Response to Reviewer 1

The authors improved the manuscript mainly by rephrasing the sections dedicated to instrument characterization and by including a NOx-interference experiment for the ANs channel. Especially after comparing with recent publications on organic nitrate instruments, the publication seems to meet current requirements to justify publication. Due to this and since the main idea of this instrument (separately quantifying total organic nitrates in both gas- and particle phase) is innovative, I recommend publication once the authors have considered my comments below (line numbers refer to the revised version of the manuscript).

General comments:

If the authors intend to ensure they retrieve meaningful data from field measurements, I highly encourage them to carefully characterize the thermal dissociation inlets for multifunctional organic nitrates. I appreciate that the ANs channel has been further characterized for NOx interference. However, the fact that the authors only found a marginal effect for 2-EHN simply confirms Wüst et al. (2025) and does not necessarily imply that the instrument performs well in the field due to the reasons outlined in my first review. It is not clear to me, why the authors refrain from choosing another surrogate. However, since this kind of characterization using multifunctional surrogates does not seem to be standard (as reflected in recently published organic nitrate instrumentation papers), I leave this point optional.

Response: We thank the reviewer for highlighting this important limitation. We agree that the 2-EHN experiment constrains the ΣAN response only for this surrogate and the tested NO/NO_2 conditions; it cannot establish the instrument response for the diverse multifunctional ANs present in ambient air. Wüst et al. (2025) showed that NO-dependent inlet chemistry can vary substantially among saturated and biogenic AN surrogates, reinforcing the need for compound-specific characterization.

Accordingly, we have narrowed our interpretation and added an explicit limitation in the revised manuscript (lines 520-529). We now state that the <20% variation observed for 2-EHN should not be generalized to isoprene-, monoterpene-, or aromatic-derived nitrates and that validation with multifunctional surrogates is required before the field response can be considered composition-independent. We appreciate the reviewer allowing the additional experiments to remain optional; rather than presenting 2-EHN as comprehensive validation, we report ΣANs as an operational quantity for the present inlet configuration and identify characterization with multifunctional surrogates as a priority for future work.

The following sentences have been added in the revised manuscript (lines 520-529):

"We acknowledge that 2-EHN provides a useful operational benchmark for instrument calibration. However, ambient organic nitrates comprise a diverse suite of multifunctional species, including nitrates derived from isoprene, monoterpenes, and aromatics. These compounds may differ in thermal dissociation behaviour and in their susceptibility to NOx-related interference. The marginal NOx effect observed for 2-EHN under the tested conditions is consistent with the broader finding of Wüst et al. (2025) that NO-dependent inlet responses can be compound specific. It should therefore not be taken to imply comparable performance across all classes of organic nitrates. Future work should extend this characterization to multifunctional surrogates to better constrain the instrument response under atmospherically relevant conditions."

Specific comments:

L98: I think you rather want to say "NO_2 transmission losses" rather than "NOx bias".

Response: We agree and have replaced "NOx biases" with "NO_2 transmission losses" at line 98 of the revised manuscript.

L142: This was shown in Dewald et al. (2021), not in Sobanski at al. (2016)

Response: Thank you for identifying the incorrect attribution. We have replaced Sobanski et al. (2016) with Dewald et al. (2021) at line 142; the accompanying citation to Wüst et al. (2025) has been retained.

L205: The fact that they are widely used does not necessarily mean they are an appropriate choice.

Response: We agree that prevalence of use is not evidence of suitability. We have removed "widely used in TD studies" as the justification (lines 205-206). Section 2.3.2 now gives the narrower rationale: isopropyl nitrate and isobutyl nitrate are used as operational laboratory standards because pure compounds are commercially available, their thermal behaviour is well characterized, and they permit reproducible controlled tests. We also state explicitly that they are not comprehensive proxies for ambient multifunctional ANs (lines 214-221).

L213-214: "...and therefore provide useful benchmark compounds for instrument testing". Do we know that? What is the fractional contribution of these compounds to the total ANs in urban areas? A study by Li et al. (2023) rather implies that ANs derived from isoprene and aromatics may be more relevant.

Response: We agree that ambient detection does not establish representativeness and that the fractional contribution of individual alkyl nitrates is site- and chemistry-

dependent. We have therefore removed the phrase "and therefore provide useful benchmark compounds for instrument testing" and no longer imply that isopropyl nitrate and isobutyl nitrate represent the urban total-AN budget. The revised text acknowledges the importance of isoprene- and aromatic-derived nitrates reported by Li et al. (2023) and makes clear that our standards were selected for controlled instrument characterization rather than for atmospheric dominance (lines 214-221):

"Isopropyl nitrate and isobutyl nitrate were selected as benchmark compounds for this instrument test. While these compounds have been detected in the urban atmosphere (Zeng et al., 2018), we acknowledge that they do not necessarily represent the full composition of ambient alkyl nitrates, particularly in urban environments where isoprene- and aromatics-derived nitrates can be more important (Li et al., 2023). Our selection was instead based on their well-characterised thermal behaviour, commercial availability, and suitability for controlled laboratory experiments to characterise the instrumental response."

L352: This is where Dewald et al. (2021) could be cited.

Response: We have added Dewald et al. (2021) at the indicated passage (now lines 355), where we state that partial dissociation of multifunctional ANs in the lower-temperature channel cannot be excluded. The full citation is included in the reference list.

L485-487: Why should the addition of ozone increase the measurement uncertainty? NO_3/N_2O_5 formation can be avoided by carefully choosing the amount of ozone to be added (Friedrich et al., 2020).

Response: We agree. Our original wording incorrectly treated O_3 addition as an inherent source of measurement uncertainty. We have deleted that statement and revised lines 485-486 to clarify that, when the amount of added O_3 is optimized, formation of NO_3 and N_2O_5 can be avoided, consistent with Friedrich et al. (2020). The ozone-supplemented design is therefore described as an alternative instrument configuration rather than as an intrinsically less certain method. The following clarification is added to the revised manuscript (Lines 485-486):

"by carefully optimizing the concentration of the ozone-supplemented, the formation of NO_3 and N_2O_5 can be avoided."

L488/489: No further correction is necessary as long as the added O_3 remains present during both zeroing and sampling (Wüst et al., 2025).

Response: We agree. We have removed the statement that O_3 absorption at 405 nm necessitates an additional correction. The revised manuscript (lines 486-490) now states

that, because O_3 is added continuously during both zeroing and sampling, its background absorption cancels in the differential measurement and no separate O_3 absorption correction is required (Wüst et al., 2025). The revised sentence (lines 486-490) now reads:

"Although ozone exhibits weak absorption at 405 nm (Wild et al., 2014), this background absorption cancels out in differential measurements because an O_3 flow is continuously injected during both zeroing and sampling; therefore, no additional correction is required (Wüst et al., 2025)."

References:

Dewald, P., Dörich, R., Schuladen, J., Lelieveld, J., and Crowley, J. N.: Impact of ozone and inlet design on the quantification of isoprene-derived organic nitrates by thermal dissociation cavity ring-down spectroscopy (TD-CRDS), Atmos. Meas. Tech., 14, 5501-5519, https://doi.org/10.5194/amt-14-5501-2021, 2021.

Friedrich, N., Tadic, I., Schuladen, J., Brooks, J., Darbyshire, E., Drewnick, F., Fischer, H., Lelieveld, J., and Crowley, J. N.: Measurement of NOx and NOy with a thermal dissociation cavity ring-down spectrometer (TD-CRDS): instrument characterisation and first deployment, Atmos. Meas. Tech., 13, 5739-5761, https://doi.org/10.5194/amt-13-5739-2020, 2020.

Li, C., Wang, H., Chen, X., Zhai, T., Ma, X., Yang, X., Chen, S., Li, X., Zeng, L., and Lu, K.: Observation and modeling of organic nitrates on a suburban site in southwest China, Sci. Total Environ., 859, 160287, https://doi.org/10.1016/j.scitotenv.2022.160287, 2023.

Wild, R. J., Edwards, P. M., Dubé, W. P., Baumann, K., Edgerton, E. S., Quinn, P. K., Roberts, J. M., Rollins, A. W., Veres, P. R., Warneke, C., Williams, E. J., Yuan, B., and Brown, S. S.: A measurement of total reactive nitrogen, NOy, together with NO_2, NO, and O_3 via cavity ring-down spectroscopy, Environ. Sci. Technol., 48, 9609-9615, https://doi.org/10.1021/es501896w, 2014.

Wüst, L., Dewald, P., Türk, G., Lelieveld, J., and Crowley, J. N.: Influence of ambient NO and NO_2 on the quantification of total peroxy nitrates (ΣPNs) and total alkyl nitrates (ΣANs) by thermal dissociation cavity ring-down spectroscopy (TD-CRDS), Atmos. Meas. Tech., 18, 1943-1959, https://doi.org/10.5194/amt-18-1943-2025, 2025.

Zeng, L. W., Lyu, X. P., Guo, H., Zou, S. C., and Ling, Z. H.: Photochemical formation of C1-C5 alkyl nitrates in suburban Hong Kong and over the South China Sea, Environ.

Sci. Technol., 52, 5581-5589, https://doi.org/10.1021/acs.est.8b00256, 2018.