNA and ΣPAN fully dissociated, though their TD profiles partially overlap. Furthermore, interference from ozone (O₃) was observed at temperatures above 150 °C, rationalized by its partial dissociation to O atoms which react with C₂H₆ to form C₂H₅ and OH radicals. Quantification of PNA and ΣPAN in laboratory-generated mixtures containing O₃ was achieved by simultaneously monitoring the TD-PERCA responses in multiple parallel CRDS channels set to different temperatures in the 60 to 130 °C range. The (1 s, 2σ) limit of detection (LOD) of TD-PERCA-CRDS is 6.8 pptv for PNA and 2.6 pptv for ΣPAN and significantly lower than TD-CRDS without chemical amplification. The feasibility of TD-PERCA-CRDS for ambient air measurements is discussed.

1 Introduction

The ROₓ (≡ OH + HO₂ + ΣRO₂) radicals and the nitrogen oxides (NOₓ = NO + NO₂) are important trace constituents of the atmosphere that drive diverse processes such as the photochemical production of ozone (O₃) in the troposphere (Kirchner and Stockwell, 1996; Fleming et al., 2006), the catalytic destruction of O₃ in the stratosphere (Bates and Nicolet, 1950; Stenke and Grewe, 2005; Solomon, 1999; Portmann et al., 1999), and the chemistry of organic aerosol formation (Ziemann and Atkinson, 2012; Ehn et al., 2014; Crounse et al., 2013). In the troposphere, the concentrations of these species are frequently buffered by ROₓ and NOₓ reservoir species, of which peroxynitric acid (PNA, HO₂NO₂), alkyl peroxy nitrates such as methyl peroxynitrate (CH₃O₂NO₂, MPN), and peroxyacyl nitrates (PANs, RC(O)O₂NO₂) are important examples (Singh et al., 1992; Roberts, 1990). Much insight into ROₓ and NOₓ chemistry has been gained by measuring the atmospheric abundances of these reservoirs. Significant PNA concentrations, for example, have been observed in the polar regions (Slusher et al., 2001; Davis et al., 2004; Jones et al., 2014), aloft in the
Table 1. Typical a PNA and PAN mixing ratios in various environments where both were quantified.

<table>
<thead>
<tr>
<th>Location</th>
<th>PNA (pptv)</th>
<th>PAN (pptv)</th>
<th>PNA / PAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antarctica – summer</td>
<td>20, Slusher et al. (2001)</td>
<td>15.6, Eisele et al. (2008)</td>
<td>1.3</td>
</tr>
<tr>
<td>Antarctica – summer</td>
<td>22, Jones et al. (2014)</td>
<td>15.6, Eisele et al. (2008)</td>
<td>1.4</td>
</tr>
<tr>
<td>Antarctica – summer</td>
<td>2.5, Jones et al. (2014)</td>
<td>9.2, Mills et al. (2007)</td>
<td>0.27</td>
</tr>
<tr>
<td>Remote troposphere – spring</td>
<td>–</td>
<td>–</td>
<td>0.13 b</td>
</tr>
<tr>
<td>Free troposphere – summer</td>
<td>45, Kim et al. (2007)</td>
<td>280, Singh et al. (2006)</td>
<td>0.16 b</td>
</tr>
<tr>
<td>Uintah Basin – winter 2014</td>
<td>100, Veres et al. (2015)</td>
<td>300, Lee et al. (2015)</td>
<td>0.33</td>
</tr>
<tr>
<td>Atlanta – winter 3.7, D. X. Chen et al. (2017)</td>
<td>640–800, Lee et al. (2013)</td>
<td>&lt; 0.01</td>
<td></td>
</tr>
<tr>
<td>Atlanta – summer</td>
<td>11.7, D. X. Chen et al. (2017)</td>
<td>640–800, Lee et al. (2013)</td>
<td>0.01–0.02</td>
</tr>
</tbody>
</table>

* Average values.
* Calculated assuming all non-PAN and PPN peroxy nitrate is PNA.
* Averages of data posted on ftp://ftp-air.larc.nasa.gov/pub/INTEXA/DC8_AIRCRAFT/.

Table 2. Selected thermal dissociation methods for quantification of daytime NO y species.

<table>
<thead>
<tr>
<th>Species quantified</th>
<th>NO 2 detection method</th>
<th>Group</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO 2, ΣPAN, ΣAN, HNO 3</td>
<td>LIF</td>
<td>Berkeley</td>
<td>Day et al. (2002)</td>
</tr>
<tr>
<td>ΣPN</td>
<td>LIF</td>
<td>Berkeley</td>
<td>Murphy et al. (2004)</td>
</tr>
<tr>
<td>HONO</td>
<td>CL</td>
<td>Berkeley</td>
<td>Perez et al. (2007)</td>
</tr>
<tr>
<td>NO 2, ΣPAN, ΣAN</td>
<td>CRDS</td>
<td>Calgary</td>
<td>Paul et al. (2009)</td>
</tr>
<tr>
<td>Aerosol nitrates</td>
<td>CRDS</td>
<td>Calgary</td>
<td>Rollins et al. (2010)</td>
</tr>
<tr>
<td>CINO 2</td>
<td>CRDS</td>
<td>Calgary</td>
<td>Thaler et al. (2011)</td>
</tr>
<tr>
<td>NO 2, ΣPAN, ΣAN, HNO 3</td>
<td>LIF</td>
<td>L’Aquila</td>
<td>Di Carlo et al. (2013)</td>
</tr>
<tr>
<td>NO, NO 2, HONO, NO y, Ammonium nitrates</td>
<td>CRDS</td>
<td>NOAA</td>
<td>Wild et al. (2014); Womack et al. (2017)</td>
</tr>
<tr>
<td>NO 2, ΣPAN, ΣAN</td>
<td>CRDS</td>
<td>Max Planck Institute</td>
<td>Thieser et al. (2016)</td>
</tr>
<tr>
<td>NO 2, ΣPAN, ΣAN</td>
<td>CAPS</td>
<td>Osaka</td>
<td>Sadanaga et al. (2016)</td>
</tr>
<tr>
<td>NO 2, RNO 2</td>
<td>CRDS</td>
<td>Hefei</td>
<td>J. Chen et al. (2017)</td>
</tr>
<tr>
<td>ΣPN, ΣPAN</td>
<td>PERCA-CRDS</td>
<td>Calgary</td>
<td>this work</td>
</tr>
</tbody>
</table>

There is ongoing interest to develop improved techniques for quantification of PANs (Roberts, 2007; Wooldridge et al., 2010; Zheng et al., 2011; Tokarek et al., 2014) and PNA (Murphy et al., 2004; Spencer et al., 2009; Veres et al., 2015; D. X. Chen et al., 2017). TD methods (Table 2) such as TD coupled to laser-induced fluorescence (TD-LIF) (Wooldridge et al., 2010; Day et al., 2002; Di Carlo et al., 2013), to cavity ring-down spectroscopy (TD-CRDS) (Paul et al., 2009; Thaler et al., 2011; Paul and Osthoff, 2010; Thieser et al., 2016; Sobanski et al., 2016; Womack et al., 2017), or to cavity phase-shift spectroscopy (TD-CAPS) (Sadanaga et al., 2016) detection of NO 2 are attractive as they can be used to monitor all components of odd nitrogen (NO y) in parallel, including NO 2 (inlet operated at ambient temperature), total peroxy nitrates (ΣPN = PNA + MPN +; inlet heated to ~ 100 °C), total peroxyacyl nitrates (ΣPAN = PAN + peroxypipinoic nitric anhydride (C 2 H 5 C(O)O 2 NO 2 +); ~ 250 °C), total alkyl nitrates + CINO 2 (ΣAN; ~ 420 °C), and HNO 3 (~ 600 °C), simply by deploying multiple detection channels and setting appropriate inlet temperatures. Molecules such as NO and HONO can be quantified through the addition of O 3 following TD (Wild et al., 2014; Womack et al., 2017; Fuchs et al., 2009).
Table 3. List of chemical reactions.

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
<th>$k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>$k_{298}$ K (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1)</td>
<td>CH$_3$O$_2$ + NO $\rightarrow$ CH$_3$O + NO$_2$</td>
<td>$2.3 \times 10^{-12} \times e^{(360/T)}$</td>
<td>$7.7 \times 10^{-12}$</td>
</tr>
<tr>
<td>(R2)</td>
<td>CH$_3$O + O$_2$ $\rightarrow$ HCHO + HO$_2$</td>
<td>$7.2 \times 10^{-14} \times e^{(-1080/T)}$</td>
<td>$1.9 \times 10^{-15}$</td>
</tr>
<tr>
<td>(R3)</td>
<td>HO$_2$ + NO $\rightarrow$ HO + NO$_2$</td>
<td>$3.5 \times 10^{-12} \times e^{(270/T)}$</td>
<td>$8.5 \times 10^{-12}$</td>
</tr>
<tr>
<td>(R4)</td>
<td>C$_2$H$_6$ + HO + O$_2$ $\rightarrow$ H$_2$O + C$_2$H$_5$O$_2$</td>
<td>$6.9 \times 10^{-12} \times e^{(-1000/T)}$</td>
<td>$2.4 \times 10^{-13}$</td>
</tr>
<tr>
<td>(R5)</td>
<td>C$_2$H$_6$O$_2$ + NO $\rightarrow$ C$_2$H$_5$O + NO$_2$</td>
<td>$6.5 \times 10^{-12} \times e^{(380/T)} \times 0.99$</td>
<td>$9.1 \times 10^{-12}$</td>
</tr>
<tr>
<td>(R6)</td>
<td>C$_2$H$_5$O + O$_2$ $\rightarrow$ C$_2$HCHO + HO$_2$</td>
<td>$2.4 \times 10^{-14} \times e^{(-525/T)}$</td>
<td>$8.1 \times 10^{-15}$</td>
</tr>
<tr>
<td>(R7)</td>
<td>PAN $\rightarrow$ CH$_3$CO$_3$ + NO$_2$</td>
<td>See Table 4</td>
<td>$4.4 \times 10^{-4}$ s$^{-1}$</td>
</tr>
<tr>
<td>(R8)</td>
<td>CH$_3$(CO)O$_2$ + NO $\rightarrow$ NO$_2$ + CH$_3$C(O)O$\rightarrow$NO$_2$ + CH$_3$ + CO$_2$</td>
<td>$7.5 \times 10^{-12} \times e^{(290/T)}$</td>
<td>$2.0 \times 10^{-11}$</td>
</tr>
<tr>
<td>(R9)</td>
<td>PPN $\rightarrow$ C$_2$H$_5$CO$_3$ + NO$_2$</td>
<td>See Table 4</td>
<td>$3.7 \times 10^{-4}$ s$^{-1}$</td>
</tr>
<tr>
<td>(R10)</td>
<td>C$_2$H$_5$CO$_3$ + NO + O$_2$ $\rightarrow$ C$_2$H$_5$O$_2$ + NO$_2$ + CO$_2$</td>
<td>$6.7 \times 10^{-12} \times e^{(340/T)}$</td>
<td>$2.1 \times 10^{-11}$</td>
</tr>
<tr>
<td>(R11)</td>
<td>HO + NO + M $\rightarrow$ HONO + M</td>
<td>$7.4 \times 10^{-31} \times (T/300)^{-2.4} \times [M]$</td>
<td>$9.7 \times 10^{-12}$</td>
</tr>
<tr>
<td>(R12)</td>
<td>HO$_2$ + NO$_2$ + M $\rightarrow$ HO$_2$NO$_2$ + M (termolecular)</td>
<td>(termolecular)</td>
<td>(termolecular)</td>
</tr>
<tr>
<td>(R13)</td>
<td>HO$_2$ + HO$_2$ + M $\rightarrow$ H$_2$O$_2$ + M (termolecular)</td>
<td>(termolecular)</td>
<td>(termolecular)</td>
</tr>
<tr>
<td>(R14)</td>
<td>CH$_3$CO$_3$ $\rightarrow$ 0.7 CH$_3$CO$_2$ + 0.3 CH$_3$CO$_2$H</td>
<td>$5.0 \times 10^{-12} \times \sum$RO$_2$</td>
<td>$5.0 \times 10^{-12} \times \sum$RO$_2$</td>
</tr>
<tr>
<td>(R15)</td>
<td>C$_2$H$_5$CO$_3$ $\rightarrow$ 0.7 C$_2$H$_5$CO$_2$ + 0.3 C$_2$H$_5$CO$_2$H</td>
<td>$5.0 \times 10^{-12} \times \sum$RO$_2$</td>
<td>$5.0 \times 10^{-12} \times \sum$RO$_2$</td>
</tr>
<tr>
<td>(R16)</td>
<td>CH$_3$O$_2$ $\rightarrow$ 0.330 CH$_3$O + 0.335 HCHO + 0.335 CH$_3$OH</td>
<td>$1.8 \times 10^{-13} \times e^{(416/T)} \times \sum$RO$_2$</td>
<td>$7.4 \times 10^{-13} \times \sum$RO$_2$</td>
</tr>
<tr>
<td>(R17)</td>
<td>C$_2$H$_5$O$_2$ $\rightarrow$ 0.6 C$_2$H$_2$O + 0.2 CH$_3$CHO + 0.2 C$_2$H$_5$OH</td>
<td>$3.1 \times 10^{-13} \times \sum$RO$_2$</td>
<td>$3.1 \times 10^{-13} \times \sum$RO$_2$</td>
</tr>
</tbody>
</table>

$^a$ Rate constant expressions are from the Master Chemical Mechanism (MCM); Jenkin et al. (1997); Saunders et al. (2003) version 3.3.1, except Reactions (R7) and (R9), which are from Kabir et al. (2014).

$^b$ Calculated using $[O_2] = 4.2 \times 10^{16}$ molecules cm$^{-3}$.

When used in polluted (i.e., high-NO$_x$) environments, however, a drawback of the TD methods is that quantification of ΣPN (and, to a lesser degree, also of ΣPAN) is compromised because of the large error introduced from subtraction of the NO$_2$ background, which is often 2–4 orders of magnitude larger than the ΣPN abundance. In such high-NO$_x$ environments, however, mixing ratios of RO$_x$ radicals are generally much smaller, < 100 pptv (Wood et al., 2016), than those of NO$_2$, such that a better strategy may be to quantify the peroxy and peroxyacetyl radicals generated in stoichiometric amounts during TD of ΣPN and/or ΣPAN rather than NO$_2$.

The RO$_x$ radicals may be quantified by chemical ionization mass spectrometry (CIMS) (Hanke et al., 2002; Edwards et al., 2003; Chen et al., 2004; Slusher et al., 2004; Hornbrook et al., 2011); in fact, a TD-CIMS method has been developed to quantify PAN by titrating the peroxyacetyl radical with iodide reagent ion (Slusher et al., 2004). Other RO$_x$ radical detection methods include LIF (Faloona et al., 2004; Heard, 2006; Fuchs et al., 2008; Dusanter et al., 2009) and peroxy radical chemical amplification (PERCA) coupled to NO$_2$ detection (Cantrell et al., 1984; Hastie et al., 1991; Green et al., 2006; Liu and Zhang, 2014; Horstjann et al., 2014). The PERCA method is attractive as it allows the infrastructure of existing TD instruments with NO$_2$ detection to be utilized.

In PERCA coupled to NO$_2$ detection, concentrations of RO$_x$ radicals are amplified by factors of between ~ 20 and ~ 190 through a series of catalytic reactions, usually involving parts-per-million by volume (ppmv, 10$^{-6}$) mixing ratios of nitric oxide (NO) and percent levels of either carbon monoxide (CO) (Cantrell et al., 1984) or a short-chain hydrocarbon such as ethane (C$_2$H$_6$) (Mihele and Hastie, 2000; Wood et al., 2016) (Reactions R1–R6, Table 3). Under these conditions, the peroxy radicals catalytically convert NO to NO$_2$, and the amount of NO$_2$ produced over a constant reaction period is proportional to the number of radicals that were present originally.

The measurement of peroxy radicals by PERCA is prone to matrix effects and interferences. For instance, a key operational parameter of any PERCA instrument is the radical chain length (CL) or amplification factor, which must be carefully calibrated. This chain length is suppressed by water vapor, whose presence increases the rates of radical loss on the inner walls of the PERCA chamber and the rates of certain gas-phase reactions, e.g., the reaction between the hydroperoxyl radical and water dimer (HO$_2$·H$_2$O) with NO to peroxy nitrous acid (HOONO), which isomerizes to nitric acid (HONO$_2$) (Mihele and Hastie, 1998, 2000; Mihele et al., 1999).

The most obvious way to minimize wall reactions and to prevent weakly bound clusters such as HO$_2$·H$_2$O from forming is to apply heat. When quantification of ambient RO$_x$ radicals is the goal, this is avoided to prevent TD of ΣPN or ΣPAN (which are more abundant than free RO$_x$ radicals). TD of ΣPN or ΣPAN produces radicals that in-
terfere with the measurement of free ROx radicals (Mihele and Hastie, 2000). In contrast, if measurement of ΣPN or ΣPAN is desired (such as in this paper), this interference is turned into a measurement principle. We are aware of only one prior attempt to quantify peroxy nitrates in this manner: Blanchard et al. (2013) thermally decomposed PAN eluting from a chromatographic column in the presence of NO and CO and quantified the amplified NO2 using luminol chemiluminescence.

In this paper, we probe the feasibility of selectively quantifying ΣPN and ΣPAN through their respective peroxy radical TD fragments by thermal decomposition peroxy radical chemical amplification cavity ring-down spectroscopy (TD-PERCA-CRDS). The instrument uses a 405 nm blue diode laser CRDS (Paul and Osthoff, 2010) to monitor NO2 and the ethane-based chemical amplification scheme described by Wood et al. (2016), chosen because of ethane’s lower toxicity compared to CO. Thermal dissociation profiles were determined for PAN, PPN, and PNA. Quantification of trace levels of PAN, PPN, and PNA by TD-PERCA-CRDS is demonstrated and compared to parallel measurements by iodide CIMS. The suitability of TD-PERCA-CRDS as a highly sensitive (sub-pptv) ΣPN and ΣPAN detection method for ambient measurements is discussed.

2 Experimental section

2.1 TD-PERCA-CRDS

2.1.1 Single-channel inlet

The majority of the experiments described in this paper were conducted using a single-channel TD-PERCA inlet that is described and depicted as Fig. S1 of the Supplement of Taha et al. (2018). Briefly, NO in N2 (100.2 ppmv, Scott-Marrin, Riverside, CA) was scrubbed of NO2 by passing through iron(II) sulfate heptahydrate (99 %, Sigma-Aldrich, Oakville, ON) prior to being combined with either a flow of N2 gas (Praxair) or ethane (CP grade, 99 %, Matheson, Baskin Ridge, NJ). The gas mixture was directed towards the 80 cm long PERCA chamber (1.27 cm or 1 in. outer diameter – o.d.). When NO and N2 were mixed prior to the PERCA chamber, a “PERCA off” signal was observed, and ethane was added after the PERCA chamber to maintain constant flow (and pressure) through the system. Conversely, when NO and ethane were directed towards the PERCA chamber a “PERCA on” signal was observed. To maintain flows and pressures through the system during “PERCA on” mode, N2 was added to the inlet at an addition point after the PERCA chamber.

The inlet was connected to a four-channel CRDS described elsewhere (Odame-Ankrah, 2015). Briefly, concentrations of NO2 were monitored via its absorption at 405 nm (Paul and Osthoff, 2010). A flow containing ppmv levels of O3 in O2 was added to one CRDS channel to monitor NO2 (Fuchs et al., 2009). The remaining two channels were equipped with heated quartz tubes to monitor NO2 + ΣPN and NO2 + ΣPAN + total alkyl nitrates (ΣAN) (Paul et al., 2009). Each channel was connected to a MFC set to a flow rate of ~0.84 slpm All four CRDS cells were connected to sample the gases exiting the single-channel TD-PERCA inlet, though in principle a single CRDS detection channel would have sufficed to carry out the measurements.

When radical free “zero” air was sampled with the single-channel inlet, a negative offset (up to 1 ppbv) was observed when the three-way solenoid valves were switched between PERCA “on” and “off” (data not shown). This artifact was not observed with the dual-channel setup (Sect. 2.1.2) and was not further investigated but may have been caused by differences in the ethane flows through the needle valve induced by pressure changes (up to 15 Torr) during switching between PERCA on and off.

2.1.2 Dual-channel TD-PERCA-CRDS

Time resolution, signal-to-noise ratio, and subtraction of background NO2 can be significantly improved in a PERCA instrument by implementing dual detection channels where both amplified and background signals are simultaneously monitored (Green et al., 2006; Cantrell et al., 1996). The dual-channel TD-PERCA setup used in this work is shown in Fig. 1. The NO reagent gas is added at the same flow rate and concentration as in the single-channel version near the tip of the inlet (after the zero air and calibration gas ports). The residence time prior to the ethane addition point (~2.0 s) suffices to destroy ROx radicals (via reaction with NO) prior to chemical amplification. Addition of either NO or ethane is on–off modulated using two-way normally open valves connected to a pump via 50 µm critical orifices (Lenox Laser, Glen Arm, MD) in a similar fashion as described earlier (Odame-Ankrah and Osthoff, 2011).

A portion of the sample flow of ~0.74 slpm was diverted prior to TD to monitor the “background” NO2 concentration in one CRDS channel. The remaining flow (~2.2 slpm) was passed through the heated quartz tube and PERCA chamber as described earlier and sampled by the other three CRDS channels to monitor background NO2 plus the amplified NO2 signal.

2.1.3 Four-channel differential temperature

TD-PERCA-CRDS

An instrument with four identical measurement channels was set up to enable simultaneous quantification of NO2, NO2 + ΣPN, and NO2 + ΣPAN + ΣAN. This version was similar to dual-channel setup described above and simply added two additional PERCA chambers; all three PERCA chambers were connected to separate CRDS channels. The quartz PERCA chamber was replaced with three identical
Figure 1. Schematic of the dual-channel thermal decomposition peroxy radical chemical amplification inlet. The inlet consists of a 60 cm long, 0.635 cm (1/4 in.) o.d. quartz heater and an 80 cm long, 1.27 cm (1/2 in.) o.d. FEP Teflon™ reaction chamber. Reaction gases were added upstream of the PERCA chamber by closing the normally open valves connected to a waste pump via 50 µm critical orifices. Background NO$_2$ levels were monitored in a parallel detection channel by tapping into the inlet prior to thermal dissociation of peroxy nitrates.

1.27 cm (1/2 in.) o.d. and 0.95 cm (3/8 in.) inner diameter (i.d.) fluorinated ethylene propylene (FEP) Teflon™ tubes externally heated using stretch-to-fit heaters (Watlow, St. Louis, MO) to 60, 80, and 100 °C, respectively. A common inlet filter was placed between the PERCA chambers and the ethane addition point. A flow restriction was placed ahead of the common filter to achieve a pressure of 380–400 Torr at a flow rate of 0.8 slpm per channel (total flow rate ∼3.2 slpm).

2.2 Synthesis and delivery of PAN and PPN

The synthesis of PAN and PPN from their corresponding anhydrides was described earlier (Mielke and Osthoff, 2012; Furgeson et al., 2011). Aliquots in tridecane were stored in 2.0 mL centrifuge tubes (VWR) in a freezer until needed.

To separate PAN and PPN from impurities generated during synthesis and storage (i.e., NO$_2$, HNO$_3$, and alkyl nitrates; Grosjean et al., 1994), a preparatory-scale gas chromatography (GC) setup (Fig. 2) was used. First, the contents of two tubes containing PAN and PPN in tridecane were combined in a three-valve glass vessel. This vessel was connected to a two-position GC Valve (VICI Valco EH4C10WE, Houston, TX) and mildly pressurized (∼0.1 atm above ambient) using oxygen (Praxair) delivered through a 10 µm critical orifice. Two megabore capillary GC columns (Restek RTX-1701, 0.53 mm i.d., 1.00 µm film thickness, State College, PA) of equal lengths (3 m) were connected to the ports adjacent to the one connected to the glass vessel. The outlet of one GC column was connected to the PERCA inlet, whereas the other was exhausted into a waste line. The port opposite to the glass vessel was also pressurized with oxygen such that both columns remained under flow at all times. Gases were delivered by switching the valve to position A (Fig. 2) for ∼40 s. The output of the preparatory-scale GC was diluted with zero air or air passed through a custom-built scrubber system to meet the sample flow requirements of the TD-PERCA CRDS and/or CIMS. The relative humidity (RH) of the gases delivered was monitored using a temperature–RH probe (VWR) placed inline.

The preparatory-scale GC setup allowed delivery of short “bursts” of PAN and PPN. To deliver a constant and low PAN concentration over prolonged time periods, air was drawn from a 4000 L Teflon chamber, initially filled with scrubbed (i.e., PAN-free) air and to which the head space above a PAN / tridecane solution had been added. An internal mixing fan ensured constant output.

2.3 Synthesis and delivery of PNA

2.3.1 Batch sample

A batch PNA sample was synthesized from reaction of nitronium tetrafluoroborate (NO$_2$BF$_4$; Sigma-Aldrich) with H$_2$O$_2$ as described by D. X. Chen et al. (2017). Briefly, a 50 % H$_2$O$_2$ solution (Sigma-Aldrich) was concentrated using a gentle N$_2$ flow over a period of several days. A small
aliquot (200 µL) of concentrated H$_2$O$_2$ was placed in a threevalve glass vessel cooled to 0 °C using an external circulating chiller, and 120 mg of NO$_2$BF$_4$ were added. The headspace of the glass vessel was flushed with a 50 sccm flow of N$_2$ delivered by a MFC. This flow delivered very high concentrations and contained substantial and variable amounts of impurities (mainly HNO$_3$), even when the vessel temperature was lowered to −20°C. The batch sample was used to calibrate the CIMS against TD-CRDS (Sect. 2.4).

2.3.2 Photolysis source

Gas flows containing low and reproducible concentrations of PNA were generated dynamically in a similar fashion to the method described by Veres et al. (2015) by combining the output of a HO$_2$ photochemical source with NO$_2$. Ultrapure N$_2$ (Praxair) was passed through a bubbler filled with deionized water at a flow rate of 100 sccm and combined with 2 sccm of O$_2$ (Praxair). This mixture was passed through a 1/4 in. (0.635 cm) o.d. quartz tube partially illuminated by a low-pressure 185 nm mercury quartz lamp (Jelight 95-2100-2, Irvine, CA). This generated a mixture of O$_3$ (~30 ppbv after dilution), OH and HO$_2$, whose concentrations were controlled with a sliding metal sleeve (VWR) which modified the length of the quartz tubing that was illuminated. This flow was combined with between 4 and 16 ppmv NO$_2$ to yield a gas mixture containing PNA which was immediately (< 5 cm tube length) diluted with zero or scrubbed air flowing at a rate slightly greater than the amount sampled by the instruments. The NO$_2$ gas stream was generated by mixing between 1.4 and 3.0 sccm of NO (100.2 ppmv in N$_2$; Scott-Marrin, Riverside, CA) with a slightly less than stoichiometric amount of O$_3$ in ~20 sccm O$_2$, generated by illuminating O$_2$ with a low-pressure 254 nm mercury quartz lamp (Jelight). The amount of PNA delivered from this source was quantified by TD-CRDS.

2.4 Chemical ionization mass spectrometry

The CIMS and its operation have been described elsewhere (Mielke et al., 2011; Mielke and Osthoff, 2012; Abida et al., 2011). For measurements of PAN or PPN, the instrument was operated with iodide reagent in declustering mode (collisional dissociation chamber voltage = −8.9 V); under these conditions, ~5 × 10$^5$ I$^-$ and ~2 × 10$^4$ I$^-$ · H$_2$O ions were observed. Mixing ratios of PAN were monitored primarily using NO$_2^−$ at m/z 62, which is formed via PNA decomposition within the IMR (Abida et al., 2011). The HNO$_3$ · I$^−$ and HO$_2$NO$_2$ · I$^−$ clusters at m/z 190 and m/z 206 (Veres et al., 2015; D. X. Chen et al., 2017) were also monitored.

The PNA response factors were determined using TD-CRDS (i.e., without added PERCA gases) with its inlet operated at 120 °C (Fig. 3). Assuming that one equivalent of NO$_2$ is generated for each PNA molecule thermally dissociated, the CIMS response factors, normalized to 10$^6$ I$^-$ counts, were 34.7 ± 0.2 Hz pptv$^{-1}$ and 0.023 ± 0.002 Hz pptv$^{-1}$ at m/z 62 and 206, respectively. These response factors are consistent with calibration factors by other groups (Veres et al., 2015; D. X. Chen et al., 2017), with the low response at m/z 206 rationalized by the low number of I$^−$ · H$_2$O ions. Even though the CIMS response at m/z 62 is not specific (Abida et al., 2011), it was used in the laboratory experiments presented here to monitor PNA rather than m/z 206 because of its larger response factor and thus higher sensitivity.

2.5 Box model simulations

Box model simulations were carried out using a subset of the Master Chemical Mechanism (MCM) V3.3.1 obtained from http://mcm.leeds.ac.uk/MCM (Jenkin et al., 1997, 2012; Saunders et al., 2003) and the Kinetic Preprocessor (KPP) (Sandu and Sander, 2006) to aid in the interpretation of observations. Details are given in the Supplement.
Table 4. Arrhenius parameters for thermal dissociation of selected PN, PAN, PPN, PAA, and O₃.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>A (s⁻¹)</th>
<th>E_a (kJ mol⁻¹)</th>
<th>Reference</th>
<th>T needed to dissociate 0.1 % (°C)b</th>
<th>T needed to dissociate 99.9 % (°C)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO₂NO₂ (PNA)</td>
<td>7.3 × 10¹⁴ᵇ</td>
<td>88.1 ± 4.4</td>
<td>Atkinson et al. (1997)</td>
<td>24</td>
<td>123</td>
</tr>
<tr>
<td>CH₃O₂NO₂ (MPN)</td>
<td>1.1 × 10¹⁶</td>
<td>88.1 ± 4.4</td>
<td>Atkinson et al. (1997)</td>
<td>3</td>
<td>86</td>
</tr>
<tr>
<td>C₂H₅O₂NO₂ (EPN)</td>
<td>8.8 × 10¹⁵</td>
<td>86.5 ± 8.7</td>
<td>Atkinson et al. (1997)</td>
<td>0</td>
<td>82</td>
</tr>
<tr>
<td>CH₃C(O)O₂NO₂ (PAN)</td>
<td>2.8 × 10¹⁶</td>
<td>113 ± 2</td>
<td>Kabir et al. (2014)</td>
<td>73</td>
<td>174</td>
</tr>
<tr>
<td>C₂H₅C(O)O₂NO₂ (PPN)</td>
<td>2.36 × 10¹⁶</td>
<td>113 ± 2</td>
<td>Kabir et al. (2014)</td>
<td>75</td>
<td>176</td>
</tr>
<tr>
<td>CH₃C(O)O₂H (PAA)</td>
<td>10¹⁴</td>
<td>134 ± 8</td>
<td>Schmidt and Sehon (1963)</td>
<td>206</td>
<td>377</td>
</tr>
<tr>
<td>CH₃C(O)O₂H (PAA)</td>
<td>1.15 × 10¹³</td>
<td>136</td>
<td>Devush et al. (1983)</td>
<td>247</td>
<td>450</td>
</tr>
<tr>
<td>CH₃C(O)O₂H (PAA)</td>
<td>5 × 10¹⁴</td>
<td>168 ± 4</td>
<td>Sahetchian et al. (1992)</td>
<td>300</td>
<td>492</td>
</tr>
<tr>
<td>O₃</td>
<td>1.3 × 10¹⁰ᵃ</td>
<td>92.8</td>
<td>Jones and Davidson (1962); Heimerl and Coffee (1979)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Calculated assuming a pressure of 550 Torr and temperature of 298 K.
b Assuming a contact time of 4 ms at the maximum temperature (Paul et al., 2009).

3 Results

3.1 Thermal dissociation profiles

The TD profiles of PNA, PAN, and PPN were measured by TD-CRDS (i.e., without amplification) with the single-channel inlet and are shown in Fig. 4. The superimposed trend lines are simulations based on the TD model introduced by Paul et al. (2009) and the Arrhenius parameters in Table 4 and are consistent with the observations. The TD profiles of PNA and PAN/PPN partially overlap and are consistent with the 5% / 95% ranges given in Fig. 3 of Wooldridge et al. (2010). PNA and PAN or PPN fully dissociated at temperatures of 120 and 250°C, respectively. These temperatures were used in subsequent experiments when complete dissociation of either PNA or PAN and PPN was desired. Also shown in Fig. 4 is the TD-PERCA-CRDS signal observed when sampling O₃, an interfering species (see Sect. 3.6.1).

3.2 Measurement of PAN and PPN by TD-PERCA-CRDS

A time series demonstrating amplification of PAN and PPN in the TD-PERCA-CRDS is shown in Fig. 5. In this experiment, PAN and PPN were delivered via the preparatory-scale GC (Fig. 2), and the single-channel setup (Sect. 2.1.1) was used.

PAN and PPN eluted from the GC column after 3 and 6 min, respectively. The compounds eluted as plateaus because of the relatively long (~30 s) injection time. In Fig. 5a, PAN and PPN are observed only by the heated (NO₂ + ΣPAN) TD-CRDS channel. This channel was operated with its quartz inlet at 250°C to quantitatively (see Fig. 5 of Paul et al., 2009) decompose PAN and PPN to NO₂. In this example, mixing ratios of 2.00 ± 0.09 ppbv and 1.86 ± 0.12 ppbv were observed, respectively (errors are 1σ of 1 s data). After the PERCA heater was set to 250°C as well, similar amounts of NO₂, 2.04 ± 0.09 ppbv and 1.97 ± 0.12 ppbv were observed in the ambient temperature channel for PAN and PPN, respectively. Marginally higher amounts were observed in the heated CRDS channel (2.42 ± 0.10 and 2.06 ± 0.14 ppbv) (Fig. 5b). The lower amounts observed in the unheated CRDS channel result from recombination of peroxyacyl radicals with NO₂ (mostly in the unheated PERCA chamber), which suppresses the signal in the unheated CRDS channel but not in the heated one. Hence, the NO₂ + ΣPAN data are a more accurate measure of the PAN and PPN concentrations delivered.
Figure 5. Peroxy radical chemical amplification of peroxyacetic and peroxypropionic nitric anhydride (PAN and PPN) delivered via a megabore GC column. (a) Time series of the signal observed by cavity ring-down spectroscopy in the ambient temperature (NO$_2$; green) and heated (NO$_2$ + ΣPAN; purple) channels with the PERCA heater off. (b) Same as (a) with the PERCA heater switched on. (c) Same as (b) with 0.75 ppmv NO added. (d) Same as (c) with 1.5 % C$_2$H$_6$ added. The amplification factor is determined from the ratio of the ambient temperature (i.e., NO$_2$) CRDS signal observed in (d) divided by that observed in (b).

Figure 6. TD-PERCA-CRDS amplification factors of ∼0.5 ppbv PAN and ∼1.3 ppbv PPN as a function of NO mixing ratio at RH = 0 %. The error bars represent standard deviations of 1 s data.

Because PAN and PPN dissociate with 1 : 1 stoichiometry, the amount of peroxyacyl radicals produced during thermal dissociation is the same as the amount of NO$_2$ generated. When ∼0.75 ppmv of NO was added (Fig. 5c), the peroxyacyl and, subsequently, the methyl (or ethyl) peroxy and the hydroperoxyl radicals oxidize NO to NO$_2$ (Reactions R8/R10, R1/R5, and R3; Table 3) and the NO$_2$ signal relative to the signal obtained in the absence of NO is amplified by a factor of 4. The ratios observed (Fig. 5c relative to Fig. 5b) were 4.0 ± 0.2 and 3.8 ± 0.3 for PAN and PPN, respectively, and are consistent with earlier observations at lower NO mixing ratios (i.e., Fig. 6 of Paul and Osthoff, 2010).

Next, NO and ethane were added at mixing ratios (0.75 ppmv NO and 1.5 % C$_2$H$_6$) that Wood et al. (2016) determined to be optimal for ambient temperature PERCA. Under these conditions, the signals amplified to 116.0 ± 1.3 ppbv and 109.3 ± 0.7 ppbv (Fig. 5d), corresponding to CLs (relative to Fig. 4b) of 48 ± 2 and 53 ± 4 for PAN and PPN, respectively.

In the presence of ethane, marginally lower NO$_2$ concentrations (98.7 and 98.1 %) were observed in the heated, NO$_2$ + ΣPAN TD-CRDS channel (compared to the absence of ethane). Partial scrubbing of NO$_2$ in heated quartz cells has been anecdotally observed in our group’s and also others’ (Womack et al., 2017) TD instruments; this effect varies between quartz cells and with sample history. Since the effect was relatively minor, it was neglected in this work.

3.3 Optimization of TD-PERCA amplification factors

Sequences, such as the one shown in Fig. 5, were used to determine conditions leading to optimum amplification factors. The largest amplification factors were obtained with an ethane mixing ratio of ∼1.6–1.7 % (data not shown).

Figure 6 shows how the chain length varies with NO mixing ratio. In the absence of ethane, amplification factors of ∼4 were observed (Fig. 6, open symbols), consistent with the results shown in Fig. 5c. When 1.7 % ethane was added, the amplification factor increased with NO mixing ratio up to a maximum at 550 ± 150 ppbv and then decreased, qualitatively consistent with the results reported by Wood et al. (2016).

The amplification factors shown in Fig. 6 were slightly larger for PAN than for PPN mainly because the PPN mixing ratio of ∼1.3 ppbv exceeded the optimum concentration range for PERCA (see Sect. 3.5.2).

3.4 Parallel measurement of PNA by TD-PERCA-CRDS and CIMS

A sample time series showing TD-PERCA-CRDS measurements of photochemically generated PNA in scrubbed air is presented in Fig. 7. Here, the TD-PERCA-CRDS was operated with the dual-channel inlet (Fig. 1) at 120 °C and with 1.6 % C$_2$H$_6$ and 316 ± 3 ppbv of NO (suboptimal NO mixing ratios). Figure 7a shows the NO$_2$ mixing ratios in the reference NO$_2$ channel (green trace) and in the TD-PERCA-CRDS channel (grey trace). In this example, the mixing ratio of PNA was changed approximately every 2 min by moving a sliding cover within the photochemical source.
The difference between these two signals is displayed in Fig. 7b (red trace, left-hand axis). Superimposed in Fig. 7b (right-hand axis) are the CIMS responses at \( m/z \) 62 (NO\(_2\)), \( m/z \) 206 (HONO \( \cdot \) \( \cdot \) \( \cdot \)), multiplied by a factor of 100 for clarity), and \( m/z \) 190 (HNO\(_3\) \( \cdot \) \( \cdot \) \( \cdot \)).

The photochemical source co-generates OH which is lost on the inner walls of the quartz tubing or is titrated by NO to HNO\(_3\) or HONO, respectively. Conceivably, the co-generation of HNO\(_3\) could interfere with quantification of PNA by CIMS at \( m/z \) 62. However, when the photolysis source was turned off at \( \sim 19:59 \) (Fig. 7), HNO\(_3\) was still observed for some time after at \( m/z \) 190 due to slow desorption from the inner walls of the connecting tubing, whereas the ion counts at \( m/z \) 62 quickly (<10 s) returned to background values close to 0 Hz, indicating that the contribution of HNO\(_3\) to ion counts at \( m/z \) 62 was negligible.

The scatter plot of the TD-PERCA-CRDS and CIMS data at \( m/z \) 62, multiplied by the CIMS response factor determined in Fig. 3a, is shown in Fig. 8a as dark blue circles. The signals by the two instruments are highly correlated \( (r^2 = 0.979) \), consistent with both instruments measuring the same molecule, PNA. The slope of this plot \( (26.3 \pm 0.4) \) equals the TD-PERCA-CRDS amplification factor for PNA. In contrast, the scatter plot of TD-PERCA-CRDS with the CIMS response at \( m/z \) 206 was unusable because of the latter’s poor signal-to-noise ratio (Fig. 3b).

### 3.5 Factors affecting amplification factors

The amplification factor for PNA shown in Fig. 8a is less than observed for PAN in Fig. 8b and for PAN and PPN under optimal conditions (Fig. 6). Though in this particular example the lower amplification factor was due to the less than optimal amount of NO added, lower amplification factors for PNA than for PAN were generally observed, even when optimum NO mixing ratios were used.

The obvious difference is that different radicals, HO\(_2\) in the case of PNA and a peroxyacyl radical (RC(O)O\(_2\)) in the case of PAN or PPN, are generated initially. However, in both cases, the HO\(_2\) / HO radical pair is the main carrier of the amplification, such that this initial difference should only have a marginal effect. Wood et al. (2016) estimated the uncertainty arising from the range in peroxy radical reactivity to ±9 %.

Experimental parameters that can affect the amplification factor include relative humidity, radical concentration, and the PERCA inlet temperature; these factors are probed separately in the following sections. In each case, box model simulations were carried out (see the Supplement) to aid in the interpretation of the data.

#### 3.5.1 Dependence of chain lengths on relative humidity

We repeated the experiment described in Sect. 3.4 with the scrubbed air humidified to 75 % RH by passing the make-up air through a bubbler. The resulting scatter plot is superimposed in Fig. 8a as red squares. Indeed, the amplification factor for PNA was lowered from 26.3 ± 0.4 to 18.0 ± 0.2 when the RH was increased from 20 to 75 %. Following these observations, the RH dependence was investigated systematically at constant NO and ethane concentrations. The results are summarized in Fig. 9.

The amplification factor decreased by \( (2.0 \pm 0.6) % \) for every 10 % increase in RH. This RH dependence is less than reported for ambient temperature PERCA: between a RH of...
0 and 50 %, for example, the response of room temperature PERCA dropped by 30 % (Wood et al., 2016), whereas that of TD-PERCA decreased by 15 %. A reduced RH dependence is expected as the elevated temperature suppresses formation of HO2 + H2O (Kanno et al., 2006), whose reaction with NO is a major radical sink (Mihele and Hastie, 1998, 2000; Mihele et al., 1999). This interpretation is supported by box model simulations, which show a reduced RH dependence of the CL at higher temperatures (Fig. S4 in the Supplement). In addition, we speculate that reactions of radicals on the inner walls of PERCA tubing are reduced at higher inlet temperature.

### 3.5.2 Dependence of chain lengths on radical concentration: dynamic range

It is well known in the PERCA community that the chain lengths decrease at high radical concentrations due to radical–radical reactions. Figure 8a and b demonstrate that the response of TD-PERCA-CRDS is linear for both PNA and PAN / PPN at low, atmospherically relevant mixing ratios (i.e., below ∼600 pptv). The linear dynamic range is similar for PNA and PAN and PPN since the radical chain carriers are the same for both.

Figure 10 summarizes the PERCA responses as functions at larger PAN / PPN mixing ratios. The largest amplification factor, 69 ± 5, was observed when the TD-PERCA inlet was operated at 250 °C with PAN or PPN mixing ratios ≤ 600 pptv. Shorter chain lengths were observed at higher mixing ratios (e.g., 62 ± 2 at 1300 pptv, 53 ± 4 at 2100 pptv, and 48 ± 2 at 2400 pptv, respectively). Thus, the amplification factor is concentration-dependent at RO2 mixing ratios above 600 pptv and is constant under atmospherically relevant trace conditions.

PERCA reactors utilizing CO as a chain carrier show non-linearity at RO2 mixing ratios above ∼200 pptv (Hastie et al., 1991), while room temperature ethane-based PERCA has a reported linear dynamic range up to ∼800 pptv (Wood et al., 2016). The greater dynamic range with ethane arises because of lower chain lengths and radical concentrations in the reactor and hence reduced radical–radical termination reactions (Wood et al., 2016). The linear range of the ethane TD-PERCA reactor of ∼600 pptv falls in between these two extremes, as the CL and radical concentrations are greater than ethane PERCA at room temperature but less than those achievable with CO PERCA.

The linear range observed is consistent with box model simulations, in particular when wall loss reactions are taken into account (Fig. S6 in the Supplement).

### 3.5.3 Dependence of chain lengths on inlet temperature

Next, we investigated the temperature dependence of the TD-PERCA-CRDS signal when sampling photochemically generated PNA at constant RH and PNA mixing ratio. Figure 11 shows such a temperature scan of ∼180 pptv PNA (measured in parallel by CIMS). The non-amplified TD profile observed by TD-CRDS is superimposed for comparison.

A striking feature in Fig. 11 is the very large increase in the amplified NO2 signal observed at temperatures above ∼150 °C. This is an artifact that arises from O3 co-emitted by the photochemical source and is commented on further in Sect. 3.6.1.

It is obvious from Fig. 11 that the amplification factor is strongly dependent on temperature; even though PNA fully dissociates at temperatures > ∼90 °C in our inlets (Fig. 4),
the amplified signal increases by $\sim 60\%$ in the region from 90 to 135°C (Fig. 11, insert), corresponding to amplification factors of $\sim 15$ and $\sim 22$, respectively. This increase is qualitatively consistent (if extrapolated) with the higher amplification factor observed with PAN or PPN at 250°C.

Box model simulations using only gas-phase chemistry from the MCM V3.3.1 (Fig. S3 in the Supplement) show that the CL is expected to decrease with increasing temperature, opposite to what is observed. This occurs in the model because the chain-carrying reactions of HO$_2$ and RO$_2$ with NO (e.g., Reaction R3, Table 3) have negative activation energies and are hence slower at higher temperatures, yielding a lower CL at higher temperature. This is partially offset when the chemistry of HO$_2$ + H$_2$O is added to the mechanism (Figs. S4 and S5 in the Supplement) but does not suffice to achieve a higher CL at higher temperature; the latter is only predicted by the box model simulations if much lower wall loss reactivity of OH and HO$_2$ is assumed (see S1.3 and S1.4 in the Supplement).

3.6 Interferences

3.6.1 Interference from O$_3$ in the measurement of $\Sigma$PAN at 250°C

When sampling ambient air (data not shown) or when sampling photochemically generated PNA (Fig. 11) the amplified NO$_2$ increases sharply at PERCA inlet temperatures above $\sim 150°C$. These observations can be rationalized by thermal decomposition of O$_3$. Even though only a small fraction of O$_3$ dissociates to O$_2$ + O at $\sim 150°C$ in the TD inlet ($\sim 0.1\%$; Fig. 5; Jones and Davidson, 1962; Heimerl and Coffee, 1979), a comparatively large signal is generated because the O atom reacts with C$_2$H$_6$ to form two radicals, OH and C$_2$H$_3$ (Baulch et al., 1994). This reaction is competitive in the PERCA inlet (compared to reaction of O with O$_2$) because of the high C$_2$H$_6$ concentration (1.7%); the lifetime of O with respect to reaction with C$_2$H$_6$ is $\sim 0.34\ ms$, which is of similar magnitude as the expected lifetime of O with respect to reaction with O$_2$ of $\sim 0.15\ ms$ (Hippler et al., 1990).

We considered an alternate inlet configuration in which the inlet length between the NO and ethane addition points is increased to allow for sufficient residence time completely titrate O$_3$ with the added NO. However, at the optimum NO mixing ratio for PERCA, the $1/e$ lifetime of O$_3$ is $\sim 6\ s$, making this approach unfeasible.

Hence, if O$_3$ is sampled with an ethane-based TD-PERCA instrument heated above 150°C, radicals are generated that are amplified by PERCA. Since O$_3$ is typically present at mixing ratios in the tens of ppbv in ambient air, quantification of $\Sigma$PAN with an ethane-based TD-PERCA-CRDS would be challenging. In contrast, TD-PERCA instruments using CO will not have this limitation, as CO reacts with O to CO$_2$ and would not generate RO$_x$ radicals.

3.6.2 Interference from peroxyacetic acid in the measurement of $\Sigma$PAN at 250°C

In a previous paper (Taha et al., 2018), we reported interference from peroxyacetic acid (PAA) when the inlet was operated at 250°C. However, the mixing ratios delivered on those experiments were well above what is expected in ambient air. Further, it is unclear what fraction of PAA dissociates at 250°C, since the Arrhenius parameters for TD of PAA are uncertain (Table 4). Regardless of whose Arrhenius parameters are assumed, the temperature needed to dissociate 0.1% of PAN is greater than that needed to dissociate 99.9% of PAN (Table 4). In ambient air, PAA is present at concentrations of up to 1 order of magnitude greater than that of PAN (Phillips et al., 2013). We estimate that under typical conditions, the interference from PAA dissociation is $<1\%$ and likely be completely prevented if the inlet is operated at a temperature below 250°C.

3.6.3 Interference from $\Sigma$PN in the measurement of $\Sigma$PN at 95–110°C

A temperature of 95°C (110°C) is required to dissociate $>90\%$ (>99.9%) of PNA in the TD-PERCA inlet; at these temperatures, $\sim 12\%$ ($\sim 39\%$) of PAN dissociates (Fig. 4). Since [PAN] $>$ [PNA] (Table 1) and hence $\Sigma$PN $>$ $\Sigma$PN in most environments, the contribution of $\Sigma$PN to the $\Sigma$PN signal in ambient air is substantial (and likely also variable given the slope of the PAN TD curve in this region). Hence, measurement of $\Sigma$PN in ambient air by TD-PERCA-CRDS with a single channel relative to an NO$_2$ background measurement is unfeasible.

3.7 Differential temperature TD-PERCA-CRDS for measurement of $\Sigma$PN and $\Sigma$PAN

3.7.1 Synthetic air mixtures

To overcome the limitations outlined in Sect. 3.6, a multi-channel, differential temperature approach was used. Here, two channels were operated at constant temperatures set in the 60 to 110°C range to avoid the interference from O$_3$ dissociation and ensure that response for $\Sigma$PN remains linear (by dissociating only a fraction of its concentration). Since the amount of NO$_2$ generated by TD-PERCA is a function of temperature and radical chain length (CL$_T$) as well as a fraction dissociated ($F_T$) of PNA and $\Sigma$PAN, the responses in the two PERCA channels operated at different temperatures, T1 and T2, are

$$[\text{NO}_2]_{T1} = \text{CL}_{T1} \times F_{\text{PAN},T1} \times [\Sigma\text{PAN}] + \text{CL}_{T1} \times F_{\text{PNA},T1} \times [\Sigma\text{PN}] + [\text{NO}_2]_{\text{ref}}.$$  \hspace{1cm} (1a)

$$[\text{NO}_2]_{T2} = \text{CL}_{T2} \times F_{\text{PAN},T2} \times [\Sigma\text{PAN}] + \text{CL}_{T2} \times F_{\text{PNA},T2} \times [\Sigma\text{PN}] + [\text{NO}_2]_{\text{ref}}.$$  \hspace{1cm} (1b)
Table 5. Products of CL and F for PAN and PNA at 110, 80, and 60°C (RH = 34%).

<table>
<thead>
<tr>
<th></th>
<th>CL_{110°C} \times F_{110°C}</th>
<th>CL_{80°C} \times F_{80°C}</th>
<th>CL_{60°C} \times F_{60°C}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNA</td>
<td>41.8 \pm 0.2</td>
<td>39.5 \pm 0.2</td>
<td>31.9 \pm 0.1</td>
</tr>
<tr>
<td>\Sigma PNA</td>
<td>10 \pm 1</td>
<td>7.6 \pm 0.9</td>
<td>1.2 \pm 0.2</td>
</tr>
</tbody>
</table>

Table 6. Statistics (average ± 1 standard deviation) of the 1 s data shown in Fig. 12.

<table>
<thead>
<tr>
<th>Time period</th>
<th>PNA (pptv)</th>
<th>PAN (pptv)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T1 = 110°C</td>
<td>T1 = 80°C</td>
</tr>
<tr>
<td>T2 = 60°C</td>
<td>T2 = 80°C</td>
<td>T2 = 60°C</td>
</tr>
<tr>
<td>21:48:45–21:49:15</td>
<td>266 \pm 4</td>
<td>267 \pm 4</td>
</tr>
<tr>
<td>21:51:15–21:52:45</td>
<td>261 \pm 5</td>
<td>261 \pm 6</td>
</tr>
</tbody>
</table>

If the CL\_T and F\_T values are measured at temperatures T1 and T2 independently (i.e., offline), and [NO\_2]_ref is quantified in an unheated, parallel reference channel, the mixing ratios of \Sigma PN and \Sigma PAN can be calculated by rearranging Eq. (1a) and (1b):

\[
\begin{align*}
[\Sigma PN] &= \frac{[NO_2]_{T1} - [NO_2]_{ref}}{CL_{T2}F_{PNAN,T2} \times CL_{T1}F_{PNAN,T1}} - \frac{[NO_2]_{T2} - [NO_2]_{ref}}{CL_{T2}F_{PNAN,T2} \times CL_{T1}F_{PNAN,T1}} \times [\Sigma PAN] \quad \text{(2a)} \\
[\Sigma PAN] &= \frac{[NO_2]_{T1} - [NO_2]_{ref}}{CL_{T2}F_{PNAN,T2}} - \frac{[NO_2]_{T2} - [NO_2]_{ref}}{CL_{T2}F_{PNAN,T2} \times [\Sigma PAN]} \quad \text{(2b)}
\end{align*}
\]

A time series demonstrating this approach using the four-channel setup is presented in Fig. 12a. Here, a constant mixing ratio of PAN (along with NO\_2 and O\_3 from the photolysis source) was added to the inlet between 21:44 and 21:55.

At 21:48:30 and at 21:50:45, PAN was added via the GC pre-column. The product of CL and F for PAN and PNA at 110, 80, and 60°C was determined offline and summarized in Table 5, assumed to be the same for all \Sigma PN and \Sigma PAN species.

The time series of PNA and PAN mixing ratios derived from Eq. (2a) and (2b) are presented in Fig. 12b. Consistent results were obtained independent of which pair of channels was used in the calculations (Table 6).
and TD-PERCA-CRDS in reality quantifies
6
ests that the chain lengths and dissociated fractions had not
55x225]
ited by the instrument’s ability to detect differences in NO
55x134]
The ability of TD-PERCA-CRDS to detect radicals is lim-
3.7.2 Laboratory air
The differential temperature TD-PERCA-CRDS was then
used to sample and determine ΣPN and ΣPAN in laboratory
The calibration parameters summarized in Table 5 were
were used since they were determined with scrubbed air, which
has the same RH as the air intake (i.e., the laboratory). The
results are summarized in Table 7.

The calculated room air ΣPN values mixing ratios are neg-
ative (i.e., not physically possible). In contrast, the ΣPAN
mixing ratios are unreasonably large as we have never ob-
served similarly high mixing ratios in our laboratory by GC,
TD-CRDS, or CIMS. Taken together, these observations sug-
gest that there is a species (or several) that dissociates in the
TD inlet and generates RO₃ radicals or, perhaps, atomic oxy-
gen other than ΣPAN. These unknown interfering species
seem to have different TD profiles than PAN and PNA as
the differential response differs when different pairs of chan-
nels are used in the calculation. Furthermore, the response
to the unknown species is more prominent when the hottest
(110°C) channel is used in the calculation.

When ∼260 pptv of PNA and ∼480 pptv PAN (using
the same setup as for Fig. 12 and Table 6) were added to the
sampled laboratory air, the responses (i.e., Δ (ΣPN) and
Δ (ΣPAN) are consistent in all channels, which sug-
gests that the chain lengths and dissociated fractions had not
changed. This observation corroborates that the ethane-based
TD-PERCA-CRDS in reality quantifies ΣPAN*, which in-
cludes PAN, PPN, etc. plus one or more unidentified species.
In Sect. 4, we speculate as to the potential identity of the in-
terfering species.

3.8 Figures of merit
The ability of TD-PERCA-CRDS to detect radicals is lim-
ited by the instrument’s ability to detect differences in NO₂
concentration after amplification, calculated using (Brown et
al., 2002)

\[
[NO_2]_{\text{min}} = \frac{R_L}{\sigma_{\text{NO}_2}} \left( \frac{\Delta \tau_{\text{min}}}{\tau_0^2} \right). \tag{3}
\]

Here, [NO₂]_{\text{min}} is the smallest NO₂ concentration that can
be detected, Δτ_{\text{min}} is the smallest measurable difference
between ring-down time constants in the presence (τ) and
absence (τ₀) of NO₂, c is the speed of light, σ_{\text{NO}_2} is the
NO₂ absorption cross section at 405 nm (6.1 × 10⁻¹⁹ cm²
molecule⁻¹, Paul and Osthoff, 2010), and \( R_L \) is a correction
factor. At the 1σ level, Δτ_{\text{min}} is approximately (Brown et al.,
2002)

\[
\Delta \tau_{\text{min}} = \sqrt{2} \times \sigma(\tau_0). \tag{4}
\]

The precision of the NO₂ measurement (and hence the limit
of detection, LOD) varied slightly between detection chan-
nels and from day to day. Typically, when sampling zero air,
the LOD for NO₂ was ∼100 pptv (1 s, 2σ). In the presence
of NO and ethane reagent gases, the LOD was larger, typically
∼174 pptv (1 s, 2σ).

Employing the dual-channel TD-PERCA-CRDS with the
PERCA heater at 250°C, a CL of 69 factored in, and in the
absence of NO₂, the (1 s, 2σ) LOD for ΣPAN* (calculated on
the basis of observed precision after subtraction of the refer-
ence channel signal, multiplying by 2√2, and dividing this
precision by the CL) was 2.6 pptv. At an inlet temperature of
120°C and with a CL of 26, the LOD for PAN was 6.8 pptv.
When averaging for 90 s, the minimum of an Allan variance
plot (Fig. 7 of Paul and Osthoff, 2010), the LOD improved
to 17 pptv for NO₂, 0.26 pptv for ΣPAN*, and 0.66 pptv for
PNA. Under field conditions, where NO, NO₂, and O₃ con-
centration vary, the LOD is expected to be higher, though this
was not evaluated in this work.

The accuracy of TD-PERCA-CRDS is limited by uncer-
tainties in CL (±7 % for dry air) and variability in the re-
sponse to different type of peroxy radicals (±9 %) (Wood
et al., 2016), and of the NO₂ measurement (±4 %), which
is dominated by uncertainties in the absorption cross section
and \( R_L \) (Paul and Osthoff, 2010). Adding these in quadrature
gives a combined uncertainty of ±12 % for dry air.

An additional uncertainty factor for the differential tem-
perature TD-PERCA-CRDS is the uncertainty in \( F_T \). The
chambers are operated at temperatures where \( F_T \) is highly
sensitive to temperature (Fig. 4). Judging from the scatter

Table 7. Statistics (average ± 1 standard deviation) of the 1 s data of laboratory air (first time period), laboratory air spiked with ∼260 pptv PNA (second period), and laboratory air spiked with 260 pptv PNA and ∼480 pptv PAN (third period).

<table>
<thead>
<tr>
<th>Time period</th>
<th>ΣPN (ppbv)</th>
<th>ΣPAN (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T₁ = 110°C</td>
<td>T₁ = 80°C</td>
</tr>
<tr>
<td></td>
<td>T₂ = 60°C</td>
<td>T₂ = 60°C</td>
</tr>
<tr>
<td>Room air</td>
<td>−0.08 ± 0.01</td>
<td>−0.29 ± 0.03</td>
</tr>
<tr>
<td>Room air + PNA</td>
<td>0.19 ± 0.01</td>
<td>−0.03 ± 0.02</td>
</tr>
<tr>
<td>∆ (ΣPN)</td>
<td>0.27 ± 0.01</td>
<td>0.26 ± 0.04</td>
</tr>
<tr>
<td>Room air + PNA + PAN</td>
<td>0.19 ± 0.01</td>
<td>−0.02 ± 0.02</td>
</tr>
<tr>
<td>∆ (ΣPAN)</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

n/a indicates not applicable.
observed (for example, in Table 6), we estimate that an additional ± 5% random error is introduced, raising the combined measurement uncertainty to ± 13%. Not included in this estimate are systematic errors that might arise from the unknown and potentially variable TD profile of the interferences included in ΣPAN*. 

4 Discussion

The main goal of this work was to evaluate the feasibility of using ethane-based TD-PERCA to quantify ΣPN and ΣPAN in ambient air. This work has identified several stumbling blocks that on aggregate insinuate that such a measurement would be difficult and error-prone in practice.

On the one hand, the ethane-based TD-PERCA-CRDS has demonstrated great LODs (< 1 pptv for ΣPAN* and PAN). This constitutes a considerable improvement compared to our previous generation TD-CRDS, whose LOD was in the hundreds of pptv (Paul and Osthoff, 2010), and represents the first optical absorption measurement of PNA at concentration levels of the same magnitude as found in ambient air (Table 1). In addition, the measurement can tolerate a large NO2 background through selective amplification of the desired signal: in Fig. 12, for example, the NO2 background was > 30 ppbv, yet PNA and PAN were quantified with a 1 s σ precision of < 6 and < 40 ppbv, respectively (Table 6). Moreover, the sensitivity of the ethane-based TD-PERCA is better than the room temperature measurement of ROx radicals (1.6 pptv; 90 s, 2σ) (Wood et al., 2016), mainly because of the greater amplification (~ 69 vs. ~ 25) and in spite of the CAPS sensor being slightly more sensitive to NO2 than our CRDS. Furthermore, the instrument’s sensitivity is comparable to (or better than) what is achievable with commonly used GC and CIMS methods. For example, at an inline temperature of 120 °C, the sensitivity of TD-PERCA-CRDS for PNA was of the same order of magnitude as our CIMS at its non-specific ion at m/z 62 and the optimized CIMS recently described by D. X. Chen et al. (2017).

The TD-PERCA-CRDS owes its good sensitivity to its high CL, which increases with temperature. Our attempts to rationalize the temperature through model simulations (see the Supplement) were limited because models simulating PERCA need to take wall loss rates into account and are generally poor predictors of experimental chain lengths. From a gas-phase kinetics perspective, reactions of HO2 and RO2 with NO (e.g., Reaction R3, Table 3) have a negative activation energy and are thus expected to slow down at higher temperatures, decreasing turnover rates and the CL. However, the RH dependence is reduced by heating, in part because one of the radical chain-terminating reaction, HO2 + NO → HNO3, proceeds via a water adduct (HO2 · H2O) (Butkovskaya et al., 2007, 2009). The temperatures within the PERCA reaction heater are sufficiently elevated to dissociate this intermediate, shutting down this radical sink reaction. In addition, the elevated temperatures inside the reactor may lessen reactions at the reactor inner wall surfaces (by driving off adsorbed water molecules, for example) though we lack direct evidence for this happening.

On the other hand, the TD-PERCA-CRDS method has several drawbacks, some of which still need to be overcome to make ambient measurements a reality.

The first challenge is posed by the TD profiles of PAN and PNA (Fig. 4) which are not completely separated. This overlap is particularly problematic in ambient air because the signal generated by the typically much smaller PNA concentrations could be overshadowed by a much larger ΣPAN signal. In this work, the overlap of the TD profiles of PNA and PAN (and the rather limited dynamic range of < 500 pptv) was overcome by the differential temperature–linear combination method (Sect. 3.7) in which ΣPAN was only partially dissociated and PNA close to completely dissociated.

A complication is that methyl and ethyl peroxy nitrate have TD profiles that are similar, but not identical, to that of PNA; these molecules dissociate at lower temperatures than PNA (Table 4). This does not matter if the TD-PERCA inlets are operated at temperatures at which all three molecules are fully dissociated (or nearly so) as in this work.

The differential temperature approach has the additional advantage of avoiding the O3 interference that occurs above 150 °C, which would otherwise have been a serious issue because of the typically much larger O3 than PAN or PNA concentrations in ambient air, and it gave consistent results in synthesized air mixtures and room air.

A second drawback of TD-PERCA is the RH-dependent CL, which necessitates frequent calibrations to determine CL × F at each channel’s temperature, though this could in principle be straightforward with photochemical sources of PNA and PAN and automated switching. At the same time, frequent calibrations of CL and F would relax the need to carefully match the responses in each of the TD channels, which is a requirement in conventional TD instruments.

The third and most substantial drawback are the interferences. The O3 interference is easily avoided by switching the instrument from ethane to CO operation. With CO, any O generated from O3 dissociation would react to form CO2 and be of no further consequence. However, CO-PERCA is somewhat unappealing because of CO’s high toxicity and lack of smell, making its use impractical and impermissible in some university laboratories due to legitimate safety concerns. Mihele and Hastie (2000) used PAN as a radical source by heating a short section of the inlet of their CO-PERCA to 200 °C and found the CL to be the same as other radical sources (which included passing H2 past a heated wire and a Cl2 photolysis source), which suggests that the CL in a CO-based PERCA is less dependent on temperature than with an ethane-based PERCA, which would be another advantage of CO-based PERCA.

The unknown interference observed in laboratory air is by far the biggest hurdle. We do not know the identity of the...
molecule or class of molecules interfering, and if the interference is present in ambient air, away from anthropogenic sources, or found only within a chemistry laboratory. We previously reported (Taha et al., 2018) that the ethane-based TD-PERCA-CRDS responds to peroxide explosives and also responds when sampling the head space above common skin cream and moisturizer products, which contain organosiloxanes. Organosiloxanes have become ubiquitous in the environment and have been found in indoor air in ppbv levels (Rücker and Kümmnerer, 2015). Their barriers to dissociation have been reported (Davidson and Thompson, 1971) and are too large for decomposition to occur at the inlet temperatures used in this work. However, Kulyk et al. (2016) recently suggested that pyrolysis of certain polysiloxanes may occur at temperatures as low as 70 °C. Clearly, more work is needed to identify which molecules or class of molecules interfere in TD-PERCA-CRDS and are included in ΣPAN∗. It is possible that the interfering species thermally dissociate(s) to release O atoms; if that is the case, this interference would not be present in a CO-based TD-PERCA. Hence, measurements using a CO-based TD-PERCA should be attempted. Furthermore, such measurements should be complemented by parallel measurements of PNA, PAN, and PPN by CIMS.

Data availability. The data used in this study are available from the corresponding author upon request (hosthoff@ucalgary.ca).

The Supplement related to this article is available online at https://doi.org/10.5194/amt-11-4109-2018-supplement.

Author contributions. YT and HO designed the experiments and carried them out. MS and YT constructed the single-channel inlet described in Sect. 2.1.1. FA synthesized the PAN and PPN samples (Sect. 2.2). XC and CY designed the setup for PAN delivery shown in Fig. 2. NG operated the CIMS and reduced the CIMS data. YT and HO prepared the manuscript with contributions from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

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