"Interactive comment on "Laser induced fluorescence based detection of atmospheric nitrogen dioxide and comparison of different techniques during the PARADE 2011 field campaign" by Umar Javed et al."

Response: Umar Javed et al.

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"Anonymous Referee #2"

"The manuscript of Umar Javed and colleagues is an interesting study on a new laser induced fluorescence instrument for the measurement of atmospheric nitrogen dioxide. It describes the set-up of this instrument with an emphasis on its calibration system and the analysis of possible cross-sensitivities. An important part of the

10 manuscript focuses on the results of an intercomparison field campaign where different nitrogen dioxide measurement techniques have been compared. Nitrogen dioxide is an important atmospheric trace gas and imposes quite some efforts to perform good measurements with different techniques. This manuscript makes a valuable contribution to improve nitrogen dioxide measurement techniques. I recommend this manuscript for publication; however there are some points that should be addressed before."

15 *Response:* We appreciate the time given by the Anonymous Referee (#2) for the review. The helpful comments of the reviewer will provide more clarity to the draft.

"Specific comments:"

"**L16:** Abstract: I suggest that in the abstract the field campaign PARADE should be mentioned; also the location and

20 time of the field campaign."

Response:

The name of the campaign along location and time is added in the abstract.

"**L 32:** Aircraft emissions as well are directly affecting the free troposphere."

25 **Response:**

Aircraft emissions, as a source for the NO_x in the upper troposphere (Strand and Hov, 1996), are included.

"**L 96:** The wavelength of the laser is given but not the wavelength of the fluorescence."

Response:

30 The NO_2 fluorescence has a broad spectrum. It starts at the excitation wavelength and extends into the infra-red region (Wehry, 1976). But still, the major fraction of the fluorescence still lies in the visible region (Sakurai and Broida, 1969;Sugimoto et al., 1982). In our case, we block the light with the interference filter at wavelengths < 550 nm. The cut-off band of the PMT is at about 890 nm. So the wavelength range of the detection window of the fluorescence signal is roughly between 550-890 nm. Still, we expect the major portion would be in the visible region. This is already explained in the text, so we have added also the lower

35 limit "$\lambda \geq 449nm$" for the emitted fluorescence in "R.2".

"**L 103:** In this context: What is the definition of zero air?"

Response:

The zero air is Synthetic air (hydrocarbon-free) as specified by Westfalen (99,999 mol% pure mixture of 20.5% O_2 in N_2, H_2O <

40 5 ppmv, HC < 0.1 ppmv, NO_x < 0.1 ppmv). Some studies e.g., (Thieser et al., 2016) showed that it is not fully free of NO_2

contamination, though levels are generally much smaller than the 0.1 ppmv specified. They estimate up to 20 ppt NO_2 in their supply of synthetic air cylinders. The Synthetic air was used during the PARADE field campaign for the background measurements of our instrument. The quality of the air is discussed in the section 3 (related to PARADE) of the draft.

Ideally, the zero air should be a replica of ambient-air but without the NO_2. In the past, it has been tried to use scrubbing techniques, based on active charcoal, coated surface with a certain chemical etc., to remove NO_2 from the ambient-air and use the scrubbed air for the background measurements (Matsumoto and Kajii, 2003). This can be done for a lower sampling rate, but at our high sampling flow rates (>4SLM) oversized scrubbing filters would be required to provide sufficient residence times.

"L 125 / L 144: What is the PMT temperature? Is the PMT actively cooled? What causes the background signal? Would the background decrease, if the PMT was cooled down at temperatures below 0°C by an active cooling unit?"

Response:

The internal temperature of the PMT is 0°C. It is regulated by a built-in thermoelectric cooler and this feature is part of the hardware from the manufacturer. We only have the control to regulate the surface temperature of the PMT. This is done externally by using a water chiller at 20°C or 25°C (avoiding condensation) according to manufacturer recommendations. The dark counts on the PMT signal are generally less than 50 counts s^{-1} for the channels used for the NO_2 fluorescence detection. The major reason for the background signal, larger than the dark signal typically by a factor >25, is expected to be fluorescence contamination from the Herriot cell mirrors existing in the red region of wavelength.

"L 223: ". . . at a lower temperature . . ." Which temperature?"

Response:

The sentence was to give a general statement.

Under lower temperature conditions, the reaction between NO and O_3 slows down. This can lead to a change in the conversion efficiency from NO to NO_2. In our case, many electrical parts (electronic valves, ozone generator, and mass flow controllers) are installed inside the calibration unit. In a fully operational mode for one day, the temperature build up in the calibration unit is 8-10°C higher than ambient temperatures. From our experience/observations, conditions with a temperature lower than 20°C inside the calibrator do not occur.

"L 237: Is there an explanation for the change in sensitivity? What is the range of sensitivity change?"

Response:

Generally, some factors can contribute to a change in the sensitivity e.g., stability of the optics alignment, cleanness of the optics, temperature related effect of electronics, stability of the calibration signal etc. Frequent calibrations were performed during the PARADE-2011 to assess the stability of the sensitivity. Based on calibrations (> 130) performed during PARADE-2011 by using dry-air (< 25 ppm of water), the relative variation in the sensitivity of the instrument was better than ± 2.7 % (1σ). Further, the sensitivity of the instrument decreases by 5 % (relative to the dry-air) at 1 % of atmospheric H_2O vapour. This is corrected by using simultaneous measurement of H_2O vapour.

"L 268: Figure 8 shows the relative precision obtained during different calibrations. But how exactly do you determine the relative precision? Does it include for example only the variability of the sensitivity or the variability of the background, etc.? Please describe in more detail."
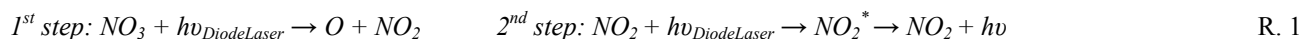
Response:

The text in this section of the draft is simplified and the figure is now presented as a function of NO_2 mixing ratios. The relative precision 0.5 % (1 min^{-1}) was calculated based on the standard deviation of the PMT NO_2-signal (in s^{-1} time resolution) during the calibration period for different NO_2 concentrations. Since the selected signals were based on higher levels of NO_2 concentrations (> 0.5 ppb). So the number 0.5 % (1 min^{-1}) is true representative of precision at higher NO_2 concentrations.

85 Standard deviation of signals at different NO_2 concentrations can be extrapolated to zero for determination of the precision at background level. It can also be calculated from the standard deviation of the zero-air signal. Both approaches give a similar result of about 3 ppt precision for our instrument. Hence, the total precision was defined by considering the both values i.e., 0.5% (1 min^{-1}) + 3 ppt (1σ).

90 <u>**"L 318:** R6 is not a valid chemical reaction (both sides of the reaction arrow should be balanced)."</u>

Response:

It is modified as follows

1st step: $NO_3 + h\upsilon_{DiodeLaser} \rightarrow O + NO_2$ 2nd step: $NO_2 + h\upsilon_{DiodeLaser} \rightarrow NO_2^* \rightarrow NO_2 + h\upsilon$ R. 1

95 <u>**"L 337:** I agree the short residence time of the sample air inside the instruments minimizes the thermal decomposition of the respective species. But please give at least a few calculated lifetimes against thermal decomposition for the most important interfering gases that illustrate this statement."</u>

Response:

At this line, the discussion was referring to the sampling line prior to the orifice. This information is further clarified in the text.

100 The ambient lifetime based on thermal decomposition is added for different species. The lifetime inside the instrument would be much larger as the cell pressure is about a factor 100 smaller compared to the ambient pressure.

<u>**"L505:** I suggest that in the summary the authors underline the main advantage and disadvantage of this measuring system, also in comparison with other measurement techniques. What is the future of Gandalf (besides LOTR)? Are</u>

105 <u>there specific plans to use this instrument during other field campaigns?"</u>

Response:

Following "sentences" are included in the summary of the draft.

"In general, all instruments performed well. GANDALF showed a very good correlation ($R^2 \approx 0.99$) in comparison to other in situ instruments (Fig. S11 in the supplement) and even with LP-DOAS the correlation was $R^2 \approx 0.9$. The differences in the

110 absolute values were within the specified range of individual measurement errors. The main advantages and disadvantages of GANDALF compared to the other instruments are summarized as follows.

In comparison to the CRDS instrument, the main advantage for GANDALF is that the sampling can be achieved without an inlet-line. This is not possible for the close-path CRDS system. This provides the capability of the detection at ambient temperature for GANDALF, which is especially of an advantage for aircraft measurements of NO_2 where avoiding

115 interference from CH_3OONO_2 and HO_2NO_2 (via unwanted thermal dissociation) is very important. The requirement of calibration is the main disadvantage for GANDALF compared to CRDS (absolute technique). However, both instruments require frequent zero-air measurements. The limit of detection for both instruments was of similar magnitude during PARADE-2011.

The CE-DOAS instrument is comparable to the CRDS instrument. It also needs frequent background measurements but no absolute calibration. GANDALF has a much better in the sensitivity compared to the CE-DOAS instrument. During

120 PARADE-2011, the detection limit for CE-DOAS was around 300 ppt (2σ, 30 s) while for GANDALF the detection limit was

5 – 10 ppt (min^{-1}). A low-cell-pressure is typically required to achieve a good sensitivity for LIF instruments (Table 1) while the detection in the other instruments (CRDS and CE-DOAS) is performed at sub-ambient pressures (>800 hPa). The requirement of calibration and usage of a larger scroll-pump (to achieve a low-cell-pressure) adds extra effort/cost to the GANDALF measurements.

125   The basic requirements for a calibration and background measurements are same in CLD and GANDALF. In the case of CLD, the maintenance is relatively easy compared to GANDALF. But GANDALF provides a direct detection of NO_2 compared to the indirect detection of NO_2 (via $NO_2 \rightarrow NO$) in the CLD instrument. The sensitivity of GANDALF was better than the CLD instrument during PARADE-2011.

     LP-DOAS does not require calibration or the zero-air measurement. For this reason, the uncertainty of the data is also
130 very small compared to GANDALF or other in situ measurements. This is the main advantage of the LP-DOAS instrument over GANDALF. The restriction of this method is that it does not provide a local measurement. Also, the temporal resolution is limited compared to other in situ instruments. The sensitivity of the LP-DOAS instrument generally depends on the length of a light path, and variations in visibility. It was on average about 0.11 ppb (2σ, 11 s) during PARADE-2011.

     Outlook: NO_2 in the free troposphere is variable (seasonally) and generally lower than 50 ppt (Gil-Ojeda et al., 2015).
135 Depending on the location, in the free troposphere and the marine boundary layer, NO_2 can be as low as a few ppt (Beygi et al., 2011;Schreier et al., 2016). These NO_2 ranges are below the detection limit for the instrument (GANDALF) for short time resolutions of 1s, for example. Improvements for future use on aircraft are possible by further reducing the background of the instrument. Since most of the background signal is from the fluorescence contamination of the Herriot's cell mirrors, this could be avoided by using a single beam (as demonstrated by (Di Carlo et al., 2013)) of the laser for detection without a Herriott cell or
140 by using different coatings on the Herriott cell mirrors to increase reflectivity and reduce fluorescence. The current CW diode laser of the instrument may be replaced by an already available mono-mode dual diode laser [λ (online) = 445 nm and λ (offline) = 442 nm] for on and off resonance measurements of NO_2. Replacement of current laser to the dual diode laser will decrease partially the dependency on the frequent zero-air background measurements.

     The formation of $RONO_2$ is an important sink for NO_x and effects the ozone production efficiency (Browne and Cohen,
145 2012). The accurate measurement of $RONO_2$ is important for the assessment of local O_3 abundances. LIF systems in combination with the thermal dissociation method (Day et al., 2002) are also used and very useful for the detection of $RONO_2$, $RONO_2$, and HNO_3. GANDALF will be capable (currently under development) of measuring these species by coupling with the thermal dissociation inlets. This further development could provide very useful data for the future to constrain models."

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"**L 508:** The authors are mentioning that the instrument is capable for measurements throughout the troposphere with a time resolution of 1 s to 1 min. However, the whole preceding discussion has been focused on ground based measurements at a time resolution of 1 min. Also the concentration of NO2 in the free troposphere is much lower than in the boundary layer. LOD would increase significantly if you reduced the sampling time from 60 s to 1s. Please
155 outline in short what improvements would be necessary to achieve this goal."

Response:

NO_2 in the free troposphere is variable (seasonally) and generally lower than 50 ppt (Gil-Ojeda et al., 2015). Depending on the location, in the free troposphere and the marine boundary layer, NO_2 can be as low as a few ppt (Beygi et al., 2011;Schreier et al., 2016). These NO_2 ranges are below the detection limit for the instrument for short time resolutions of 1s, for example.
160 Improvements for future use on aircraft are possible by further reducing the background of the instrument. Since most of the

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background signal is from the fluorescence contamination of the Herriot's cell mirrors, this could be avoided by using a single beam (as demonstrated by (Di Carlo et al., 2013)) of the laser for detection without a Herriott cell or by using different coatings on the Herriott cell mirrors to increase reflectivity and reduce fluorescence.

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"Technical Corrections:"

"L 298: . . . about 8 time higher than the cross section of . . ."
Response:
170   It is done.

"Tables:"

"Table 3: ±δ – explanation in the caption is missing."
175   **Response:**
It is done.

"Table 4: Uncomplete caption - which ratios?"
Response:
180   It is modified as follows.
"Average the ratios of NO_2 measurements from the different instruments, taking into account all available data from PARADE-2011."

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"Figures:"
"In general the figure captions are often not sufficient in explaining the content of the figures."
"Figure 1: The numbers in the caption of this figure have different orientations and do not facilitate the reading. All numbers should have the same conventional orientation (like the numbers "9, 10, . . ."?. "SF" - This is not quite
190   consistently. All other objects of this figure stand for units of the instrument. "Sampling flow" is the gas stream into the instrument (I assume) and not part of the instrument. So it would be more suitable to write: Inlet orifice or sampling flow line, or . . . ."
Response:
The numbering in the figure/text is simplified, and synchronized.
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"Figure 4: . . . as a function of O3 concentration in . . . Please explain "arb" in the y-axis label. The caption is incomplete; "Box-Model NO2" is not mentioned."
Response:
It is modified as follows.

200 "The PMT NO$_2$ signals in counts (cts) are shown as a function of O$_3$ concentrations in the calibrator (y-axis scale on the left side), together with NO$_2$ calculated from a box model of the NO$_2$ production in the calibrator (y-axis scale on the right side)."

"Figure 5: "also theoretically calculated residence time (7.73s). . ." I assume the red line in this figure is meant."

Response:

205 Yes, the red line is showing the theoretical residence time. This information is now added to the caption in the draft.

"Figure 6: What do you mean by calibration signal? I assume it is the number of counts at the PMT?"

Response:

210 Yes, these are counts at the PMT. It is corrected in the caption.

"L 250 – L 265 / Figure 7: The description in the text and in the figure caption is a little bit confusing and should be clarified. E.g. an ozone analyzer is shown in the figure but not mentioned in the text. In the text blue, red and white arrows are mentioned; in the figure you find additionally orange arrows. In the text only red arrows in L2 are

215 mentioned, but there also white arrows found in L2. I assume that the valves EV3 and EV2 have to point at the position P1(P2) at the same time? Above the Gandalf-box in Figure 7 there are three times written "4100 sscm" in different colors and different orientation. As long as you do not discuss it explicitly in the text, one "4100 sccm" label is enough. Figure caption: "outdoor – operations"? - Better during field campaigns or during the PARADE field campaign."

220 **Response:**

The ozone analyser is used to check the concentration of O$_3$ in the calibration gas, and this information is now included in the text. The orange arrow has been removed. The white arrow was representing ambient air flow during along the overflow of the calibration gas. P1 and P2 where switched around. The figure has been revised along with the text to correct it and make it easier to understand in the updated version of the draft.

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"Figure 8: JD = Julian Days. The formulation of this caption is a little bit unclear. Please improve."

Response:

The relative precision in this figure is now shown as a function of NO$_2$ mixing ratios instead of time. The caption of the figure is

230 also accordingly changed.

"Figure 12 and 13: "Ratios. . ." – The readability would be improved if you would write in the caption which ratio is meant. Please choose the same y-scale for all figures."

Response:

235 All the figures are modified for as suggested by the reviewer.

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