

Responses to Reviewer

Reviewer #1:

Tian et al. demonstrate a newly developed instrument to detect NO₂ as well as total peroxy and alkyl nitrates in both gaseous and condensed phase. Detection of organic nitrate species relies on their thermal decomposition to NO₂ through different heated inlets, which is monitored by a cavity enhanced absorption spectrometer. To distinguish between particle and gas phase organic nitrates, paired heated inlets equipped with particle filters positioned either upstream or downstream are used. The different species are quantified by channel differencing from subsequent measurements through each inlet within a measurement cycle. The NO_x-induced bias in PAN quantification with the gPNs inlet has been thoroughly characterized and validated with a GC-ECD. These results provide basis for a nonlinear regression approach to correct field data. The pANs measurements have been validated with particulate 2-ethylhexyl nitrate, thermal decomposition behaviour of the gANs channel has been tested with isobutyl and isopropyl nitrate.

There is only very little instrumentation dedicated to the quantification of total particulate organic nitrate species and the instrumental idea is thus of general interest to the geoscience community. The presentation is clear and the manuscript is well written. However, as detailed in my comments below, major revisions are necessary before the manuscript can be considered for publication: The instrument's ability to detect all of the above-mentioned species accurately in the presence of high NO_x concentrations is insufficiently verified (especially for gANs, pPNs and pANs). The use of a NO₂-based detection approach (rather than NO_x), an empirical nonlinear regression model, and inappropriate reference compounds to characterize the ANs channels does not adequately take the current state-of-the-art knowledge into account.

Major concerns/ General comments

1. Monofunctional alkyl nitrates as reference compound

Dewald et al. (2021) demonstrated that monofunctional alkyl nitrates, such as isopropyl or 2-ethylhexyl nitrate, are not suitable for instrument characterization due to their oversimplified dissociation behavior. In urban atmospheres, organic nitrates typically originate from the oxidation of anthropogenic or biogenic VOCs and are therefore often multifunctional (Hamilton et al., 2021; Kumar et al., 2023). As shown for isoprene-derived organic nitrates, such complex compounds can dissociate at lower temperatures in quartz inlets in the presence of ambient ozone. As a result, ANs may partially dissociate in the PN channels. The authors should therefore either characterize the inlets using atmospherically relevant RONO₂ compounds to rule out this bias or modify the design of the PN inlet (e.g., by using a PFA tube with increased residence time enabling operation at lower temperatures).

Response: We thank the reviewer for this important comment. We agree that monofunctional alkyl nitrates cannot represent the full structural and thermal diversity of ambient multifunctional ONs, and our original wording overstated their representativeness. We have therefore revised the manuscript to describe isobutyl nitrate, isopropyl nitrate, and 2-EHN explicitly as operational standards for the present

inlet design, rather than as chemically comprehensive surrogates for urban AN mixtures. Specifically, in Section 2.3.2 we now state that these compounds were selected because pure standards are commercially available and have been used in previous TD studies, but that they do not span the full thermal behavior of ambient multifunctional ANs. In Section 3.1 we also added an explicit limitation statement that, because the TD setpoints were derived from surrogate standards, partial dissociation of some multifunctional ANs in the lower-temperature channel cannot be excluded.

We also clarified the design trade-off relevant to the reviewer's PFA suggestion. We agree that a lower-temperature PFA-based PN inlet is a valuable strategy for dedicated PN measurements (as shown by Dewald et al., 2021). In the present five-channel differential design, however, our AN channel requires 450 °C operation, and using materially different reactor environments for the 250 and 450 °C channels would introduce an additional differential uncertainty. We therefore retained matched quartz reactors and now present this explicitly as a compromise of the current design rather than as an optimal solution for all ON classes.

2. Lacking characterisation of biases in the ANs channels

Wüst et al. (2025), a reference that the authors cite themselves, showed that the presence of NO can also create substantial biases in the quantification of alkyl nitrates that even vary extremely for different parent compounds (e.g. isoprene versus limonene; note that biogenic VOCs are also present in urban areas). The potential biases caused by NO_x when dissociating PNs (preferably work with a diffusion source here, see below) and atmospherically relevant ANs in the ANs channels (gas and particle phase) have to be assessed and discussed by the authors if they aim at quantifying ANs accurately.

Response: We thank the reviewer for this important point. We agree that our original wording was too strong and did not sufficiently separate what is supported by the present experiments from what remains uncertain for ambient multifunctional ANs. We therefore revised both the response letter and the manuscript so that the Σ AN result is presented as an operational, compound-limited measurement, not as a bias-free quantification of all atmospheric AN classes.

We added two pieces of supporting evidence and one explicit limitation. First, we revised Figure S4 so that the 450 °C channel is evaluated as $[\text{NO}_2]_{450} - [\text{NO}_2]_{\text{RT}}$, which is a cleaner diagnostic of source-related behavior in the Σ AN channel than the original 450–250 expression. Second, we added new Figure 6, in which NO and NO₂ were introduced to a 2-EHN diffusion source. The normalized 2-EHN response varied by less than 20% across the tested NO_x range and did not show a systematic monotonic dependence on either NO or NO₂. Third, we now state explicitly in Section 3.3.2 that these tests are sufficient to justify not introducing a separate empirical AN correction term for the present dataset, but they do not rule out compound-specific biases for multifunctional ambient ANs.

Accordingly, we changed the manuscript text from an overly broad claim that “elevated NO_x does not affect the Σ AN channel” to a more defensible statement: for the present inlet design and the compounds tested here, 450–250 differencing provides the best available operational Σ AN estimate, while additional validation with atmospherically

relevant multifunctional ANs remains necessary.

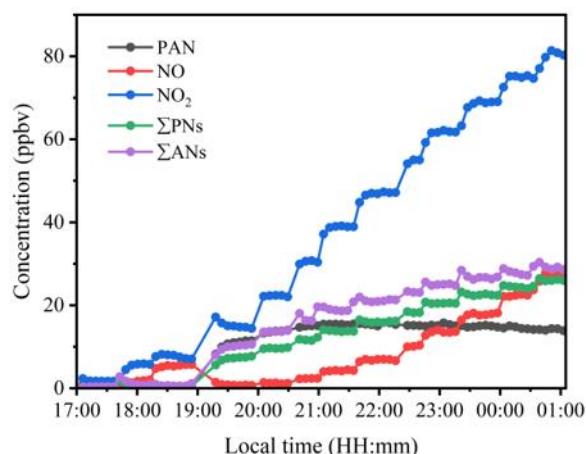


Figure S4 Measurements of PAN, NO, NO₂, ΣPNs and ΣANs when different NO concentrations are introduced into acetone/air gas under 285 nm UV lamp irradiation. ΣPNs is calculated as $[\text{NO}_2]_{250} - [\text{NO}_2]_{\text{RT}}$, ΣANs is calculated as $[\text{NO}_2]_{450} - [\text{NO}_2]_{\text{RT}}$.

Discussion added in the Section 3.3.2 (Lines 494-505):

“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 indicate 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.”

In addition, we added NO and NO₂ to the 2-EHN diffusion source to verify the interference of NO_x with ANs measurement in the supplementary experiments, Figure 6 has been added to the revised manuscript:

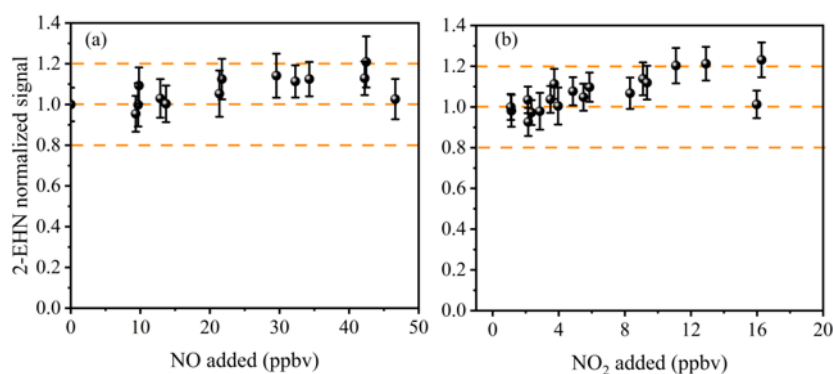


Figure 6. 2-EHN normalized signal at Σ ANs channel with (a) NO added, and (b) NO₂ added. The error bars represent 1σ standard deviation. In the NO and NO₂ addition experiments, the initial concentrations of 2-EHN were 37.4 and 56.1 ppbv, respectively.

The corresponding discussion in revised Section 3.3.2 now states that the 2-EHN response shows no systematic monotonic dependence on the added NO or NO₂, that the normalized response varies by less than 20% across the tested range, and that this evidence supports reporting Σ ANs as a 450–250 operational difference for the present dataset without introducing a separate empirical AN correction term.

Discussion added in Section 3.3.2 (lines 506-515):

“To further verify the effect of NO_x on Σ ANs 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. Insufficient characterization of the PNs channels

The authors only performed experiments with PAN, admittedly by far the most relevant PNs species in the gas phase. In urban areas, mixtures of different PNs species (e.g. PAN/PPN/MPAN) can occur, which dissociate to NO₂ and different RO₂, which may substantially differ in their chemical behaviour, thereby also resulting in a different NO_x-induced bias (similar to the different behaviour of isoprene- and limonene-derived alkyl nitrates as shown in Wüst et al. (2025)). Their regression model might only be applicable to PAN or for a certain NO/NO₂ ratio (please also indicate which amounts of NO and NO₂ have been added to get an idea of the NO/NO₂ ratios!). The authors should at least discuss this issue. Could the authors please also demonstrate that their instrument is capable of detecting peroxy nitrates in the particle phase?

Response: We agree with the reviewer. PAN-only characterization does not establish composition-independent Σ PN accuracy, and the manuscript needed to state that boundary more clearly.

We made three corresponding revisions. First, we now report the NO/NO₂ ranges used in model development, validation, and field application (0.044–2.015, 0.040–0.246, and 0.021–0.607, respectively), so that the reader can judge the envelope of conditions actually tested. Second, we revised the discussion in Sections 4.2–4.3 to state explicitly that the correction is PAN-anchored and that the corrected daytime g Σ PNs should be interpreted as an operational Σ PN estimate rather than a composition-independent absolute total when the ambient PN mixture departs strongly from PAN. Third, we softened the language regarding particle-phase PNs: p Σ PN is retrieved operationally by channel differencing, but it has not been directly validated with a particulate PN

standard. That limitation is now stated explicitly in the field discussion and in the Conclusions.

We therefore no longer present the instrument as having fully validated particle-phase PN quantification. Instead, we present $p\Sigma\text{PN}$ as an operational output of the five-channel design whose absolute magnitude still requires dedicated laboratory validation with a particulate PN standard.

Revisions made in Lines 460-468:

“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 (RO_2) 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/NO_2 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/NO_2 ratios encountered under various conditions.”

4. Detection based on NO_2

If the authors aim to use this instrument in urban areas, where the NO_x bias is highly significant, why did they refrain from detecting NO_x instead of NO_2 as demonstrated in various publications (Friedrich et al., 2020; Gingerysty, 2021; Ohara et al., 2024; Wild et al., 2014; Wüst et al., 2025) in order to easily circumvent the (often compound-specific) NO_x biases as well as the majority of the problems discussed herein?

Response: We thank the reviewer for this important conceptual point. We fully agree that NO_x -based TD instruments are a powerful strategy for reducing part of the compound-specific NO -mediated bias, and our original response did not explain clearly enough why we retained NO_2 detection in the present study.

The reason is not that we regard NO_x detection as less valid; rather, we made a different instrument-design trade-off. Our goal here was to build a compact five-channel system that could retrieve gas- and particle- phase ON classes with a single optical detector and a simple filter-differencing architecture. Retaining direct NO_2 detection keeps that architecture compact, but it also requires an explicit correction framework for coupled NO/NO_2 chemistry.

We therefore rewrote the relevant manuscript text to present this as a deliberate trade-off rather than as a claim of superiority. We now state explicitly that ozone-assisted NO_x detection remains highly attractive, especially when maximal suppression of inlet chemistry is the primary goal, while a NO_2 -based design offers a simpler hardware configuration at the cost of requiring careful interference characterization and correction.

Minor concerns/ Specific comments

1. L88-98: After this section, it might be worth outlining the NO_x bias in the ANs channel (see e.g. Sobanski et al., 2016; Thieser et al., 2016) as well.

Response: We agree with the reviewer’s comment. We have added the outlining of

NO_x bias in ANs channels in the revised manuscript (lines 93-99):

“Regarding bias in NO₂ measurements in the ANs channel, Sobanski et al. (2016) conducted a laboratory study on the transmission efficiency of NO₂ in heated glass tubes equipped with filters and filled with glass beads, finding that NO₂ losses in the 448K and 648K channels were within 2% and 5%, respectively. Furthermore, Thieser et al. (2016) also noted that losses due to TD temperature settings and pipe wall effects are negligible. Therefore, NO_x biases in the PNs/ANs channel are typically disregarded in both laboratory experiments and field deployments.”

2. L102/103: This approach has also been used by Sobanski et al. (2016) before the instrument has been modified by Dewald et al. (2021).

Response: We sincerely appreciate this valuable comment. We have added more references to support this idea, including (Sobanski et al., 2016; Dewald et al., 2021), in the revised manuscript (line 104).

3. L105: This approach has also been shown in Friedrich et al. (2020), Gingerysty (2021), Ohara et al. (2024) and Wild et al. (2014).

Response: We sincerely appreciate this valuable comment. We have added more references (Friedrich et al., 2020; Gingerysty 2021; Ohara et al., 2024; Wild et al., 2014) to support this idea in the revised manuscript (lines 106-107).

4. L111-115: It might be worth citing Wüst et al. (2025) here, who thoroughly discussed problems associated to this type of PAN source.

Response: We sincerely appreciate this valuable comment. We have added references “(Wüst et al., 2025)” to support this idea in the revised manuscript (lines 121).

5. L115-117: I agree with this statement. 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 (as implied by the authors in L334) and surface chemistry. The authors should mention it in this section.

Response: As suggested by the reviewer, we have incorporated this suggestion by adding the text in the introduction section (lines 122-127):

“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.”

6. L122: How do the authors ensure accurate ANs quantification?

Response: We appreciate your time and effort. We have included a review of the precise quantification of ANs in the revised manuscript (lines 136-146):

“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.”

7. L181-183/185: These reference compounds are only of limited atmospheric significance (see general comment above).

Response: We thank the reviewer for this follow-up comment. In line with the major comment above, we have revised this section to avoid claiming broad atmospheric representativeness. The revised manuscript now describes isobutyl nitrate, isopropyl nitrate, and 2-EHN as operational benchmark compounds used to characterize the present inlet/detector configuration. We retained these compounds because they are accessible, stable, and commonly used in TD studies, but we now state explicitly that they do not cover the full chemical diversity of ambient multifunctional ONs. This clarification has been inserted in Section 2.3.2 (lines 213-220 in the revised manuscript): *“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.”*

8. L201-204: Did the authors perform any transmission experiments for different particle sizes during “UF” sampling periods?

Response: This is an excellent point. We did not perform particle transmission experiments. However, according to the literature (Rollins et al., 2010; Garner et al., 2020), non-volatile particles have a relatively high transmission efficiency, and it may be even higher for volatile particles. Nevertheless, to address this comment, we have added the following text after that section (lines 244-260):

“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.”

9. L207-214: As the accurate quantification relies on NO₂ and channel differencing, did the authors verify that the NO₂ transmission does not vary with the inlet temperature? Sobanski et al. (2016) found small but significant NO₂ losses in heated quartz inlets with glass beads.

Response: We thank the reviewer for this important question. We did not perform a standalone NO₂ transmission experiment for each temperature channel in the present study, so the original wording was too categorical. We have revised the manuscript to frame this point more carefully: our assumption of negligible temperature-dependent NO₂ loss is based on the literature for unpacked heated quartz tubes, whereas the small NO₂ losses reported by Sobanski et al. (2016) were associated with packed channels. The revised text now cites this distinction explicitly and avoids implying that we directly verified it in our own system (lines 273-277):

“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).”

10. Section 2.6: Could the authors please discuss the uncertainties associated with their measurements?

Response: We thank the reviewer for this suggestion. We agree that the original uncertainty statement was too compressed and could be read as a complete method uncertainty, which it is not. We therefore revised Section 2.6 to distinguish between: (1) instrumental calibration and repeatability for simple NO₂ inputs, and (2) additional method uncertainty associated with TD chemistry, aerosol transmission, channel subtraction, and representativeness of the surrogate standards. The revised manuscript now makes clear that the 6% CEAS calibration uncertainty and 1.4% repeatability do not by themselves fully describe the uncertainty of ambient Σ PN/ Σ AN retrievals, which are reported as operational measurements for the present configuration:

“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.” (lines 306-315)

11. L251-255: The authors should mention that these values are used as ballpark values and do not necessarily reflect the wall losses of their own inlets since they vary with inlet geometry and operating conditions (flow, temperature etc.).

Response: We agree with the reviewer’s comment. We have incorporated this suggestion by adding the sentence in the revised manuscript (lines 323-325):

“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.”

12. L259: “Thermal spectrum” does not appear to be a physically correct term in this context. I therefore rather recommend “thermogram” or “(thermal) decomposition profile”, as indicated in other publications.

Response: We agree that “thermogram” or “(thermal) decomposition profile” are better contexts. And “Thermal spectrum” has been corrected to “thermal decomposition profile” in the sentence (lines 330, 346 and 1011-1012).

13. L346/347: Here, the authors compared to the lookup table method proposed by Li et al. (2021). But how well does your method perform in comparison to the explicit numerical simulation approach using a more complex model as e.g. shown by Sobanski et al. (2016) under field conditions? In addition, it would be good to explicitly differentiate between a lookup table approach (which is based on numerical simulations of laboratory data) and the explicit numerical simulation approach with field data input throughout the text.

Response: We thank the reviewer for this useful suggestion. We agree that the explicit numerical simulation approach of Sobanski et al. (2016) and the lookup-table approach of Li et al. (2021) should not be conflated. We therefore revised the manuscript to keep these two methods conceptually separate throughout the discussion.

We were not able to reproduce the full explicit simulation framework of Sobanski et al. (2016) because the published paper does not provide the complete implementation details needed for a faithful field-data comparison. Rather than present a partial or potentially misleading reproduction, we limited our quantitative comparison to the published lookup-table approach of Li et al. (2021) and stated this explicitly. We also expanded the text around Figure S7 so that the reader can see that our comparison is against a lookup table, not against an explicit field-constrained chemical simulation (Lines 442-445):

“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.”

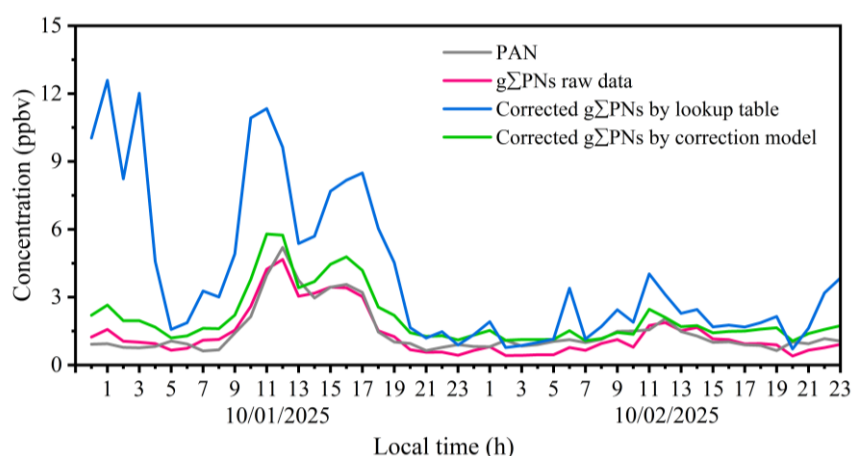


Figure S7 Comparison of gΣPNs raw data, measured PAN and correction results from two correction methods. The gray line represents PAN measured by GC-ECD, the red line shows raw gΣPNs measured by TD-CEAS, the green line indicates gΣPNs corrected by correction model, the blue line represents gΣPNs corrected by lookup table.

14. L351-357: Can the authors provide a reason for the overestimation of PAN by the lookup table approach under the high concentration conditions? The model by Li et al. (2021) seems to include the bias induced by both NO and NO₂.

Response: We thank the reviewer for the suggestion. In the revised manuscript, we explain the reason for the overestimation of the lookup table (lines 446-454):

“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.”

15. L371-373: Why would it be an advantage having to rely on measured NO/NO₂? The addition of ozone is easily feasible during field deployment as well (e.g. Friedrich et al., 2020).

Response: We thank the reviewer for this comment. Following the reviewer’s concern, we removed our earlier wording that implied an inherent advantage of avoiding ozone addition. The revised manuscript now presents the comparison more fairly: ozone-assisted NO_x detection is treated as a strong alternative design, while our method is framed as a correction strategy tailored to a compact single-cavity NO₂-based instrument. The revised text now emphasizes the instrument-design trade-off rather

than claiming that one approach is universally preferable (Lines 479-492):

“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.”

16. L366-368: Could the authors please justify their statements with additional plots and/or experiments? Previous studies reported indeed a NO_x-bias in the detection of PAN in the ANs channel that significantly differs (usually weaker) from that in the PNs channel (Sobanski et al., 2016) presumably due to thermal decomposition of the acetyl peroxy radical (Thieser et al., 2016).

Response: We thank the reviewer for this question. Sobanski et al. (2016) reported that the weak bias (~3–5 %) in the measurement of PAN in the ANs channel is attributable to the thermal dissociation of the peroxyacetyl radical. A plausible explanation is that Sobanski et al. (2016) packed both the PNs and ANs channels with glass beads and glass fiber filters, which effectively scavenge organic radicals generated during thermal dissociation. This approach has also been reported in the studies of Lin et al. (2024) and Dewald et al. (2021). To further investigate the measurement bias of PAN in the ANs channel, we have revised Figure S4 in the manuscript, as detailed above. In addition, following the reviewer’s suggestion, we conducted supplementary experiments to quantify the effect of NO_x on the measurement bias in the ANs channel (see new Figure 6). A dedicated discussion has been added in the newly Section 3.3.2, as detailed above (see lines 493-515).

17. In addition, the presence of alkyl nitrates is highly speculative. Wüst et al. (2025) showed that the photochemical PAN source as deployed by the authors can create an artefact signal in the ANs signal in the presence of NO due to impurities of H₂O₂ and peracetic acid. Also, Fig. S3 shows very well some NO_x-induced deviations in the ANs channel. The authors could work with a diffusion PAN source to properly characterize the behaviour of PAN in the ANs channel while avoiding impurities (alkyl nitrates, peroxides...).

Response: We thank the reviewer for this suggestion. We agree that a clean diffusion PAN source would be preferable for isolating PAN behavior in the Σ AN channel. Because we did not have such a validated source available for the present revision, we

chose a more conservative response: rather than claiming that Figure S4 resolves the question, we reframed Figure S4 as a source-diagnostic plot and restricted the AN interpretation to the additional 2-EHN NO/NO₂ experiments and to explicitly operational language in Section 3.3.2.

18. In any case, the NO_x-bias during the detection of an alkyl nitrate in the ANs channel has to be performed as well (see general comment above).

Response: We agree. We have now addressed this point directly by adding the new NO/NO₂ addition experiments with 2-EHN (Figure 6) and by revising Section 3.3.2 so that the resulting AN interpretation is clearly limited to an operational, compound-tested range rather than generalized to all ANs.

19. L429: Please specify the type of filter you used.

Response: As suggested by the reviewer, we have added the type of filter “(PTFE, retention efficiency of 99.5% or higher for 0.3 μm particles)” in the revised manuscript (Line 623).

20. L454/455: As commented above, the lacking correction of the ANs data is not sufficiently justified in the current form of the manuscript.

Response: We thank the reviewer for this comment. We agree that the original justification was insufficient. We have now strengthened it in two ways: by adding the new NO/NO₂ experiments with 2-EHN (Figure 6), and by rewriting the manuscript text so that “no additional AN correction” is justified only for the present dataset and tested compound space. We no longer present this as a general conclusion for all ambient AN mixtures.

21. L519-522: Most of these aspects are crucial to consider before publication. It is not clear why the authors consider this as future work.

Response: We thank the reviewer for this important comment. We agree that these points should not have been deferred loosely to “future work”. We therefore rewrote the Conclusions so that the present scope and the remaining limitations are stated explicitly in the main claims of the paper. The revised conclusion now identifies, within the current study itself, the main unresolved issues: the PAN-anchored nature of the ΣPN correction, the limited surrogate basis for the ΣAN channel, the lack of direct particulate PN and NH₄NO₃ validation, and the restricted use of nighttime gas-phase data. Future work is mentioned only after these current limitations are made explicit.

Revisions made in the Conclusions (Lines 741-751):

“Several limitations remain important. First, the ΣPN correction is anchored to PAN and may not fully capture the behavior of mixed ambient PN ensembles. Second, the ΣAN channel was evaluated with a limited set of surrogate standards, and direct laboratory validation for particle-phase PNs and NH₄NO₃ 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.”

22. L528: As far as I am aware, this statement does not meet Copernicus’ submission guidelines.

Response: We thank the reviewer for bringing this important oversight to our attention. We acknowledge that our manuscript availability statement is not meet Copernicus’ submission guidelines. In the revised manuscript on lines 753-755, we have corrected the “Data are available upon request from the corresponding author (wangxm@gig.ac.cn).” to “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.” We appreciate the reviewer’s diligence in enforcing the journal’s policies.

23. L680: Same here, please reconsider the term “thermal spectrum”.

Response: We agree that “thermogram” or “(thermal) decomposition profile” are better contexts. And “Thermal spectrum” has been corrected to “thermal decomposition profile” in the sentence (lines 1011-1012).

24. Fig. 2: Could the authors please discuss the negative intercept? What would the slope be if the fit were forced through zero? Also, it seems to me that the first three points behave differently to the rest.

Response: Thank you for raising this concern. We have added an explanation of the negative intercept in the revised manuscript (lines 362-365):

“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.”

When the fitted curve in Figure 3 is forced through the origin, the slope becomes 0.88, which represents a slight deterioration in fit, although the correlation improves ($R^2 = 0.99$). The first three data points deviate from the remainder of the dataset. This deviation is attributed to a small amount of NO₂ generated during the photochemical production of PAN, which introduces a minor bias in the TD-CEAS measurements, as discussed in Sect. 3.3.1.

25. Fig. S3: Where does the NO_x before 19:00 LT come from? Does it originate from the PAN source? And referring to one of my comments above: Could the signal in the ANs channel originate from H₂O₂/peracetic acid impurities in the source in the presence of NO as discussed by Wüst et al. (2025)?

Response: We thank the reviewer for this careful reading. We agree that Figure S4 should not be over-interpreted as evidence for ambient AN behavior, because the photochemical PAN source can contain reactive by-products. We have therefore revised

both the SI caption and the main text so that Figure S4 is presented explicitly as a diagnostic of source-related/common-mode behavior in the 250 and 450 °C channels, not as a compound-specific validation of the Σ AN channel.

Regarding the NO_x present before 19:00 LT, this signal arises from the photochemical PAN generation system itself, in which low acetone and NO were continuously introduced under UV irradiation. We now state this more clearly in Text S1. We also acknowledge directly that impurities such as peracetic acid or H₂O₂, as discussed by Wüst et al. (2025), are part of the reason why Figure S4 must be treated as a source-diagnostic plot rather than a definitive AN-channel characterization.

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