

Response to reviewers for the paper “Nitrate radical generation via continuous generation of dinitrogen pentoxide in a laminar flow reactor coupled to an oxidation flow reactor.”

We thank the referee for his/her comments on our paper. To guide the review process, we have copied the referee’s comments in black text. Our responses are in blue text. Alterations to the paper are indicated in bold text below and in annotations to the revised manuscript.

Anonymous Referee #2

General comments.

1. a) Section 2.2.1, the section cited some references about the wall loss of NO₃ and N₂O₅ in Teflon/Pyrex tube, and the NO₃ and N₂O₅ wall loss in LFR and OFR is extrapolating or interpolation based on the reported results, which weak the results as the wall loss of NO₃ and N₂O₅ in the system is an important source of uncertainty. The lab quantification of the wall loss in LFR and OFR in the future works can further improve the value of this study.

Our results suggest that NO₃ wall loss is not an important source of uncertainty because NO₃ is too short-lived for NO₃ wall loss to compete with NO₃ oxidative loss. We modified the text as follows to underscore the importance of characterizing N₂O₅ wall loss rates for a specific LFR-OFR configuration (changes bolded):

P12, L8-12: “Because OFR-iN₂O₅ can continuously generate N₂O₅ and NO₃ at room temperature, it is significantly easier to apply in continuous flow reactor studies than related techniques. However, in addition to the aforementioned considerations, high N₂O₅ and HNO₃ concentrations that are generated using OFR-iN₂O₅ complicate the application of techniques such as iodide-adduct chemical ionization mass spectrometry due to efficient reactions between the iodide reagent ion and N₂O₅ or HNO₃ (Lee et al.,2014). **Additionally, the humidity-dependent N₂O₅ wall loss rate must be accurately characterized to model the performance of a specific OFR-iN₂O₅ configuration.**”

b) Additionally, page 5, line 9-10, the fixed condition of OFR is ambiguous, please clear it, at least add the simulation results in SI.

We modified the text as follows (changes bolded):

P5, L6-10: “Published k_{wLFR,NO_3} values onto tubing with 1 cm (**Teflon**) and 4 cm (**Pyrex**) ID are 0.2 and 0.1 s⁻¹ respectively [...] Assuming k_w is inversely proportional to the internal diameter of the tube, we assumed $k_{wLFR,NO_3} = 0.15$ s⁻¹. Extrapolating this value to the OFR yielded $k_{wOFR,NO_3} = 0.02$ s⁻¹. At fixed OFR-iN₂O₅ conditions **that are summarized in Table S3**, varying k_{wLFR,NO_3} between 0 and 0.3 s⁻¹ changed NO_{3exp} achieved in the OFR by 0.3%.”

We added the following table to the Supplement:

Table S3. Sensitivity analysis of the effect of varying k_{wLFR,NO_3} on NO_{3exp} . The following inputs to the KinSim mechanism were assumed: $[NO_2]_{0,LFR} = [O_3]_{0,LFR} = 300$ ppm, $T_{LFR} = T_{OFR} = 24^\circ C$, $RH_{LFR} = RH_{OFR} = 1\%$, $k_{wLFR,N_2O_5} = 0.1 s^{-1}$, $k_{wOFR,N_2O_5} = 0.014 s^{-1}$, $\tau_{LFR} = 20$ s, $\tau_{OFR} = 120$ s, dilution factor = 4.4 between LFR and OFR.

| $k_{wLFR,NO_3} [s^{-1}]$ | $NO_{3exp} [\text{molecules cm}^{-3} \text{ s}]$ | Normalized NO_{3exp} |
|--------------------------|--|------------------------|
| 0 | 1.277×10^{14} | 1 |
| 0.1 | 1.275×10^{14} | 0.9984 |
| 0.2 | 1.273×10^{14} | 0.9969 |
| 0.3 | 1.272×10^{14} | 0.9965 |

c) Page 5, line 11-13, the Extrapolating results is confuse, the reference said 0.04 and 0.009 s⁻¹ corresponding to ID (4 and 7 cm), what is corresponding parameter of the k_{wLFR} of 0.07 and 0.03 s⁻¹ mentioned here?

We assumed $k_{wLFR,N_2O_5} = 0.05 s^{-1}$ by calculating the average of the cited $k_{wLFR,N_2O_5} = 0.03$ and $0.07 s^{-1}$ values that were obtained after extrapolating to the ID of the LFR. We clarified this by modifying the text as follows (changes bolded):

P5, L11-13: “Published k_{w,N_2O_5} values onto dry (RH≈20%) Pyrex/PFA tubing with 4 and 7 cm ID are 0.04 and 0.009 s⁻¹ [...] Extrapolating these values to the LFR used here **and then averaging them together yielded** $k_{w,N_2O_5} = 0.05 s^{-1}$ **that was applied** in the LFR-KinSim model.”

Specific comments.

- Page 2, line 29-34, this introduction of the LFR is confusing. The authors can use a schematic figure to show more details about the OFR-iN₂O₅ (rather than Figure 1 from references), which would increase the paper’s readability.

Figure 1 in this manuscript, reproduced below, already shows the OFR-iN₂O₅ schematic that we think the reviewer is requesting:

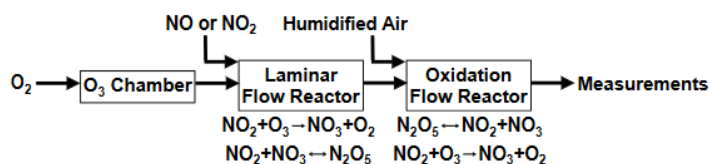


Figure 1. Process flow diagram of the OFR-iN₂O₅ technique used to generate nitrate radicals (NO₃).

We are assuming that the references to Wood et al. (2003) and Boyd et al. (2015) caused the confusion, based on the reviewer’s statement regarding “Figure 1 from references”. To clarify this section, we modified the text as follows (changed bolded):

P2, L29-31: “Figure 1 shows a process flow diagram of the OFR-iN₂O₅ method. Separate flows containing NO₂ and O₃ were input to a PFA tube with 2.54 cm outer diameter, 2.22 cm inner diameter, and 152.4 cm length that was operated as an LFR. **Previous studies used a similar process to generate N₂O₅** (Wood et al., 2003; Boyd et al., 2015) **although the LFR materials, flow rates, and reagent concentrations were different.**”

3. Page 4, line 8. Romanini et al. (1997) is not the right reference of the IBBCEAS principle, I suggest the author replace it by e.g., Fiedler et al., 2003.(Fiedler, S. E., Hese, A., and Ruth, A. A.: Incoherent broad-band cavity-enhanced absorption spectroscopy, Chem Phys Lett, 371, 284-294, 2003.)

We made the substitution suggested by the reviewer.

4. In Eq .2 the kNO_2 or kNO_3 should revised to kNO_2+RO_2 or kNO_3+RO_2 , the similar change also applied in Eq. 3 and Eq. 4

We made the revisions suggested by the reviewer.