1 **Thermal dissociation cavity enhanced absorption spectrometer for detecting NO₂,**

2 **RO₂NO₂ and RONO₂ in the atmosphere**

3 Chunmeng Li[1], Haichao Wang[1, 2, 3*], Xiaorui Chen[1], Tianyu Zhai[1], Shiyi Chen[1], Xin Li[1], Limin Zeng[1], Keding Lu[1, *]

4 [1] State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences
5 and Engineering, Peking University, Beijing, 100871, China.
6 [2] School of Atmospheric Sciences, Sun Yat-sen University, Zhuhai, Guangdong, 510275, China.
7 [3] Guangdong Provincial Observation and Research Station for Climate Environment and Air Quality Change in the
8 Pearl River Estuary, Key Laboratory of Tropical Atmosphere-Ocean System, Ministry of Education, Southern
9 Marine Science and Engineering Guangdong Laboratory (Zhuhai), Zhuhai, 519082, China.
10 * Corresponding author: wanghch27@mail.sysu.edu.cn; k.lu@pku.edu.cn

11 **Abstract.** We developed a thermal dissociation cavity enhanced absorption spectroscopy (TD-CEAS) for the in-situ
12 measurement of NO_2, total peroxy nitrates (PNs, RO_2NO_2), and total alkyl nitrates (ANs, $RONO_2$) in the atmosphere. PNs
13 and ANs are thermally converted to NO_2 at the corresponding pyrolysis temperatures and detected by CEAS at 435 - 455
14 nm. The instrument samples sequentially from three channels at ambient temperature, 453K and 653K, with a cycle of 3
15 minutes, for measuring NO_2, NO_2+PNs, and NO_2+PNs+ANs, respectively. The absorptions between the three channels are
16 used to derive the mixing ratios of PNs and ANs by the spectral fitting. The limit of detection (LOD) is estimated to be 97
17 pptv (1σ) at 6 s intervals for NO_2. The measurement uncertainty of NO_2 is estimated to be 8%, while the uncertainties of
18 PNs and ANs detection is larger than NO_2 due to some chemical interferences in the heating channels, such as the reaction
19 of NO (or NO_2) with the peroxy radicals produced by the thermal dissociation of organic nitrates. Based on the laboratory
20 experiments and numerical simulations, we set up a lookup table method to correct these interferences in PNs and ANs
21 channel under various concentrations of ambient organic nitrates, NO, and NO_2. Finally, we present the first field
22 deployment and compared it with other instruments during a field campaign in China, the advantage and limitations of this
23 instrument are outlined.

1. Introduction

24

25 Organic nitrates (ONs) act as the temporary NOx reservoir species, which affects the atmospheric circulation and has
26 impacts on air quality and climate (Mellouki et al., 2015). Peroxy nitrates (PNs, RO_2NO_2) and alkyl nitrates (ANs,
27 $RONO_2$) are the two important kinds of organic nitrates. They are closely related to the distribution of oxidants in the
28 atmosphere by terminating HOx cycle. ONs are also the important precursors of secondary organic aerosol (SOA)
29 (Berkemeier et al., 2016; Lee et al., 2016; Ng et al., 2017; Rollins et al., 2012). Volatile organic compounds (VOCs)
30 are oxidized by OH or O_3 to produce peroxy radicals (RO_2), then the RO_2 reacts with NO_2 to produce PNs (R1). In
31 addition, the aldehydes formed during the process of NO_3 oxidizing isoprene at night react with NO_3 to form PNs.
32 PNs can be divided into two categories depending on the nature of the RO_2 group. One is peroxy acyl nitrates (PANs)
33 when RO_2 is R'C(O)OO, among which PPN (peroxypropionyl nitrate) and PAN dominate PNs with the percentage
34 of 75%-90% due to the relatively high thermal stability. While some peroxy nitrates without acyl group are only
35 abundant in the cold regions (Roberts, 1990; Roberts et al., 1998b; Thieser et al., 2016; Wooldridge et al., 2010). The
36 sink pathways of PNs include deposition, thermal decomposition, photolysis, and OH oxidation, and the thermal
37 decomposition dominates in the troposphere with a temperature dependence (R2). Therefore, the lifetime of PAN is
38 various from less than one hour to several months, depending on the environmental conditions.
39 $RO_2 + NO_2 + M \rightarrow RO_2NO_2 + M$ (R1)
40 $RO_2NO_2 + M \rightarrow RO_2 + NO_2 + M$ (R2)
41   At the high NOx region, RO_2 reacts primarily with NO to produce ANs. ANs can be also emitted directly from
42 biomass combustion and the ocean. The ocean emission is regarded as the main source of short-chain ANs (C_1-C_3),
43 and up to tens of pptv of species above have been measured in marine areas (Atlas et al., 1993; Chuck et al., 2002;
44 Talbot et al., 2000). The NO_3-initiated ANs during the night is generally considered to be important, which has a
45 higher organic nitrate yield compared with OH-initiated ANs (Horowitz et al., 2007; Perring et al., 2013). During the
46 daytime, there is a branch reaction in forming ANs (R3) with a small branch ratio (1%-30%) (Arey et al., 2001;
47 Reisen et al., 2005; Russell and Allen, 2005; Wennberg et al., 2018). Ambient ANs are removed by photolysis or
48 oxidation to produce NOx or HNO_3, be deposited or transported as NOx reservoirs. ANs play a significant role in
49 SOA formation (Lee et al., 2016; Zare et al., 2018). Monofunctional ANs are stable and account for a small proportion
50 of ANs, among which the ones formed from alkanes can be the tracers of human activities in remote areas (Simpson
51 et al., 2006; Wang et al., 2003). Polyfunctional ANs are hard to detect since they are more reactive than
52 monofunctional ANs.
53 $RO_2 + NO + M \rightarrow RO_2NO + M$ (R3a)
54 $RO_2 + NO + M \rightarrow RO + NO_2$ (R3b)
55   The various sources and sinks of ONs complicate their atmospheric distribution. The measurement of ANs and
56 PNs has been developed by gas chromatography (GC). GC is used for separation of species, and then the separated
57 substances are quantified by using electron capture detectors (ECD), luminol chemiluminescence (CL), or mass
58 spectrometry (MS) (Atlas, 1988; Blanchard et al., 1993; Flocke et al., 2005; Gaffney et al., 1998; Hao et al., 1994;
59 Luxenhofer et al., 1994; Tanimoto et al., 1999). These methods measure individual species accurately (Roberts et al.,
60 2003), but the individual standards are incomprehensive. Meanwhile, the methods suffer from relatively low time
61 resolution (Blanchard et al., 1993). Day et al. (2002) used the feature of gradient pyrolysis of reactive nitrogen
62 compounds and determined NO_2 product by TD-LIF (thermal-dissociation laser-induced fluorescence), achieving the
63 measurement of PNs, ANs, and gaseous HNO_3 (Day et al., 2002). After that, chemical ionization mass spectrometry
64 (CIMS) and cavity enhanced spectroscopy have been used to quantify the pyrolysis products (Paul and Osthoff, 2010;
65 Slusher et al., 2004; Thieser et al., 2016; Wild et al., 2014). The detection limits and response times of TD-CIMS are
66 excellent, but ^{13}C-labeled PAN is required as an internal standard. TD-CRDS (cavity ring-down spectroscopy) and

67 TD-CAPS (cavity attenuated phase shift spectroscopy) have achieved measurements of PNs and ANs (Sadanaga et
68 al., 2016; Sobanski et al., 2016), which showed high spatial and temporal resolution and good measurement capability.
69   Organic nitrates have a large range of mixing ratios in the atmosphere that vary from several pptv in the warm and
70 remote regions to several ppbv in polluted regions. The field measurements of organic nitrates have been extensively
71 conducted in the United States and Europe (Fischer et al., 2000; Glavas and Moschonas, 2001; Kastler and
72 Ballschmiter, 1999; Perring et al., 2009; Roberts et al., 1998a; Sobanski et al., 2017),but the related studies are
73 sparse in China (Chen et al., 2017; Song et al., 2018; Sun et al., 2018; Zhang et al., 2018). Ozone pollution in China
74 has occurred frequently in recent years (Ma et al., 2019; Shu et al., 2019; Wang et al., 2009; Wang et al., 2017b; Yin
75 et al., 2019), but the importance of PNs and ANs in regulating ozone formation has not been well studied. Here we
76 developed a pyrolysis measurement system based on cavity enhanced absorption spectroscopy (CEAS) to detect NO_2,
77 PNs, and ANs in the atmosphere. In this study, the detailed setup of the instrument, laboratory characterizations, and
78 its first field applications in China are presented.

79 ## 2. Methods

80 ### 2.1 Instrumentation of TD-CEAS
81 Our instrument is designed to measure NO_2, ANs and PNs in the atmosphere, which has the characteristics of good
82 stability, low energy consumption and portability. The total weight of the instrument is less than 30 kg, the overall
83 size is $110 \times 60 \times 50$ cm, and the power consumption is less than 300 W. The measurement of NO_2 is achieved by
84 CEAS. Due to the feature of gradient pyrolysis of ANs and PNs, the sample gas flowing out from three different
85 channels contains the total amount of NO_2 at different temperatures. The gradient of NO_2 concentration absorption
86 at different pyrolysis temperatures is used to retrieve the mixing ratio of NO_2, PNs, and ANs. The time resolution of
87 the instrument measurement is 6 s, the measurement time of each channel is 1 minute, and each cycle is 3 minutes.
88   The CEAS system has been described in detail in previous literature (Duan et al., 2018; Fiedler et al., 2003;
89 Gherman et al., 2008; Jordan and Osthoff, 2020; Jordan et al., 2019; Langridge et al., 2006; Liang et al., 2019; Liu
90 et al., 2019; Min et al., 2016; Tang et al., 2020; Ventrillard-Courtillot et al., 2010; Wang et al., 2017a; Yi et al., 2016),
91 so there is a brief introduction to the principle of the instrument. NO_2 molecules have a specific absorption structure
92 in the wavelength range of 400-500 nm (Fig. S1). Based on Lambert-Beer's law, the extinction coefficient (α) is
93 proportional to the absorber's concentration and the optical path. Here α is mainly contributed by the molecular
94 absorption, Rayleigh scattering and Mie scattering. Besides, it can also be obtained by comprehensive calculation
95 through the intensity of sampling spectrum, reference spectrum, mirror reflectivity, and effective cavity length (d_{eff}).
96   In Eq.1, λ is the wavelength of light, $I_0(\lambda)$ is the intensity of the reference spectrum, $I(\lambda)$ is the sample spectrum,
97 d_{eff} is the effective cavity length (see Sec. 3.2 in detail), $R(\lambda)$ is the mirror reflectivity, $\alpha_{Mie}(\lambda)$ is the extinction
98 due to Mie scattering, $\alpha_{Rayl}(\lambda)$ is the extinction due to Rayleigh scattering, n_i and $\sigma_i(\lambda)$ are the number density
99 and absorption cross-section of i_{th} gas compounds, respectively. According to Eq.1, it is necessary to quantify the
100 mirror reflectivity, effective cavity length, and NO_2 absorption cross-section.

101 $$\alpha(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1\right)\left(\frac{1-R(\lambda)}{d_{eff}}\right)$$

102 $$= \sum_i n_i \times \sigma_i(\lambda) + \alpha_{Mie}(\lambda) + \alpha_{Rayl}(\lambda) \qquad (1)$$

103   As shown in Fig.1a, the optical layout of the CEAS consists of the light source, collimating optics, cage system,
104 high-finesse cavity and a commercial spectrograph with a charge-coupled device (CCD) detector. The core of the
105 light source module is a single-color LED (M450D3, Thorlabs, Newton, NJ, USA), centering at 445 nm with a full
106 width at half maximum (FWHM) of 18 nm. To obtain a stable output of the light source, the input current and

107   operating temperature of the light source are stabilized to reduce the intensity and wavelength drift. The switching

108   power supply is 12 VDC with a current of 1.00 ± 0.01 A. The constant current control is achieved through a stable

109   current source. The temperature of the light source is controlled by the Proportion Integration Differentiation (PID)

110   algorithm and stabilized at 24.0 ± 0.1 °C.

111   Four stainless steel columns are used to collimate two opposing high-mirror mounting bases. The two endplates in

112   the middle of the cage structure further enhance the stability of the system. The light source is introduced into the

113   system through a fiber connected to a two-dimensional adjustment frame (CXY1, Thorlabs, Newton, NJ, USA)

114   through a connector. The plano-convex lens (f = 30 mm) is installed in another adjustment frame, and the two

115   adjustment frames are connected by a custom X-shaped adapter, which is fixed at the end with the light source. The

116   center alignment of the light source, the lens, and the high-reflectivity module are achieved by adjusting the

117   adjustment frame in the vertical and horizontal directions. Then blue light is thus introduced into an optical cavity

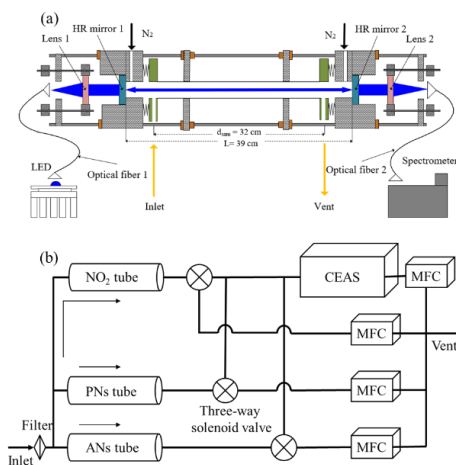
118   composed of a pair of high-reflectivity mirrors. The high-reflectivity mirror (CRD450-1025-100, Advanced thin films,

119   Colorado, USA) is reported to be greater than 0.9999 (440 – 460 nm) with a radius curvature of 1.0 m and a diameter

120   of 25.4 mm. The high-reflectivity mirrors are installed in the groove of the special custom base and sealed by an O-

121   ring, and then the three-dimensional micro-adjustment is achieved by squeezing the lens and the O-ring to adjust

122   their pitch and yaw finely. The distance between mirrors is 39.0 cm, and high-purity nitrogen (> 99.999 %), which

123   passes through the small hole before the mirror base, is used as a purge gas to protect the mirror surface.

124

125   Figure 1. The overall schematic of CEAS (a) and the instrument (b). CEAS is mainly composed of LED, collimating optics, cage structure,

126   high-finesse cavity and spectrometer. After filtering the PM, the gas goes through three quartz tubes, and then the alternate measurements

127   of NO_2, NO_2+PNs and NO_2+PNs+ANs is achieved by three-way solenoid valves.

128

129   The cavity system is sealed by two welded bellows, two polytetrafluoroethylenes (PTFE) connecting pieces, and

130   a stainless-steel sampling cell which is internally polished. The PTFE connecting piece connects the sampling cell

131   and the bellows and also acts as a sample inlet and outlet. As shown in Fig. 1a, the distance between the inlet and the

132   outlet (d_{sam}) is 32.0 cm. After passing through the sampling cavity, the blue light is converged by another plano-

133   convex mirror (f = 50 mm). It enters the detector-spectrometer (QE65PRO, Ocean Optics, Dunedin, FL, USA) for

134   signal acquisition through an optical fiber. The dark current in the CCD of the spectrometer is reduced by controlling

135   the temperature of CCD at -20.0 °C; the width of the entrance slit is 100 μm and the corresponding wavelength

136   resolution is 0.39 nm; the detection wavelength range is 413.48 - 485.48 nm.

137   The schematic of TD-CEAS is shown in Fig. 1b. The flow system mainly includes the particulate matter filtering
138   in the front end of the sampling line, the quartz tubes for species pyrolysis conversion, the three-way system switching
139   module, the detection module (CEAS) and the flow control module. The sample gas firstly passes through a PTFE
140   filter membrane (25 μm thickness, 4.6 cm diameter, 2.5 μm pore size, Typris, China) to remove ambient aerosols.
141   The sample gas enters the system through 1/4 inch PFA (polytetrafluoroethylene) tube, and then is divided into three
142   channels (NO_2 channel, ANs channel, and PNs channel) by using two T-shaped PFA three-way connection. The gas
143   flow at the end of each channel is controlled at 0.8 L min^{-1} and the total flow rate (sample flow gas and purge gas) is
144   2.6 L min^{-1} maintained by mass flow controllers and a diaphragm pump.

145   The quartz tubes have a length of 35 cm, which has an inner diameter of 5 mm and an outer diameter of 10 mm,
146   connected to the system through a 10 mm to 1/4 inch PTFE connection. The quartz tubes of the ANs channel and the
147   PNs channel are heated by resistance wire, and the temperature is controlled by the PID algorithm. An asbestos sleeve
148   on the quartz tube's surface is used to achieve the insulation of heat exchange with the external environment. The
149   heating power of PNs channel and ANs channel are about 20 W and 50 W, respectively. The length of the heating
150   module is 15 cm. According to the pyrolysis efficiency experiment (see Sec. 3.4 for details), the heating temperatures
151   for the ANs and PNs channels are controlled at 180 °C and 380 °C, respectively. If it is assumed that the temperature
152   of the heating part is uniform, the gas residence times of the ANs and PNs channels are 92.3 ms and 141.9 ms,
153   respectively. One CEAS is used to detect the NO_2 absorption of different channels to reduce the cross-interference
154   due to the difference of multi-detectors. A solenoid valve is connected behind the quartz tube of each channel. At the
155   same time, a time relay is used to control the three T-shaped solenoid valves periodically. Each channel has the same
156   constant flow rate no matter the sampling air draw into the CEAS or vent. At the end of the channels, mass flow
157   controllers are used to restricting the flow rate.

2.2 Laboratory experiments setup

159   To characterize the performance and potential interferences of this instrument, we used a photochemical PAN source
160   in the laboratory experiments. Acetone undergoes photolysis at 285 nm from Hg lamp, and then generates excess PA
161   radicals (peroxyacetyl radicals) in the zero air. At this time, a small amount of NO reacts with PA to form NO_2, and
162   then NO_2 further reacts with PA to form PAN. We got a standard PAN source in this way, which generated a source
163   at a level of 1-10 ppbv. The source level was double-checked by a GC-ECD instrument. To investigate the potential
164   interferences caused by the pyrolysis organic radical products react with ambient NO and NO_2 in TD-CEAS, a multi-
165   gas calibrator (146i, Thermo Fisher Scientific Inc., USA) was used to generate O_3 gas by photolysis of oxygen, and
166   output well-mixed gases by mixing NO or NO_2 with zero air according to the requirements. NO (1 ppmv) and NO_2
167   (10 ppmv) bottle gases were connected to the multi-gas calibrator. An ozone monitor was used to detecting O_3 levels
168   in these experiments (49i, Thermo Fisher Scientific Inc., USA). A NO_x monitor was used to detecting NO and NO_2
169   level in these experiments (42i, Thermo Fisher Scientific Inc., USA). Pure N_2 (>99.9999%) and He (>99.9999%)
170   bottle gas were used to calibrate the mirror reflectivity of CEAS and purge the mirrors.

2.3 Box model

172   A box model was established to mimic the experimental results and study the potential interferences of NO and NO_2
173   in PNs and ANs measurement. The chemical mechanism is followed by previous work (Thieser et al., 2016). These
174   reactions in the pyrolysis process in the box model are listed in Text S1, and the reaction rate of these reactions is
175   mainly taken from the MCM. As the wall loss has an important effect on the lifetime of free radicals, we set the wall
176   loss constant (k_{wall}) of RO_2 as the value of 0.3 /s (Thieser et al., 2016; Wooldridge et al., 2010). The wall loss rate
177   coefficients of HO_2 and OH are selected as the values of 0.5 and 5.4 /s (Fuchs et al., 2008). The residence time of the
178   sampling gas in each channel is calculated by considering the temperature distribution. The time step of the model is
179   set to 0.001s.

3. Instrument characterization

3.1 Mirror reflectivity

The spectra of the pure N_2 (>0.99999) or He (>0.99999) filling the cavity are collected to calibrate the mirror reflectivity, as the Rayleigh scattering section of the two is significantly distinct, so $R(\lambda)$ can be calibrated according to Eq.2 (Chen and Venables, 2011; Min et al., 2016).

$$R(\lambda) = 1 - d \times \left(\frac{I_{N_2}(\lambda) \times n_{N_2} \times \sigma_{Rayl,N_2}(\lambda) - I_{He}(\lambda) \times n_{He} \times \sigma_{Rayl,He}(\lambda)}{I_{He}(\lambda) - I_{N_2}(\lambda)} \right) \qquad (2)$$

Where d is the distance between two high-reflectivity mirrors, λ is the wavelength, $I_{N_2}(\lambda)$ and $I_{He}(\lambda)$ are spectrums obtained when the cavity is filled with pure N_2 and He, respectively, n_{N_2} and n_{He} are the number density calculated at measurement temperature and pressure in the cavity, respectively, $\sigma_{Rayl,N_2}(\lambda)$ and $\sigma_{Rayl,He}(\lambda)$ are the Rayleigh scattering section of N_2 and He, respectively (Shardanand, 1977; Sneep and Ubachs, 2005). Fig. 2 shows the average of mirror reflectivity calibration results. The $R(\lambda)$ is above 0.9999 in 435-465 nm, and up to 0.99992 at 450 nm. The total uncertainty of the mirror reflectivity is 5%, which comes from the uncertainty in the scattering section of N_2. The blue line is the average optical path length when the sampling flow rate in the cavity is 0.8 L min^{-1}, which is equal to $d_{eff}/(1\text{-}R)$ (d_{eff} is 31.84 cm), with the value up to 5.2 km at 450 nm.

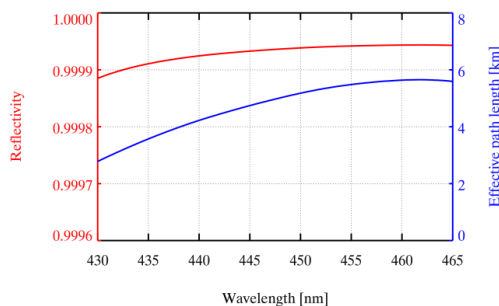
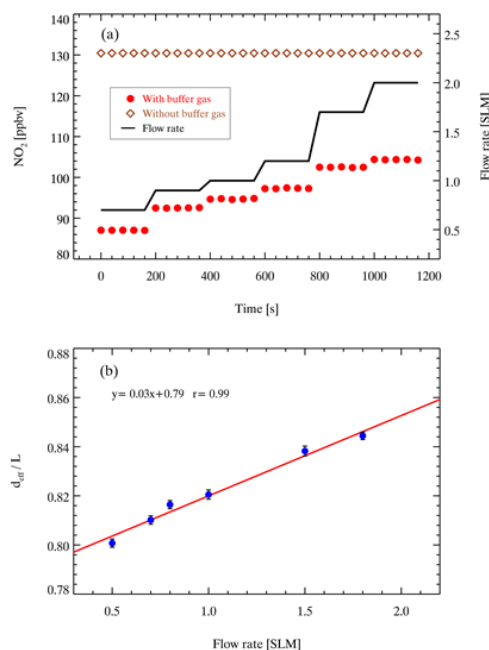



Figure 2. Mirror reflectivity and optical path length calibrated by He (>0.99999) and N_2 (>0.99999). The red line is the average $R(\lambda)$, and the blue line is the optical path length.

3.2 Effective cavity length

The effective length of absorbers (named effective cavity length, d_{eff}) in the detection cell is shorter than the physical distance of the cavity; thus, it needs to be calibrated. We performed the concentration determination on the NO_2 standard source (130 ppbv) under two experimental settings with or without purging and then used Eq. 1 to calculate d_{eff}. The ratio of NO_2 absorption with and without purging is equal to the ratio of the effective cavity length to the physical distance L between the mirrors (d_{eff}/L). NO_2 stand was prepared from a bottled standard (5 ppmv NO_2) and diluted with high-purity N_2 in the multi-gas calibrator (146i, Thermo Fisher Scientific Inc., Waltham, MA, USA). As shown in Fig. 3a, the retrieved concentration of NO_2 shows a positive correlation trend with the flow rate with N_2 purging; the concentration of NO_2 is 130 ppbv without a purge. The d_{eff}/L at different sampling flow rates is shown in Fig. 3b. It is found that the ratio of the effective cavity length increases as the flow rate increases, suggesting the importance of airflow rate stability during sampling. The uncertainty of the prepared NO_2 standard source is estimated to be 2.0%, while the uncertainty of the NO_2 absorption cross-section is 4.0%, according to Voigt et al. (2002). As a result, the total uncertainty of d_{eff} calibration is 4.5% (Voigt et al., 2002).

211

212

213   Figure 3. The results of the effective cavity length. (a) The black line represents the flow rate, the red points, and brown diamonds

214   represent the retrieved NO_2 concentration with and without nitrogen purge (100 sccm×2), respectively; (b) The correlation dependence

215   of the ratio of the effective cavity length (d_{eff}) to cavity physical distance (L) on the sampling flow rate.

3.3 Spectral fitting

216

217   The absorption cross-section of NO_2 measured by (Voigt et al., 2002) is used to retrieve NO_2 concentration in this

218   study. The absorption cross-section of NO_2 between 435-455nm is selected to perform the spectral fitting. It was

219   reported that the NO_2 cross-section is not sensitive to the temperature change (Vandaele et al., 2002; Voigt et al.,

220   2002), so the convolution is only performed for our instrument setup at ambient temperature. The peak at 436.2 nm

221   of Hg spectrum measured by the spectrometer is used to generate a wavelength-dependent instrument slit function

222   that accounts for the change of spectral resolution over the CCD pixels. The convoluted cross-section of NO_2 is

223   shown in Fig. S1. The measured absorption coefficient (α) is processed by DOASIS (Differential Optical Absorption

224   Spectroscopy Intelligent System). The fitting shift is constrained within ±0.2 nm. Glyoxal has strong absorption in

225   the same optical window (Liu et al., 2019; Min et al., 2016; Thalman et al., 2015; Thalman and Volkamer, 2010;

226   Washenfelder et al., 2008), but here we do not take into consideration in spectrum fitting. Fig. 4 shows two examples

227   of the spectral fitting of measured absorption of high and low NO_2 at 6 s integration time during the ambient

228   measurement. The retrieved mixing ratio of NO_2 is 18.2 ppbv and 1.8 ppbv, respectively. The corresponding fitting

229   residual is in the range of $10×10^{-9}$ at 435-455 nm, suggesting the system can guarantee the accuracy for different

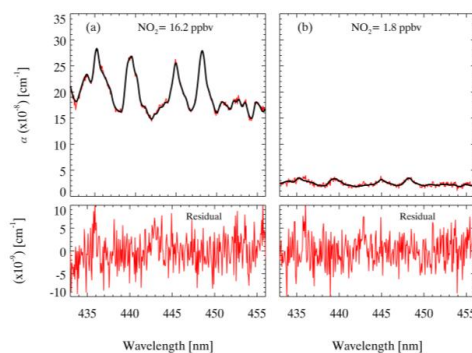
230   levels of NO_2 measurement. A typical measurement sequence during the ambient measurement is illustrated in Fig.

231   5, which displays NO_2 mixing ratios after three channels alternatively. The mixing ratio of NO_2 in different channels

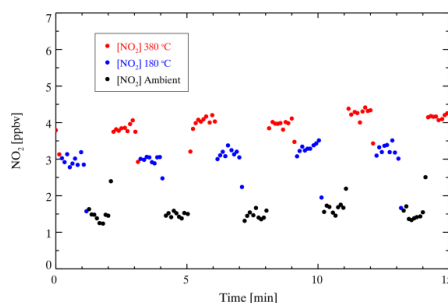
232   is detected periodically, and there are several transitional points due to switching measurement phases. As we discuss

233   later, the mixing ratio of ANs and PNs can be calculated by subtracting the NO_2 mixing ratio measured from different

234   channels.

235

236

237   Figure 4. An example of the spectral fit for an extinction spectrum measured (6 s average) during field measurements. The fitted results

238   of NO₂ are shown and the total fit result, and the residual at high concentration (a) and low concentration (b).

239

240   Figure 5. An example of typical measurements performed in a field study with 6 s spectrum integral time. A measurement cycle includes

241   three phases whose duration is 60 s. The red points denote the NO₂ mixing ratio measured in the ANs channel ([NO₂] 380℃), the blue

242   ones denote the NO₂ mixing ratio measured in the PNs channel ([NO₂] 180℃), and the black ones denote the NO₂ mixing ratio measured

243   in the reference channel ([NO₂] Ambient).

244

245   There are two methods to determine the mixing ratio of ONs and PNs. One is the differential concentration method.

246   The differential NO₂ concentration is gradient subtracted between different measurement channels after the spectrum

247   fitting, as shown in Eqs. 3-6, and the I_0 is fixed during the data analysis by using pure nitrogen spectrum ('CONC'):

248   I_{TD380} and I_{TD180} are spectrums obtained by ONs and PNs measurement channels, respectively; I_{N_2} is a spectrum

249   obtained when the cavity is filled with N₂ (>0.99999); α_{TD380} and α_{TD180} are absorption coefficients when I_{N_2} is

250   set as the reference spectrum, and I_{TD380} or I_{TD180} is set as sample spectrum, respectively; after eliminating the

251   abnormal points caused by switching, [ONs] is obtained by subtracting the average of the effective points of

252   [NO₂]$_{TD380}$ and [NO₂]$_{REF}$, and [PNs] is obtained by subtracting the average of the effective points of [NO₂]$_{TD180}$ and

253   [NO₂]$_{REF}$. The other method is the differential absorption method, by using the dynamic background spectrum

254   method ('SEPC') for spectral fitting (Eqs.7-8): I_{REF} is the spectrum obtained at the ambient temperature

255   measurement channel; ONs can be retrieved based on I_{TD380} and I_{REF}; PNs can be retrieved by I_{TD180} and I_{REF}.

256   An intercomparison of field measurement shows that the 'SEPC' method results in fewer outliers (Fig. 6). For the

257   'SEPC' method, the shift and squeeze of the spectrum is performed only once during the spectrum fitting, which

258   reduces the uncertainty caused by the second spectrum fitting. Therefore, we selected the 'SEPC' method to retrieve

259   the concentration of NO$_2$, PNs, and ANs in the following data processes.

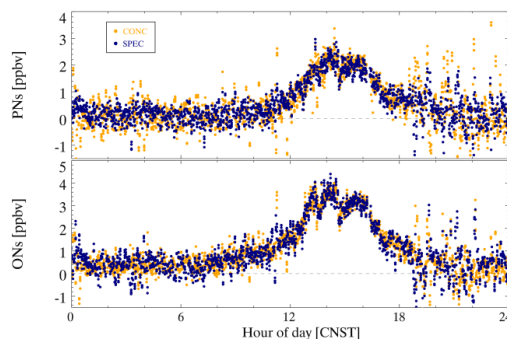
260     $\alpha_{TD380} = \left(\frac{I_{TD380}}{I_{N_2}} - 1\right)\left(\frac{1 - R(\lambda)}{d_{eff}}\right)$ (3)

261     $\alpha_{TD180} = \left(\frac{I_{TD180}}{I_{N_2}} - 1\right)\left(\frac{1 - R(\lambda)}{d_{eff}}\right)$ (4)

262     $[ONs] = [NO_2]_{TD380} - [NO_2]_{REF}$ (5)

263     $[PNs] = [NO_2]_{TD180} - [NO_2]_{REF}$ (6)

264     $\alpha_{[ONs]} = \left(\frac{I_{TD380}}{I_{REF}} - 1\right)\left(\frac{1 - R(\lambda)}{d_{eff}}\right)$ (7)

265     $\alpha_{[PNs]} = \left(\frac{I_{TD180}}{I_{REF}} - 1\right)\left(\frac{1 - R(\lambda)}{d_{eff}}\right)$ (8)

266

267   Figure 6. An example of the calculation results of the fixed I_0 ('CONC') and dynamic I_0 ('SPEC') methods performed in the field

268   measurements. Orange dots represent the results of the 'CONC' method, and dark blue dots represent the calculation results of the 'SPEC'

269   method.

3.4 The efficiency of thermal dissociation

271   The strength of the bond between the NO$_2$ group and the organic group determines the temperature to pyrolyze the

272   organic nitrates. The cleavage of the NO$_2$ group in PNs requires about 85-115 kJ/mol (Kirchner et al., 1999), while

273   for ANs, the pyrolysis process requires about 160-170 kJ/mol (Roberts, 1990), so PNs are more prone to dissociate

274   thermally. For the pyrolysis measurement of organic nitrates, the exact temperature setting for complete pyrolysis

275   varies, mainly due to the many factors that affect the efficiency of thermal dissociation, such as the specificity of the

276   quartz tube, the heating residence time, and temperature distribution of the heating part (Womack et al., 2017). The

277   thermal dissociation of PAN was tested separately in the PNs and ANs channels, and the efficiency curves are the

278   same between ANs channel and PNs channel. The heating temperature is the temperature of the quartz tube surface

279   rather than the airflow temperature in the quartz tube. The experiments were done under normal sampling conditions,

280   and the heating temperature was evaluated from room temperature to 440 ℃ to determine the appropriate heating

281   temperature. Fig. 7 shows the pyrolysis of PAN start when the heating temperature is about 50 ℃. The curve seems

282   to reach a platform when the heating temperature is around 180 ℃. However, the normalized signal of thermal

283   dissociation of PAN reaches the final platform once the temperature is above 360 ℃. Similarly, the PAN is reported

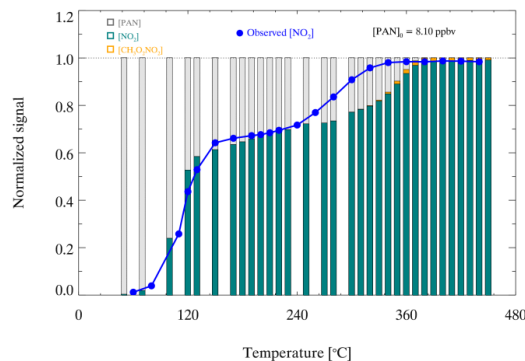
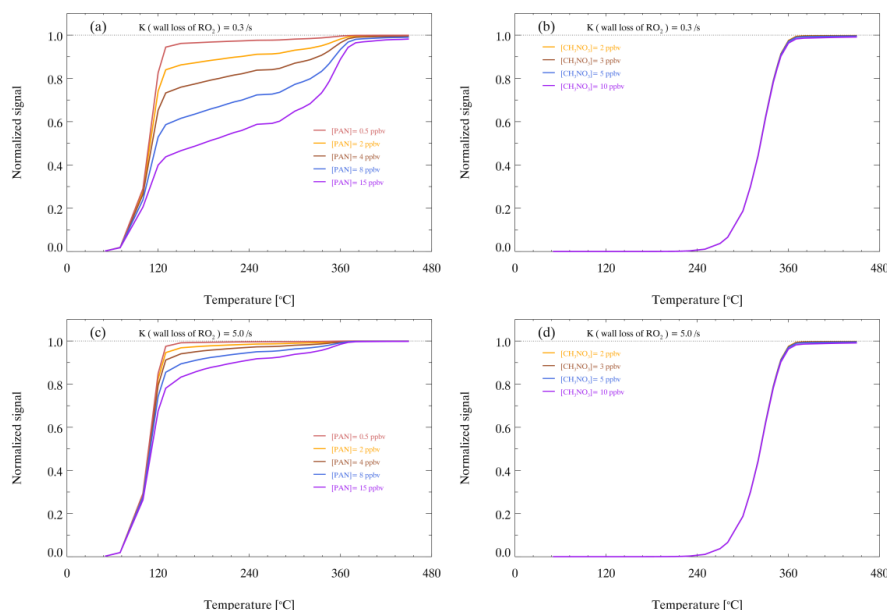
284   thermally dissociated totally about 400 ℃ (Friedrich et al., 2020). The occurrence of the dual-platform phenomenon

285   is due to the competitive progress of pyrolysis and recombination reactions. PAN will produce NO$_2$ and PA after

286   thermal dissociation, but PA will recombine with NO$_2$ if PA is not lost on the wall surface in time (R7-R8). Therefore,

287   the thermal curve shows two platforms as the heating temperature increases.

288   To further study the thermal dissociation of organic nitrates in the heated channels, the box model simulations are
289   conducted to reproduce the response relationship between heating temperature and NO_2 generated by pyrolysis. As
290   shown in Fig. 7, PAN gradually transforms into NO_2 and $CH_3O_2NO_2$ as the setting temperature increases. The
291   simulated signals of thermal dissociation of PAN show two platforms similar to the experimental results generally.
292   However, there are some differences between 260 to 360 °C, which may come from the simulation uncertainties such
293   as the temperature profile in the heating channel, the follow-up reactions of PA radicals and their reaction rates. The
294   first platform at 180 °C is caused by the recombination of PA and NO_2 after the pyrolysis of PAN, so the recombination
295   cannot be ignored when the heating temperature level is around the first platform. The second temperature platform
296   period indicates that almost all PAN is transformed into NO_2, which is due to the increase in the pyrolysis loss of PA
297   and the pyrolysis of PAN enhanced with the temperature increases. The concentration of PAN source and wall loss
298   rate of RO_2 influence the fraction of related species. Fig. 8(a) and (c) show that the gap between the two platforms
299   increases with PAN concentration and decreases with the wall loss rate coefficients of RO_2 increasing. The wall loss
300   of RO_2 competes with the recombination of PA radical and NO_2. Therefore high wall loss rate coefficient of RO_2
301   reduces the recombination for PAN.
302   The consistent between observed and simulated thermal efficiency of PAN suggests that the model simulation is
303   reliable. Without the ANs source to quantify the thermal efficiency of ANs, we try to use the model simulation to
304   determine the heating temperature of the ANs channel. Based on the same parameter settings of the model, MeN
305   (methyl nitrate, CH_3NO_3) is selected as the representative of ANs to simulate the pyrolysis efficiency curve. Fig. 8(b)
306   and (d) show that the MeN can be thermally dissociated totally when the temperature over 380 °C, indicates that the
307   temperature set to 380 °C for ANs channel is reasonable. The simulation also showed that the two factors have almost
308   no effect on the pyrolysis of MeN, which is completely pyrolyzed to produce NO_2 when the temperature is 380 °C.
309   The simulation results are similar to previous reports about the thermal dissociation of ANs, whose heating
310   temperatures are set in the range from 350 to 450 °C (Day et al., 2002; Sadanaga et al., 2016; Sobanski et al., 2016;
311   Thieser et al., 2016). Therefore, 180 °C and 380 °C are selected as the heating temperature of the PNs channel and
312   ANs channel, respectively.

313
314

315
316   Figure 7. Normalized signals of thermal dissociation of PAN. The blue points represent the normalized signal of the observed NO_2
317   mixing ratio during thermal dissociation. The histogram represents the simulated distribution of thermal dissociation products at different
318   temperatures, in which the gray, green and orange columns represent PAN, NO_2 and HNO_3, respectively.
319

320

321 Figure 8. Model simulated thermal decomposition profiles of PAN and MeN with different amounts of PAN or MeN under different wall

322 loss rate coefficient of RO_2. Panel (a) and (b) show that the NO_2 signal of PAN and MeN when the wall loss rate coefficient of RO_2 is

323 0.3 /s. Panel (c) and (d) show that the NO_2 signal of PAN and MeN when the wall loss rate coefficient of RO_2 is 5 /s.

4. Results and discussion

4.1 Measurement interference

326 Previous studies have shown that the filter losses and wall losses of NO_2, PNs and ANs are small (Paul et al., 2009;

327 Thieser et al., 2016). As shown in Fig. S2, the response to concentration changes of PAN was nearly instantaneous

328 under the normal sampling, suggesting the memory effects on the inlet and cavity tubing are insignificant. As shown

329 in Fig. S3 and Fig. S4, the filter loss and sampling tube are negligible. The transmission efficiency for PAN is > 97%

330 if there is a fresh filter membrane in the holder. We purpose that changing the filter once a day can ensure a high

331 transmission efficiency of the species to be detected. In the heating channels, organic nitrates will be thermally

332 dissociated to produce NO_2, but some simultaneous reactions will affect the NO_2 mixing ratio. The potential

333 interferences mainly come from the following reactions: formation NO_2 via NO and O_3, pyrolysis of O_3, reactions of

334 organic radicals with NO and NO_2, pyrolysis of other reactive nitrogen oxides.

335   The formation of NO_2 in a dark reaction between NO and O_3 should be considered in NO_2 measurement. If the

336 reaction has continued for a certain time (t) during the sampling, the amount of NO_2 formed $[NO_2]t$ can be calculated:

337 $[NO_2]t = k \times [NO] \times [O_3] \times t$, where k is the rate coefficient for Reaction (R4) and is given as 2.07×10^{-12} exp (-

338 1400/T) cm^3/molecule/s (Atkinson et al., 2004). According to the temperature distribution and the airflow

339 temperature measurements changing with the distance after the heating quartz tube, the heated channel temperature

340 profiles under normal sampling are shown in Fig. S5. Based on the temperature profile, the reaction of NO and O_3 in

341 the three channels can be calculated. As the residence time of airflow in three channels is short and similar (0.806 s

342 in reference channel; 0.697 s in ANs channel; 0.730 s in PNs channel), the results of simulations show the inference

343 is small. For example, in a case on an ozone pollution day with O_3 = 100 ppbv, NO = 2 ppbv and NO_2 = 5 ppbv, the

344 NO_2 produced by the reaction of NO and O_3 in the reference channel is 0.07 ppbv, corresponding to 1.3% of

345   atmospheric NO_2. Similarly, the interferences in ANs channel and PNs channel are 0.14 ppbv (2.7% of NO_2) and

346   0.10 ppbv (2.0% of NO_2), respectively.

347   The thermal degradation of O_3 occurs at high temperatures, which reduces NO_2 to NO via $O(^3P)$ (R5-R7). The

348   interference was once ignored in the process of PNs and ANs pyrolysis (Day et al., 2002). However, the subsequent

349   studies have shown that the reaction can cause significant negative deviations in the measurements of NO_2 under

350   higher temperature, and the degree of interference is closely related to the temperature change of the pyrolysis module

351   (Lee et al., 2014; Thieser et al., 2016). To determine the reduction reaction effect, we did the experiments in which

352   NO_2 was detected in three different channels when the various NO_2 and O_3 were added. The experiment results are

353   shown in Table 1 with various amounts of NO_2, and O_3 added. No significant NO_2 mixing ratio difference was

354   observed between the reference and ANs channels. We showed a negligible interference here, which is different from

355   previous reports (Lee et al., 2014; Thieser et al., 2016). This is likely caused by a much lower temperature setting of

356   our ANs measurement channel. Since the pyrolysis rate constant of O_3 is highly temperature-dependent, the lower

357   temperature would largely reduce the level of O atom as well as this interference.

358    $NO + O_3 \rightarrow NO_2$ (R4)

359    $O_3 \rightarrow O + O_2$ (R5)

360    $O + O_2 + M \rightarrow O_3 + M$ (R6)

361    $O + NO_2 \rightarrow O_2 + NO$ (R7)

362

363   Table 1. The measurements of NO_2 mixing ratio in three channels of TD-CEAS with different added amounts of NO_2 and O_3.

Order	[NO_2]	[O_3]	[O_3]×[NO_2]	[NO_2]$_{TD380}$	[NO_2] -[NO_2]$_{TD380}$
	[ppbv]	[ppbv]	[ppbv×ppbv]	[ppbv]	[ppbv]
0	7.45±0.27	48.19	359	7.79±0.27	-0.34
1	7.89±0.27	67.47	532	8.17±0.28	-0.28
2	15.58±0.29	48.19	751	15.84±0.28	-0.26
3	8.23±0.27	96.38	793	8.22±0.28	0.01
4	15.77±0.25	67.47	1064	15.94±0.27	-0.17
5	8.43±0.27	144.57	1218	8.64±0.28	-0.21
6	16.18±0.28	96.38	1559	16.20±0.28	-0.02
7	16.28±0.30	144.57	2354	16.26±0.31	0.02

364

365   The RO_2 recombines with NO_2 or reacts with NO interfere with the measurement of ANs and PNs. Taking PAN

366   as an example, the organic radicals may trigger interference as described above (R8-R15). The PA produced after

367   thermal dissociation of PAN (R8) can recombine with NO_2 (R9). RO_2 can oxidize NO to produce NO_2 while

368   generating another organic radical (R10). CH_3O_2 can further initiate a series of reactions that affect the distribution

369   of NO_2 (R11-R15). Therefore, the lifetime and fate of PA generated by PAN pyrolysis will cause the interference,

370   and atmospheric NO and NO_2 will affect the degree of measurement interference.

371    $CH_3C(O)O_2NO_2 + M \rightarrow CH_3C(O)O_2 + NO_2 + M$ (R8)

372    $CH_3C(O)O_2 + NO_2 + M \rightarrow CH_3C(O)O_2NO_2 + M$ (R9)

373    $CH_3C(O)O_2 + NO (+ O_2) \rightarrow NO_2 + CH_3O_2 + CO_2$ (R10)

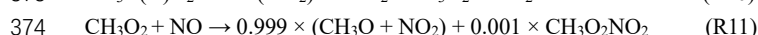
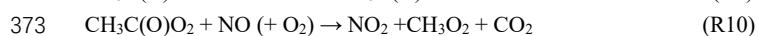
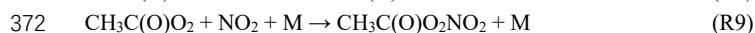
374    $CH_3O_2 + NO \rightarrow 0.999 \times (CH_3O + NO_2) + 0.001 \times CH_3O_2NO_2$ (R11)

375    $CH_3O \rightarrow HCHO + HO_2$ (R12)

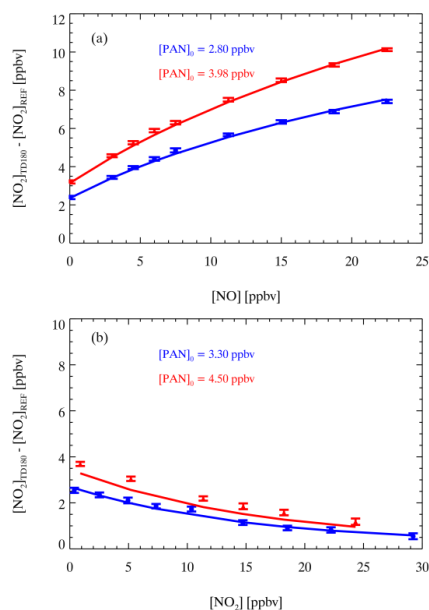
376    $CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$ (R13)

377    $HO_2 + NO \rightarrow OH + NO_2$ (R14)

378    $OH + NO_2 \rightarrow HNO_3$ (R15)

379    $CH_3NO_3 \rightarrow CH_3O + NO_2$ (R16)

380   A set of laboratory experiments was conducted to measure the interference in the PNs channel with different NO, NO$_2$ and PAN levels. Fig. 9a shows the measurement and simulation results of different PAN concentration mixed with different concentrations of NO. With the increase in NO added, the detected PNs mixing ratio (the signal difference between PNs channel and REF channel) also gradually increased. More NO reacted with PA radicals generated during thermal dissociation to produce additional NO$_2$ within the residence time in the PNs channel, which led to the measurements higher than the PAN source level. In contrast, as shown in Fig. 9b, the measured PNs were lower than PAN source level when NO$_2$ was added to the source, and the bias increased with the increase of NO$_2$ added. The addition of NO$_2$ in the system improves the overall concentration of NO$_2$ in the PNs channel, promoting the reformation to PAN.

389   We conducted numerical simulations by a box model to mimic the observation and check the chemical reactions in the PNs channel. Fig. 9a shows the simulations have a good consistency with the experiment result under different NO levels. Fig. 9b shows that the model can capture the trend of experimental results on NO$_2$ interferences, except the case of PAN source of 4.5 ppbv, which might due to reaction of small excess RO$_2$ in the PAN source line and extra NO$_2$ added to generate additional PAN before sampling into the instrument. Overall, these experiments proved that NO and NO$_2$ interfere with the measurement of PNs. However, the agreement of experiments and model results indicates that the interference of NO, NO$_2$ for PNs measurements can be corrected. In the field measurements, the correction factor refers to the ratio between the real value and the measured value of PNs. For example, in a typical case during field measurements where PAN = 3 ppbv, NO = 8 ppbv and NO$_2$ = 5 ppbv, the difference between PNs channel and reference channel is equal 4.54 ppbv (equivalent to the measured PAN), which require a correction factor of 0.66. Here, nearly 40000 simulations are done under various initial concentrations of NO (0-70 ppbv), NO$_2$ (0-60 ppbv) and PAN (0-10 ppbv) to get the correction factor look-up table for our first field measurement (detailed in Sect. 4.3). The correction factor for PNs measurements can be determined by the look-up table according to the atmospheric NO and NO$_2$ and the raw data of PNs measurements with linear interpolation.

403

404

405   Figure 9. Modeled (lines) and measured (points) difference between the NO₂ signal in the PNs channel and reference channel for different
406   PAN samples with different added amounts of NO (a) and NO₂ (b). The error bars show one standard deviation.

407   Fig. 10 displays the interference of NO and NO₂ to the PAN measurements in the ANs channel. The thermal
408   dissociation of PA radical is rapid, and the reformation of PAN is also suppressed at higher temperatures. So, the
409   PAN measurement response to NO and NO₂ added are weakened. The laboratory experiments showed that the
410   measured signal difference increased with NO (Fig. 10a). Hence, the presence of NO still led to the higher
411   measurement result of ONs than the source value. However, the interference was weaken compared with the
412   measured results in the PNs channel at the same NO and PAN source level (Fig. 9a). Similarly, the experiments with
413   NO₂ added showed the underestimated measurements of ONs, and the interference was significantly weakened
414   compared with that in the PNs channel. We used the same box model except updating the temperature distribution
415   and the corresponding residence time in the ANs tube to simulate the interference of NO or NO₂ under different PAN
416   source levels. However, there are still some uncertainties about the reaction mechanism and reaction rate for the
417   thermal dissociation of PAN at such high temperatures. Similar to the simulation results of (Thieser et al., 2016), we
418   did the sensitivity tests about the follow-up reactions of PA, and found that the isomerization of PA to CH₂C(O)OOH
419   has a great effect on the consistency of the experiments and the simulation results. If the reaction rate of the branching
420   reaction is set to zero, as shown in Fig. 10, the simulation results capture the trend well when NO₂ or NO is added.
421   Many factors affect the signal of NO₂ produced by the thermal dissociation of PAN, so the mechanism scheme
422   mentioned above provides a reasonable assumption to the interference process. Overall, the box model predicts the
423   interference of PAN measurement caused by NO and NO₂. Therefore, the correction factors of different cases under
424   various NO, NO₂ and PAN added are simulated to form the second look-up table, and then we can capture the signal
425   contribution of PNs to the ONs measurements in ANs channel.

426   MeN is pyrolyzed to produce NO₂ and CH₃O in the ANs channel (R16), and CH₃O is an important intermediate
427   product of the reactions about PA (R10 - R12). Therefore, the mechanism scheme about PAN applies to simulations
428   to correct the interference of atmospheric NOx to the ANs measurements. Similarly, the different cases under various
429   NO, NO₂ and MeN added were simulated to form the third look-up table for the corrections of ANs measurements
430   in the ANs channel. Through the look-up tables, the method to correct ANs measurements are established. Based on
431   the 'SEPC' method, the raw concentration of ONs ([ONs]) and PNs ([PNs_180]) can be gained, which need further
432   corrections. As for PNs measurements, the related cases can be found by the atmospheric NOx and the detected
433   [PNs_180] in PNs channel according to the first look-up table. Then the right correction factor ($C1$) is calculated
434   based on linear interpolation between the correction factor and detected signal of PAN measurement under the same
435   NOx distribution. As shown in Eq. 9, the corrected PNs mixing ratio ([PNs_C]) is derived by [PNs_180] and $C1$. The
436   interference relationships between atmospheric NOx and PNs are different in two TD channels, so it is necessary to
437   determine the contribution of PNs to ONs signal before subtracted in the ANs channel. We use the [PNs_C] derived
438   by the first look-up table and the atmospheric NOx to determine the correction factor ($C2$) for PNs signal based on
439   the second look-up table. Then the contribution of PNs to ONs measurements ([PNs_380]) is determined by Eq. 10.
440   Therefore, the raw concentration of ANs ([ANs]) is calculated by subtracting [PNs_380] from [ONs] (Eq. 11). As
441   for the correction of ANs, the correction factor ($C3$) is determined by the third look-up table, and then the result is
442   multiplied [ANs] to obtain the corrected ANs mixing ratio ([ANs_C]) (Eq. 12).

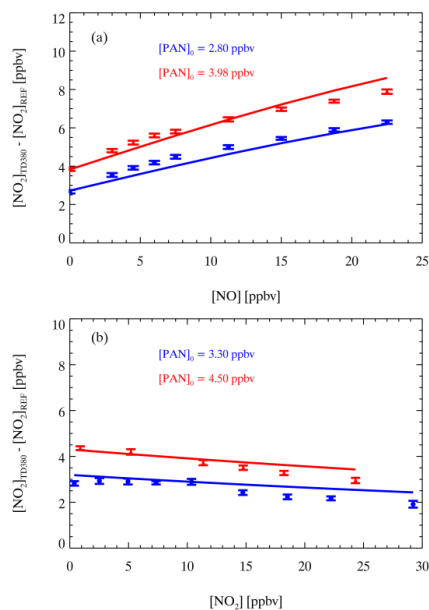
443   $[PNs\_C] = [PNs\_180] \times C1$ (9)

444   $[PNs\_380] = \dfrac{[PNs\_C]}{C2}$ (10)

445   $[ANs] = [ONs] - [PNs\_380]$ (11)

446   $[ANs\_C] = [ANs] \times C3$ (12)

447   In addition to the interference mentioned above, other nitrogen compounds may undergo pyrolysis to generate NO_2
448   in the heating channels, such as N_2O_5 and $ClNO_2$ (Li et al., 2018; Wang et al., 2017a; Womack et al., 2017), which
449   may be a source of uncertainty for measurements of organic nitrates. These interferences can be extracted with the
450   simultaneous measurement of N_2O_5 and $ClNO_2$.

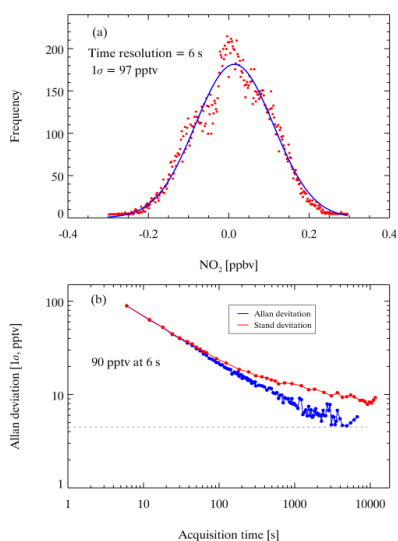
451

452

453   Figure 10. Modeled (lines) and measured (points) difference between the NO_2 signal in the ANs channel and reference channel for
454   different PAN sources with different amounts of NO (a) and NO_2 (b). The error bars show one standard deviation.

4.2 Uncertainty and detection limit

456   The uncertainty of CEAS measurement of NO_2 is contributed by absorption cross-section, mirror reflectivity, and
457   effective cavity length. The absorption cross-section of NO_2 is taken from Voigt et al. (2002), whose uncertainty is
458   about 4% (Voigt et al., 2002); the uncertainty of mirror reflectivity is about 5%, determined by the error of the
459   scattering cross-section of N_2; the uncertainty of effective cavity length is about 4.5%. According to the Gaussian
460   error propagation, the associated uncertainty of the ambient NO_2 measurement is ±8% based on the above parameters.
461   The precision of the instrument can be assessed by the Allan deviation and standard deviation. We continuously
462   measured 21077 spectra when the cavity was filled with N_2 under purge. The integration time was 3 s and the
463   sampling time was 6 s as every two spectra average before saving. The first 100 nitrogen spectra collected were
464   averaged as I_0, and all the spectrums were analyzed based on the I_0. The data set was divided into 300 gradients for
465   Gaussian fitting, and 1σ is 97 pptv, as shown in Fig. 9a. The 21077 spectra were averaged at different time intervals
466   (from 6 s to 11400 s). The Allan deviations at different time intervals were calculated (Duan et al., 2018; Langridge
467   et al., 2008; Wang et al., 2017a). As shown in Fig. 9b, the Allan deviation decreases as sampling time increases when
468   the sampling time is smaller than 1300 s, and the minimum is 5 pptv. When the sampling time is 6 s, the Allan
469   variance can reach 90 pptv, close to 1σ. ANs and PNs are detected by the same CEAS system and calculated by the
470   dynamic I_0 ('SEPC') method, so their precision is identical with NO_2 measurement. The uncertainty of [ANs] and
471   [PNs] mainly comes from the spectrum fitting to derive the concentration of NO_2 and the interference correction in

472   heated channels, which should be larger than 8%.

473

474

475   Figure 11. The instrument performance with different integration times. (a) the standard deviation of the measurements of NO_2 for a 6 s

476   integration time. (b) Allan deviation plots for measurements of NO_2 for a 6 s integration time.

4.3 The performance in field observation

478   TD-CEAS has deployed the first field observation in Xinjin County, Chengdu, China, in 2019, referred to as the

479   CHOOSE campaign (Yang et al., 2020). As shown in Fig. S6, there is a residential area at 5 km from the northwest

480   of the site; the surrounding area is lush with trees and is close to a forest park and a national wetland park; there is

481   an industrial park at about 12 km to the west and 8 km to the south separately. During the CHOOSE campaign, TD-

482   CEAS was deployed in a container. The sampling inlet protruded from the container top and was supported by a

483   bracket, with a height of 4 m above the ground. We determined the raw data of PNs and ONs during the observation

484   period. Base on the NO, NO_2, and raw PNs measured simultaneously, the specific correction factor picked from look-

485   up table can be referred to, and then the raw data is corrected. The raw concentration of ANs can be obtained by

486   subtracting the simulated PNs based on the second look-up table from the measured ONs in the ANs channel, and

487   then the raw ANs are corrected according to the third look-up table. Fig. 12a shows the time series of raw data and

488   the corrected data of PNs from August 9th to August 18th during the CHOOSE campaign, and Fig. 12b shows the time

489   series of ANs measurements before and after corrected. The correction factors used during corrections are shown in

490   Fig. S7. The value of *C1* is generally greater than 1.0 (except during the morning), suggesting the role of NO_2 is more

491   significant than NO in this site. The tendency of *C2* and *C3* is similar to *C1* during measurements, but the daily

492   change of *C2* and *C3* relatively smaller as the decrease of the sensitivity of interferences in ANs channel as mentioned

493   above. Fig. 12c shows that NO_2 was constantly increasing at night, reaching a peak near the early morning, and

494   maintaining a high value around 11 a.m. High mixing ratios of PNs were observed during the measurement, and the

495   diurnal variation of PNs was clear. The peak of ANs appeared in the noontime and several hours before that of PNs.

496   A photolytic conversion chemiluminescence detector (PC-CLD) was used to measure NO and NO_2 in the campaign.

497   The time series of NO_2 measured by TD-CEAS and PL-CLD with 5 min average is shown in Fig. 13a, which are

498   from August 9th to August 16th. The trend of NO_2 measured by two instruments agree well, but the results of PL-CLD

499   are higher when the mixing ratio of NO₂ is low at noon. Fig. 13b shows that the correlation coefficient of the NO₂
500   concentration measured by two instruments is up to 0.99. The results of TD-CEAS is a little higher than the results
501   of PL-CLD as the slope is 0.95, which is reasonable when considering the instrument uncertainties. The time series
502   of PNs (TD-CEAS) and PAN (GC-ECD) is shown in Fig. 13c, and the trends are relatively consistent, but the results
503   of PNs are higher than the results of PANs measured by GC-ECD, especially in the noontime. The result is reasonable
504   since the PAN is the most but not equal to the total PNs. The correlation between the two instruments is good as the
505   correction coefficient is up to 0.85 (Fig. 13d), suggesting our instrument's feasibility in PNs measurement.
506

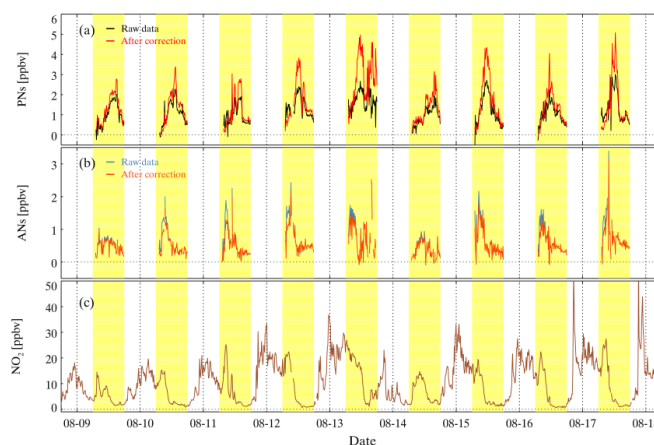
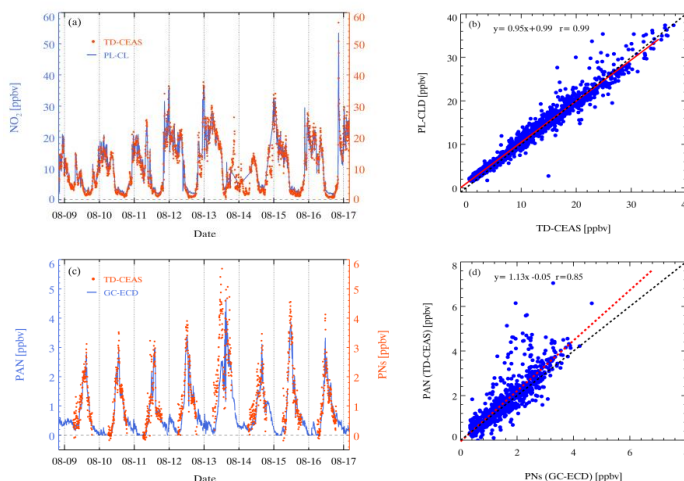



Figure 12. Time series of the observed mixing ratios of PNs, ANs and NO₂, during ozone pollution from the CHOOSE campaign in
2019. The yellow regions indicate the period for the daytime. (a) The black lines represent the raw measurements of PNs, and the red
lines are the corrected measurements of PNs according to the lookup table. (b) The blue lines represent the raw measurements of ANs,
and the orange lines are the corrected measurements of ANs according to the lookup tables. (c) The measurements of NO₂ in the reference
channel.

515   Figure 13. Comparison of TD-CEAS and PL-CLD in the CHOOSE campaign: Panel (a) shows the time series of NO_2 measurements.

516   Orange points represent the results of TD-CEAS, and blue line represents the results of PL-CLD. Panel (b) shows the NO_2 correlation

517   between the two instruments. Comparison of the PNs measured by TD-CEAS and the PAN measured by GC-ECD: Panel (c) shows the

518   time series of PNs and PAN, orange dots represent the results of TD-CEAS, and blue line represents the results of GC-ECD; Panel (d)

519   shows the PNs correlation of the two instruments.

5. Conclusions and outlook

521   We developed a new TD-CEAS instrument to measure PNs, ANs and NO_2 in the atmosphere. The instrument uses

522   only one CEAS to measure NO_2, PNs and ANs to avoid the error caused by different detectors. This TD-CEAS is a

523   combination of CEAS and pyrolysis technology for organic nitrates measurement. CEAS uses the small cavity cell

524   of the cage system, with a total length of about 60 cm, a small overall volume and low energy consumption. The use

525   of a NO_2-CEAS system to detect three classes of compounds reduces the instrument uncertainty. The short cycle

526   period meets the atmospheric lifetime requirements of organic nitrates for measurement time resolution in general.

527   The time resolution of the instrument is 6 s, one measurement cycle is 3 min, and sample gas from each channel is

528   measured for 1 min. The instrument has a lower detection limit of 97 pptv (1σ). The interferences in the heating

529   channels are characterized under different levels of ambient NO, NO_2 and ONs (PAN or MeN) by laboratory

530   experiments and model simulations. Three look-up tables were established to correct the PNs and ANs concentration

531   based on the detected NOx and organic nitrates.

532   The instrument was deployed in field measurement in Chengdu, China, and the PNs measured by TD-CEAS

533   showed a good consistency with PAN measured by GC-ECD during the daytime. However, when the ambient NO_2

534   in the sampled air masses change drastically, the difference in NO_2 between adjacent measurement modes in a cycle

535   will be erroneous, resulting in the unfeasible measurement (Fig. S8). The simultaneous measurements show that the

536   N_2O_5 mixing ratio during nighttime is low and zero during the daytime. Therefore, the interferences of the N_2O_5 is

537   negligible for the ONs measurements during the day for the CHOOSE campaign. Nevertheless, the observed ANs

538   may be subject to the level of $ClNO_2$ without the simultaneous $ClNO_2$ measurement. Overall, this instrument is very

539   suitable for detecting NO_2, PNs, and ANs in the chamber studies or ambient measurements with relatively stable air

540   masses free of intensive emission interferences. Multiple detectors can be used for simultaneous observation to avoid

541   limited measurement conditions. More importantly, the ways to reduce the impact of interference reaction in heated

542   channels shall be investigated, such as improving the wall loss of RO_2 through increasing surface areas of the

543   sampling lines or reducing the residence time during the sampling.

545   **Data availability.** The datasets used in this study are available from the corresponding author upon request

546   (k.lu@pku.edu.cn).

548   **Author contributions.** K.D.L. and H.C.W. designed the study. C.M.L, H.C.W. set up and characterized the

549   instrument, analyzed the data and wrote the paper with the input of K.D.L. All authors contributed to the field

550   measurements, discussed and improved the paper.

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

554   **Acknowledgments**. This work was supported by the National Natural Science Foundation of China (Grants No.

555   21976006); the National Research Program for Key Issue in Air Pollution Control (Grants No. DQGG0103-01);

556   Beijing Municipal Natural Science Foundation for Distinguished Young Scholars (Grants No. JQ19031).

559 **References.**

560 Arey, J., Aschmann, S. M., Kwok, E. S. C., and Atkinson, R.: Alkyl nitrate, hydroxyalkyl nitrate, and hydroxycarbonyl formation from
561 the NOx-air photooxidations of C-5-C-8 n-alkanes, J. Phys. Chem. A, 105, 1020-1027, 2001.

562 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated
563 kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of O-x, HOx, NOx and SOx species, Atmos.
564 Chem. Phys., 4, 1461-1738, 2004.

565 Atlas, E.: EVIDENCE FOR GREATER-THAN-OR-EQUAL-TO-C-3 ALKYL NITRATES IN RURAL AND REMOTE
566 ATMOSPHERES, Nature, 331, 426-428, 1988.

567 Atlas, E., Pollock, W., Greenberg, J., Heidt, L., and Thompson, A. M.: ALKYL NITRATES, NONMETHANE HYDROCARBONS,
568 AND HALOCARBON GASES OVER THE EQUATORIAL PACIFIC-OCEAN DURING SAGA-3, J. Geophys. Res.-Atmos., 98,
569 16933-16947, 1993.

570 Berkemeier, T., Ammann, M., Mentel, T. F., Poschl, U., and Shiraiwa, M.: Organic Nitrate Contribution to New Particle Formation and
571 Growth in Secondary Organic Aerosols from alpha-Pinene Ozonolysis, Environ. Sci. Technol., 50, 6334-6342, 2016.

572 Blanchard, P., Shepson, P. B., Schiff, H. I., and Drummond, J. W.: DEVELOPMENT OF A GAS-CHROMATOGRAPH FOR TRACE-
573 LEVEL MEASUREMENT OF PEROXYACETYL NITRATE USING CHEMICAL AMPLIFICATION, Anal. Chem., 65, 2472-2477,
574 1993.

575 Chen, J. and Venables, D. S.: A broadband optical cavity spectrometer for measuring weak near-ultraviolet absorption spectra of gases,
576 Atmos. Meas. Tech., 4, 425-436, 2011.

577 Chen, J., Wu, H., Liu, A. W., Hu, S. M., and Zhang, J.: Field Measurement of NO2 and RNO2 by Two-Channel Thermal Dissociation
578 Cavity Ring Down Spectrometer, Chinese J Chem Phys, 30, 493-498, 2017.

579 Chuck, A. L., Turner, S. M., and Liss, P. S.: Direct evidence for a marine source of C-1 and C-2 alkyl nitrates, Science, 297, 1151-1154,
580 2002.

581 Day, D. A., Wooldridge, P. J., Dillon, M. B., Thornton, J. A., and Cohen, R. C.: A thermal dissociation laser-induced fluorescence
582 instrument for in situ detection of NO2, peroxy nitrates, alkyl nitrates, and HNO3, J. Geophys. Res.-Atmos., 107, 2002.

583 Duan, J., Qin, M., Ouyang, B., Fang, W., Li, X., Lu, K. D., Tang, K., Liang, S. X., Meng, F. H., Hu, Z. K., Xie, P. H., Liu, W. Q., and
584 Hasler, R.: Development of an incoherent broadband cavity-enhanced absorption spectrometer for in situ measurements of HONO and
585 NO2, Atmos. Meas. Tech., 11, 4531-4543, 2018.

586 Fiedler, S. E., Hese, A., and Ruth, A. A.: Incoherent broad-band cavity-enhanced absorption spectroscopy, Chem Phys Lett, 371, 284-
587 294, 2003.

588 Fischer, R. G., Kastler, J., and Ballschmiter, K.: Levels and pattern of alkyl nitrates, multifunctional alkyl nitrates, and halocarbons in
589 the air over the Atlantic Ocean, J. Geophys. Res.-Atmos., 105, 14473-14494, 2000.

590 Flocke, F. M., Weinheimer, A. J., Swanson, A. L., Roberts, J. M., Schmitt, R., and Shertz, S.: On the measurement of PANs by gas
591 chromatography and electron capture detection, J. Atmos. Chem., 52, 19-43, 2005.

592 Friedrich, N., Tadic, I., Schuladen, J., Brooks, J., Darbyshire, E., Drewnick, F., Fischer, H., Lelieveld, J., and Crowley, J. N.:
593 Measurement of NOx and NOy with a thermal dissociation cavity ring-down spectrometer (TD-CRDS): instrument characterisation and
594 first deployment, Atmos. Meas. Tech., 13, 5739-5761, 2020.

595 Fuchs, H., Holland, F., and Hofzumahaus, A.: Measurement of tropospheric RO2 and HO2 radicals by a laser-induced fluorescence
596 instrument, Rev. Sci. Instrum., 79, 12, 2008.

597 Gaffney, J. S., Bornick, R. M., Chen, Y. H., and Marley, N. A.: Capillary gas chromatographic analysis of nitrogen dioxide and PANs
598 with luminol chemiluminescent detection, Atmos. Environ., 32, 1445-1454, 1998.

599 Gherman, T., Venables, D. S., Vaughan, S., Orphal, J., and Ruth, A. A.: Incoherent broadband cavity-enhanced absorption spectroscopy
600 in the near-ultraviolet: Application to HONO and NO2, Environ. Sci. Technol., 42, 890-895, 2008.

601 Glavas, S. and Moschonas, N.: Determination of PAN, PPN, PnBN and selected pentyl nitrates in Athens, Greece, Atmos. Environ., 35,
602 5467-5475, 2001.

603 Hao, C. S., Shepson, P. B., Drummond, J. W., and Muthuramu, K.: GAS-CHROMATOGRAPHIC DETECTOR FOR SELECTIVE AND

604 SENSITIVE DETECTION OF ATMOSPHERIC ORGANIC NITRATES, Anal. Chem., 66, 3737-3743, 1994.

605 Horowitz, L. W., Fiore, A. M., Milly, G. P., Cohen, R. C., Perring, A., Wooldridge, P. J., Hess, P. G., Emmons, L. K., and Lamarque, J.

606 F.: Observational constraints on the chemistry of isoprene nitrates over the eastern United States, J. Geophys. Res.-Atmos., 112, 13,

607 2007.

608 Jordan, N. and Osthoff, H. D.: Quantification of nitrous acid (HONO) and nitrogen dioxide (NO2) in ambient air by broadband cavity-

609 enhanced absorption spectroscopy (IBBCEAS) between 361 and 388 nm, Atmos. Meas. Tech., 13, 273-285, 2020.

610 Jordan, N., Ye, C. Z., Ghosh, S., Washenfelder, R. A., Brown, S. S., and Osthoff, H. D.: A broadband cavity-enhanced spectrometer for

611 atmospheric trace gas measurements and Rayleigh scattering cross sections in the cyan region (470-540 nm), Atmos. Meas. Tech., 12,

612 1277-1293, 2019.

613 Kastler, J. and Ballschmiter, K.: Identification of alkyl dinitrates in ambient air of Central Europe, Fresenius J. Anal. Chem., 363, 1-4,

614 1999.

615 Kirchner, F., Mayer-Figge, A., Zabel, F., and Becker, K. H.: Thermal stability of peroxynitrates, Int. J. Chem. Kinet., 31, 127-144, 1999.

616 Langridge, J. M., Ball, S. M., and Jones, R. L.: A compact broadband cavity enhanced absorption spectrometer for detection of

617 atmospheric NO2 using light emitting diodes, Analyst, 131, 916-922, 2006.

618 Langridge, J. M., Ball, S. M., Shillings, A. J. L., and Jones, R. L.: A broadband absorption spectrometer using light emitting diodes for

619 ultrasensitive, in situ trace gas detection, Rev. Sci. Instrum., 79, 2008.

620 Lee, B. H., Mohr, C., Lopez-Hilfiker, F. D., Lutz, A., Hallquist, M., Lee, L., Romer, P., Cohen, R. C., Iyer, S., Kurten, T., Hu, W., Day,

621 D. A., Campuzano-Jost, P., Jimenez, J. L., Xu, L., Ng, N. L., Guo, H., Weber, R. J., Wild, R. J., Brown, S. S., Koss, A., de Gouw, J.,

622 Olson, K., Goldstein, A. H., Seco, R., Kim, S., McAvey, K., Shepson, P. B., Starn, T., Baumann, K., Edgerton, E. S., Liu, J., Shilling, J.

623 E., Miller, D. O., Brune, W., Schobesberger, S., D'Ambro, E. L., and Thornton, J. A.: Highly functionalized organic nitrates in the

624 southeast United States: Contribution to secondary organic aerosol and reactive nitrogen budgets, Proc. Natl. Acad. Sci. U. S. A., 113,

625 1516-1521, 2016.

626 Lee, L., Wooldridge, P. J., Gilman, J. B., Warneke, C., de Gouw, J., and Cohen, R. C.: Low temperatures enhance organic nitrate formation:

627 evidence from observations in the 2012 Uintah Basin Winter Ozone Study, Atmos. Chem. Phys., 14, 12441-12454, 2014.

628 Li, Z., Hu, R., Xie, P., Chen, H., Wu, S., Wang, F., Wang, Y., Ling, L., Liu, J., and Liu, W.: Development of a portable cavity ring down

629 spectroscopy instrument for simultaneous, in situ measurement of NO3 and N2O5, Opt. Express, 26, A433-A449, 2018.

630 Liang, S., Qin, M., Xie, P., Duan, J., Fang, W., He, Y., Xu, J., Liu, J., Li, X., Tang, K., Meng, F., Ye, K., Liu, J., and Liu, W.: Development

631 of an incoherent broadband cavity-enhanced absorption spectrometer for measurements of ambient glyoxal and NO2 in a polluted urban

632 environment, Atmos. Meas. Tech., 12, 2499-2512, 2019.

633 Liu, J., Li, X., Yang, Y., Wang, H., Wu, Y., Lu, X., Chen, M., Hu, J., Fan, X., Zeng, L., and Zhang, Y.: An IBBCEAS system for

634 atmospheric measurements of glyoxal and methylglyoxal in the presence of high NO2 concentrations, Atmos. Meas. Tech., 12, 4439-

635 4453, 2019.

636 Luxenhofer, O., Schneider, E., and Ballschmiter, K.: SEPARATION, DETECTION AND OCCURRENCE OF (C2-C8)-ALKYL

637 NITRATES AND PHENYL-ALKYL NITRATES AS TRACE COMPOUNDS IN CLEAN AND POLLUTED AIR, Fresenius J. Anal.

638 Chem., 350, 384-394, 1994.

639 Ma, M., Gao, Y., Wang, Y., Zhang, S., Leung, L. R., Liu, C., Wang, S., Zhao, B., Chang, X., Su, H., Zhang, T., Sheng, L., Yao, X., and

640 Gao, H.: Substantial ozone enhancement over the North China Plain from increased biogenic emissions due to heat waves and land cover

641 in summer 2017, Atmos. Chem. Phys., 19, 12195-12207, 2019.

642 Mellouki, A., Wallington, T. J., and Chen, J.: Atmospheric Chemistry of Oxygenated Volatile Organic Compounds: Impacts on Air

643 Quality and Climate, Chemical Reviews, 115, 3984-4014, 2015.

644 Min, K. E., Washenfelder, R. A., Dube, W. P., Langford, A. O., Edwards, P. M., Zarzana, K. J., Stutz, J., Lu, K., Rohrer, F., Zhang, Y.,

645 and Brown, S. S.: A broadband cavity enhanced absorption spectrometer for aircraft measurements of glyoxal, methylglyoxal, nitrous

646 acid, nitrogen dioxide, and water vapor, Atmos Meas Tech, 9, 423-440, 2016.

647 Ng, N. L., Brown, S. S., Archibald, A. T., Atlas, E., Cohen, R. C., Crowley, J. N., Day, D. A., Donahue, N. M., Fry, J. L., Fuchs, H.,
648 Griffin, R. J., Guzman, M. I., Herrmann, H., Hodzic, A., Iinuma, Y., Jimenez, J. L., Kiendler-Scharr, A., Lee, B. H., Luecken, D. J., Mao,
649 J. Q., McLaren, R., Mutzel, A., Osthoff, H. D., Ouyang, B., Picquet-Varrault, B., Platt, U., Pye, H. O. T., Rudich, Y., Schwantes, R. H.,
650 Shiraiwa, M., Stutz, J., Thornton, J. A., Tilgner, A., Williams, B. J., and Zaveri, R. A.: Nitrate radicals and biogenic volatile organic
651 compounds: oxidation, mechanisms, and organic aerosol, Atmos Chem Phys, 17, 2103-2162, 2017.

652 Paul, D., Furgeson, A., and Osthoff, H. D.: Measurements of total peroxy and alkyl nitrate abundances in laboratory-generated gas
653 samples by thermal dissociation cavity ring-down spectroscopy, Rev. Sci. Instrum., 80, 2009.

654 Paul, D. and Osthoff, H. D.: Absolute Measurements of Total Peroxy Nitrate Mixing Ratios by Thermal Dissociation Blue Diode Laser
655 Cavity Ring-Down Spectroscopy, Anal Chem, 82, 6695-6703, 2010.

656 Perring, A. E., Bertram, T. H., Wooldridge, P. J., Fried, A., Heikes, B. G., Dibb, J., Crounse, J. D., Wennberg, P. O., Blake, N. J., Blake,
657 D. R., Brune, W. H., Singh, H. B., and Cohen, R. C.: Airborne observations of total RONO2: new constraints on the yield and lifetime
658 of isoprene nitrates, Atmos. Chem. Phys., 9, 1451-1463, 2009.

659 Perring, A. E., Pusede, S. E., and Cohen, R. C.: An Observational Perspective on the Atmospheric Impacts of Alkyl and Multifunctional
660 Nitrates on Ozone and Secondary Organic Aerosol, Chemical Reviews, 113, 5848-5870, 2013.

661 Reisen, F., Aschmann, S. M., Atkinson, R., and Arey, J.: 1,4-hydroxycarbonyl products of the OH radical initiated reactions of C-5-C-8
662 n-alkanes in the presence of N0, Environ. Sci. Technol., 39, 4447-4453, 2005.

663 Roberts, J. M.: THE ATMOSPHERIC CHEMISTRY OF ORGANIC NITRATES, Atmospheric Environment Part a-General Topics, 24,
664 243-287, 1990.

665 Roberts, J. M., Bertman, S. B., Parrish, D. D., Fehsenfeld, F. C., Jobson, B. T., and Niki, H.: Measurement of alkyl nitrates at Chebogue
666 Point, Nova Scotia during the 1993 North Atlantic Regional Experiment (NARE) intensive, J. Geophys. Res.-Atmos., 103, 13569-13580,
667 1998a.

668 Roberts, J. M., Jobson, B. T., Kuster, W., Goldan, P., Murphy, P., Williams, E., Frost, G., Riemer, D., Apel, E., Stroud, C., Wiedinmyer,
669 C., and Fehsenfeld, F.: An examination of the chemistry of peroxycarboxylic nitric anhydrides and related volatile organic compounds
670 during Texas Air Quality Study 2000 using ground-based measurements, J. Geophys. Res.-Atmos., 108, 2003.

671 Roberts, J. M., Williams, J., Baumann, K., Buhr, M. P., Goldan, P. D., Holloway, J., Hubler, G., Kuster, W. C., McKeen, S. A., Ryerson,
672 T. B., Trainer, M., Williams, E. J., Fehsenfeld, F. C., Bertman, S. B., Nouaime, G., Seaver, C., Grodzinsky, G., Rodgers, M., and Young,
673 V. L.: Measurements of PAN, PPN, and MPAN made during the 1994 and 1995 Nashville Intensives of the Southern Oxidant Study:
674 Implications for regional ozone production from biogenic hydrocarbons, J. Geophys. Res.-Atmos., 103, 22473-22490, 1998b.

675 Rollins, A. W., Browne, E. C., Min, K. E., Pusede, S. E., Wooldridge, P. J., Gentner, D. R., Goldstein, A. H., Liu, S., Day, D. A., Russell,
676 L. M., and Cohen, R. C.: Evidence for NOx Control over Nighttime SOA Formation, Science, 337, 1210-1212, 2012.

677 Russell, M. and Allen, D. T.: Predicting secondary organic aerosol formation rates in southeast Texas, J Geophys Res-Atmos, 110, 2005.

678 Sadanaga, Y., Takaji, R., Ishiyama, A., Nakajima, K., Matsuki, A., and Bandow, H.: Thermal dissociation cavity attenuated phase shift
679 spectroscopy for continuous measurement of total peroxy and organic nitrates in the clean atmosphere, Rev. Sci. Instrum., 87, 2016.

680 Shardanand, S. a. R., A. D. P.: Absolute Rayleigh scattering cross sections of gases and freons of stratospheric interest in the visible and
681 ultraviolet regions, NASA Technical Note, 1977. 1977.

682 Shu, L., Wang, T., Han, H., Xie, M., Chen, P., Li, M., and Wu, H.: Summertime ozone pollution in the Yangtze River Delta of eastern
683 China during 2013-2017: Synoptic impacts and source apportionment, Environmental pollution (Barking, Essex : 1987), doi:
684 10.1016/j.envpol.2019.113631, 2019. 113631-113631, 2019.

685 Simpson, I. J., Wang, T., Guo, H., Kwok, Y. H., Flocke, F., Atlas, E., Meinardi, S., Rowland, F. S., and Blake, D. R.: Long-term
686 atmospheric measurements of C-1-C-5 alkyl nitrates in the pearl river delta region of southeast China, Atmos Environ, 40, 1619-1632,
687 2006.

688 Slusher, D. L., Huey, L. G., Tanner, D. J., Flocke, F. M., and Roberts, J. M.: A thermal dissociation-chemical ionization mass spectrometry
689 (TD-CIMS) technique for the simultaneous measurement of peroxyacyl nitrates and dinitrogen pentoxide, J Geophys Res-Atmos, 109,
690 2004.

691   Sneep, M. and Ubachs, W.: Direct measurement of the Rayleigh scattering cross section in various gases, J. Quant. Spectrosc. Radiat.
692   Transf., 92, 293-310, 2005.

693   Sobanski, N., Schuladen, J., Schuster, G., Lelieveld, J., and Crowley, J. N.: A five-channel cavity ring-down spectrometer for the
694   detection of NO2, NO3, N2O5, total peroxy nitrates and total alkyl nitrates, Atmos. Meas. Tech., 9, 5103-5118, 2016.

695   Sobanski, N., Thieser, J., Schuladen, J., Sauvage, C., Song, W., Williams, J., Lelieveld, J., and Crowley, J. N.: Day and night- time
696   formation of organic nitrates at a forested mountain site in south-west Germany, Atmos Chem Phys, 17, 4115-4130, 2017.

697   Song, J., Zhang, Y., Huang, Y., Ho, K. F., Yuan, Z., Ling, Z., Niu, X., Gao, Y., Cui, L., Louie, P. K. K., Lee, S.-c., and Lai, S.: Seasonal
698   variations of C-1-C-4 alkyl nitrates at a coastal site in Hong Kong: Influence of photochemical formation and oceanic emissions,
699   Chemosphere, 194, 275-284, 2018.

700   Sun, J., Li, Z., Xue, L., Wang, T., Wang, X., Gao, J., Nie, W., Simpson, I. J., Gao, R., Blake, D. R., Chai, F., and Wang, W.: Summertime
701   C-1-C-5 alkyl nitrates over Beijing, northern China: Spatial distribution, regional transport, and formation mechanisms, Atmos. Res.,
702   204, 102-109, 2018.

703   Talbot, R. W., Dibb, J. E., Scheuer, E. M., Bradshaw, J. D., Sandholm, S. T., Singh, H. B., Blake, D. R., Blake, N. J., Atlas, E., and
704   Flocke, F.: Tropospheric reactive odd nitrogen over the South Pacific in austral springtime, J. Geophys. Res.-Atmos., 105, 6681-6694,
705   2000.

706   Tang, K., Qin, M., Fang, W., Duan, J., Meng, F., Ye, K., Zhang, H., Xie, P., He, Y., Xu, W., Liu, J., and Liu, W.: Simultaneous detection
707   of atmospheric HONO and NO2 utilising an IBBCEAS system based on an iterative algorithm, Atmos. Meas. Tech., 13, 6487-6499,
708   2020.

709   Tanimoto, H., Hirokawa, J., Kajii, Y., and Akimoto, H.: A new measurement technique of peroxyacetyl nitrate at parts per trillion by
710   volume levels: Gas chromatography/negative ion chemical ionization mass spectrometry, J. Geophys. Res.-Atmos., 104, 21343-21354,
711   1999.

712   Thalman, R., Baeza-Romero, M. T., Ball, S. M., Borras, E., Daniels, M. J. S., Goodall, I. C. A., Henry, S. B., Karl, T., Keutsch, F. N.,
713   Kim, S., Mak, J., Monks, P. S., Munoz, A., Orlando, J., Peppe, S., Rickard, A. R., Rodenas, M., Sanchez, P., Seco, R., Su, L., Tyndall,
714   G., Vazquez, M., Vera, T., Waxman, E., and Volkamer, R.: Instrument intercomparison of glyoxal, methyl glyoxal and NO2 under
715   simulated atmospheric conditions, Atmos. Meas. Tech., 8, 1835-1862, 2015.

716   Thalman, R. and Volkamer, R.: Inherent calibration of a blue LED-CE-DOAS instrument to measure iodine oxide, glyoxal, methyl
717   glyoxal, nitrogen dioxide, water vapour and aerosol extinction in open cavity mode, Atmos. Meas. Tech., 3, 1797-1814, 2010.

718   Thieser, J., Schuster, G., Schuladen, J., Phillips, G. J., Reiffs, A., Parchatka, U., Pohler, D., Lelieveld, J., and Crowley, J. N.: A two-
719   channel thermal dissociation cavity ring-down spectrometer for the detection of ambient NO2, RO2NO2 and RONO2, Atmos Meas Tech,
720   9, 553-576, 2016.

721   Vandaele, A. C., Hermans, C., Fally, S., Carleer, M., Colin, R., Merienne, M. F., Jenouvrier, A., and Coquart, B.: High-resolution Fourier
722   transform measurement of the NO2 visible and near-infrared absorption cross sections: Temperature and pressure effects, J. Geophys.
723   Res.-Atmos., 107, 13, 2002.

724   Ventrillard-Courtillot, I., O'Brien, E. S., Kassi, S., Mejean, G., and Romanini, D.: Incoherent broad-band cavity-enhanced absorption
725   spectroscopy for simultaneous trace measurements of NO2 and NO3 with a LED source, Appl. Phys. B-Lasers Opt., 101, 661-669, 2010.

726   Voigt, S., Orphal, J., and Burrows, J. P.: The temperature and pressure dependence of the absorption cross-sections of NO2 in the 250-
727   800 nm region measured by Fourier-transform spectroscopy, J Photoch Photobio A, 149, 1-7, 2002.

728   Wang, H., Chen, J., and Lu, K.: Development of a portable cavity-enhanced absorption spectrometer for the measurement of ambient
729   NO3 and N2O5: experimental setup, lab characterizations, and field applications in a polluted urban environment, Atmos. Meas. Tech.,
730   10, 1465-1479, 2017a.

731   Wang, T., Poon, C. N., Kwok, Y. H., and Li, Y. S.: Characterizing the temporal variability and emission patterns of pollution plumes in
732   the Pearl River Delta of China, Atmos. Environ., 37, 3539-3550, 2003.

733   Wang, T., Wei, X. L., Ding, A. J., Poon, C. N., Lam, K. S., Li, Y. S., Chan, L. Y., and Anson, M.: Increasing surface ozone concentrations
734   in the background atmosphere of Southern China, 1994-2007, Atmos Chem Phys, 9, 6217-6227, 2009.

735 Wang, T., Xue, L., Brimblecombe, P., Lam, Y. F., Li, L., and Zhang, L.: Ozone pollution in China: A review of concentrations,
736 meteorological influences, chemical precursors, and effects, Sci. Total Environ., 575, 1582-1596, 2017b.

737 Washenfelder, R. A., Langford, A. O., Fuchs, H., and Brown, S. S.: Measurement of glyoxal using an incoherent broadband cavity
738 enhanced absorption spectrometer, Atmos. Chem. Phys., 8, 7779-7793, 2008.

739 Wennberg, P. O., Bates, K. H., Crounse, J. D., Dodson, L. G., McVay, R. C., Mertens, L. A., Nguyen, T. B., Praske, E., Schwantes, R.
740 H., Smarte, M. D., St Clair, J. M., Teng, A. P., Zhang, X., and Seinfeld, J. H.: Gas-Phase Reactions of Isoprene and Its Major Oxidation
741 Products, Chemical Reviews, 118, 3337-3390, 2018.

742 Wild, R. J., Edwards, P. M., Dube, W. P., Baumann, K., Edgerton, E. S., Quinn, P. K., Roberts, J. M., Rollins, A. W., Veres, P. R., Warneke,
743 C., Williams, E. J., Yuan, B., and Brown, S. S.: A Measurement of Total Reactive Nitrogen, NOy, together with NO2, NO, and O-3 via
744 Cavity Ring-down Spectroscopy, Environ. Sci. Technol., 48, 9609-9615, 2014.

745 Womack, C. C., Neuman, J. A., Veres, P. R., Eilerman, S. J., Brock, C. A., Decker, Z. C. J., Zarzana, K. J., Dube, W. P., Wild, R. J.,
746 Wooldridge, P. J., Cohen, R. C., and Brown, S. S.: Evaluation of the accuracy of thermal dissociation CRDS and LIF techniques for
747 atmospheric measurement of reactive nitrogen species, Atmos Meas Tech, 10, 1911-1926, 2017.

748 Wooldridge, P. J., Perring, A. E., Bertram, T. H., Flocke, F. M., Roberts, J. M., Singh, H. B., Huey, L. G., Thornton, J. A., Wolfe, G. M.,
749 Murphy, J. G., Fry, J. L., Rollins, A. W., LaFranchi, B. W., and Cohen, R. C.: Total Peroxy Nitrates (Sigma PNs) in the atmosphere: the
750 Thermal Dissociation-Laser Induced Fluorescence (TD-LIF) technique and comparisons to speciated PAN measurements, Atmos. Meas.
751 Tech., 3, 593-607, 2010.

752 Yang, Y., Li, X., Zu, K., Lian, C., Chen, S., Dong, H., Feng, M., Liu, H., Liu, J., Lu, K., Lu, S., Ma, X., Song, D., Wang, W., Yang, S.,
753 Yang, X., Yu, X., Zhu, Y., Zeng, L., Tan, Q., and Zhang, Y.: Elucidating the effect of HONO on O3 pollution by a case study in southwest
754 China, The Science of the total environment, doi: 10.1016/j.scitotenv.2020.144127, 2020. 144127-144127, 2020.

755 Yi, H. M., Wu, T., Wang, G. S., Zhao, W. X., Fertein, E., Coeur, C., Gao, X. M., Zhang, W. J., and Chen, W. D.: Sensing atmospheric
756 reactive species using light emitting diode by incoherent broadband cavity enhanced absorption spectroscopy, Opt. Express, 24, 10, 2016.

757 Yin, C., Deng, X., Zou, Y., Solmon, F., Li, F., and Deng, T.: Trend analysis of surface ozone at suburban Guangzhou, China, Sci. Total
758 Environ., 695, 2019.

759 Zare, A., Romer, P. S., Tran, N., Keutsch, F. N., Skog, K., and Cohen, R. C.: A comprehensive organic nitrate chemistry: insights into
760 the lifetime of atmospheric organic nitrates, Atmos. Chem. Phys., 18, 15419-15436, 2018.

761 Zhang, Y., Sun, J., Zheng, P., Chen, T., Liu, Y., Han, G., Simpson, I. J., Wang, X., Blake, D. R., Li, Z., Yang, X., Qi, Y., Wang, Q., Wang,
762 W., and Xue, L.: Observations of C1-C5 alkyl nitrates in the Yellow River Delta, northern China: Effects of biomass burning and oil
763 field emissions, The Science of the total environment, 656, 129-139, 2018.

764