

Response to Anonymous Referee #1

We are grateful to the first anonymous reviewer for his review and the valuable comments which helped improving our manuscript. For clarity, the comments are reproduced in blue below, followed by our replies.

Abstract and later discussion: A clear motivation for the investigation of the OPR sensitivity to NO additions is missing. Some hint in the abstract and further explanation in the text would help the reader to better understand the purpose of this investigation.

As suggested by the reviewer we modified the abstract and the introduction to motivate the investigation of the OPR sensitivity to NO as follows (changes in bold italics):

“... However, an attempt was made to investigate the OPR sensitivity to NO_x by adding NO inside the instrument. This type of investigations ***allows checking whether our understanding of the turnover point between NO_x-limited and NO_x-saturated regimes of ozone production is well understood and*** does not require measuring ambient OPR but only probing the change in ozone production when NO is added. During IRRONIC, changes in ozone production rates ranging from the limit of detection (3σ) of 6.2 ppbv h⁻¹ up to 20 ppbv h⁻¹ were observed when 6 ppbv of NO was added into the flow tubes.”

We also modified the following paragraph in the introduction section:

“When ozone is produced, reactions of peroxy radicals with NO also lead to the formation of OH, which can then oxidize other molecules of VOCs to produce more peroxy radicals, and as a consequence, more ozone. The propagation chemistry between RO_x (OH, HO₂ and RO₂) radicals, which fuels ozone production, is terminated either by NO_x-RO_x reactions or by cross reactions of RO_x radicals in NO-rich and NO_x-poor environments, respectively. These two types of termination reactions lead to different regimes of ozone production referred as NO_x-limited or NO_x-saturated when the rate of ozone production increases or decreases with NO_x, respectively. The turnover point between the two regimes depends on NO_x concentrations, VOC reactivity, and radical production rates (Kleinman, 2005). Since different air quality regulations have to be implemented for the two different regimes, i.e either NO_x or VOC emission regulations, ***investigating the sensitivity of ozone production rates to its precursors during field studies, such as NO_x, is important to test our understanding of the turnover point.*** Understanding this complex and non-linear radical chemistry is key for the design of efficient emission control strategies.”

p8: How is the zeroing of the CAPS monitor done? How stable was the zero and what is the uncertainty of the NO₂ measurement and the end of the P(O_x) measurement connected to this issue?

The zero was checked frequently during the field campaign by providing dry zero air to the monitor and was found to change by less than 0.3 ppbv over 12 hours. It is worth noting that a slow drift of the zero does not impact the measurements since the same CAPS monitor was used to measure Ox at the exit of both flow tubes with a switching time of 1 minute. The calculation of P(O₃) implies a subtraction of the measured Ox concentrations, which cancels out any offset in the monitor's zero.

The CAPS monitor was calibrated with a NO₂ standard mixture certified at 190±3 ppb (2σ) by LNE (French National Metrology Institute). This uncertainty of 1.5% from the NO₂ calibration will propagate in quadrature to P(O₃).

These two points have been clarified in the manuscript in section 2.1.

p14 I3: Is there an influence from the 4m long heated inlet line on the Ox concentration?

No tests were performed to check whether the heated lines could lead to a change in Ox concentrations. The rationale behind the use of these lines was to make sure to get the best transmission of Ox species from the flow tubes to the O₃-to-NO₂ converter and to avoid any condensation of water when the lines are sent inside the laboratory for quantification with the CAPS monitor.

p14 I19: It is not clear what is meant by keeping the NO level constant for days for the NOx additions every 40 min.

The NO addition was turned ON and OFF every 40 minutes all along the campaign. The level of NO added in the flow tubes when the addition was turned ON was kept at a constant level for several days. For instance, the flow rate of NO was adjusted to get an addition of 6 ppbv for the time period shown in Figure 8 (10-14 July). The flow was adjusted to other values during other time periods, leading to different mixing ratios of NO. We modified the manuscript to clarify this point.

p16 I6-8: Is there an influence from nighttime chemistry Ox losses (NO₃/N₂O₅ chemistry) expected in the dark tube compared to the illuminated tube?

We do not expect a different impact of the NO₃/N₂O₅ chemistry between the reference and ambient flow tubes during daytime for the reason that the filter covering the tube does not strongly affect J(NO₃). A spectroradiometer (METCON) was used to quantify the change in J-values due to the absorption of the Ultem film. These measurements showed that J(NO₃) was reduced by less than 20%, leading to the conclusion that the photolysis frequency of NO₃ in the reference tube was still high enough to keep NO₃ at a similar level than in the ambient flow tube, which is negligible during daytime.

p22 / Fig. 5: Why is the NO still relatively high in the dark tube? If this is due to photolysis, why is sunlight not further suppressed? What is the impact of the residual NO on the P(O₃) measurement?

As shown in Fig. S6, NO mixing ratios range from 10-200 ppt for 30 May after 271 s of residence time in the reference (dark) flow tube. As noted by the reviewer, these mixing ratios are larger than what is expected if ambient NO is titrated by O₃ in the flow tube without any other process to reform NO. For this day, NO mixing ratios at the exit of the reference flow tube should range from 0.05-100 ppt when the measured ambient ozone mixing ratios are considered. As mentioned above, the

transmission of the Ultem filter was characterized using a spectroradiometer. These measurements showed that $J(\text{NO}_2)$ in the reference flow tube is approximately 2% of ambient $J(\text{NO}_2)$, which is sufficient to convert a fraction of NO_2 into NO , leading to higher NO mixing ratios than expected.

This residual NO contributes to ozone formation in the reference flow tube as shown in Figure 6 for 30 May.

Section 3.2.2: I was searching for the assessment of the impact in the sections before. Maybe the authors want to integrate the content of section 3.2.2 in the discussion of the results before.

We thank the reviewer for this suggestion. However, including the content of section 3.2.2 in the previous discussion will make the discussion more complex and we decided to keep section 3.2.2 as is for the sake of clarity.

Technical points: p2 l5: disturbs instead of disturb ; p12 l14: There is a double point after the equation that might not be necessary ; p12 l21: bias instead of Bias ; p15 l25: subscript in Ox ; p16 l3: subscript in P(Ox) ; p17 l11: revealed instead of reveal ; p29 l15: subscript in P(Ox)

These corrections have been done.