

1 **Five-channel TD–CEAS measurements of gaseous and**
2 **particulate organic nitrates with NO/NO₂ interference**
3 **correction under high-NO_x conditions**

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Abstract

Organic nitrates (ONs) are important temporary reservoirs of atmospheric NO_x and, for sufficiently low-volatility species, contributors to secondary organic aerosol formation. However, online measurements of particle-phase ONs remain limited, hindering quantitative constraints on ON abundance and gas–particle partitioning. Here we present a five-channel thermal dissociation cavity-enhanced absorption spectrometer (TD–CEAS) for in situ, time-resolved measurements of NO₂ and operationally defined ON classes in both the gas and particle phases. The instrument combines a room-temperature channel for ambient NO₂ with thermal dissociation channels operated at 250 and 450 °C to quantify total peroxy nitrates (ΣPNs) and total alkyl nitrates (ΣANs), respectively. Gas–particle separation is achieved using paired inlet/filter configurations, and gas- and particle-phase ΣPNs and ΣANs are retrieved by channel differencing. The 1σ (1 s) detection limits are 49 pptv for gΣPNs, 49 pptv for pΣPNs, 48 pptv for gΣANs, and 68 pptv for pΣANs. Laboratory characterization included temperature-dependent dissociation measurements, cross-validation of PAN against GC–ECD ($R^2=0.988$; slope = 0.987), and an operational calibration for particulate ΣANs using 2-ethylhexyl nitrate (recovery slope=1.036±0.028; method detection limit =0.029 μg NO₂). Dedicated interference experiments showed that NO and NO₂ can introduce substantial nonlinear biases in ΣPN measurements; these effects were parameterized using a multiple nonlinear regression model. The instrument was deployed at an urban site in Guangzhou during September–October 2025 and provided 6 min measurements of NO₂, gas- and particle-phase ΣPNs, and gas- and particle-phase ΣANs under high-NO_x conditions. During the October intensive period, corrected gas-phase ΣPNs covaried well with independently measured PAN ($R^2=0.83$), and PAN accounted for 78 % of daytime gΣPNs. This five-channel TD–CEAS provides a framework for continuous observations of ON phase partitioning and reactive nitrogen processing in polluted urban atmospheres.

Keywords: thermal dissociation; cavity-enhanced absorption spectroscopy; NO₂; peroxy nitrates; alkyl nitrates; gas–particle partitioning

1 Introduction

Organic nitrates (ONs), defined here as organic compounds containing the -ONO_2 functional group, are ubiquitous in the atmosphere. They are produced primarily during the oxidation of volatile organic compounds (VOCs) in the presence of NO_x via daytime OH chemistry and nighttime NO_3 chemistry. By temporarily sequestering NO_x and subsequently releasing it through thermal decomposition, photolysis, and further oxidation (Kirchner et al., 1999; Neu et al., 2008; [Zare, et al., 2018](#)), ONs act as both reservoirs and sinks of reactive nitrogen, thereby influencing ozone production and the redistribution of NO_x on regional scales (Perring et al., 2013). In addition, many ONs are sufficiently low in volatility, or become so through continued oxidation and accretion, that they partition to the particle phase and contribute to secondary organic aerosol (SOA) formation (Atkinson, 2000; Rollins et al., 2012; [Fisher et al., 2016](#); [Day et al., 2022](#)). Quantifying ON abundance and gas-particle partitioning is therefore important for constraining both reactive nitrogen budgets and coupled oxidant–aerosol chemistry.

Operationally, ONs are often grouped into peroxy nitrates (RO_2NO_2 , ΣPNs) and alkyl nitrates (RONO_2 , ΣANs), which differ in formation pathways, thermal stability, and atmospheric lifetimes (Roberts, 1990). Acyl peroxy nitrates such as peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) are relatively thermally stable and can represent a substantial fraction of ΣPNs , whereas non-acyl peroxy nitrates such as HO_2NO_2 and $\text{CH}_3\text{O}_2\text{NO}_2$ are much less stable under typical boundary-layer conditions (Murphy et al., 2004). ΣANs are produced in both OH- and NO_3 -initiated oxidation, with especially important contributions from nighttime NO_3 chemistry and implications for SOA formation and reactive nitrogen cycling (Rollins et al., 2012; Perring et al., 2013; [Kiendler-Scharr et al., 2016](#)). The structural diversity, multifunctionality, and

composition-dependent volatility of ONs make them challenging targets for comprehensive, in situ measurements, particularly when both gas- and particle-phase ONs are of interest.

Thermal dissociation (TD) coupled with fast NO₂ detection has emerged as a practical approach for class-resolved ON measurements because the O–NO₂ bond strengths differ between RO₂NO₂ and RONO₂, enabling ΣPNs and ΣANs to be converted to NO₂

at different temperatures (Roberts, 1990; Kirchner et al., 1999). Measurement techniques include

~~TD has been combined with a range of sensitive NO₂ detectors, including~~ laser-induced fluorescence (LIF) (Day et al., 2002), cavity ring-down spectrometry (CRDS) (Paul et al., 2009), chemical ionization mass spectrometry (CIMS) (Zheng et al., 2011), cavity attenuated phase shift spectrometry (CAPS) (Sadanaga et al., 2016), and cavity-enhanced absorption spectrometry (CEAS) (Li et al., 2021).

These instruments have enabled sensitive measurements of gas-phase ON classes, and recent work has also extended TD-based approaches to the particle phase (Keehan et al., 2020). Nevertheless, online measurements of particle-phase ONs remain comparatively limited. In many studies, particle-phase ONs are inferred indirectly from aerosol mass spectrometry or derived from offline filter analysis, both of which have limitations in chemical specificity, time resolution, or operational simplicity (Yu et al., 2019; Chen et al., 2022). Extending TD-based measurements to particle-phase ONs requires careful inlet design, phase separation, and evaluation of potential sampling artifacts.

A central challenge in TD-based ΣPN measurements is that thermal dissociation of peroxy nitrates generates RO₂ radicals, which can react with NO (positive bias) or recombine with NO₂ (negative bias).
~~A central challenge in TD-based ΣPN measurements is that thermal dissociation does not simply convert the analyte to NO₂;~~

95 ~~it also produces radical intermediates that can participate in secondary chemistry within~~
96 ~~the heated inlet. In particular, dissociation of peroxy nitrates yields RO₂ radicals, which~~
97 ~~can react with NO to form additional NO₂, biasing ΣPNs high, or recombine with NO₂~~
98 ~~to re-form peroxy nitrates, biasing ΣPNs low (Day et al., 2002; Li et al., 2021; Lin et~~
99 ~~al., 2024). Regarding bias in NO₂ measurements in the ANs channel, Sobanski et al.~~
100 ~~(2016) conducted a laboratory study on the transmission efficiency of NO₂ in heated~~
101 ~~glass tubes equipped with filters and filled with glass beads, finding that NO₂ losses in~~
102 ~~the 448K and 648K channels were within 2% and 5%, respectively. Furthermore,~~
103 ~~Thieser et al. (2016) also noted that losses due to TD temperature settings and pipe wall~~
104 ~~effects are negligible. Therefore, NO_x biases in the PN/ANs channel are typically~~
105 ~~disregarded in both laboratory experiments and field deployments. The direction and~~
106 ~~magnitude of the bias depend on the chemical regime in the inlet and are therefore~~
107 ~~expected to be especially important under high NO_x conditions, where NO and NO₂~~
108 ~~coexist at elevated concentrations and vary rapidly. This issue is not merely a~~
109 ~~calibration detail: for TD instruments deployed in polluted urban air, inaccurate~~
110 ~~treatment of NO/NO₂-dependent chemistry can directly compromise the quantitative~~
111 ~~retrieval of ΣPNs.~~

112
113 Several strategies have been proposed to reduce or correct these interferences.
114 Hardware-based approaches include decreasing the residence time available for
115 secondary chemistry by modifying inlet pressure or flow conditions (Day et al., 2002),
116 adding downstream packing materials intended to remove radical intermediates
117 (Sobanski et al., 2016; Dewald et al., 2021; Lin et al., 2024), or redesigning the
118 dissociation channel and introducing O₃ downstream so that NO is converted to NO₂

and the instrument effectively measures NO_x rather than NO₂ alone (Friedrich et al., 2020; Gingerysty 2021; Ohara et al., 2024; Wüst et al., 2025). Calibration-based approaches have also been used, in which known NO or NO₂ perturbations are applied to PAN standard gas and the resulting deviations are represented as correction factors or lookup tables for ambient data processing (Li et al., 2021). ~~These approaches have improved TD measurements substantially, but they also have limitations. These approaches have improved TD measurements substantially, but they also involve different trade-offs. NO_x-based architectures can suppress part of the NO-mediated bias, but they require additional post-inlet conversion chemistry and careful control of ozone-derived interferences. Calibration-based approaches retain simpler hardware, but their validity depends on how well the laboratory source represents the inlet chemistry encountered in ambient air. The net bias depends on the chemical regime in the inlet and becomes particularly important under high-NO₂ conditions, where NO and NO₂ coexist in ambient air. In addition, PAN standards are commonly generated photochemically from acetone-containing systems, which may introduce excess peroxyacetyl radicals and other secondary products that complicate the interpretation of separate NO and NO₂ addition experiments (Wüst et al., 2025). Inaccurate treatment of this interference can compromise quantitative ΣPN retrieval in polluted urban air.~~ In ambient air, NO and NO₂ generally vary simultaneously rather than independently, and the relative importance of the competing pathways is governed by the chemical regime rather than by either species alone. In addition, PAN standards are commonly generated photochemically from acetone-containing systems, which may introduce excess peroxyacetyl radicals and other secondary products that complicate the interpretation of separate NO and NO₂ addition experiments. Under high-NO_x conditions, where both interferences may occur simultaneously, treating NO and NO₂ effects independently

~~may therefore be insufficient.~~ For that reason, the secondary inlet chemistry is modelled explicitly for some instruments in order to correct the data (Keehan et al., 2020; Sobanski et al., 2016; Taha et al., 2018; Thieser et al., 2016). In that case input of measured ambient NO, NO₂ and uncorrected ANs/PNs is required in order to account for the simultaneous bias by NO and NO₂ as well as the chemical regime and surface chemistry. In the present work, we retain a compact single-detector NO₂-based architecture and evaluate whether a laboratory-constrained correction can make such a design operationally useful in high-NO_x urban air.

These considerations are particularly important for multi-channel instruments designed to retrieve both gas- and particle-phase Σ PNs and Σ ANs. In such systems, a bias in the Σ PN channel propagates directly into the derived gas-phase signal and can also affect the particle-phase product through channel differencing. A robust treatment of NO/NO₂-dependent interference is therefore essential not only for accurate Σ PN quantification, but also for reliable gas-particle partitioning in polluted environments. There remains controversy regarding the interference of NO and NO₂ on the quantification of ANs, which is related to the standard sample systems employed in different studies. When experiments were conducted using pure standards as diffusion sources, no dependence of ANs on NO and NO₂ was observed (Paul et al., 2009). In contrast, when NO and NO₂ were added to ANs generated from the oxidation of VOCs by NO₃ or OH, significant measurement biases were observed, accompanied by a broad thermal decomposition range (Sobanski et al., 2016; Wüst et al., 2025). This discrepancy may be attributed to the formation of byproducts, such as peroxy nitrates, during the reaction process. Therefore, careful selection of the standard sample system and consideration of potential interference from byproducts are necessary when conducting experiments.

At the same time, there remains a practical need for compact instruments that can measure ON classes in both phases using a single NO₂ detector and a field-deployable inlet architecture.

In this work, we develop a five-channel thermal dissociation TD-CEAS that extends TD-CEAS for in situ measurements of gaseous and particulate ONs. The instrument combines a single CEAS NO₂ detector with two TD setpoints (250 °C for ΣPNs and 450 °C for ΣANs) and paired filter configurations to retrieve gas- and particle-phase ΣPNs and ΣANs by channel differencing. Particular emphasis is placed on the characterization and correction of NO/NO₂-dependent interference in the ΣPN channels under high-NO_x conditions. To this end, we perform dedicated laboratory experiments, develop a multiple nonlinear regression correction model for the combined effects of NO and NO₂, and compare its performance with a previously reported lookup-table approach. We further characterize the instrument response, evaluate its precision and detection limits, and demonstrate its performance during an urban field deployment in Guangzhou. This study aims to provide both a practical measurement framework for continuous ON observations in gas and particle phases and a correction strategy for improving TD-based ΣPN measurements in chemically complex, high-NO_x environments, enabling derivation of gas- and particle-phase ON classes by channel differencing. ~~We provide systematic laboratory characterization, including dissociation behavior, calibration strategies for gaseous and particulate standards, and quantification of interferences relevant to high-NO_x environments, and we demonstrate the instrument performance during an urban field deployment.~~

2 Instrumentation and methods

2.1 Thermal dissociation (TD) inlets

TD is implemented using heated quartz-tube reactors. Each TD inlet consists of a quartz tube (60 cm length; 1/4" outer diameter; 3.9 mm inner diameter) wrapped with 20 cm Ni–Cr heating wire and insulated with thermal cotton to minimize heat loss. A K-type thermocouple positioned at the center of the heated region monitors the tube outer-wall temperature and is regulated by a temperature controller (stability ± 2 °C). The thermocouple accuracy is ± 1 °C over -20–1000 °C.

Sample air is delivered through 1/4" PTFE tubing with PTFE straight/tee fittings (Swagelok). During operation, the sampling flow is 1 L min⁻¹, corresponding to a residence time of 0.048 s in the heated region. This short residence time is designed to promote rapid dissociation of thermally labile ONs while minimizing post-dissociation chemistry within the heated section. Because the thermocouple measures the tube wall temperature rather than the gas temperature, the reported TD setpoints are expected to be higher than the corresponding gas temperature. Therefore, TD setpoints reported here should be interpreted as operational setpoints for this specific reactor design and are not necessarily directly comparable with other TD geometries.

2.2 CEAS NO₂ spectrometer

Thermally generated NO₂ is detected by CEAS near 405 nm. In CEAS, an optical cavity provides a long effective absorption pathlength through multiple reflections between high-reflectivity mirrors, enabling sensitive absorption-based NO₂ measurements while retaining the selectivity of optical spectroscopy. NO₂ has strong, structured absorption in the 405 nm region, allowing retrieval via spectral fitting. A single CEAS NO₂ spectrometer is used for all five inlet channels. The CEAS instrument used here has been characterized previously (Zhou et al., 2022). In the present configuration, the CEAS reports NO₂ mixing ratios for each channel segment, and all TD-derived quantities are obtained by differencing of channel measurements (Sect. 2.5).

2.3 Standards and laboratory generation

2.3.1 PAN (representative Σ PNs)

PAN is used as a representative PN for laboratory characterization of the Σ PN channel. PAN is produced photochemically by UV photolysis (285 nm) of excess acetone in O₂ to generate peroxyacetyl (PA) radicals, followed by reaction with NO (He et al., 2023). PAN mixing ratios are adjusted by varying the NO flow. PAN is quantified independently using a GC-ECD and is used for cross-validation of the TD-CEAS response.

2.3.2 Alkyl nitrates (representative Σ ANs) and aerosol tests

Isobutyl nitrate and isopropyl nitrate (95% purity, Macklin, China) are used as representative gas-phase AN for characterization of the Σ AN response. These standards are generated by dilution of their vapor into zero air following established approaches (Paul et al., 2009). They were selected because pure standards are commercially available and have been widely used in TD studies, but they are not intended to span the full thermal behavior of ambient multifunctional ANs.

For particle-phase tests, 2-ethylhexyl nitrate (2-EHN, Aladdin, China) solution is aerosolized to produce organic nitrate-containing particles, which are introduced into the TD-CEAS to evaluate particle-phase response and quantification. Because particulate inorganic nitrate may also generate NO₂ upon heating, sodium nitrate aerosol is generated in a similar manner to characterize its temperature-dependent contribution and assess potential interference in the particle-phase channels.

Isobutyl nitrate and isopropyl nitrate are detectable atmospheric ANs (Zeng et al., 2018) and therefore provide useful benchmark compounds for instrument testing. Although 2-EHN is not expected to be a dominant ambient ON species, it is a stable and accessible high-molecular-weight organic nitrate (MW = 175.23 g mol⁻¹) and has been used in

previous TD studies as a practical particulate organic nitrate surrogate (Paul et al., 2009; Lin et al., 2024). We therefore use these compounds as operational standards for the present inlet design rather than as chemically comprehensive proxies for all ambient ANs.

2.4 Five-channel configuration, sampling sequence, and channel definitions

The five-channel TD-CEAS combines two TD temperatures (250 °C and 450 °C) with two filter placements (upstream versus downstream) to enable separation of gas and particle phases (Figure S1). Ambient air is sampled through a PM_{2.5} cyclone prior to entering the inlet manifold. A multi-channel inlet selection unit sequentially routes each channel to the shared CEAS detector. When the multi-channel inlet unit is in operation, only the sample flow from the currently selected channel is allowed to enter the analyzer. Since there is a transition period during which the NO₂ signal stabilizes after switching channels, the data from the first 15 seconds following the channel switch should be discarded, as shown in Figure S2.

The instrument samples five channels plus an ultra-high-purity N₂ reference segment. The ultra-high-purity N₂ is supplied from cylinders and fed directly into the CEAS zero-air inlet, the N₂ flow rate matches the sampling. Each channel is sampled for 1 min, followed by a 1 min N₂ segment, yielding a 6-min measurement cycle. The N₂ segment is used as a reference for instrument baseline and stability (Sect. 2.6).

We denote “F” as a particle filter placed upstream of the TD (gas-only enters TD), and “UF” as an inlet without an upstream filter (gas + particle enter TD), with a particle filter placed downstream of the TD reactor to prevent particles from entering the CEAS cavity. The filters are made of PTFE and has a diameter of 47 mm, with retention efficiency of 99.5% or higher for 0.3 μm particles. The filter is replaced once a week

during field campaigns, or earlier if the analyzer's flow rate decreases and in the event of air pollution. Table S1 summarizes the channel definitions and the corresponding quantities measured as NO₂ mixing ratios by CEAS.

According to a study by Rollins et al. (2010), particulate transmission experiments using non-volatile NaCl particles revealed significant loss of small-particle-size (≤ 100 nm) particles, while the transmission efficiency for particles larger than 100 nm exceeded 85% (represent a lower limit to the transmission and detection efficiency for semi volatile particles). As for volatile particles, they rapidly evaporate and thermally decompose into NO₂ within the TD. In addition, Garner et al. (2020) performed a cross-validation of NaNO₃ aerosols using TD-CRDS and SMPS; the correlation coefficient between NaNO₃ and the NO₂ produced by its quantitative conversion was 0.98 ± 0.03 , which further demonstrates the high transmission efficiency of the particles. Although there may be transmission losses for small particles, these losses are generally acceptable. One line of evidence suggesting that wall losses of organic nitrates (ONs) are negligible is that the uncertainty in the recovery of 2-EHN is below 4 % (Fig. 4). This indicates that ANs rapidly decompose into NO₂ during transport through the TD inlet, and that no significant back-reaction loss of RO radicals with NO₂ occurs. Of course, for high-molecular-weight ONs, wall loss effects are largely dependent on compound volatility, tubing material, and temperature. In this study, we used PTFE tubing and ambient-temperature sampling to minimize such effects.

2.5 Retrieval of g/p Σ PNs and g/p Σ ANs

For each 1 min segment, the CEAS reports an NO₂ mixing ratio for the selected channel. Let C_{RTF} , $C_{250\text{F}}$, $C_{450\text{F}}$, $C_{250\text{UF}}$, and $C_{450\text{UF}}$ denote the NO₂ mixing ratios (pptv or ppbv) measured by CEAS in the corresponding channels. Gas- and particle-phase ON classes are retrieved by channel differencing:

$$g\Sigma PNs = C_{250F} - C_{RTF} \quad (1)$$

$$p\Sigma PNs = C_{250UF} - C_{250F} \quad (2)$$

$$g\Sigma ANs = C_{450F} - C_{250F} \quad (3)$$

$$p\Sigma ANs = (C_{450UF} - C_{250UF}) - (C_{450F} - C_{250F}) \quad (4)$$

These expressions correspond to the field configuration in which the RT/250/450 channels are operated with upstream particle filtration for gas-phase retrieval, while paired 250/450 channels without upstream filtration (but with downstream particle removal) provide total (gas + particle) ON classes. Sobanski et al. (2016) noted that heated quartz tubes packed with frit and glass beads exhibit a small but significant loss of NO₂, which may be attributed to the packing material increasing the collision area for NO₂, resulting in a small loss of NO₂. No NO₂ transmission losses were observed in heated quartz tubes without packing material (Thieser et al., 2016; Lin et al., 2024).

Because channels are sampled sequentially, each derived quantity is timestamped at the midpoint of the corresponding 1-min segment. When longer averaging periods are applied (e.g., hourly means), within-cycle timing offsets are typically small compared with the averaging window.

2.6 Uncertainty propagation, detection limits, and reporting conventions

Detection limits are reported as 1 σ precision inferred from Allan deviation analyses with ultra-high purity N₂ continuously introduced to each channel. For the RT, 250 °C, and 450 °C channels, the 1 σ NO₂ detection limits at 1 s integration are 34, 35, and 33 pptv, respectively; at 10 s integration they are 12, 13, and 12 pptv.

Derived ON quantities are calculated as differences between channels. Assuming independent noise among channel measurements, the uncertainty for a difference $A-B$ is propagated as:

$$\sigma_{A-B} = \sqrt{\sigma_A^2 + \sigma_B^2} \quad (5)$$

Using the 1 s NO₂ precision for relevant channels, the resulting 1σ (1 s) detection limits for derived gas-phase ΣPNs and ΣANs are:

$$\sigma(g\Sigma PNs) = \sqrt{\sigma_{250F}^2 + \sigma_{RTF}^2} \approx \sqrt{35^2 + 34^2} = 49 \text{ pptv} \quad (6)$$

$$\sigma(g\Sigma ANs) = \sqrt{\sigma_{450F}^2 + \sigma_{250F}^2} \approx \sqrt{33^2 + 35^2} = 48 \text{ pptv} \quad (7)$$

And for particle-phase ONs are:

$$\sigma(p\Sigma PNs) = \sqrt{\sigma_{250UF}^2 + \sigma_{250F}^2} \approx 49 \text{ pptv} \quad (8)$$

$$\sigma(p\Sigma ANs) = \sqrt{\sigma_{450UF}^2 + \sigma_{250UF}^2 + \sigma_{450F}^2 + \sigma_{250F}^2} \approx 68 \text{ pptv} \quad (9)$$

These values correspond to the reported field-operation performance. Table 2-1 compares the detection limits of the present TD-CEAS with those reported for representative TD-based techniques. Overall, the detection limits achieved here are within the range of recent TD instruments, while the present configuration additionally enables sequential retrieval of gas- and particle-phase PNs and ANs using a single NO₂ spectrometer. Because published detection limits are reported at different integration times and for different instrument configurations, the comparison is intended as a general benchmark rather than a strict ranking of sensitivity.

The uncertainty of the reported ON classes includes detector calibration, channel differencing, and inlet-related artifacts. For the underlying NO₂ measurements, the CEAS calibration uncertainty is approximately 6% (Zhou et al., 2022), and the repeatability for continuous 10 ppbv NO₂ passed through the TD-CEAS configuration

is 1.4%. These values describe instrumental accuracy and stability for simple NO₂ inputs. They do not include composition-dependent TD chemistry, aerosol transmission losses, or the representativeness of surrogate standards, which may dominate the uncertainty of ambient ΣPN and ΣAN retrievals. Accordingly, quantitative results reported below are best interpreted as operational ON measurements for the present inlet geometry and correction framework.

2.7 Box model

A zero-dimensional box model was implemented to reproduce the correction-factor lookup table reported by (Li et al., (2021) and to compare that approach with the regression-based correction proposed in this study. The chemical mechanism followed previous work and was based on the Master Chemical Mechanism (MCM) v3.3. The wall loss rate constants for RO₂, HO₂, and OH radicals were set to 0.3, 0.5 and 5.4 s⁻¹, respectively, following Fuchs et al. (2008), Wooldridge et al. (2010), Thieser et al. (2016), and Li et al. (2021). These values are used as ballpark and do not necessarily reflect the wall losses of the inlets since they vary with inlet geometry and operating conditions such as flow and temperature. The model was used only for method comparison and not for interpretation of ambient observations.

3 Laboratory characterization

3.1 TD temperature selection and dissociation behavior

To define operational TD temperature for ΣPNs and ΣANs, we measured temperature-dependent NO₂ yields (“thermal decomposition profile~~thermal—spectra~~”) for representative organic nitrates. PAN was used as a surrogate acyl peroxy nitrate, isopropyl nitrate and isobutyl nitrate were used as surrogate alkyl nitrates, and 2-ethylhexyl nitrate (2-EHN) aerosol was used as a surrogate particulate organic nitrate.

Sodium nitrate aerosol was used to evaluate potential interference from particulate inorganic nitrate.

For each compound, the TD setpoint was stepped across the temperature range and the NO₂ enhancement in the heated channel (relative to room temperature) was used to infer dissociation completeness. As shown in Figure 24, PAN reaches a stable plateau in NO₂ yield at temperatures above ~250 °C, indicating near-complete conversion at and above this temperature. In contrast, isopropyl nitrate and isobutyl nitrate show minimal dissociation below 250 °C (<10% of the high-temperature plateau), increase sharply near ~300 °C, and reach stable plateau by ~350 °C. The particulate 2-EHN shows a similar trend, stabilizing near ~400 °C. Particulate inorganic nitrate behaves differently: the NO₂ yield remains <10% below 400 °C and does not reach a stable plateau until ~750 °C, implying that particulate inorganic nitrate contributes minimally to the NO₂ signal at 450 °C for this TD geometry and residence time.

Based on these measured ~~thermal spectra~~ thermal decomposition profile, we selected 250 °C as the operational setpoint for ΣPNs and 450 °C as the operational setpoint for ΣANs. These setpoints are specific to the present TD reactor design (Sect. 2.1) and correspond to wall temperatures measured at the tube exterior. Because they were derived from surrogate standards, they should not be interpreted as compound-independent thresholds for all ambient ONs; in particular, partial dissociation of some multifunctional ANs in the lower temperature channel cannot be excluded.

3.2 Calibration and quantitative performance

3.2.1 PAN calibration and GC-ECD cross-validation

PAN was generated using the photochemical source described in Sect. 2.3.1 and quantified independently by GC-ECD (Zhang et al., 2012). Over 0–20 ppb supplied NO, the relationship between NO input and generated PAN indicates stable PAN

production with an average conversion efficiency of $\sim 84\%$ ($R^2 = 0.99$). PAN derived from the TD–CEAS channel agrees closely with GC-ECD ($R^2 = 0.988$; slope = 0.987; Fig. 3) from clean background (e.g., PAN < 1 ppbv) to heavily polluted conditions (e.g., PAN > 10 ppbv) across trace to heavily polluted levels ($R^2 = 0.988$; slope = 0.987; Fig. 2). This agreement supports quantitative retrieval of Σ PNs for representative acyl peroxy nitrates under the tested conditions. The slope in Fig. 3 reflects the difference in detection limits between TD-CEAS and GC-ECD. Owing to its higher measurement accuracy and sensitivity, CEAS is able to resolve the differences between channels at low concentrations.

3.2.2 Particle-phase Σ AN calibration via filter thermolysis of 2-EHN

Because stable gas-phase AN standards at known mixing ratios were not available in our setup, we established an operational particulate Σ ANs calibration using filter thermolysis of 2-EHN (Yu et al., 2021). Stable gas-phase Σ AN standards at specified mixing ratios are difficult to generate reproducibly by vapor dilution. Therefore, we established an operational particulate Σ AN calibration using filter thermolysis of 2-EHN (Yu et al., 2021). A known volume of 2-EHN solution was injected onto a pre-baked quartz filter (0.5 cm²; baked at 450 °C for 4 h) placed inside a quartz TD tube held at 450 °C. A second 450 °C TD stage was installed downstream to promote complete conversion prior to NO₂ detection. The resulting NO₂ signal was measured by CEAS in dry, clean air.

This calibration was conducted through the complete heated inlet configuration rather than by direct injection into the optical cell, so it reflects the integrated response of the present inlet-plus-detector system. It should therefore be viewed as an operational

calibration for this configuration, not as an absolute molecular sensitivity applicable to all particulate ANs compositions.

The recovered NO₂ mass from each injection was calculated by integrating the NO₂ time series:

$$m_{NO_2}(\mu g) = \frac{M_{NO_2} Q}{V_m * 10^6} \sum_i ([NO_2]_i \Delta t) \quad (10)$$

where [NO₂]_i is the NO₂ mixing ratio in ppb at time step *i*, M_{NO₂} is the molar mass of NO₂ (g mol⁻¹), Q is the CEAS sampling flow (16.67 mL s⁻¹), Δt = 1 s, and V_m = 24.5 L mol⁻¹ at 25 °C and 101 kPa. The 10⁶ factor converts ppbv and flow units to mass in μg.

Seven blank-filter runs were used to determine method detection limit of 0.029 μg NO₂.

2-EHN calibration using five injection volumes (1, 2, 5, 8, 10 μL) shows excellent linearity (R² = 0.99; Fig. 43). The recovery regression slope is 1.036 ± 0.028 with a small intercept (−0.020 ± 0.046), indicating quantitative recovery for this surrogate

particulate ΣAN standard under the calibration conditions. It is important to note that we conducted the experiments using the complete sampling system and subtracted the blank from the results.

3.3 Interferences and correction strategies

3.3.1 NO and NO₂ interferences on ΣPNs

Thermal dissociation of ΣPNs produces RO₂ radicals that can participate in rapid secondary chemistry within the heated inlet. In the presence of NO₂, these radicals can recombine to re-form peroxy nitrates and bias ΣPNs low. In the presence of NO, they can convert NO to NO₂ and bias ΣPNs high (Day et al., 2002; Sobanski et al., 2016; Li

et al., 2021; Lin et al., 2024). These competing pathways are expected to be especially important under high-NO_x conditions, where NO and NO₂ coexist at elevated concentrations and the competing reactions take place in parallel.~~These competing pathways are expected to be especially important under high-NO_x conditions, where NO and NO₂ coexist at elevated concentrations and vary simultaneously.~~

To characterize these effects for the present TD geometry, we conducted laboratory interference experiments using PAN as a representative acyl peroxy species. As described in Text S1, PAN was generated photochemically in an acetone/air system while the NO input was progressively increased. PAN was measured by GC-ECD, NO and NO₂ was measured by a Thermo Scientific 42i-TL analyzer, and ΣPNs and ΣANs were measured by TD-CEAS. This configuration enabled direct comparison between the reference PAN concentration and the uncorrected TD-CEAS ΣPNs signal over a range of NO/NO₂ regimes.

During the gradient experiments, the acetone concentration was held constant and only the NO input was varied. At acetone-rich, low-NO conditions, most added NO was converted to NO₂, which promoted PAN formation. Under these conditions, the measured ΣPN signal was biased low because of excess peroxyacetyl (PA) radicals, together with PA radicals produced by PAN dissociation in the TD inlet, could recombine with NO₂ downstream of the heated section. As the NO mixing ratio increased, PAN formation was increasingly suppressed, while PA radicals generated by PAN dissociation reacted increasingly with NO to form additional NO₂, causing the measured ΣPNs signal to become biased high. These experiments therefore show that both the sign and the magnitude of the bias are governed by the chemical regime in the inlet rather than by NO or NO₂ alone.

To account for the combined effects of NO and NO₂, we developed a multiple nonlinear regression model based on the experimental dataset. Because temperature was held constant in these experiments and PAN formation and dissociation are closely related to the NO/NO₂ ratio (Zhang et al., 2015), the NO/NO₂ ratio was used as the explanatory variable to represent the relevant chemical regime:

$$[\Sigma PNs]_{real} = a \times [\Sigma PNs]_{meas} \times e^{\left(b \times \frac{[NO]}{[NO_2]}\right)} + c \quad (11)$$

where $[\Sigma PNs]_{real}$ is the PAN reference concentration measured by GC-ECD, $[\Sigma PNs]_{meas}$ is the uncorrected TD-CEAS concentration, and [NO] and [NO₂] are expressed in ppbv. The *a*, *b*, and *c* are the fitting coefficients, with values of 1.57, -3.44, and 0.58 respectively.

For comparison, we also reproduced the correction-factor lookup-table correction approach of Li et al. (2021) using the box model configuration described in Sect. 2.7.

Figure 54 compares corrected ΣPNs values obtained with the two approaches against the reference PAN measurements with GC-ECD. The multiple nonlinear regression model reproduced the reference PAN values well ($R^2 = 0.993$; RMSE = 0.49 ppbv) across both low and high PAN ranges. By comparison, the reproduced lookup-table approach did not perform well across the entire concentration range, despite an overall correlation of 0.975 (R^2), the method increasingly overestimated PAN, especially under high-NO_x conditions. ~~By comparison, the reproduced lookup-table approach performed well at low concentrations ($R^2 = 0.975$) but increasingly overestimated PAN at high concentrations, particularly under high-NO_x conditions.~~ The corresponding evaluation metrics for both methods are summarized in Table S24. Relative to the lookup-table method, the regression model provides a more compact correction framework and better

captures the coupled effects of NO and NO₂ across the experimental range. In addition, we compared the performance of the two calibration methods on field observation data, as shown in Figure S7. As can be seen, regardless of whether the PAN concentration is low or high, the lookup table calibration results significantly overestimate. In this experiment, the lookup table correction for PAN resulted in substantial overestimation. This is because the lookup table was constructed by simply combining experimental data from Box model simulations that had been validated separately for experiments with NO or NO₂ addition. Consequently, this approach does not account for the combined bias arising from the simultaneous presence of NO and NO₂. The experimental results of Li et al. (2021) further indicate that the positive measurement bias induced by NO addition is considerably larger than the negative bias induced by NO₂ addition. Therefore, the lookup table method introduces significant uncertainty under high NO_x conditions.

To further assess robustness, replicate experiments were performed under otherwise identical conditions but with a series of NO concentrations~~different NO gradients~~. As shown in Fig. S54, the corrected ΣPNs agreed well with the measured PAN, with correlation coefficient of 0.98 and slopes of 1.06, indicating that the regression-based correction was reproducible across independent ~~gradient~~ experiments.

In terms of proportion, PAN accounts for more than 70% of ΣPNs (Wooldridge et al., 2010), however, ΣPNs also include PPN, MPAN, and non-acyl peroxy nitrates. Given their similar pyrolysis characteristics, these species can be measured separately. Moreover, their pyrolysis products (RO₂) exhibit comparable chemical properties, so they are typically treated as a single class of compounds for experimental analysis and discussion. In this experiment, the NO/NO₂ ratio ranged from 0.044 to 2.015; in validation tests, it ranged from 0.040 to 0.246; and in the real atmosphere, it ranged

from 0.021 to 0.607 (see Section 4). Thus, the measured ratios essentially cover the NO/NO₂ ratios encountered under various conditions.

Previous studies have reported the presence of alkyl nitrates and other by-products in photochemical PAN sources (Paul et al., 2009; Wüst et al., 2025), consistent with the Σ ANs signal observed in the 450 °C channel during these experiments (Fig. S43). The key point for the present instrument is that the source-related perturbation varied only weakly with the NO and NO₂ and was present in both heated channels. We therefore treated the residual 450-250 signal as the best available operational Σ ANs estimate for this configuration, while explicitly acknowledging that composition-dependent AN biases may remain. However, the Σ ANs signal varied only weakly with the NO and NO₂ perturbations. ~~Because NO/NO₂-induced deviations are present in both the 250°C and 450°C channels, and largely cancel in the 450-250 channel subtraction, no additional correction was applied to Σ ANs in this study.~~ During field observations, the correction model was applied to the 250 °C channel measurements using simultaneously measured NO and NO₂, and the corrected 250 °C data were then used to derive Σ PNs. ~~Unlike approaches that require downstream ozone addition (Wüst et al., 2025), this method relies only on measured NO and NO₂ and can therefore be implemented directly during field deployment.~~

The ozone-supplemented method has been successfully applied in several studies (e.g., Friedrich et al., 2020; Wüst et al., 2025; Shao et al., 2026; Wild et al., 2014), yielding satisfactory results. We do not regard these NO_x-based designs as inferior; rather, they represent a different instrument trade-off. In the present study, we retained a single-cavity NO₂-based architecture because it keeps the five-channel system compact and

avoids adding post-inlet conversion chemistry to every channel. This choice requires an explicit correction for coupled NO/NO₂ effects. At the same time, ozone addition introduces additional measurement uncertainties, particularly under high NO_x conditions, along with potential interference from the formation of NO₃ and N₂O₅. Furthermore, ozone exhibits weak absorption at 405 nm (Wild et al., 2014), which necessitates additional correction measures. The regression approach proposed here is therefore intended as a practical correction strategy for a compact NO₂-based instrument, whereas NO_x-based architectures remain attractive when the highest possible suppression of compound-specific inlet chemistry is the overriding priority.

3.3.2 NO and NO₂ interferences on ΣANs

Previous studies reported only weak PAN interference in the ΣANs channel when radical-scavenging packing materials (glass beads and glass fiber filters) are used (Sobanski et al., 2016). In our unpacked quartz configuration, Figure S4 should be interpreted primarily as a diagnostic of common-mode source artifacts and relative channel behavior rather than as a clean quantification of PAN chemistry in the 450 °C channel. The NO₂ signal observed in the ΣANs channel follows the same general NO-dependent trend as in the ΣPNs channel, while the offset between the channels is likely influenced by secondary products from the photochemical PAN source (Li et al., 2021). This behaviour indicates that much of the PAN source interference is shared by both heated channels and is therefore reduced by 450–250 channel differencing, but it does not exclude compound-specific biases for atmospherically relevant multifunctional ANs.

To further verify the effect of NO_x on ΣANs measurements, this study conducted experiments involving the addition of NO and NO₂ using a 2-EHN diffusion source. The results are shown in Figure 6 and show no systematic monotonic dependence on

the added NO or NO₂. Across the tested range, the normalized 2-EHN response varied by less than 20%, and the remaining scatter is consistent with the stability of the diffusion source and flow control. We therefore did not introduce an additional empirical AN correction term for the present field dataset. Instead, Σ ANs is reported as an operational quantity derived from 450–250 channel differencing. This conclusion is supported for 2-EHN under our test conditions, but it should not be generalized to all ambient multifunctional ANs without further validation.

3.3.32 O₃ interference

O₃ thermally dissociates at elevated temperatures (>330 °C), producing O atoms that can perturb the NO/NO₂ partitioning in the heated region. Prior laboratory studies indicate that even high O₃ (200–240 ppb) mixed with 25.1 ppb NO₂ results in only ~3.5% NO₂ loss at 600 °C, and no significant NO₂ bias is observed across typical O₃ levels in comparable TD systems (Day et al., 2002). Kinetic estimates under representative polluted conditions (e.g., O₃ 100 ppb, NO 2 ppb, NO₂ 5 ppb) suggest that O₃-related NO₂ perturbations in heated channels are within ~3%, smaller than the overall measurement uncertainty. The experiment further demonstrated that variations in the amounts of introduced NO₂ and O₃ did not produce significant differences in NO₂ concentrations across the different measurement channels. (Li et al., 2021). On this basis, O₃ interference is neglected for the present analysis.

3.3.43 Other interferences (nitro-aromatics, ClNO₂, N₂O₅, HONO, HNO₃, NH₄NO₃)

Nitro-aromatics and nitrophenols can potentially generate NO₂ upon heating. To evaluate this potential interference in the Σ AN channel, we tested 3-nitrophenol and 1-nitropyrene (1 mg mL⁻¹; 1 μ L injection) at 450 °C. The integrated NO₂ masses were

below the detection limit, suggesting negligible interference for Σ ANs under these test conditions.

Reactive nitrogen species such as ClNO_2 and N_2O_5 can thermally dissociate near the chosen TD temperatures ($\sim 450^\circ\text{C}$ and $\sim 210^\circ\text{C}$, respectively), which could bias gas-phase Σ ANs and Σ PNs at night (Thaler et al., 2011; Sobanski et al., 2016). Because these species are largely nocturnal and photolyze rapidly after sunrise, daytime gas-

phase ON retrievals are expected to be less affected (Li et al., 2021). Ambient concentrations of N_2O_5 and ClNO_2 exhibit substantial variability depending on atmospheric conditions. According to the literature, N_2O_5 concentrations in urban environments typically range from 0.1 to 1 ppbv, with occasional peaks reaching several ppbv (Wang et al., 2017). ClNO_2 concentrations are generally lower, typically ranging from tens of pptv to several ppbv, i.e., 0.1–0.5 ppbv (Mielke et al., 2011; Riedel et al., 2014). Consequently, considerable uncertainty exists in the nighttime measurement of gaseous Σ ANs and Σ PNs, and such interferences are difficult to quantify due to the variability of ambient conditions. Li et al. (2021) refrained from analyzing nighttime measurements because of these interferences. In contrast, in this study, the nighttime observational datasets were retained only to support the particulate-phase retrievals in Section 4. Because particle-phase ONs are obtained by paired-channel differencing, common gas-phase contributions are reduced substantially; however, complete cancellation cannot be guaranteed if interfering species behave differently in the gas-only and particle-inclusive paths. Nighttime $\text{p}\Sigma$ PNs and $\text{p}\Sigma$ ANs should therefore be regarded as more robust than nighttime gas-phase data, but still operational rather than fully interference-free. In addition, particle-phase ONs are retrieved by differencing configurations that largely cancel common gas-phase contributions; therefore, $\text{p}\Sigma$ PNs

and Σ ANs are less sensitive to nocturnal gas-phase species under the present retrieval framework.

HONO undergoes thermal or photolytic decomposition to yield NO. Pérez et al. (2007) and Friedrich et al. (2020) reported initial decomposition temperatures of HONO at 450 °C and 400 °C, respectively, with complete thermal decomposition occurring only in the range of 650–700 °C. Consequently, in the Σ PNs channel (250 °C) of this study, HONO is not thermally decomposed, while in the Σ ANs channel (450 °C), the decomposition efficiency does not exceed 10 %. Ambient HONO concentrations at urban sites are typically below 3 ppbv (Wang et al., 2025), resulting in NO production from thermal decomposition of less than 300 pptv. Moreover, HONO is rapidly photolyzed after sunrise, thus exerting minimal influence on daytime TD measurements. Overall, the thermal decomposition of HONO in the ANs channel produces only trace amounts of NO, which may nonetheless interfere with TD channels and systems that target NO₂ as the analyte.

It should be noted that the thermal tests described above were conducted using NaNO₃ as a proxy for particulate inorganic nitrate. While NaNO₃ is thermally refractory, NH₄NO₃ is likely to dominate much of the urban inorganic nitrate burden in China and is substantially more semivolatile. Literature data indicate that NH₄NO₃ begins to decompose at temperatures as low as ~400 °C, and that its conversion to NO₂ at 450 °C is less than 50% (Garner, et al., 2020). Because this temperature range overlaps with the Σ ANs setpoint used here, ambient NH₄NO₃ could contribute a positive artifact to measured Σ ANs. Using a typical Pearl River Delta NH₄NO₃ mass concentrations of <10 $\mu\text{g m}^{-3}$ (Liu et al., 2026) and a conservative 50% conversion efficiency, we obtain an order-of-magnitude upper bound of ~1.4 ppbv NO₂ equivalent. The exact magnitude for our inlet remains unquantified because NH₄NO₃ was not tested directly in the

laboratory. This is an important limitation of the current study, especially for cool or heavily polluted conditions.

3.4 Precision and detection limits (Allan deviation)

Instrument precision was assessed using Allan deviation analysis with ultra-high-purity N_2 introduced to the inlet. The 1σ (1 s) NO_2 detection limits are 34 pptv (RT), 35 pptv (250 °C), and 33 pptv (450 °C), improving to 12–13 pptv at 10 s integration (Fig. 75).

Propagating these channel precisions through the channel-differencing retrieval (Sect. 2.6) yields 1σ (1 s) detection limits of 49 pptv for $\text{g}\Sigma\text{PNs}$, 49 pptv for $\text{p}\Sigma\text{PNs}$, 48 pptv for $\text{g}\Sigma\text{ANs}$, and 68 pptv for $\text{p}\Sigma\text{ANs}$, consistent with values used for field reporting.

Table 2-1 compares detection limits reported for representative TD-based techniques.

The present TD-CEAS achieves detection limits comparable to the lower end of reported TD methods, while providing simultaneous gas/particle partitioning using a

single, compact NO_2 spectrometer framework. In terms of temporal resolution, single-cavity configurations are limited by channel switching, resulting in a lower time resolution. Multi-cavity designs therefore represent a promising direction for future instrumental development. Various strategies have been explored to mitigate measurement interferences, including the use of glass bead packing (which reduces but does not fully eliminate interference), correction factor lookup tables, and post-inlet ozone addition. In this study, we propose a correction model based on the NO/NO_2 ratio that accounts for the coupled effects of both interferents. Existing TD setups for particulate-phase measurements mainly employ either denuders or filter. Denuders require careful monitoring of absorption efficiency and saturation, whereas filter membranes only need to be replaced periodically, making them more convenient to use.

4 Field deployment and example observations

4.1 Site description and ancillary measurements

The five-channel TD-CEAS was deployed on the rooftop (~15 m a.g.l.) of an office building at the Guangzhou Institute of Geochemistry (GIG), Guangzhou, China (113°21'49" E, 23°8'46" N), as shown in Figure S6. The site is located in a densely populated urban area influenced by nearby traffic corridors (~350 m). Two short intensive observation campaigns were conducted during 4-7 September 2025 and 1-2 October 2025 under clear, rain-free conditions.

When measuring ambient air, the air passes through a PM_{2.5} cyclone separator into a 1/2-inch stainless steel main sampling tube with a high-flow pump used to draw air at the end (Fig. S6). The TD-CEAS system collects samples via a bypass line (PTFE, ~2 m) connected to the main sampling tube. Ancillary reactive nitrogen measurements were used to support evaluation of TD-CEAS performance and to enable post-processing correction of TD artifacts. NO was measured with a chemiluminescence NO_x analyzer (Thermo Scientific 42i-TL). During the October deployment, PAN was measured concurrently by a GC-ECD system for intercomparison with the TD-CEAS gas-phase PN signal. Unless otherwise stated, times are reported in local time (UTC+8).

4.2 Measurement cycle, field configuration, and data processing

Ambient air was sampled through a PM_{2.5} cyclone upstream of the inlet manifold. The instrument was operated in the five-channel configuration described in Sect. 2, with paired inlet/filter arrangements used to separate gas-only and total (gas + particle) signals. The gas-phase channels (RT-F, 250-F, 450-F) used an upstream particle filter (PTFE, retention efficiency of 99.5% or higher for 0.3 μm particles) to remove particles prior to the TD reactors and CEAS, thereby providing NO₂, gΣPNs, and gΣANs by channel differencing. The particle-inclusive channels (250-UF, 450-UF) sampled air without upstream filtration so that both gas and particles entered the TD reactors, while a downstream filter removed particles immediately before the CEAS cavity. These

channels therefore provided total (gas + particle) Σ PNs and Σ ANs, and particle-phase quantities (p Σ PNs and p Σ ANs) were obtained by differencing the total and gas-only channels.

Each channel was sampled for 1 min, after all five channels have been measured, a 1 min ultra-high-purity N₂ segment was introduced, yielding a 6-min measurement cycle. One-minute mean NO₂ values were calculated for each channel segment, and the derived ON products were reported at the 6 min cadence of the cycle. For clarity in time-series presentation, hourly means were calculated from the 6 min data (Sect. 4.3).

Because thermally labile nocturnal species such as N₂O₅ and ClNO₂ can decompose in the TD inlets and bias gas-phase ON retrievals, the quantitative discussion in this work focuses on daytime gas-phase ONs, when such interferences are expected to be less important. Nighttime gas-phase ON data are shown for completeness and should be

interpreted with caution. This is because the presence of other reactive nitrogen oxides at night, such as ClNO₂, N₂O₅, and HONO, as described in Section 3.3.4 (which form at night and photolysis during the day), can significantly interfere with ON measurements. In contrast, particle-phase ONs were retained for both daytime and nighttime because the differencing approach reduces gas-phase interferences that are common to the gas-only and total configurations, although it may not remove them completely.~~largely cancels gas-phase interferences that are common to the gas-only and total configurations.~~

Laboratory-derived NO/NO₂ interferences in the Σ PN channels (Sect. 3.3.1) are expected to be most relevant under urban, high-NO_x conditions. Accordingly, the correction model obtained from PAN-based laboratory experiments was applied to the 250 °C channel measurements using simultaneously measured NO from the chemiluminescence analyzer and NO₂ from the RT channel. The corrected 250 °C data

were then used to derive gΣPNs and pΣPNs. No additional correction was applied to ΣANs beyond the 450–250 differencing described above, and the resulting ΣAN values are interpreted operationally.

4.3 Time series and evaluation against PAN

Figure ~~8~~6 shows hourly mean time series for NO, NO₂, gΣPNs, pΣPNs, gΣANs, and pΣANs during the two intensive observation periods. NO and NO₂ exhibited typical urban variability, with higher concentrations at night and lower concentrations during the day. The mean NO and NO₂ mixing ratios were 1.5 ± 2.1 ppbv and 14.8 ± 9.3 ppbv (mean $\pm 1\sigma$) in September, and 1.4 ± 1.3 ppbv and 18.2 ± 14.4 ppbv in October.

Daytime gΣPNs are elevated in both campaigns, with mean values of 2.8 ± 1.2 ppbv in September and 2.1 ± 1.2 ppbv in October and corresponding maxima of 8.4 and 5.8 ppbv, respectively. Particle-phase ΣPNs were smaller (e.g., 1.1 ± 0.5 ppbv in September) and showed less distinct diel structure. gΣANs displayed clear daytime maxima, with a mean of 1.0 ± 0.5 ppbv and 1.2 ± 0.5 ppbv in September and October, respectively. In contrast, pΣANs (1.0 ± 0.4 ppbv in September; 0.9 ± 0.5 ppbv in October) tended to peak at night, consistent with enhanced nighttime nitrate chemistry contributions and the expected nocturnal partitioning/production of low-volatility ONs (Fry et al., 2013).

The trends in daytime gΣPNs and temperature are positively correlated, as shown in Figure 9. The fractions of gΣPNs ($\text{g}\Sigma\text{PNs} / (\text{g}\Sigma\text{PNs} + \text{p}\Sigma\text{PNs})$) increases from less than 60 % in the morning (08:00, ~29 °C) to nearly 80 % in the afternoon (16:00, ~34 °C), which is qualitatively consistent with warmer conditions favoring the gas phase. We therefore regard the daytime evolution of gΣPNs as robust in a relative sense. By contrast, the absolute magnitude of pΣPNs should be interpreted more cautiously because pΣPN is obtained by channel subtraction and has not been directly validated

with a particulate PN standard. The residual particulate signal may reflect a combination of less volatile PN components, temperature-dependent partitioning, and subtraction uncertainty. Relative humidity may also influence Σ PNs through PAN hydrolysis and heterogeneous uptake on particles (Salas et al., 2020; Sun et al., 2022). The nighttime increase in g Σ PNs is not interpreted quantitatively because ClNO₂, N₂O₅, and HONO can contribute to gas-phase channels after dark. For Σ ANs, the particle-phase fraction increases as temperature decreases, which is consistent with partitioning of lower-volatility organic nitrates towards the condensed phase during nighttime conditions.

During the October campaign, corrected g Σ PNs were evaluated against independently measured PAN from the GC-ECD system. The two measurements agreed well in temporal variability, and linear regression yielded $R^2 = 0.83$. The regression slope indicates that PAN accounted for approximately 78% of daytime g Σ PNs (Figs. S75–S86). This proportion ranges from 48% to 78% at the temperate forest site in Paris, France (Andersen et al., 2025). This ~~comparison~~ supports the quantitative performance of the TD–CEAS gas-phase Σ PNs retrieval under urban conditions and provides an observational constraint on the extent to which PAN dominated the measured g Σ PNs pool during the deployment. Based on the comparison of raw Σ PNs and PAN (where g Σ PNs are, at certain times, unreasonably lower than PAN), it is necessary to correct the raw data because the uncorrected values occasionally imply a physically implausible negative inlet bias. At the same time, the correction remains PAN-anchored. In the real atmosphere, Σ PNs comprise a mixture of peroxy nitrates, whose thermal dissociation products may not behave identically to the PA radical. The corrected daytime g Σ PNs values should therefore be interpreted as operational Σ PN estimates constrained by PAN, rather than as composition-independent absolute totals.

These field observations demonstrate the capability of the five-channel TD–CEAS to provide continuous measurements of NO₂ and operational ON classes in both gas and particle phases at a 6 min cadence, with performance evaluation supported by independent PAN measurements and correction for NO/NO₂-dependent artifacts relevant to high-NO_x environments.

5 Conclusions and outlook

We developed and characterized a five-channel TD-CEAS system for in situ measurements of NO₂ and operationally defined ON classes in both the gas and particle phases. The instrument couples a single NO₂ detector (405 nm) with two thermal dissociation setpoints (250 °C and 450 °C) and paired inlet/outlet configurations (upstream filtration for gas-only; downstream filtration for particle-inclusive sampling) to enable retrieval of gas- and particle-phase ΣPNs and ΣANs by channel differencing. In the field configuration used here, the system cycles through the five channels plus an N₂ reference segment, providing a complete set of NO₂, g/p ΣPNs, and g/p ΣANs at a 6 min cadence.

Laboratory characterization of PN_s and AN_s standards supported the selection of operational TD temperatures~~Laboratory characterization supported the selection of operational TD temperatures, with PAN (proxy for ΣPN_s) exhibiting near-complete conversion at 250 °C and alkyl nitrate standards (proxies for ΣAN_s) reaching stable conversion at 450 °C for the residence time and reactor geometry employed.~~ Under these conditions, particulate inorganic nitrate (NaNO₃) showed minimal contribution to the NO₂ signal at 450 °C. Allan deviation analysis yielded 1 σ (1 s) detection limits of 49 pptv for gΣPN_s, 49 pptv for pΣPN_s, 48 pptv for gΣAN_s, and 68 pptv for pΣAN_s. The gas-phase ΣPN response was validated using PAN, with TD–CEAS PAN-equivalent

774 mixing ratios agreeing with GC–ECD measurements (slope = 0.987; $R^2 = 0.988$). For
775 particle-phase Σ ANs, an operational calibration based on filter thermolysis of 2-EHN
776 produced a linear response (slope = 1.036 ± 0.028) and a method detection limit of
777 $0.029 \mu\text{g NO}_2$. Dedicated interference experiments demonstrated that NO and NO_2 can
778 introduce substantial, nonlinear biases in Σ PNs retrievals through radical chemistry in
779 the TD inlet. These effects are reduced using a regression-based correction model that
780 outperformed the reproduced lookup-table approach across the tested NO_x conditions.
781 Field deployment at an urban site in Guangzhou during September–October 2025
782 demonstrated stable instrument operation under high- NO_x conditions and produced
783 continuous time series of gas- and particle-phase ON classes. During the October
784 intensive period, corrected g Σ PNs covaried well with independently measured PAN,
785 with R^2 of 0.83, and PAN accounted for approximately 78% of daytime g Σ PNs. The
786 observed diurnal variation of gas-phase ONs and the day-night pattern of particle-phase
787 ONs provide a useful approach for investigating the daytime phase partitioning of ONs
788 and the transformation processes of reactive nitrogen in urban air.~~The observed diel~~
789 ~~behavior, characterized by daytime enhancement of gas-phase ONs and nighttime~~
790 ~~enhancement of p Σ ANs, illustrates the utility of this approach for probing ON phase~~
791 ~~partitioning and reactive nitrogen processing in urban air.~~ Because thermally labile
792 nocturnal species such as N_2O_5 and ClNO_2 may interfere with gas-phase ON retrievals,
793 nighttime gas-phase data should be interpreted cautiously and are not used here for
794 quantitative discussion.

795 Several limitations remain important. First, the Σ PN correction is anchored to PAN and
796 may not fully capture the behavior of mixed ambient PN ensembles. Second, the Σ AN
797 channel was evaluated with a limited set of surrogate standards, and direct laboratory
798 validation for particle-phase PNs and NH_4NO_3 interference is still lacking. Third,

nighttime gas-phase data are not used quantitatively, and nighttime particle-phase data, although less sensitive to common gas-phase interferences, should still be regarded as operational. Finally, parallel multi-cavity or multi-detector designs would further reduce artifacts associated with channel switching. Within these bounds, the five-channel TD-CEAS provides a practical framework for continuous, class-resolved monitoring of organic nitrates in both phases while explicitly addressing NO/NO₂-dependent TD chemistry in high-NO_x environments. Future work should focus on strengthening traceability and expanding applicability of the method, including potential gas-particle separation artifacts, calibration representativeness, interference generalization with the goal of enabling reliable gas-phase ON detection across environments with reproducible processing. Overall, the five-channel TD-CEAS provides a practical measurement framework for continuous, class-resolved monitoring of organic nitrates in both phases, while explicitly addressing key challenges, particularly NO/NO₂-dependent TD chemistry, in high-NO_x environments.

Data availability

Datasets are presented in figures and summarized in tables throughout the paper and the Supplement. Raw data from these resources are available from the corresponding author (wangxm@gig.ac.cn) upon request. Data are available upon request from the corresponding author (wangxm@gig.ac.cn).

Author contributions

XW acquired funds. XT designed and characterized the instrument with the support of XW and WS. XT carried out the instrument assessments. XT, HL, XY, and WS carried out the ONs measurements in the field. XT prepared the manuscript. XW and WS

823 supervised the study. XW revised and edited the manuscript.

824 **Competing interests**

825 The authors declare that they have no conflict of interest.

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Table 1. Channel definitions and the corresponding quantities measured as NO₂-mixing ratios by CEAS.

Channel	TD-setpoint	Filter-placement	What enters TD	CEAS measures
RT-F	RT	upstream	gas-only	NO ₂
250-F	250 °C	upstream	gas-only	NO ₂ + gΣPNs → NO ₂
450-F	450 °C	upstream	gas-only	NO ₂ + gΣPNs + gΣANs → NO ₂
250-UF	250 °C	downstream	gas + particles	NO ₂ + (g+p)ΣPNs → NO ₂
450-UF	450 °C	downstream	gas + particles	NO ₂ + (g+p)ΣPNs + (g+p)ΣANs → NO ₂

Table 12. Summary of reported 1σ detection limits (pptv) for thermal-dissociation-based measurements of gSPNs, pSPNs, gΣANs and pΣANs from the literature and this study, with the integration time (s) indicated in parentheses. For this study, ΣPN and ΣAN detection limits are obtained by propagating Allan-deviation-derived NO₂ precision through the channel-differencing retrieval. Reported detection limits as given in the cited studies. “/” indicates not reported. Time resolution refers to the time for all species to complete one cycle.

Reference	Instrument	Detection limit (pptv)				<u>Time resolution</u>
		gSPNs	gΣANs	pSPNs	pΣANs	
(Day et al., 2002)	TD-LIF	90 (10s)	90 (10s)	/	/	<u>10 s</u>
(Paul et al., 2009)	TD-CRDS	/	100 (1s)	/	/	<u>1 s</u>
(Rollins et al., 2010)	TD-LIF			/	45 (60s)	<u>60 s</u>
(Sobanski et al., 2016)	TD-CRDS	47 (1s)	40 (1s)	/	/	<u>1 s</u>
(Sadanaga et al., 2016)	TD-CAPS	7 (120s)	/	/	/	<u>6 min</u>
(Thieser et al., 2016)	TD-CRDS	28 (1s)	28 (1s)	/	/	<u>/</u>
(Chen et al., 2017)	TD-CRDS	/	100 (1s, RNO ₂)	/	/	<u>3 s</u>
(Keehan et al., 2020)	TD-CRDS	220	220	/	/	<u>8 min</u>
(Li et al., 2021)	TD-CEAS	90 (6s)	90 (6s)	/	/	<u>3 min</u>
(Lin et al., 2024)	TD-CRDS	20.5 (1s)	18.3 (1s)	/	/	<u>1 s</u>
(Lin et al., 2026)	TD-CRDS	5.5 (30s)	6.2 (30s)	5.5 (30s)	6.2 (30s)	<u>5 min</u>
This study	TD-CEAS	49 (1s)	48 (1s)	49 (1s)	68 (1s)	<u>6 min</u>

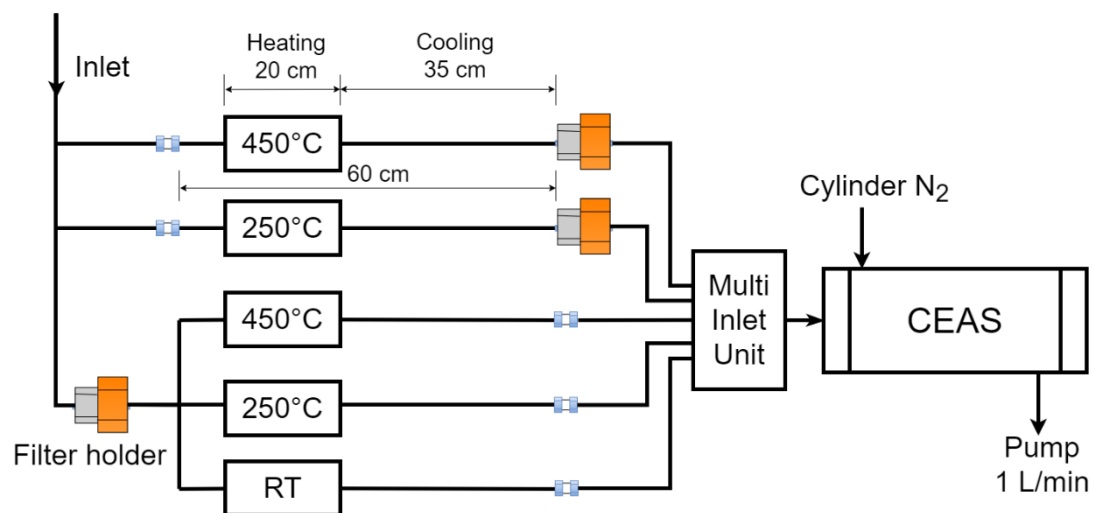


Figure 1. Schematic diagram of the five-channel TD-CEAS instrument.

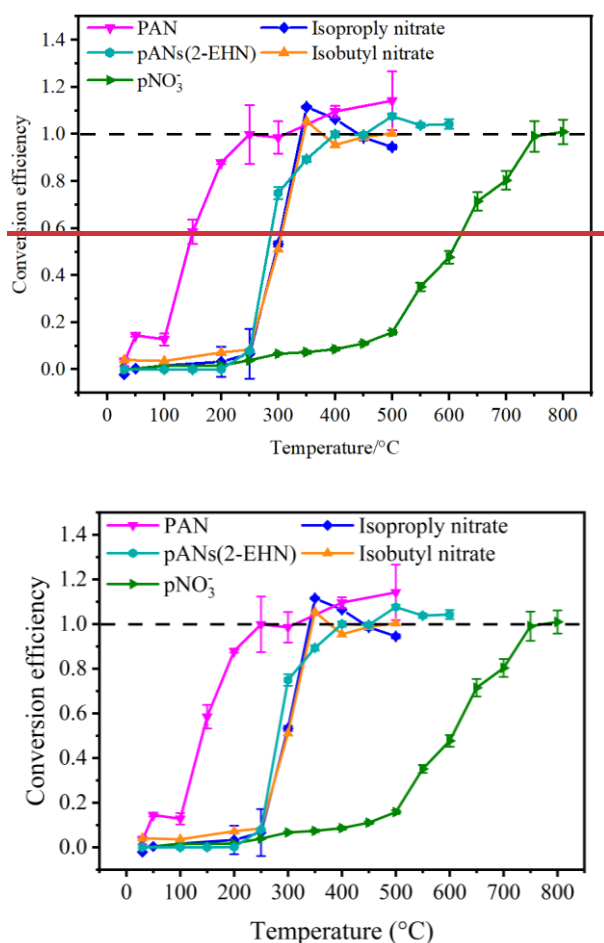


Figure 24. Temperature-dependent thermal dissociation response (“thermal decomposition profile~~thermal spectrum~~”) for representative organic nitrate standards and aerosol nitrate in the TD inlet. Shown are peroxyacetyl nitrate (PAN; proxy for Σ PNs), isopropyl nitrate and isobutyl nitrate (proxies for gas-phase Σ ANs), particulate 2-ethylhexyl nitrate (2-EHN; proxy for particle-phase organic nitrates), and particulate inorganic nitrate (pNO_3^- , generated from NaNO_3 aerosol). The conversion efficiency (unitless) is calculated as the NO_2 yield at each setpoint normalized to the high-temperature plateau for each compound; the dashed line denotes unity (complete conversion). Error bars indicate $\pm 1\sigma$ from replicate measurements. Temperature refers to the TD tube wall temperature at the thermocouple location.

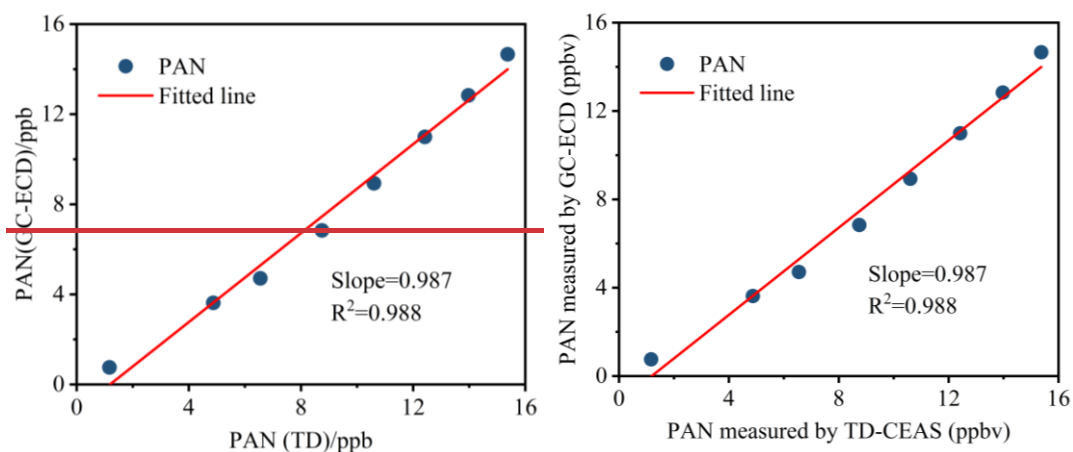


Figure 32. Cross-validation of PAN measured TD-CEAS against an independent gas chromatography–electron capture detector (GC–ECD) measurement. PAN (TD) is derived from the TD–CEAS 250 °C channel after subtraction of the room-temperature NO₂ channel. The red line shows a least-squares linear regression; the slope and coefficient of determination (R^2) are reported in the panel.

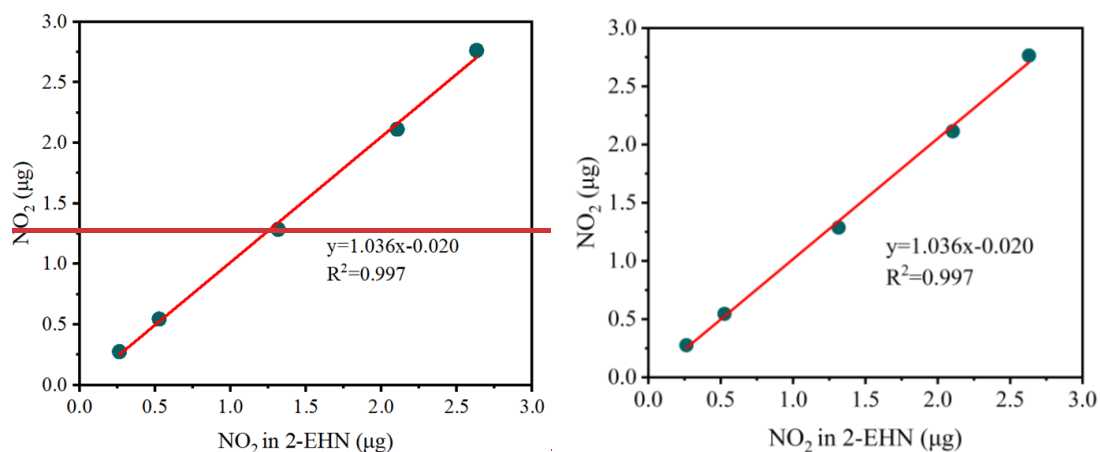


Figure 34. Calibration of particulate Σ AN response using filter thermolysis of 2-ethylhexyl nitrate (2-EHN). The recovered NO₂ mass (integrated CEAS signal) is plotted as a function of the expected NO₂ mass associated with the injected 2-EHN amount. The red line denotes a linear regression; the fit equation and R^2 are given in the panel.

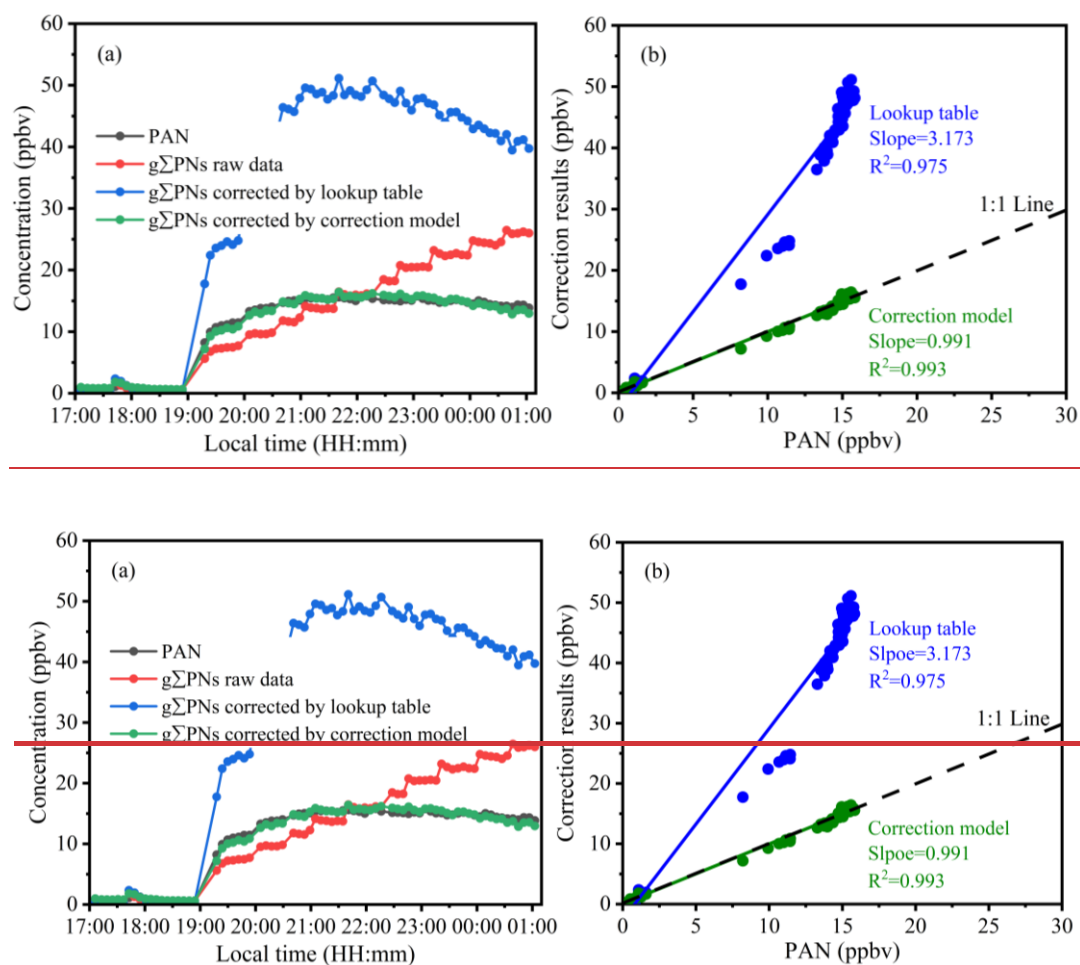


Figure 45. (a) The measured PAN and gΣPNs alongside the correction ΣPNs by lookup table and correction model, (b) Linear fit of correction results of lookup table and correction model with measured PAN. PAN is measured by GC-ECD, and gΣPNs is measured by TD-CEAS through the difference subtraction method.

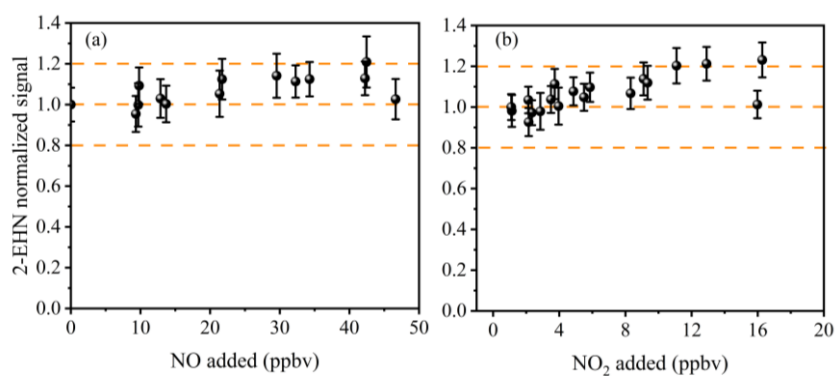


Figure 6. 2-EHN normalized signal at Σ ANs channel with (a) NO added, and (b) NO₂ added. The error bars represent 1σ standard deviation. In the NO and NO₂ addition experiments, the initial concentrations of 2-EHN were 37.4 and 56.1 ppbv, respectively.

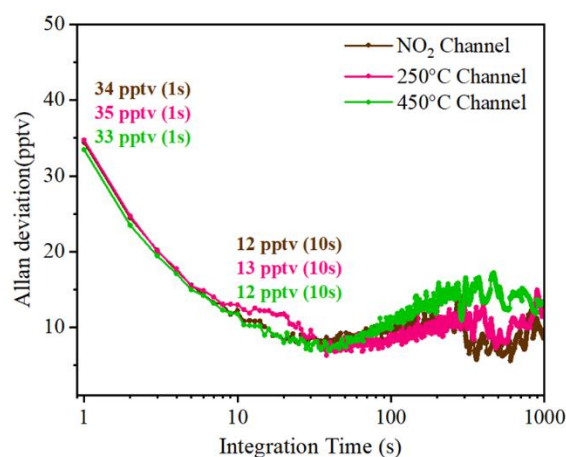


Figure 57. Allan Deviation of NO₂ mixing ratios retrieved by CEAS for the room-temperature NO₂ channel and the heated TD channels (250 °C and 450 °C), calculated from continuous ultra-high-purity N₂ sampling. The Allan deviation quantifies 1 σ precision as a function of integration time; annotated values indicate the 1 s and 10 s precisions for each channel.

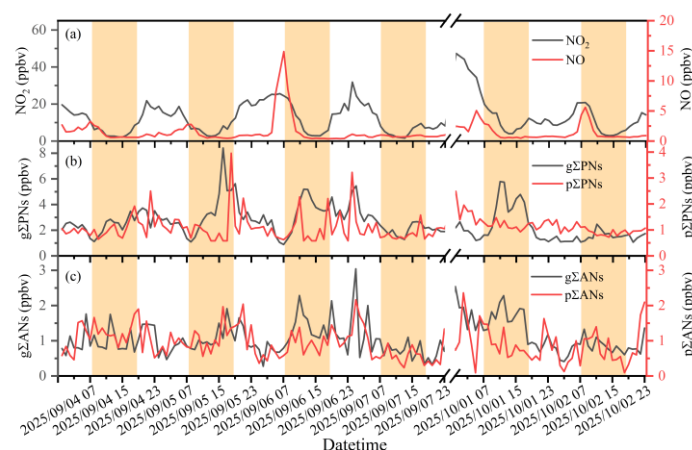


Figure 68. Hourly mean time series of NO measured by a Thermo Scientific 42i-TL analyzer, NO₂ measured by the RT channel, and class-resolved organic nitrates measured by the five-channel TD-CEAS during two intensive periods at the urban Guangzhou site (4–7 September 2025 and 1–2 October 2025; local time, UTC+8). From top to bottom, panels show NO and NO₂, gas- and particle-phase peroxy nitrates (gΣPNs and pΣPNs), and gas- and particle-phase alkyl nitrates (gΣANs and pΣANs). ΣPNs are shown after application of the NO/NO₂-dependent correction model derived from laboratory PAN experiments. Orange shading indicates daytime. All mixing ratios are in ppbv.

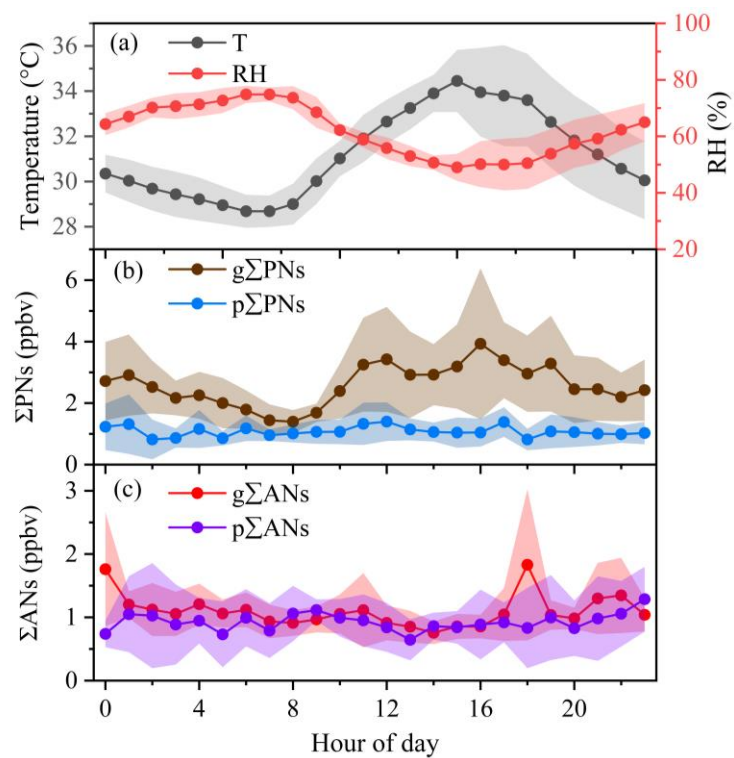


Figure 9. Daily average of (a) temperature and relative humidity, (b) gas- and particle-phase Σ PNs, and (c) gas- and particle-phase Σ ANs. Shading indicating the error of $\pm 1 \sigma$.