

**“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 #3”**

10 “This manuscript describes a laser induced fluorescence instrument that has been developed for ground and aircraft based measurements of NO<sub>2</sub>. It describes the setup of the instrument, its calibration and examines possible interferences. There is also a description of data taken with the instrument during a field campaign that involved a range of different NO<sub>2</sub> detection techniques and a comparison of the different datasets is made. NO<sub>2</sub> is a key atmospheric constituent and it is important to develop new direct measurement techniques for it, making this type of work very topical. The manuscript is generally well written and provides an important reference for others wishing to develop an LIF instrument for NO<sub>2</sub> detection. I recommend publication subject to the authors dealing with the following relatively minor comments.”

15 **Response:** We are grateful for the Anonymous Referee (#3) for accepting the draft for the review and giving time for the useful comments on the draft.

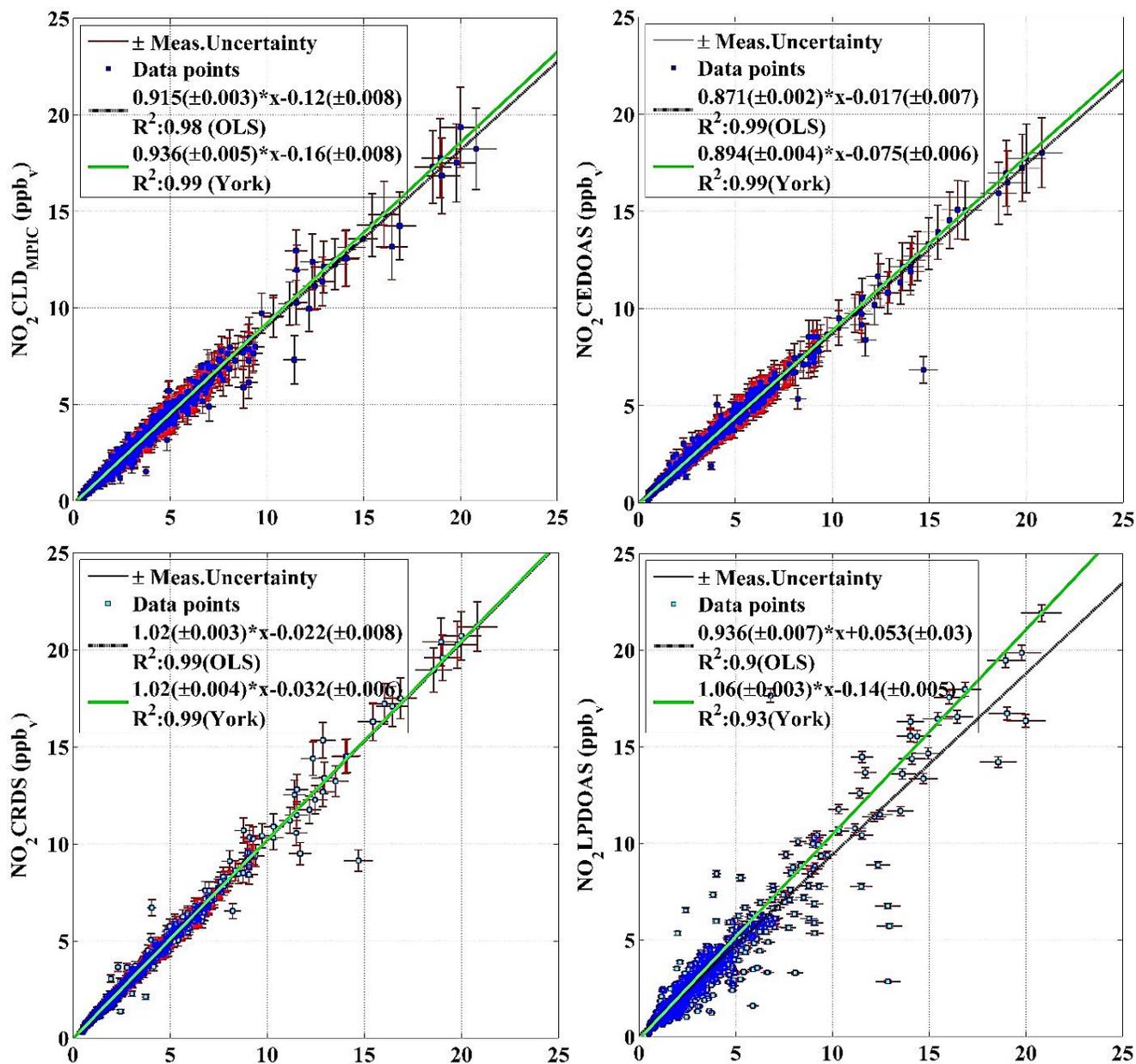
**“Specific comments:”**

20 “On line 254 it is stated that frequent zero-air measurements are necessary to monitor changes in the background signal. This is important as presumably the addition of air with zero NO<sub>2</sub> in it is the only way that the background signal of the instrument can be measured? I therefore think that more discussion should be had into this. Firstly, how is the zero air generated, is it just from a cylinder or is there some further scrubbing carried out? How do the authors know how much NO<sub>2</sub> is in their zero air, has it been measured? Some discussion should be had as to how the quality of the zero air effects the accuracy of the instrument.”

25 **Response:**

Yes, the zero NO<sub>2</sub> (zero air) measurements were the only way to determine the background of the instrument for the setup used in PARADE-2011. The zero air was directly used from the cylinder (Synthetic air, hydrocarbon free) without any extra scrubbing method. The discussion about the zero air is part of the PARADE-2011 field campaign. It is described in the section “3.1 NO<sub>2</sub> inter-comparison during PARADE (‘GANDALF’)”. For the gas supply, a gas bundle (12 × 50 L × ~200bar) was used during the campaign. We did not know the absolute value of NO<sub>2</sub> in the zero air for PARADE-2011. However, we observed differences of up to ± 8 ppt in 70 % (1σ) of the hourly based successive background measurements (> 500). This variability can be a good indicator for the uncertainty in the zero air. A NO<sub>2</sub>-contamination in zero air will not impact the precision of the instrument but (accuracy) it would lead to underestimate the ambient NO<sub>2</sub>.

35 Another indication that the NO<sub>2</sub> contamination in zero air used during PARADE-2011 was less than GANDALF’s detection limit is that in the data analysis the y-intercept of other NO<sub>2</sub> in situ instruments (y-axis) vs GANDALF (x-axis) showed always a negative number. If the GANDALF zero-measurements would have significant NO<sub>2</sub> contamination the y-intercept should be positive.



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Figure 1: The individual correlation of different NO<sub>2</sub> instruments (y-axis) versus GANDALF (x-axis) is shown for available 10 minutes data averages. The two different fitting procedures i.e. based on least square fit (Bevington and Robinson, 1992) and York method (York et al., 2004) are applied.

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"In the instrument description section I feel that a diagram showing the timing of the laser pulse, PMT detection and fluorescence signal would be beneficial. All the information is there in the paragraph but a diagram would make things much clearer."

**Response:**

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A figure (Fig. S4) showing the raw data for the laser cycle was provided in the supplement of the draft. We have transferred (with modification) this figure from supplement to the main draft as part of the "Fig. 2".

55 “On line 144 it is stated that the PMT and laser are kept at a constant temperature by a water chiller but at what temperature? Would lowering the temperature help with reducing background? Or conversely if no cooling was present, which may make the instrument easier to operate on an aircraft, how would this affect instrument performance?”

**Response:**

60 The surface temperature of the PMT and laser is kept at a temperature of 20°C or 25°C (avoiding condensation) by circulating water. This provides the heat sink for the internal thermoelectric cooling of the PMT (@ 0°C) and laser (@ 25°C). The internal cooling is the default setting from the manufacturer.

65 The internal temperature cannot be regulated by an external cooling. The external temperature should be in the range of 5-35°C along a sufficient heat exchange system (fan cooling, water circulation etc.). Moreover, the dark counts on the PMT signal are in the order of  $< 50 \text{ counts s}^{-1}$  for the channels used for the NO<sub>2</sub> 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. For a stable (parameters like power, wavelength, shape of the beam etc.) laser operation, an external temperature range is within 15-30°C. This range is sufficient to keep the internal temperature of the laser at 25°C. A laser operation out of the specified range would lead to shut-off/potentially damage the laser.

70 “On line 199 it is stated that in the calibration system, about 99% of the NO is consumed by titration with O<sub>3</sub> to produce the NO<sub>2</sub>. Why do the authors choose to titrate this much? Surely there is a danger that they could have more O<sub>3</sub> than NO in the system and hence have the potential for secondary chemistry to affect the amount of NO<sub>2</sub> present? Would it not be better to titrate around 80% of the NO to NO<sub>2</sub>?”

**Response:**

75 The secondary chemistry will always be present (from the beginning) regardless of a partial or full titration. Only the net impact would be larger/smaller with full/partial titration, respectively. Our model simulations/lab experiments have shown that the impact of secondary chemistry in our system was only around 1 %. These results were discussed in the earlier section (lines 178-195) of the submitted draft.

80 “In the abstract it is stated that the instrument could be used for airborne measurements of NO<sub>2</sub> however there is very little discussion of this in the manuscript. There should at least be some discussion as to how the instrument precision and detection limit would change for 1 second averaging (which would be required for aircraft work) and how this compares to the potentially lower levels of NO<sub>2</sub> present in the free troposphere.”

**Response:**

85 The following “discussion” is included in to the summary of the paper.

90 “NO<sub>2</sub> 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<sub>2</sub> can be as low as a few ppt (Beygi et al., 2011;Schreier et al., 2016). These NO<sub>2</sub> ranges are below the detection limit for the instrument for short time resolutions of down to 1s. 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 by using different coatings on the Herriott cell mirrors to increase reflectivity and reduce fluorescence.”

**“Technical:”**

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**“Figure 1: It would be clearer if the numbers were all the same way up on the page.”**

**Response:**

In the revised version of the draft, the numbers are synchronized with the text as suggested by the reviewer.

100 **“Reaction 2: what is the wavelength of the fluorescence?”**

**Response:**

The NO<sub>2</sub> fluorescence has a broad spectrum. It starts near 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 until 553 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 553-890 nm. Still, we expect the major portion would be in the visible region. So we have added only the lower limit “ $\lambda \geq 449nm$ ” for the fluorescence in “R.2”.

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