

In the following we list the referee's comments (black) our reply (blue) and indicate what changes have been made to the manuscript (green).

Referee Comment RC1

Türk et al. describe a compact cavity ring-down spectrometer for quantification of NO_3 and N_2O_5 . In spite of its compactness, the instrument achieves excellent limits of detection and good accuracy. Sample ambient air measurements are presented.

Numerous such instruments have been described in the literature, including by the authors. While the manuscript is written well, the authors need to revise the discussion and explain what they would consider novel or different in their approach. Essentially, the manuscript requires a section comparing this new instrument with existing methods (include a Table summarizing these) as well as a critical discussion of this instrument's performance, advantages and disadvantages compared to existing methods.

We have added text (new Section 3.8) and a Table that compares the instrument with existing setups from this laboratory as well as CRDS and BBCEAS instruments from other research groups.

3.8 Comparison with field-deployable cavity enhanced instruments for NO_3 .

During the last few decades, several instruments using cavity-enhanced absorption spectroscopy have been developed for ambient measurement of NO_3 (and N_2O_5). Table 2 lists those instruments that have been described in the literature which were designed or used for field-deployment. The Table includes instrumental parameters such as LOD (for both NO_3 and N_2O_5) and the footprint, where this information is available.

While some of the first instruments, e.g. (Brown et al., 2001), used large pulsed lasers and were mounted on optical tables, the availability of laser diodes has reduced the cost and size requirements. The most commonly deployed modern detection methods are BBCEAS and CRDS, the best of which ((Brown et al., 2001; Brown et al., 2002a; Dubé et al., 2006; Wagner et al., 2011; Sobanski et al., 2016a)) achieve < 1 pptv limits of detection within one second of integration time, as does the present instrument. Note that all of these are CRDS instruments, with BBCEAS-based methods having slightly poorer LODs. The two features of the present instrument that set it aside from most others is the small footprint and ease of mirror-adjustment / cleaning and optical stability.

The vertical alignment of the cavities in our system result in the smallest footprint among those instruments that achieve sub-pptv performance at 1 second integration time. Compared to our present instrument (Sobanski et al., 2016a), and previous versions (Schuster et al., 2009) we have greatly reduced the footprint (factor > 2) and weight (factor 2), which together allow easier transport and enhances the possibility of measurements in confined spaces such as tower-elevators. While it is not possible to compare the “ease of optical adjustment” and optimization of ring-down times with instruments that do not stem from our group, the mirror-tilting mechanism in our latest instrument and its (lack of) response to e.g. mechanical and thermal stress is superior to the use of commercial optical mounts (Sobanski et al., 2016a) as is the ease of mirror removal, cleaning and replacement. These attributes make deployment of the present instrument in confined spaces and non-laboratory environments easier to achieve than our previous setups.

Table 2: Comparison of NO₃ and/or N₂O₅ instruments using optical cavities and designed for field deployment.

Reference	Method	NO ₃ limit ¹	N ₂ O ₅ limit ¹	Footprint (cm × cm)	Height (cm)
Brown et al. (2001)	CRDS	< 1 pptv (1σ 50s)	-	61 × 122 × 122 ²	
Brown et al. (2002b)	CRDS	< 1 pptv (2σ 5s)	< 1 pptv (2σ 5s)	122 × 61	-
Simpson (2003)	CRDS	-	2.4 pptv (2σ 25s)	20 × 30 × 122 ²	
Ball et al. (2004)	BBCEAS	2.5 pptv (1σ 516s)	-	-	-
Bitter et al. (2005)	BBCEAS	1 pptv (1σ 100s)	-	300 × 120	-
Ayers et al. (2005)	CRDS	1.4 pptv (2σ 4.6s)	-	-	-
Dubé et al. (2006)	CRDS	< 1 pptv (1σ 1s)	1 pptv (1σ 1s)	110 × 52.5	-
Langridge et al. (2008)	BBCEAS	< 1 pptv (1σ 10s)	-	-	-
Schuster et al. (2009)	CRDS	2 pptv (1σ 5s)		110 × 40 ³	110 ³
Kennedy et al. (2011)	BBCEAS	< 1 pptv (1σ 2s)	< 1 pptv (1σ 2s)	110 × 55 ⁴	130 ⁴
Wagner et al. (2011)	CRDS	< 1 pptv (1σ 1s)	< 1 pptv (1σ 1s)	110 × 55 ⁴	-
Odame-Ankrah and Osthoff (2011)	CRDS	1.5 pptv (1σ 10s)	2.2 pptv (1σ 10s)	74 × 53	85
Wang et al. (2015)	CRDS	3.2 pptv (2σ 10s)	-	-	-
Sobanski et al. (2016a)	CRDS	< 1 pptv (1σ 1s)	2 pptv (1σ 1s)	130 × 60 ³	155 ³
Wang et al. (2017)	BBCEAS	2.4 pptv (1σ 1s)	2.7 pptv (1σ 1s)	90 × 40 × 25 ²	
Li et al. (2018)	CRDS	2.3 pptv (1σ 2.5s)	3.1 pptv (1σ 2.5s)	110 × 40 × 35 ²	
Nam et al. (2022)	BBCEAS	1.4 pptv (1σ 1s)	-	-	-
This work	CRDS	< 1pptv (1σ 1s)	< 2pptv (1σ 1s)	55 × 55	150

Notes: ¹ LOD or precision (typically reported for BBCEAS). ² Stated as reported, but the optical path is likely horizontally aligned, which increases the footprint. ³ Value based on personal communication. ⁴ Value based on visual estimation.

Referee Comment RC2

This well-written pre-print describes an instrument for the detection of NO_3 and N_2O_5 based on cavity-ring down spectroscopy. The instrument is state-of-the-art in this field and its experimental characterization together with field observations of NO_3 and N_2O_5 are credible and justified in the manuscript. Indeed, several instruments of this type are known in the literature (Brown et al. 2002, Dube et al. 2006, Crowley et al. 2010). Hence the authors should motivate the reasons for developing this instrument better. What kind of scientific measurements can be / will be performed with this instrument that could not be done with similar devices before?

We thank the referee for this positive and careful assessment of our manuscript. We have added text to detail our motivation to build a new instrument:

Our present instrument for measurement of NO_3 (Sobanski et al., 2016a) is a five-channel CRDS with a large footprint (1.3×0.6 m) with a weight of > 100 kg. The large size and weight of this instrument has thus far precluded its deployment outside of our measurement container and measurement of vertical profiles e.g. using a tower-elevator. In addition, while our two previous instruments have successfully measured NO_3 and N_2O_5 (Crowley et al., 2011; Schuster et al., 2009; Sobanski et al., 2016b), they have suffered from drift (presumably caused by thermal and mechanical stress impacting the optical alignment), complete loss of alignment during transport, and involved complex procedures to remove and clean the cavity mirrors, which, under campaign conditions often lead to extended down-periods in which no data were acquired. In addition, a combination of a weak source term for NO_3 (i.e. low O_3 and / or NO_2 mixing ratios) and its high reactivity of NO_3 (e.g. in forested environments) has often led to mixing ratios of NO_3 that are below the limit of detection (LOD) of many instruments that impairs assessment of its role as an oxidant in such environments. While this problem has been partially resolved by this group's measurement of NO_3 -reactivity (Dewald et al., 2025; Dewald et al., 2026; Liebmann et al., 2019; Liebmann et al., 2017), obtaining closure through measurement of NO_3 , its production rate and its reactivity have been limited by the LOD of NO_3 instruments. Our aim in developing the small-footprint instrument described here was to resolve / improve on these issues and problems and enable its deployment in e.g. tower-elevators or small-aircraft. In the following, we describe the operational principles, its design and the results from laboratory characterization measurements as well as its performance during field campaigns.

The instrument has an interesting design and is thoroughly conceptualized; the authors present enough detail to justify the claimed performance (e.g. LOD, Allan variance, inlet loss characterization). Nevertheless, below are a few observations/comments as to where the manuscript could/should potentially be improved:

Line 22-67 (Introduction): The importance of NO_3 and N_2O_5 for the nocturnal atmosphere is well outlined, and all relevant reactions and known facts are comprehensively described. However, the section is missing the motivation for improving detection of NO_3 and N_2O_5 by CRDS. Why is it important to improve some of the engineering aspects of known devices to enable better measurements? What is the envisaged deployment of the instrument and the advancement of field-based detection of NO_3 and N_2O_5 enabled by the instrument?

This comment has been answered in the reply above.

Line 55-57: Broadband methods, such as IBBCEAS, are also common alternatives to time dependent cavity ring-down methods and a couple of examples in the literature should be explicitly mentioned here; not only CEAS per se.

We have referenced the use of BBCEAS:

Broadband cavity enhanced absorption spectroscopy (BBCEAS, see e.g. Fiedler et al. (2003)) and cavity ring-down spectroscopy (CRDS, see e.g. Brown and Stutz (2012))

Line 97: "...installed in an aluminium rack..." How was this done - how is the aluminium frame connected to the carbon fibre tube cage system? Does the different thermal expansion between the carbon fibre tubes and the aluminium impinge on the alignment? See also lines 150/151.

We have addressed this in the following text:

In order to avoid transfer of mechanical stress from the rack to the cavities, the mirror mounts (see below) were attached to the aluminium rack via rubber buffers (60 Shore A, 189-3264, RS PRO) supporting the upper end of each cavity only. To mitigate the rotational force created by the weight of the "hanging" cavity the lower mirror mount is gently pressed against a rubber covered aluminium plate.

Line 105 and Line 119: The authors do not state how the flow is generated. They only mention the "exhaust system". What pump was used? Did you use any scrubber for NO?

There are several alternatives for pumping as described below. The NO is not scrubbed before entering the exhaust system.

Regulated flows through the instrument are exhausted into a vacuum manifold when the instrument is operated in our measurement container or into an external membrane pump (MD 4 T, Vacuubrand) during laboratory operation. Alternatively, the instrument can use a small, in-rack membrane pump (MD 1 VARIO-SP, Vacuubrand).

Line 106: What is the length of the heated inlet? How is the heated inlet of the (NO_3 & N_2O_5) channel thermally isolated from the NO_3 channel inlet? Are these channels thermally fully isolated?

The TD inlet is 20 cm in length. This has been mentioned. We already state that the cavities are insulated using custom made heating / insulation sleeves: "The cavities are insulated with custom-made heating / insulation sleeves (HORST GmbH)" We have added the text:

As the cavities are heavily insulated and about 20 cm apart, there is no significant transfer of heat from the "hot" cavity to the "cold" one.

Line 107/108: Where is the temperature measured - not shown in Figure 1.

Figure 1: We have added the position of multiple temperature sensors (T) and changed the symbol of the thermal dissociation inlet to "TDI" (which includes another temperature sensor as stated in the manuscript). We have modified the text, the Figure and its legend:

All temperature read-and-control units (diraView and Quantrol series, Jumo GmbH) are operated with standard PT1000 sensors (RS PRO) attached to the outside of the glass but within the thermal insulation. While the sensor for the TD inlet is located directly at its center, both cavity temperatures are measured at the midpoint of the length of one of the longer arms. For the heated channel, we use an additional sensor at the T-shape intersection.

The caption has been adjusted accordingly:

Ambient air is sampled through an automatic filter changer, after which NO can be added for zero measurement. The left-hand cavity measures $[\text{NO}_3]$ at room temperature. Sampled air in the right-hand channel passes a TD inlet set to 443 K, ensuring the thermal dissociation of N_2O_5 to measure the sum of $\text{NO}_3 + \text{N}_2\text{O}_5$ at 373 K. The walls of the filter changer and the T-shaped glass tubing are FEP-coated, while every other surface is made from PFA. The cavity mirrors are protected with purge gas, while their chambers are made from anodized aluminium. Two separate laser diodes are used to record ring-down traces with photomultipliers after the transition of bandpass filters.

Line 109/110 & 114/115: What was the aerosol filter porosity? What particle sizes were targeted (1 μm)? How often are filters changed – what criteria were used? (This is indeed discussed later, hence a cross-reference to section 3.5 should be included appropriately.)

We have added a cross-reference:
(details in Section 3.5)

Automated filter changers are non-trivial devices, hence more details on the filter changer would be great in the supplementary material.

Line 113/114: This filter changer was already described by Sobanski et al. (albeit within the supplement) and used for the new 2CH-CRDS instrument after recoating with FEP. Together with minor electronical setting changes, this was implied by “modified from Sobanski et al. (2016)”. To clarify, we now add some details and write:

We use the same filter changer device that was presented by Sobanski et al. (2016a) (which operates similar to that described by Dubé et al. (2006)) and renewed the FEP coating on the inner walls. The device uses a three-station rotary turret plate: By successive rotation of this plate by 120 ° a new filter is inserted from a supply stack, then used within the sampled air and finally ejected. During filter changes, the sample air flow is interrupted to prevent contamination.

Line 116 (&126): The MFCs for the NO line and the purge flows are not shown in Figure 1. The way these flows are controlled should be shown in Figure 1, potentially also together with typical flow rates. This will not overload Figure 1.

Figure 1 has been modified accordingly. We have:

Added four MFCs and related connections for NO line (2) and purge flows (2). Added titration valve, added typical flow rates within the instrument and modified the legend.

Line 138: “... generate a high flow velocity...”. Can you state an estimated value of the flow velocity here?

We now state the estimated flow velocity:

The diameter of the tube is sufficient to guide the laser beam through, but small enough to generate a high flow velocity of $\sim 13 \text{ cm s}^{-1}$ compared to the sample air (3.5 cm s^{-1}) within the pre-exhaust chamber that prevents back diffusion.

Line 141: Including the o-rings schematically in Figure 2 would be helpful.

We have modified Figure 2b and its caption accordingly:

Additionally, O-rings (magenta indicators) are shown to highlight critical seals like the fine adjustment screws and the window.

The three point alignment concept is not well explained. More explanations especially in Figure 2 would be good here. For field work this is critical.

We have modified the text as follows:

The use of long arms to connect the inner mirror-securing ring with the outer sealing part means that applying pressure induces bending of the arm and allows the mirror to tilt. The flexural modulus of the material enables the mirror to return to its original position when the pressure is reduced (i.e., the screw is retracted). Different metals such as stainless steel or spring steel and different arm thicknesses can achieve similar results, but poor adjustability (too high rigidity) and irreversible deformation (elastic limit exceeded) are design challenges. To maximize the stiffness of the mirror mount, the arm thickness needs to be as high as possible.

Our solution was to use a thickness of 2.5 mm which was milled from a 4 mm solid titanium disk.

How are misalignment caused by mechanical vibrations and thermal drift prevented?

We have added:

Titanium was chosen because of its mechanical properties and low thermal expansion coefficient.

Where is the seal made?

We have extended the text as follows:

The window and all metallic components are sealed to the outside using silicone O-rings (magenta circles/lines in Figure 2b), which are recessed into designated grooves.

Line 146-148: What is the distance of the off-axis alignment? What is the $(1/e^2)$ -beam diameter and how is the diameter determined/controlled? How did ring-down times compare between on- and off-axis alignment? Was that studied systematically? What losses are introduced by going "somewhat" off-axis? The authors state that there is only 4 mm diameter tube between the mirror and purge gas/sample air mixing volume. This appears to be critical. Depending on beam diameter there is very little room to "go off-axis".

We have not systematically studied on- and off-axis alignment. In our case, the term "slightly off-axis" is used to emphasize a deviation from a perfect on-axis alignment (light path perpendicularly protruding the center of every optical element). We have modified the text to indicate how far "off-axis" we enter the cavity mirror.

While the upper screws are used to adjust the position of the collimation lens relative to the laser diode, the lower ones are used to adjust the position of the laser mount for slight (< 1 mm) off-axis alignment to avoid back reflections into the laser diode, which can perturb the laser emission spectrum.

Line 160: Sentence structure. "...is driven..., is modulated..." please rephrase, e.g. delete second "is".

Sentence rewritten:

The square-wave modulated laser current (Section 2.5) is driven by a control board (MLDEVAL with MLD203CHB, Thorlabs) and results in an average optical power output of 8 mW (at 25 % duty cycle) after the optical isolator.

Line 172: Band-pass filter not shown in Figure 1. Should be included.

Bandpass filter added to Figure 1.

Line 185: "ring-downs" is a bit casual. Replace by "ring-down decays" or "ring-down waveforms" or "ring-down traces".

Change made:

For each recorded ring-down, we reject the initial 5 μ s after switching off the laser and use the following 600 μ s for fitting. We pre-average 125 individual ring-down traces to smoothen the signal and reduce computational load.

Line 188: If there is no significant difference in the averaging approach, why did the authors not reduce computational overhead by eliminating the averaging of 5 ring-down times for a "1 sec data point". Read out noise?

During the early phase of instrument development, this separate averaging (first ring-down traces, second ring-down times) seemed to improve the noise on 1-second data. Re-evaluation

in the current state showed no significant difference. Since we do not experience computational limitations, the old values are/were kept.

Line 200-205: It would be useful to show the reaction schematic in the supplementary material. Added a new figure to the Supplement. The new Figure S1 shows the schematic of the NO_3 source. Subsequently, figure labels and cross-references have been adjusted.

Figure S1: Schematics of the flow tube NO_3 source. The inflow of NO , O_3 and clean air for dilution is controlled with MFCs (Alicat). A mercury Pen-Ray lamp is used to produce ozone. Due to the high O_3 concentration and large rate coefficient, we estimate the mixing ratio of NO to be significantly less than 1 pptv less than 5 seconds after entering the NO_3 source. The source and thermal dissociation element are temperature controlled by PT1000 sensors at center-length. An O_3 monitor is used to estimate corrections (titration NO , see Section 3.3).

Line 240: "...from newly dissociated NO_3 ..." This is misleading and should read something like: "...from NO_3 formed in the dissociated of N_2O_5 ..."

We have changed the sentence to:

This accounts for a very small fraction of NO_3 that is formed "late" from N_2O_5 dissociation and has insufficient time for reaction with NO during a titration cycle.

Line 247: "...taking an O_3 level of 100 ppbv..."

The ozone concentration in the field varies and is usually probably significantly smaller than 100 ppbv, which is some sort of upper limit. The estimate of a discrepancy of +0.2 pptv is based on this maximum ozone level. The correction is dependent on ozone concentration. How can this be handled in the field? An additional ozone photometer with sufficient sensitivity and integration time would always be required. The same applies to the NO_3 & N_2O_5 channel.

Correct. We have added text related to this:

Even through the correction is small, when deploying the instrument in the field we therefore always make O_3 measurements in parallel.

Line 261: "clear air" -> "clean air" or "zero air" or "synthetic air"

This deals with instrument zeroing with zero-air. We now write:

...and its concentration can vary rather quickly during field measurements and greatly between ambient and zero-air measurements.

Line 265: This is somewhat casually phrased. The Allan variance is not simply defined as the square root of the common 1σ standard deviation.

We have added a more detailed explanation of Allan Deviation and restructured the paragraph. For both channels, the ideal LOD was determined from an Allan Deviation analysis over the respective zero signal. The Allan Deviation is obtained as the square root of the Allan Variance, which is calculated as the averaged squared difference between consecutive pairs of time-averaged (zero) measurements over a given integration time. Here, we use the Overlapping Allan Deviation (oadev by AllanTools.py version 2024.4) to evaluate about 6 hours of nighttime data and under ideal laboratory conditions (stable temperatures, sampling particle-free clean air).

Figure 4 shows the 1σ Allan Deviation for both channels for integration times up to two hours. For short integration times, both channels show the typical decrease related to the declining impact of white noise. Compared to the ideal white noise reduction (thin diagonal lines), the observed decrease is shallower indicating the presence of additional noise source. With increasing integration time, the Allan Deviation begins to rise again, which is associated with drift effects.

Line 270: Figure 4 should ideally not just show a line for each channel but the pivot (data-)points generating the line. The authors may want to consider showing the white noise ideal behaviour, i.e. a straight line with slope of -1/2 in a double log plot.

Figure 4 has been modified with added markers and reduced line width. For both channels, we added lines illustrating ideal behaviour and changed the caption accordingly:

Allan Deviation plots for both cavities based on 1 s data. The integration time of 3 minutes is indicated by the black vertical line. Thin diagonal lines represent the white noise ideal behaviour. The data were recorded while measuring clean air over a period of 6 hours at night under laboratory conditions.

Line 285: “hinder” -> “reduce”

“hinder” has been replaced by “reduce”.

Line 308: “ 98 ± 4 % which is the mean and two standard deviations of all determined T_{max} values.” -> “98% with a 2σ variation of all determined T_{max} values of +2% and -4%.”

Text changed to:

...98 % with a 2σ variation of all determined T_{max} values of ± 4 %.

Table 1: In the table are values that are physically not meaningful; e.g. Pall #3, Cytiva#4. Errors should be capped at 100% transmission. I presume that the error in T_{max} is indeed the *square root* of the covariance of the fit?

While the physical transmission can not be greater than 100 %, we are dealing with real signal and measurements in which sources of bias (i.e. drift in the NO_3 mixing ratio with time) exist. We do not see the benefit of replacing ± 4 % with asymmetric errors. We have changed the notes to Table 1:

The uncertainties of T_{max} were calculated by the square root of the covariances of the fit and do not reflect small NO_3 source fluctuations.

Line 330: After a detailed discussion of NO_3 losses by aerosol filters (including additional data in the supplementary material), the authors reveal that by far the largest loss is caused by the automatic filter changer itself. However, statistics on the establishment of the stated 80 ± 5 % are not presented. The discussion of the filter losses (while interesting from an experimental point of view) seems inappropriately long. More information on the automatic filter changer should be shown instead (what does “multiple times” mean and what were the conditions) and the bulk of the filter loss discussion could go into the Supplement.

Most of the filter transmission discussion and test are already in the SI. We have additionally moved Table 1 to the supplement (now Table S1). We have modified the manuscript text as follows:

When using the automatic filter changer (see Section 2.2), an additional NO_3 transmission factor must be considered. This was determined by the ratio of measured $[\text{NO}_3]$ when passed through the filter changer or through a PFA bypass with negligible NO_3 loss (Schuster et al., 2009). Under normal operating conditions (14 slm sampled at about 920 mbar), six switching intervals (each about 5 minutes of data) were used to determine the average NO_3 transmission (80 ± 5 %) through the filter changer. This value was subsequently verified by another measurement with ten intervals (each 6 minutes) more than a year later.

Line 342/343: Does the clamping of the carbon fiber tubes on aluminium cause additional stress when heated – depends on the clamping design.

The exact cause of the apparent loss in optical alignment (increase in noise) when using a flow of 5000 sccm is not known, but may be related to gas-flow induced temperature changes of the mirror mount away from its “best alignment”. We have amended the text as follows:

In the heated channel, measurements below flow rates of 5000 sccm were excluded due to increased noise in the ring-down signal, presumably caused by changing the temperature of the mirror mounts away from that experienced during the prior optical alignment.

Line 345 – Figure 6: Two axes are not used in Figure 6. The figure would benefit from the upper axis showing the flow rates corresponding to the different residence times.

Rather than clutter the Figure, we have added flow the ranges in the caption.

Figure 6: Determination of wall loss rates (k_{wall}) by variation of the residence times (t) for both channels. The measured values are based on the average and two standard deviations of 3 minutes of data, normalized to the initial value of a mono-exponential fit. The flow ranges were 5000 – 9000 sccm (NO_3 channel) and 5500 – 9000 sccm ($\text{NO}_3 + \text{N}_2\text{O}_5$ channel).

In the caption k_{wall} is called k_w in the main text.

We adjusted the legend to be consistent with the main text.

Line 363: Residence time stated as 0.24 s which is different from the value given in the previous section.

0.24 s refers to the estimated residence time in the absorption path (cavity) and not the whole channel (inlet + cavity). In the previous section the wrong term was used, this has now been corrected:

...the residence times are 0.43 s in the NO_3 channel and 0.34 s in the ($\text{NO}_3 + \text{N}_2\text{O}_5$) channel, ...

Lines 390 & 440: “Iupac” -> “IUPAC”

Change made.

Supplementary Material:

Figure S2: The data shown for filter #1 AW15357 "after ozone treatment" is not physically meaningful. The error bars are too small and the transmission is systematically over 100%

See above