

## **Response to reviewers:**

### **The Caltech Photooxidation Flow Tube Reactor – I: Design and Fluid Dynamics**

We sincerely thank the four anonymous reviewers and Dr. Andrew Lambe for valuable suggestions. We accept most of the reviewers' suggestions and have made substantial revisions. Here we list the major changes to the current version:

1. We have rewritten the **Introduction** to clarify the goal of building the CPOT and to carry out comparison with existing flow tube reactors.
2. We have rewritten and added two new sections in **Section 2 Design and Experimental Setup**:
  - **Section 2.2 Photolytic Environment** regarding the quantification of light intensity, details are discussed in **Appendix A**, and the light spectrum is shown in **Fig. 2**;
  - **Section 2.6 Photochemical Model** regarding the construction of a basic photochemical model.
3. We have moved the theoretical contents about diffusive penetration efficiency, Taylor dispersion, and particle motion trajectory that contain a large number of equations to the appendices as **Appendices D, E, and F**.
4. **Section 5.1 Experimental Evaluation of Penetration Efficiency and RTD** has been divided into two new sections:
  - **Section 5.1 Experimental Evaluation of Penetration Efficiency**:
    - a. We have carried out additional experiments to address the loss fraction of gas-phase species to the static mixer as a function of relative humidity in **Section 5.1.1**, and **Fig. 9** is updated with four subplots.
    - b. We have added a new paragraph and **Fig. 10** in **Section 5.1.2** discussing about the impact of coagulation on particle size distribution.
  - **Section 5.2 Experimental Evaluation of RTD**
5. **Section 5.2.1 and 5.2.2** has been emerged as a whole section. In the new version, it is **Section 5.3 Non-ideal Flow in the Reactor**.
6. We have added **Section 6 Photochemical Model** talking about the 1D axially-dispersed plug flow reactor (AD-PFR) photochemical model and **Table 1** summarizing the simulated OH exposure that can be achieved by the reactor.
7. We have rewritten the **Conclusions** focusing on the new findings of this work.

8. We have changed the manuscript title.

With these major modifications, particularly the addition of the photolytic environment and a photochemical model, we believe that this manuscript is significantly stronger and more independent. We now consider this manuscript as a stand-alone publication, as opposed to the original plan of publishing a following publication to further characterize the CPOT.

We decided to remove “I” in the title and retitled the paper as “**The Caltech Photooxidation Flow Tube Reactor - Design, Fluid Dynamics and Characterization**”.

Below are our point by point responses (in blue). All the changes are marked in the revised paper. The page and line numbers in the response correspond to the revised version.

## **Response to Anonymous Referee #1**

### **General comments:**

Huang et al. presents a nice manuscript about the new CalTech Photooxidation Flow Tube Reactor (CPOT), which will enable them to join the dozens of research groups who have been using Oxidation Flow Reactors to study the secondary particles and their properties for oxidation times scales appropriate for the atmosphere for a decade. The manuscript is well written and well organized. It contains lots of nice color figures and drawings and solid analyses. However, there are some errors and omissions which must first be addressed, but when they are, the manuscript will be suitable for AMT.

[We thank the reviewer for the valuable information about the PAM reactor and the constructive suggestions on this manuscript.](#)

### **Specific comments:**

When designing a flow reactor or chamber of any sort, the designer needs to consider how the flow reactor or chamber will be used. There are always compromises because there is no perfect flow reactor or chamber, particularly for atmospheric pressure. For instance, if you want to relate time in the reaction to reaction time, then you will have enhanced wall interactions because that is how this characteristic is achieved. For a flow tube that is at atmospheric pressure, you must have something to mix the different gases and particles to be studied completely into the carrier air flow. This mixing may be by shower heads or static mixers with lots of surface area, but then you will also have lots of possible surface interactions and losses for gases and particles before they even enter the main flow reactor.

If you want to study ambient aerosol particle chemistry or particle mass yields, then you will want to minimize wall effects and losses, which means minimizing wall interactions, but then the ability to relate time in the flow tube to reaction time may become difficult. If you want only to do laboratory studies, you still need to decide whether you want to look at chemical evolution (so that time in the reactor equals reaction time) or chemical properties that are distorted by wall interactions, such as SOA yields. Then that decision determines if you embrace wall interactions to give you laminar flow or you try to avoid walls and lose the ability to relate time in the chamber to reaction time. Which way the compromises are made depends entirely on the purpose. Of course you can decide to try to do both, and possibly compromise both.

The authors of this manuscript should have an introductory paragraph stating what they intend to study with this CPOT so that the reader can judge whether they have designed it appropriately for that purpose. They should also lay out the strengths and weaknesses of their approach for each type of study they intend to do (e.g., SOA mass yields, SOA chemical properties, time-dependent kinetic studies).

We have substantially rewritten the **Introduction**. Please refer to the revised paper.

2.5 Computational Fluid Dynamics (CFD) Simulations page 4, line 20. Assuming isothermal flow is unrealistic, which the authors say later in the manuscript. The authors should say up front that they are going to try isothermal to see what they get and then will need to modify this assumption later in the manuscript.

We have added a sentence as “The isothermal assumption will be relaxed subsequently.” (P6L7).

3.1 Injection method. Page 5, line 8. The authors are wrong about the method of injecting air into the PAM chamber. The flow does enter through a tube in the middle, but is quickly diverted by a covered cap with holes drilled sideways to divert the flow toward the outer edges of the chamber. This air is then passed through a fine-mesh screen to break the larger eddies into smaller eddies inside the actual chamber. I suggest that the authors get in touch with the builders of the PAM chamber, so that they know and are thus able to give a correct description of the actual flow in the PAM chamber.

We thank the referee for pointing this out. Together with the photo provided by Dr. Lambe, we now know exactly how the PAM injection system works. To avoid any confusion, we have removed all references to the PAM reactor at this point but kept the discussion of the straight injection style, which is referred as the sudden expansion case in the CFD simulation.

Page 5, line 16. This is not the dead volume to which Lambe et al., are referring. I recommend that the authors contact the designers of the PAM chamber to make sure they understand exactly what the PAM chamber design is, as well as the compromises that were made and why.

We have removed this part and added a discussion in a later section about loss in the inlet part. Please refer to our response to the following comment.

Page 5, line 18. The PAM chamber used in Ortega et al., is basically the same as the one used in Lambe et al.. The only difference is that the entrance plate with the flow diverter is removed so as to completely eliminate the loss of ambient particles and gases on the entrance plate and diverter by having the air flow into the chamber over almost its entire cross section. It is not to “reduce recirculation” in the reactor, as stated in this manuscript, although it might have improved the flow somewhat. The main result was that there was no longer any ambient particle loss in the PAM chamber.

We thank the referee for pointing out this fact. We have removed the sentence in question and discuss briefly the effect of the inlet design on the transmission of reactants in Section 3.1 (**P7L28**): “In addition to the flow field inside the reactor introduced by the inlet design, the transmission of different reactants (i.e. gas-phase species and particles) in the inlet system should also be considered (Karjalainen et al., 2016; Ortega et al., 2013, 2016; Palm et al., 2016; Simonen et al., 2016; Tkacik et al., 2014). Generally, a larger surface area means more interaction between the reactants and the walls, especially for “sticky” molecules. The effect of static mixer on the transmission of gas-phase species will be investigated in Section 5.1.”

Section 3.2. Page 6, Can the light from the reactor section get into the diffuser section? Is there ozone in the diffuser section? If so, then shouldn't the authors consider the diffuser section part of the reactor?

The diffuser section is covered by aluminum foil, but still a small amount of light leaks from the open side; since the residence time within the diffuser section is much shorter (30 s), as compared with the average residence time in the flow tube (1520 s), so the diffuser section as part of the reactor can be neglected without any discrepancy.

How does the lack of laminar flow in initial part of the diffuser section affect the particle formation/chemistry that the author may want to study since the diffuser is part of the reactor?

As noted above, given the weak light leakage and the short residence time, the effect of reactions occurring within the diffuser section are expected to be minor.

Section 3.3. The authors did look at issues of convection due to the temperature gradients in CPOT, but not the convection due to “hot spots” along the walls, which are likely to be important, irregular, and possibly transient.

Did the authors measure the temperature distribution of the walls in the CPOT to within 0.1 C? I would assume that there will be hot spots with differences of as much as 0.2 C or more, even with the temperature-control jackets and especially when the lights are on. My guess is that assuming an axial temperature gradient in the non-isothermal case is the best case scenario and that reality will be quite a bit worse.

We could do the following analysis with the Richardson number, but we can illustrate the problem with an even simpler calculation. Simple buoyancy calculations would suggest that air warmed by these 0.2 C hot spots would stir the reactor vertically from bottom to top in less than 10 seconds, which is a much shorter time than the 20-minute residence time. And, because the reactor is a round tube, this vertical motion will get translated into horizontal motion as the rising air hits the top half of the tube. The stirring due to these hot spots is likely to be as important as any other flow

considerations and is probably a major driving force in their eddy diffusion correction. Such eddy diffusion will do a great job of bringing the air in the chamber into close contact with the walls several times, thus increasing wall loss and exchange.

The temperature gradients that the authors determine are important are about the same as the 0.2 C difference used in this simple calculation. Thus, they have every right to be worried about thermal gradients and should include hot spots in their thinking about how convection is going to be a huge problem.

We do not measure the temperature distribution of the wall. Instead, we measure the water temperature into and out of the water jacket, and find a temperature difference of ~0.2 K. We agree with the reviewer's point that the presence of a hot spot is likely to induce secondary flow. We have added the following statement (**P16L28**):

"The spiral flow is more easily established if there are hot spots inside, which can be likely, as the sample ports on the reaction sections are not heat-insulated by the water jacket."

5. Results and Discussion 5.1 Measuring the initial value of the gases and particles downstream of the static mixer does not give a complete picture of particle and gas loss if those particles and gases will be added upstream of the static mixer during the experiments. How much of the gases and particles is lost on the static mixer? My guess is that a significant amount of the SO<sub>2</sub> and the ammonium sulfate particles will be lost, as will some of the H<sub>2</sub>O<sub>2</sub>. Now, if the authors intend to measure the amounts of gases and particles downstream of the static mixer and use these values as their initial values, then this test would be valid. Is that their intent?

Also, what about any gases / particles that are modified by interactions with the static mixer? They could be important for the chemistry that occurs in the CPOT reaction section.

Even for the way this penetration study was done, my guess is that the authors had to wait a while for the surfaces to acclimate to SO<sub>2</sub> before they were able to get it all through. Did the authors have to wait?

Yes, losses can occur in the static mixer and subsequently in the flow tube itself. We have measured the penetration efficiency of gas molecules and polydispers particles in the static mixer and the flow tube individually. The results are now discussed in **Section 5.1** and **Fig. 9**.

For each penetration study, the data in **Fig. A.1 (Appendix A)** show that at least 1 h is needed for the system to achieve steady state.

Page14, line 8. This test does not provide evidence that there was negligible interaction with the walls for the gases. All the authors can really say is that there was negligible loss, which could mean that the surfaces were (temporarily?) passivated. How that would change with the lamps on and active chemistry is anyone's guess.

It would be good to know the penetration efficiency for both initial cases – before the static mixer and just after the static mixer. The authors should measure it and report the results in the next version of the manuscript.

Also, were these penetration efficiency tests done under dry conditions? If so, then these are “best case” values, especially for SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. Unless the authors intend to do all their experiments under dry conditions (which will greatly limit the maximum OH exposure in CPOT and the applicability of the results to the real atmosphere), they should do the penetration efficiency tests under the same conditions as they will use in the experiments. My guess is that the penetration efficiency for SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> will fall rather precipitously.

In the additional experiment, we have investigated the RH-dependent penetration efficiency for both gas-phase species and polydisperse ammonium sulfate (RH smaller than its deliquescence RH). Details are now given in **Section 5.1** and **Fig. 9**.

5.1.2. page 14, line 27. It is doubtful that the 20% particle loss is due to electrostatic loss to the quartz walls. Instead, it is likely that the loss is due to more active convection taking the particles closer to the wall more frequently in the CPOT than the authors think.

Upon further consideration, we agree with the referee. We have removed the statement about the electrostatic loss and state that “The measured maximum penetration efficiency is ~ 80%, indicating a loss of particles, which is likely caused by secondary flow that actively conveys particles closer to the wall. This secondary flow will be discussed in Section 5.3.” (**P14L21**) We also added a subsequent paragraph discussing the impact from coagulation (**P14L25**).

Page 16, line 19. Why are the eddy diffusivities for ozone and particles different? I would think that they should be the same for small particles.

The two values are, in fact, relatively close. The difference may come from different experimental conditions. Since the eddy-like diffusivity,  $\sim 10^{-4} \text{ m}^2 \text{ s}^{-1}$ , is much higher than the inherent diffusivity of either gas-phase species and particles, all reactants can be viewed as having the same diffusivity.

Somewhere at the end of the discussion and results, the authors need to compare the characteristics of the CPOT to those of other flow tube reactors, such as the PAM chamber, TPOT, and the Irvine chamber. From the data provided here, CPOT appears to be not much better than any of these other existing chambers in terms of particle transmission or residence time distribution. If you look at the difference in the actual arrival time to that predicted by laminar flow and the full-width and also at the half maximum of the actual peak to that of the laminar flow case, as in Figure 10, and compare those to what is achieved in TPOT and PAM in Lambe et al. Figure 3, you will see that the actual

arrival time is about half that for the laminar case and the FWHM peak width is about double that of the laminar case for all three flow tubes.

Therefore, it is unclear to me if the authors have achieved their goal of having a flow tube that can be used for kinetic studies (in the sense of time in the chamber is equal to reaction time) any better than the existing flow reactors can.

We admit that the CPOT does not perform better in terms of RTD than other currently existing flow reactors. Consequently, we have added the following paragraph at the end of Section 5.2 (**P15L29**): “Overall, the experimental RTD results of both gas-phase species and particles in the CPOT are essentially comparable to those of present flow reactors (Lambe et al., 2011a), given the arrival time and the width of the peak. This discrepancy of the RTDs between the theoretical laminar flow and the real flow indicates the presence of non-ideal flow in the reactor.”

However, confirmed by the CFD simulation and the fitting results of the experimental data, we can use the simple parameters from fitting results, which incorporates the effect from fluid field (e.g. the axial dispersion) in the diffusion equation, to simplify the modeling of the photochemical studies (**Section 6**). From this point of view, we do have achieved the goal for kinetic studies.

Conclusions. The authors say in the conclusion that “The measured residence time distribution will enable correction for the unavoidable deviations that do occur.” The only way this statement can be made credible is for the authors to add a section that shows how they are going to do this and then demonstrate that it works with real kinetics measurements. Then they need to do an error analysis to show what the uncertainty of their kinetic measurements will be. If they do not wish to do this work for this manuscript, then I suggest that they remove this sentence.

We have removed this sentence.

Conclusions. The second-to-last sentence in the manuscript says “Finally, the perturbations from strict laminar flow in the horizontal tube are a result of buoyancy effects.” The authors recognize in this manuscript what other researchers have been saying for years – that buoyancy plays a dominant role in flow reactors with residence times of minutes to hours. They call it a perturbation, but there is nothing small about it, so I suggest that they call it “variations from strict laminar flow”.

This point about buoyancy is important, so the authors should include a sentence about it in the abstract and not just in the conclusions.

We have rewritten substantially the **Abstract** and **Conclusion** sections and now state “As confirmed by the CFD prediction, the presence of a slight deviation from strictly isothermal conditions leads to secondary flows in the reactor that produce deviations from the ideal parabolic laminar flow.” in the **Abstract**.

Conclusions. I disagree with the last statement: “If it had been feasible to mount the flow tube vertically, these effects could have been largely eliminated.” Mounting the flow tube vertically will not eliminate these buoyancy effects because it is impossible to eliminate “hot spots” that will drive the buoyancy. Instead, mounting the flow tube vertically will likely enhance the buoyancy effects. By luck or design, this enhancement can occur in a way that effectively isolates the center flow from the walls, although it greatly shortens the residence time. The flow reactor used for the Kang et al. papers was a vertical flow tube. The authors may want to contact the developers of the original PAM chamber to learn what they know about the flow characteristics in vertical flow reactors if they really want to retain this sentence in the manuscript.

We agree. We have removed this sentence in the revised version.

Technical corrections / comments:

4. page 9, line 10. Please change “may” to “will”.

Corrected.

Figure 11. Are the two dashed lines switched? I would think that the gravitational settling would cause a lower penetration efficiency for larger particles.

Thanks for pointing this out. We have corrected it in the revised version by using words instead of equation numbers.

## **Response Anonymous Referee #2**

Huang et al. Present a detailed computational fluid dynamics (CFD) model of their laminar flow tube. They highlight the importance of flow-shaping and mixing at the inlet of the reactor and how non-isothermal conditions can substantially impact on e.g. the distribution of residence times (RTD). Computed RTDs were compared with measured residence times of trace gases, especially O<sub>3</sub> following pulsed admission to the flow tube. Introduction of eddy-like diffusivity was required to align calculation and observation.

Without presenting anything particularly new or unexpected, Huang et al. compile some useful information concerning the design and construction of high pressure, laminar flow-tubes with long residence times and draw comparison with some previous designs. This paper is a good starting point for anyone looking to construct such an experiment for investigation of atmospheric processes and is thus appropriate for AMT. The manuscript is clearly written and organized, the figures are appropriate and of good quality. The authors may consider the following comments / questions.

We thank the reviewer for the valuable comments.

There is almost no indication in this manuscript (P1L15, P2L4) about what atmospheric, chemical / physical systems the flow-tube is intended to be used for. Likewise, at the end of the manuscript, apart from mention that some gas-phase organics may be lost at higher rates to the walls, there is little indication of what type of chemical systems may be problematic. This manuscript would benefit from such considerations even if only qualitative.

We have rewritten the **Introduction** to address these issues. Please refer to the revised paper.

P2L4 There are many examples of problems associated with increasing radical concentrations to reduce the time scales on which atmospheric processes take place (>days) to make them observable on typical (hours) laboratory time scales. Not all processes are linear in time x concentration. Obvious examples involve reaction terms (e.g. reactions between peroxy radicals) that are quadratic in concentration. This deserves mention.

We thank the referee for pointing this out. We agree and have replaced “concentration × time” with “integrated OH exposure” in **P2L17**. We also discuss in detail the OH exposure calculation in the new **Section 6**.

P3L4 The max. Reynolds number in the conical section is listed here. It would also be useful at this point to list the Reynolds number in the long cylindrical section of the flow tube.

We have rewritten the following sentence “Under the typical CPOT flow rate ( $2 \text{ L min}^{-1}$ ), the Reynolds numbers at the inlet cone, in the cylindrical section, and at the exit cone are 150, 20, and 450, respectively, well below the transition to turbulent flow.” in **P4L13**.

P3L9 The lamps emit mainly at 254 nm. Please indicate the relative intensity (penetrating the jackets and water coolant) of the other lines are. Perhaps a Figure of the lamp emission spectra would be useful.

We have rewritten **Section 2.2** and added a new appendix section (**Appendix A**) addressing the quantitation of irradiation from different lamps. **Figure 2** has been added as the reference for the lamp emission spectra.

P5L20 Ezell were not the first to use the shower-head design. I’m aware of others (constructed for a similar purpose) that precede this by several years (e.g. Bonn et al., J. Phys. Chem. 106, 2869, 2002).

We appreciate this comment. We have added the reference and rephrased this sentence as: “Some flow tube designs address inlet issues using flow management devices, e.g. a spoked-hub/showerhead disk inlet (Bonn et al, 2002; Ezell et al, 2010) that distributes the reactants evenly about the reactor cross-section and provides sufficient mixing (Fig. 4B).” in **P7L19**.

P11L21 The diffusivity for ozone can be accurately calculated or simply taken from previous experimental determinations found in the literature. Why assume a value of  $1\text{e-}5 \text{ m}^2/\text{s}$ ?

We agree. For reference, the diffusivity of  $\text{O}_3$  is  $1.44 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  and  $\text{SO}_2$  is  $1.12 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  (Massman, 1998). The value we choose here,  $1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ , is the typical order of magnitude of the diffusivity of vapor molecules. By using this value, we want to generalize the simulation to the behavior of typical vapor molecules, but, later on, an exact value can be used, if needed.

P17L29 the authors write: The current study indicates that secondary flows can exist in laminar flow tube reactors and affect the fluid dynamics and RTD. This is true but this is not the first time that this fact has been established. Previous users of high-pressure, laminar flow tubes have recognized this fact and done detailed characterization of the effects of mixing and non-laminar conditions by conducting kinetic experiments with well-known reaction systems (see e.g. Donanhue et al. J. Phys. Chem. 100, 5821, 1996). While the pulsed addition of a trace gas will provide an estimate of the RTD, the study of a reaction would provide even more insight as the effects of mixing of trace gases of different diffusivity and wall losses can be assessed.

We appreciate this information. We agree with the statement that the study of the reaction system also provides insight into the flow mixing effect. We constructed a 1D axially-dispersed plug flow reactor (AD-PFR) photochemical model framework (**Section 2.6**) to simulate OH+SO<sub>2</sub> with photolysis of H<sub>2</sub>O<sub>2</sub> in the absence of NO<sub>x</sub>. The fitting results from pulsed RTD experiments are used as parameters in this model. The discrepancy between the PFR model and the AD-PFR model at high reaction rate demonstrates the flow mixing effect on the reaction system. Details can be found in **Section 6**.

**Reference:**

Massman, W. J.: A review of the molecular diffusivities of H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, CO, O<sub>3</sub>, SO<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>O, NO, and NO<sub>2</sub> in air, O<sub>2</sub> and N<sub>2</sub> near STP, *Atmos. Environ.*, 32, 1111-1127, doi:10.1016/S1352-2310(97)00391-9, 1998.

### **Response to Anonymous Referee #3**

The authors present a detailed description of the design and characterisation of the new Caltech photooxidation flow tube (CPOT) reactor, using a combination of fluid dynamics calculations to determine the ideal flow behavior within the reactor and experimental characterisations to assess deviations from ideal conditions. The manuscript is well written and the design and results are presented in a clear and logical manner. The manuscript is suitable for publication in AMT. I have only minor comments listed below:

In general the introduction is quite short, and would benefit from a discussion of the various types of flow tubes currently in operation. The authors comment that flow tube reactors are an alternative to the batch chamber, but do not comment on the different timescales of processes that are often studied with flow tubes or batch reactors – they are often quite different.

The introduction would also benefit from a discussion of the limitations of previous flow tube designs, and any evidence that the fluid dynamics in previous flow tube designs are not well represented by simple models.

We thank the reviewer for these specific comments.

Page 2, line 33: Please indicate the section number where the temperature control of the inlet diffuser is described.

Corrected.

Page 3, line 9: ‘irradiate’ to ‘irradiation’.

We have changed ‘irradiate mainly at 254 nm’ to ‘emit narrow bands at 254 nm and 185 nm’.

Page 3, line 17: Please quantify ‘substantial amount of energy’.

Given the measured temperature difference (0.3 K), the circulation flow rate (13 L min<sup>-1</sup>) and the water heat capacity (4200 J kg<sup>-1</sup> K<sup>-1</sup>), assuming the heat absorption efficiency is about 50%, we roughly estimate a value of 550 W. The working power of the lamp is 45 W, thus the energy to generate heat is about 76% of the total energy consumption, which is a reasonable value.

Page 3, line 30: ‘condition’ to ‘conditions’.

Corrected.

Page 4, lines 9-11: Mixture of numbers given as ‘two’ and ‘2’. Please be consistent.

Corrected.

Page 5, line 8: Please move the references to after 'PAM reactor'.

Since the PAM reactor does not use this injection style, we have removed all the statements about the PAM reactor as well as the references in this section. Please refer to the response to Anonymous Reviewer #1 on Page 4 and comment 3 by Andrew Lambe #5 on Page 20 for details.

Page 5, line 19 (and elsewhere): 'reactor' should be included wherever 'PAM' is mentioned.

Please see the response to the previous comment.

Page 6, line 4: Although it is defined in the abstract, please also define 'RTD' here.

Corrected.

Page 10, equation 8: Please provide some explanation for the ellipsis in the equation.

(Note: the equation numbers have been changed.)

The analytical solution to Eqs. D2 - D5 is a superposition of infinite eigenvalue terms. The coefficients inside the exponential part of the 4th, 5th, and 6th terms are -107.6, -174.3, and -256.9, respectively, which is so large that as long as  $\xi$  is not small enough ( $< 0.02$ ), these terms can be omitted. Theoretically, for small values of  $\xi$ , Eq. 3 and 4 can give the same value of  $\eta$  as long as we can find an infinite series of eigenvalues with sufficient precision.

Page 10, line 11: Please provide some typical values to give a reference point for small values being less than 0.02.

In the book *The Mechanics of Aerosols* (Fuchs, 1964), Fuchs has compared Eq. 3 and 4 in Table 16. For  $\xi$  in the range of 0.01 to 0.1, the discrepancy between the two is within 1%. Thus 0.02 is a safe criterion.

Page 15, line 18: Please change 'minute' to 'small'.

Corrected.

Page 16, line 5: 'An idealized ... '.

Thanks for pointing this out. We have removed this sentence in order to merge Section 5.2.1 and 5.2.2 as a whole.

Page 26, Figure 3: The photograph is not particularly clear.

We have adjusted the contrast of the photograph to make it clear.

Page 32, Figure 9 caption (end): ‘non-diffusion’ to ‘non-diffusing’.

Corrected. Figure 9 now becomes Fig. F.2 in the new version.

**Reference:**

Fuchs, N. A.: *The Mechanics of Aerosols*. Pergamon, New York, 1964.

## **Response to Anonymous Referee #4**

The manuscript “The Caltech Photooxidation Flow Tube Reactor – I: Design and Fluid Dynamics” by Huang et al. presents a very detailed description of the design and characterization of a new laminar flowtube reactor (CPOT) for oxidation reactions of vapor molecules and particles at high oxidant levels. The paper focuses on the simulation of fluid dynamics of several fundamental components, such as inlet and exit section, and residence time distributions (RTD) under conditions deviating from the ideal situation. Modeled RTDs are finally compared to experimental RTDs in order to evaluate the performance of the CPOT. Exploring chemical aging of gas phase molecules and particles relevant in the environment and optimizing measurement techniques is certainly of fundamental interest. Given the complexity these kinetics, laboratory experiments on confined and characterized systems in a well-defined environment are required for developing a better understanding of the complex processes occurring in the atmosphere. The manuscript is well written and clearly structured, and although the novelty of the presented material is questionable, it provides a detailed summary of important factors that need to be considered when building a new flow reactor system.

We thank the reviewer for these valuable comments.

One weakness of the presented flow reactor is the high level of oxidant that is required. The authors write in the introduction that high OH exposures are equivalent to multiple days of atmospheric OH concentrations. However, whether high oxidant levels can be extrapolated to atmospherically relevant conditions has yet to be determined. In fact, it is very likely that the chemical reaction pathway might change as a function of reaction time and oxidant concentration.

We agree with the reviewer’s comment. The enhanced oxidation environment in a flow tube reactor may promote reactions, such as  $\text{RO}_2 + \text{RO}_2$ , which may change the route of formation of the secondary organic aerosol (SOA). However, this potential weakness is common to all the existing flowtube reactors, rather than one that is particularly associated with the CPOT. A recent study have found no significant discrepancy between compositions of SOA generated in the chamber and the flowtube at current detection precision (Lambe et al., 2015). Whether a molecular-level difference exists between the chamber and the flowtube SOA still remains an open question and is of great interest for the atmospheric chemistry community. We believe that a fundamentally well-characterized flowtube reactor, such as the one demonstrated in this work, will be beneficial in answering this type of questions.

The authors attribute in section 5.1.2 RTD discrepancy to the evaporation of particle-borne water. It would be interesting to see how relative humidity affects CPOT performance.

We have removed this possible interpretation since we find no relationship between the relative humidity and penetration efficiency. We attribute the discrepancy to the forced convection to the wall by the secondary flow induced by small temperature differences. We also add a new paragraph (P14L25) and **Fig. 10** in **Section 5.1.2** discussing about the effect of coagulation on the size distribution.

**Reference:**

Lambe, A., Chhabra, P., Onasch, T., Brune, W., Hunter, J., Kroll, J., Cummings, M., Brogan, J., Parmar, Y., and Worsnop, D.: Effect of oxidant concentration, exposure time, and seed particles on secondary organic aerosol chemical composition and yield, *Atmos. Chem. Phys.*, 15, 3063-3075, 2015.

## **Response to Dr. Andrew Lambe #5**

Huang and Coggon et al. present theoretical and experimental evaluation of a newly-designed Caltech Photooxidation Flow Tube Reactor (CPOT). The CPOT incorporates components of, and is evaluated against, other recently developed oxidation flow reactor techniques. The authors use COMSOL to conduct CFD simulations of various inlet configurations (e.g. conical diffusers, static mixers) and lamp-induced temperature gradients, and their effects on flow fields. The penetration efficiency ( $\eta$ ) and residence time distributions (RTDs) for vapors ( $O_3$ ,  $SO_2$ ,  $H_2O_2$ ) and particles (polydisperse ammonium sulfate) are measured experimentally. For the vapors that were studied,  $\eta = 100\%$ ; for particles,  $\eta \leq 80\%$  at  $D_p = 100$  nm. The authors use a Taylor dispersion model to simulate the observed RTDs, and specifically to reproduce behavior of temperature-gradient-induced secondary flows.

Overall, in my opinion this manuscript is well written. The CPOT technique has potential applications for laboratory SOA studies that will presumably (based on title) be examined in related publications to follow. Another, perhaps even more important contribution is the theoretical and modeling framework that is presented which is applicable to other oxidation flow reactor techniques. I would support publication in Atmospheric Measurement Techniques after consideration of my comments below.

[We thank Dr. Lambe for the constructive suggestions and details about PAM.](#)

### Comments

1. Aside from mentioning that the CPOT is equipped with UV-A, UV-B, and mercury lamps, there is no discussion of the photochemical oxidation capabilities of the CPOT despite the statement in Section 2.2 that “quantifying light fluxes for each type of lamp is the prerequisite for performing photochemical experiments in the CPOT.” In my opinion, it is critical to provide basic information in this regard in this paper. I recommend supplementing Section 2.2 and Figure 1D by adding a section (or table) summarizing the basic photochemical oxidation capabilities of the CPOT. For example:

| Lamp type | Primary/Mean Emission $\lambda$ | Minimum actinic flux | Maximum actinic flux | OH precursor(s) | Minimum [OH] | Maximum [OH] |
|-----------|---------------------------------|----------------------|----------------------|-----------------|--------------|--------------|
| UVC (Hg)  | 254                             | XX                   | XX                   | AA              | XX           | XX           |
| UVB       | 305                             | YY                   | YY                   | BB              | YY           | YY           |
| UVC       | 350                             | ZZ                   | ZZ                   | CC              | ZZ           | ZZ           |

[We have rewritten Section 2.2 and added Appendix A and Fig. 2 to illustrate the quantification of light intensity and the spectrum of the lamps. Table B1 in Appendix B shows the photolysis rate under full emission of the three types of lamps. A photochemical model is presented in Section 6 to](#)

simulate the OH exposure in the absence of NO<sub>x</sub> condition (the OH precursor is H<sub>2</sub>O<sub>2</sub>). We summarize the simulation results in “**Table 1**: Simulated OH exposure under full light emission

| Lamp type | OH <sub>exp</sub> <sup>a</sup> |                                     | Atmos. Equiv. <sup>b</sup> |                        |
|-----------|--------------------------------|-------------------------------------|----------------------------|------------------------|
|           | (molec cm <sup>-3</sup> s)     |                                     | (h)                        |                        |
|           | PFR                            | AD-PFR <sub>corr</sub> <sup>c</sup> | PFR                        | AD-PFR <sub>corr</sub> |
| Hg vapor  | 8.0×10 <sup>11</sup>           | 7.3×10 <sup>11</sup>                | 222                        | 203                    |
| UVB       | 5.4×10 <sup>10</sup>           | 4.9×10 <sup>10</sup>                | 15                         | 13.6                   |
| UVA       | 6.0×10 <sup>9</sup>            | 5.4×10 <sup>9</sup>                 | 1.7                        | 1.5                    |

<sup>a</sup>Input of OH exposure (OH<sub>exp</sub>) simulation: 1 ppm H<sub>2</sub>O<sub>2</sub> and 100 ppb SO<sub>2</sub> at RH = 5% and T = 295 K ([H<sub>2</sub>O<sub>2</sub>] = 1500 ppm).

<sup>b</sup>Atmospheric equivalent (Atmos. Equiv.) OH<sub>exp</sub> values are also converted to their equivalent hours of OH exposure in the ambient atmosphere, assuming a typical ambient OH concentration of 1×10<sup>6</sup> molecule cm<sup>-3</sup>.

<sup>c</sup>PFR and AD-PFR<sub>corr</sub> are calculated by Eqs. (6) and (7), respectively.”

2. I think it would also be useful to briefly mention how the lights are used. For example, are only UVA, UVB, or UVC lamps used depending on the experimental goals? Or are combinations of different lamp types used at the same time? How is the UV intensity adjusted and measured?

We have rewritten **Section 2.2**. In the first paragraph we state how the lights are used, including the intensity adjustment and the usage based on the particular experimental goals. In the second paragraph, we briefly explain how we measure the light intensity, with details in **Appendix A**.

3. I want to point out that the “straight tube inlet” design portrayed in Figure 3A doesn’t incorporate specific characteristics of the PAM reactor, which uses a drilled-out inlet nut on the inside of the front plate combined with a fine mesh screen or a Teflon disc (depending on version; see Figure 1 below) to promote radial mixing. If the goal of this analysis is to represent the specific characteristics of the PAM reactor -- which, for self-serving reasons, I’d be curious to see -- I suggest incorporating additional inlet components shown in the photo to evaluate the effect it has (if any). I can provide necessary specifications. Otherwise, if it is only meant to illustrate a simplified reactor geometry, it shouldn’t be specifically associated with the PAM reactor as is currently done in the Figure 3 caption.



Figure 1. PAM reactor “inlet mixer”. A mesh screen or Teflon disc is press fit into a nut with drilled-out holes to promote axial mixing.

We thank Dr. Lambe for providing this figure. To avoid any confusion, we have removed all the statements that describe the specifics of the PAM reactor regarding the “straight tube inlet” injection style. We retain Fig. 3A as the sudden expansion (90°) case that is discussed in Section 3.2.

4. There are several sections in the paper where extensive sets of equations / derivations are used:

- Section 4.2, Equations 3-7
- Section 4.3.1, Equations 10-15
- Section 4.3.2, Equations 16-22

While informative and useful for advanced readers, in my opinion, this level of detail is potentially overwhelming for basic readers. Would it be possible to move some of this material to a new Appendix C?

We have moved these developments from the main text into **Appendices D, E, and F**.

5. **P14, L9-L11**: The authors state: “The extent of wall deposition of organic vapors in the flow tube reactor requires comprehensive study and will be addressed in a future publication.” Isn’t this also applicable to the conical diffuser / static mixer described earlier in the paper (P6, L27), which has higher surface-to-volume ratio than “Reactor 1” and “Reactor 2”? I suggest briefly stating somewhere in the manuscript that a limitation to using conical diffusers/ static mixers is losses of sticky organic vapors that may be important SOA precursors.

We have included a short summary at the end of Section 3.1 concerning the large surface area related loss (**P7L28**):

“In addition to the flow field inside the reactor introduced by the inlet design, the transmission of different reactants (i.e. gas-phase species and particles) in the inlet system should also be considered (Karjalainen et al., 2016; Ortega et al., 2013, 2016; Palm et al., 2016; Simonen et al., 2016; Tkacik et al., 2014). Generally, a larger surface area means more interaction between the reactants and the walls, especially for “sticky” molecules. The effect of static mixer on the transmission of gas-phase species will be investigated in Section 5.1.”

6. **P14, L28**: “Note that since we measured the particle size distribution after the static mixer, this loss does not arise from the static mixer.” Related to #4, doesn’t this imply that there is significant loss of particles through the static mixer? I suggest briefly stating somewhere in the manuscript that a limitation to using static mixers is particle losses. This may be unimportant for CPOT-related applications, but is critical in applications of other oxidation flow reactors, particularly when a goal

is to measure SOA-to-POA-enhancement ratios (e.g. Ortega et al., 2013; Tkacik et al., 2014; Karjalainen et al., 2016; Ortega et al., 2016; Palm et al., 2016; Simonen et al., 2016).

Addressing this comment is incorporated in the response to the previous point.

7. **Section 4.3:** Please also cite the use of Taylor dispersion modeling to characterize vapor and particle residence time distributions in the PAM and TPOT reactors by Lambe et al. (2011). On a related note, an RTD comparison figure presented by Campuzano-Jost et al. (2016) is reproduced below (Figure 2). Can the authors provide any insight or hypotheses as to how the (seemingly) minor improvement in RTD obtained with the CPOT would influence the corresponding measured properties of secondary organic aerosols produced in both systems?

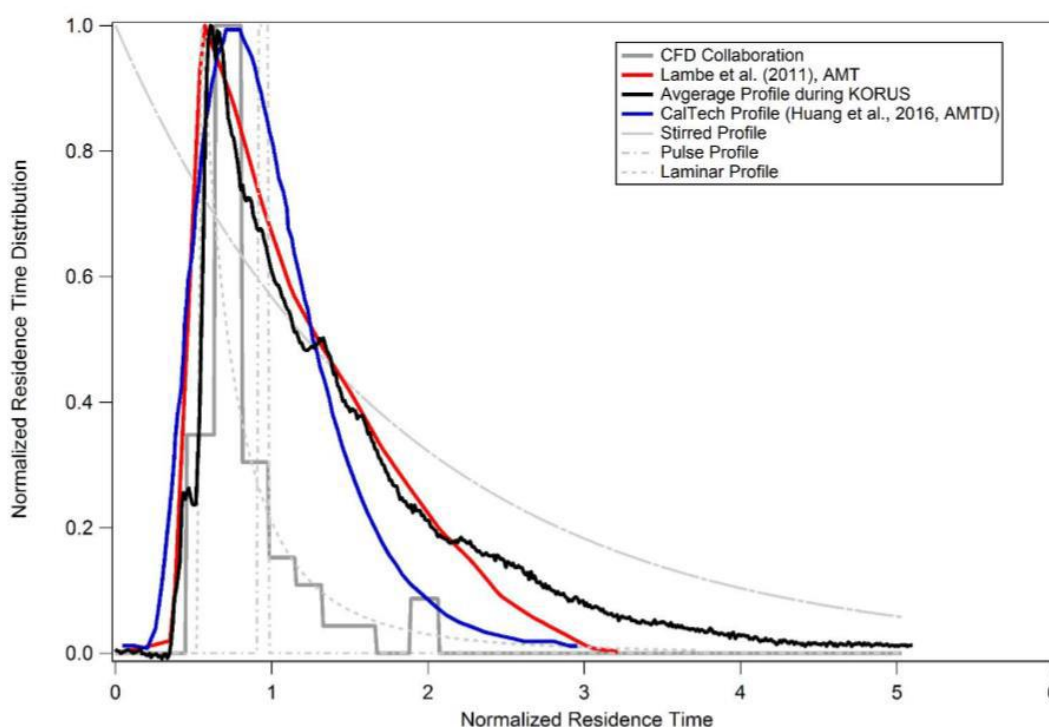


Figure 2. Comparison of theoretical and measured oxidation flow reactor residence time distributions (RTDs) in CPOT and PAM by Campuzano-Jost et al. (2016).

We have added the following statement in Section 4.3.1 about Taylor dispersion modeling (**P12L17**):  
 “In the PAM reactor (Lambe et al., 2011a), the Taylor dispersion criteria does not strictly meet the working conditions, however, the two flow regime fitting results suggest that two types of flow may exist in the reactor: a direct flow with minor dispersion and a secondary recirculation flow with significant dispersion.”

We appreciate Dr. Campuzano-Jost for compiling the RTD data from different types of flow reactor. We also thank Dr. Jimenez for making an update on this figure, proving that the RTD of CPOT looks better.

For non-ideal reactors, RTD can provide insights to the fluid field. As confirmed by our CFD simulations and Taylor dispersion fittings, we have successfully simplified the coupling of RTD with the kinetic study, i.e. the convection-diffusion ordinary differential equation (ODE). This makes the interpretation of data more reliable. Please refer to Section 6 for the details.

8. **Sect. 4.2.3:** Please define size limits for “diffusive” and “non-diffusive” particles.

Since particles always exhibit Brownian diffusivity, to avoid confusion, we note two regimes, i.e. diffusion regime (diameter smaller than ~80 nm) and settling regime (diameter larger than ~80 nm), and kept consistent with this expression in the context (**P13L14**).

9. **Figures 7-8:** I am not certain if these figures are necessary. If they are, I wonder if they could be moved to an appendix/supplement.

We have moved Figs. 8 and 9 to **Appendix F**, but kept Fig. 7 (in the new version it becomes **Fig. 8**) since it relates directly to the two regimes for the discussion about particles.

10. **Figure 9:** For “100 nm, 99%”, “200 nm, 95%”, “500 nm, 88%”, and “1000 nm, 65%”, I assume that the 99%, 95%, 88% and 65% values are penetration efficiencies. This could be made clearer, for example, “100 nm,  $\eta = 99\%$ ”. In the open area (white spaces), the authors may also consider adding an “ $\eta = 0\%$ ” label, or modifying the caption to read: “The open space between the dashed curve and the tube wall indicates the region in which particles have deposited on the tube wall ( $\eta = 0\%$ )”.

We have modified the title of each panel and the caption of the figure. The new figure now is in **Appendix F** as **Fig. F.2**.

11. **Figure 11:** Please indicate in the caption that the penetration efficiency as defined here does not include particle losses in the diffuser/static mixer, and thus represents a lower limit to the penetration efficiency of the entire CPOT.

We have replaced this figure with a more comprehensive one, showing the penetration efficiency of gas-phase species and particles (**Fig. 9** in the revised paper).

12. **Figure 13:** The authors might consider mentioning in the legend or the caption that Eq. 14 represents a Taylor dispersion model.

Done.



# The Caltech Photooxidation Flow Tube Reactor - Design, Fluid Dynamics and Characterization

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**Abstract.** Flow tube reactors are widely employed to study gas-phase atmospheric chemistry and secondary organic aerosol formation. The development of a new laminar-flow tube reactor, the Caltech PhotoOxidation flow Tube (CPOT), intended for the study of gas-phase atmospheric chemistry and secondary organic aerosol (SOA) formation, is reported here. The present work addresses the reactor design based on fluid dynamical characterization and the fundamental behavior of vapor molecules and particles in the reactor. The design of the inlet to the reactor, based on computational fluid dynamics (CFD) simulations, comprises a static mixer and a conical diffuser to facilitate development of a characteristic laminar flow profile. To assess the extent to which the actual performance adheres to the theoretical CFD model, residence time distribution (RTD) experiments are reported with vapor molecules ( $O_3$ ) and sub-micrometer ammonium sulfate particles. As confirmed by the CFD prediction, the presence of a slight deviation from strictly isothermal conditions leads to secondary flows in the reactor that produce deviations from the ideal parabolic laminar flow. The characterization experiments, in conjunction with theory, provide a basis for interpretation of atmospheric chemistry and secondary organic aerosol studies to follow. A 1D photochemical model within an axially dispersed plug flow reactor (AD-PFR) framework is formulated to evaluate the oxidation level in the reactor. The simulation indicates that the OH concentration is uniform along the reactor, and an OH exposure ( $OH_{exp}$ ) ranging from  $\sim 10^9$  to  $\sim 10^{12}$  molecules  $cm^{-3}$  s can be achieved from photolysis of  $H_2O_2$ . A method to calculate  $OH_{exp}$  with a consideration for the axial dispersion in the present photochemical system is developed.

## 1 Introduction



Experimental evaluation of atmospheric chemistry and aerosol formation is typically carried out in laboratory reactors. Such reactors comprise both chambers and flow reactors. The flow tube reactor has emerged as a widely-used platform (Bruns et al., 2015; Chen et al., 2013; Ezell et al., 2010; Kang et al., 2007, 2011; Karjalainen et al., 2016; Keller and Burtscher, 2012;

Khalizov et al., 2006; Lambe et al., 2011a, b, 2012, 2015; Li et al., 2015; Ortega et al., 2013, 2016; Palm et al., 2016; Peng et al., 2015, 2016; Simonen et al., 2016; Tkacik et al., 2014).

The flow tube reactor is generally operated under steady-state conditions. An attribute of the flow tube reactor is that, by control of the inlet concentration and oxidation conditions, it is possible to simulate atmospheric oxidation under conditions equivalent to multiple days of atmospheric exposure with a reactor residence time over a range of minutes. It should be noted that the chemistry occurring in such a highly oxidizing environment may differ from that in the atmosphere and batch chamber, even though no discrepancy between the components of the SOA generated in the flow tube reactor and the batch chamber has yet to be reported (Lambe et al., 2015). Moreover, under the steady state operating conditions, it is possible to accumulate sufficient products for detailed analytical evaluation. Key factors relevant to atmospheric processes, such as gas-phase kinetics (Donahue et al., 1996; Howard, 1979; Thornton and Abbatt, 2005), nucleation rates (Mikheev et al., 2000), uptake coefficients of vapors on particles (Matthews et al., 2014), and heterogeneous reactions on particle surfaces (George et al., 2007), can be evaluated via flow tube studies.

Since the concept of Potential Aerosol Mass (PAM) was proposed, the PAM reactor, operated as a flow tube reactor, has been widely used in laboratory and field studies of SOA formation (Chen et al., 2013; Kang et al., 2007, 2011; Keller and Bartscher, 2012; Kroll et al., 2009; Lambe et al., 2011a, 2012, 2015; Ortega et al., 2016, 2013; Palm et al., 2016; Slowik et al., 2012; Smith et al., 2009). A powerful attribute of the PAM and subsequent flow reactors is the capability to generate hydroxyl radical (OH) levels that lead to integrated OH exposure ranging as high as  $\sim 10^{12}$  molecules  $\text{cm}^{-3}$  s, at which it is possible to simulate atmospheric oxidation conditions comparable to those occurring over  $\sim 1$  week. Chemical kinetic modeling studies have investigated the free radical chemistry in the oxidation flow reactor (OFR) (e.g., Li et al., 2015; Peng et al., 2015, 2016).

Flow tube designs vary in dimension, detailed construction, and strategy for generating the oxidizing environment. Each specific design aspect of a flow reactor can significantly affect both the fluid dynamics and the chemistry within the reactor. For example, the design of the inlet to the reactor determines the extent of initial mixing of the reactants as well as the development of concentration profiles in the reactor. The classical flow tube for gas-phase kinetic measurements employs a movable inlet in the axial position surrounded by a carrier gas to achieve the flexibility in varying reaction time (Howard, 1979). The wavelength-dependent radiation source determines the choice of oxidants that initiate free radical chemistry. In the atmosphere, the ubiquitous oxidant OH is generated largely by the reaction of  $\text{H}_2\text{O}$  with  $\text{O}(^1\text{D})$ , which is produced by the photolysis of  $\text{O}_3$  at wavelengths  $< 320$  nm. In the flow reactor, a variety of OH generation strategies exist. One option is to use blacklights that center around 350 nm to gently photolyze OH precursors such as  $\text{H}_2\text{O}_2$ , HONO, and  $\text{CH}_3\text{ONO}$ . The material of the flow tube determines the placement of radiation sources. For example, the PAM reactor described by Kang et al. (2007) is constructed of Teflon which is transparent to UV radiation; consequently, the UV lamps that drive the photochemistry can be positioned outside the reactor itself. By contrast, another class of flow reactors is constructed of aluminum, for which the UV lamps must be positioned inside the reactor itself (Li et al., 2015; Ezell et al., 2010). Characterization of the behavior of the flow tube reactor requires ideally a combination of flow and residence time modeling and experiment, chemical kinetic modeling and experiment, and modeling and experimental measurement of interactions of vapor molecules and particles with reactor walls.

We present here the development and characterization of the Caltech Photooxidation flow Tube reactor (CPOT). The CPOT has been constructed as a complement to the Caltech 24 m<sup>3</sup> batch chambers (Bates et al., 2014, 2016; Schilling et al., 2015; Hodas et al., 2015; Loza et al., 2013, 2014; McVay et al., 2014, 2016; Nguyen et al., 2014, 2015; Schwantes et al., 2015; Yee et al., 2013; Zhang et al., 2014, 2015) in carrying out studies of SOA formation resulting from the oxidation of volatile organic compounds (VOCs) by oxidants OH, O<sub>3</sub>, and NO<sub>3</sub> over time scales not accessible in a batch chamber. Owing to its steady-state operation, the CPOT also affords the capability to collect sufficient quantities of SOA generated in the reactor for comprehensive composition determination by off-line mass spectrometry.

While the reactor itself is not unlike a number of those already developed and cited above, we endeavor here to describe in some detail the theoretical/experimental characterization of the reactor. Using computational fluid dynamics (CFD) simulations, we describe the design and characterization of the CPOT. We highlight fundamental consideration of the design of a laminar flow tube reactor, including methods of injection of gases and particles, the behavior of vapor molecules and particles in the reactor, and effects of non-isothermal conditions on the flow in the reactor. We evaluate the extent to which the fluid dynamics modeling agrees with experimental residence time distribution (RTD) measurements.

Experimental measurements of SOA formation in laboratory Teflon chambers are influenced by deposition of both particles and vapors to the chamber walls, and evaluation of the SOA yield from VOC oxidation must take careful accounting for such wall losses (e.g., Zhang et al., 2014; Nah et al., 2016a, b). We seek to assess the extent to which both vapor and particle deposition onto the entrance region and quartz wall of the flow tube is influential in flow tube reactor studies. While experimental measurements of these processes will be presented in future studies, the transport modeling presented here provides a basis for evaluating the effect of reactor surfaces on experimental measurements of atmospheric chemistry and SOA formation.

A photochemical kinetic model is formulated to simulate OH production in the reactor. Typically, at steady state, the flow tube reactor gives only one data point under a specific condition. Such a model is essential in evaluating oxidation data in the reactor since the model predicts how the reactants evolve along the reactor. Generally, the ideal plug flow reactor (PFR) framework is used in the modeling of a flow tube system (Li et al., 2015; Peng et al., 2015, 2016). For a non-ideal flow reactor, the axially-dispersed plug flow reactor (AD-PFR) framework couples the RTD with the chemical reaction system. The axial dispersion plays the role of backward and forward mixing of the reactants, smoothing the concentration gradients. By the comparison between AD-PFR and PFR models, we will show how the non-ideal flow reactor impacts the data interpretation and suggest a method for correction.

## 2 Design and Experimental Setup

### 2.1 CPOT Reactor

The CPOT comprises three sections: the inlet section, the main reaction section, and the outlet section (Fig. 1A). The inlet consists of two components - the static mixer and the conical diffuser (Fig. 1B). The static mixer is designed to thoroughly mix reactant streams, whereas the diffuser serves to expand the mixed flow to the diameter of the reaction section while maintaining an idealized laminar flow profile. The static mixer is constructed of stainless steel and consists of 12 helical

elements (StaticMixCo, NY). The Pyrex glass diffuser section expands from an inner diameter of 1.6 cm to 15 cm at an angle of 15°. The diffuser angle was chosen based on CFD simulations in order to minimize flow separation and recirculation. Detailed design of the inlet section is discussed in Section 3.

The CPOT reaction section consists of two 1.2 m × 17 cm ID cylindrical quartz tubes surrounded by an external water jacket (1 cm thickness) and flanged together with clamps and chemically resistant o-rings. Four ports along the reactor axis allow sampling of the reactor contents at different residence times. A transition cone at the end of the reactor concentrates the reactants into a common sampling line that can be split among multiple instruments; thus, samples extracted at the end of the reactor represent the so-called cup-mixed average of the entire reactor cross section. This design is similar to the exit cone of the UC Irvine flow tube reactor (Ezell et al., 2010). The Pyrex glass exit cone gradually reduces the diameter of the reactor from 15 cm to 0.72 cm at an angle of 15°. Similar to the inlet diffuser, the exit cone is temperature-controlled (Section 2.3).

The CPOT is designed to operate under laminar flow. The essential dimensionless group that differentiates laminar vs. turbulent flow is the Reynolds number,  $Re = \frac{\rho U D}{\mu}$ , where  $\rho$  is the fluid density,  $U$  is a characteristic velocity of the fluid,  $\mu$  is the fluid viscosity, and  $D$  is the tube diameter. For cylindrical tubes, the flow is considered laminar when  $Re < 2100$ . Under the typical CPOT flow rate (2 L min<sup>-1</sup>), the Reynolds numbers at the inlet cone, in the cylindrical section, and at the exit cone are 150, 20, and 450, respectively, well below the transition to turbulent flow.

## 2.2 Photolytic Environment

The reactor is housed within a 51 × 51 × 300 cm chamber containing 16 wall-mounted UV lamps. The arrangement of the lamps is outlined in Fig. 1D. Light intensity is adjustable (0, 25%, 50%, 75%, and 100%), and the UV spectrum can be set to a specific wavelength range with the installation of various T12 UV lamps, including Hg vapor lamps (emit narrow bands at 254 nm and 185 nm), UVB lamps (polychromatic irradiation centered at 305 nm) and UVA lamps (polychromatic irradiation centered at 350 nm), based on the experimental goals.

Quantification of light fluxes for each type of lamp is the prerequisite for performing photochemical experiments. A challenge associated with quantifying photon fluxes is that the flux emitted by the lamps is not necessarily that perceived by a molecule inside the reactor. Attenuation of photon fluxes can potentially arise from: 1) attenuation by the quartz wall and the water jacket surrounding the experimental sections; 2) reflection and/or refraction of light inside the chamber; and 3) absorption of light by gas-phase molecules (e.g. absorption of the 185 nm band by O<sub>2</sub> molecules). To overcome this challenge, we employ a method combining direct measurements and gas-phase chemical actinometry, where the directly recorded emission spectra are adjusted to the the observed photolysis rate of NO<sub>2</sub> ( $j_{NO_2}$ ). The advantage of this method is that the actual output spectra of the lamps are used, since the quantification of fluxes is based on what the molecules perceive inside the reactor. The water coolant in the jacket surrounding the tube is transparent at the UV wavelengths of interest, with the exception that it absorbs at the 185 nm band emitted by the Hg vapor lamps. Although the general UV cutoff of water is at 190 nm, we observed formation of 60 ppb of O<sub>3</sub> with a 2 L min<sup>-1</sup> flow rate under the full power of the Hg vapor lamp. The radiation intensity at 185 nm that penetrates into the reaction section is calculated to be about 10<sup>-5</sup> of that at 254 nm. The photon fluxes in the CPOT

from the three types of lamps are shown in Fig. 2 with a detailed description of the determination of photon fluxes provided in Appendix A.

### 2.3 Temperature Control in the Reaction Section

At full photolytic intensity, the lamps generate as much as 550 W of heat. To maintain a constant temperature and minimize convective mixing in the tube due to temperature inhomogeneity, each of the two reaction sections is fitted with a quartz cooling jacket, in which chilled water is circulated at a rate of 13 L min<sup>-1</sup>. Coolant is introduced into the jacket near the exit cone and exits at the inlet (Fig. 1A). Under typical operation, the cooling jacket can maintain the steady-state reactor temperature at a desired value between 20 and 38°C. Under full photolytic intensity of the UVA lamps, which produce the most heating among the three types of lamps, the temperature rise of air in the reactor is  $\leq 0.3$  K at steady state. Reactor temperature control is further addressed in Section 3.3.

### 2.4 Experimental Testing

Particles and vapor species are used to experimentally characterize the fluid dynamics inside the reactor. The injection scheme is illustrated by Fig. 1C. Polydisperse ammonium sulfate particles were generated by atomizing a 0.01 M aqueous solution with a constant rate atomizer (Liu and Lee, 1975). The atomized particles were immediately dried by a silica gel diffusion drier. The size distribution of particles was measured by a custom-built scanning mobility particle sizer (SMPS). For the particle RTD measurement, the particle counts were monitored with a TSI 3010 Condensation Particle Counter (CPC, Minneapolis, MN). Gas-phase RTD studies were performed under dark conditions. O<sub>3</sub> was generated by passing purified air through an O<sub>3</sub> generator (UVP, 97-0067-01), and the O<sub>3</sub> mixing ratio was monitored by a O<sub>3</sub> monitor (Horiba APOA-360). A Teledyne NO<sub>x</sub> Analyzer (Model T200) was used to monitor NO, NO<sub>2</sub>, and NO<sub>x</sub> in the experiment of the determination of photon flux. To measure the penetration efficiency of gas-phase species, a SO<sub>2</sub> monitor (Meloy Lab, SA285E) was used to detect SO<sub>2</sub> and a chemical ionization mass spectrometry (CIMS, Crounse et al., 2006; St. Clair et al., 2010) was employed to detect H<sub>2</sub>O<sub>2</sub>.

### 2.5 CFD Simulations

CFD simulations were performed using COMSOL Multiphysics 5.0 software (Stockholm, Sweden. www.comsol.com) to assist the design and characterization of the reactor. COMSOL uses a finite element method and has a number of built-in modules that can be utilized to simulate a specific experimental condition. Recently, several research groups have employed COMSOL in atmospheric and aerosol chemistry studies (Grayson et al., 2015; Sellier et al., 2015; Zhang et al., 2015). Here, the model geometry replicates that of the actual design; thus, the simulations include a static mixer, diffuser inlet, reaction section, and exit cone with exact dimensions (Fig. 3A).

At the design stage, the performance of the inlet section was simulated numerically using CFD models (Section 2.5). The actual static mixer containing 12 mixing elements was simulated by a 2-element mixer using the COMSOL built-in static mixer model. Flow profiles calculated using the 2-element static mixer model were found to be identical to those using static mixers

with 4 or more elements. Since static mixers yield asymmetric flow patterns, the model was solved in a 3D geometry. The entire 3D model was discretized with a fine mesh composed of approximately  $1.25 \times 10^6$  tetrahedral elements (Fig. 3B). The average element quality, which is a reflection of cell distortion (a value of 1 reflects a perfect element shape), was 0.77 with a minimum of 0.12. A finer mesh within the domain of the static mixer was applied to capture flow dynamics near the entrance to the diffuser cone (Fig. 3B). Model sensitivity to meshing was tested using a finer mesh density, and results were found to be identical. An impermeable and no-slip boundary condition was applied to all surfaces. The flow at the entrance into the static mixer was set to be  $2 \text{ L min}^{-1}$ , and the outlet pressure was assumed to be atmospheric. Simulations were conducted until a steady state was achieved, and the errors converged to  $< 10^{-6}$ .

Navier-Stokes equations were solved using the COMSOL laminar flow package in the CFD module assuming compressible, isothermal flow. The isothermal assumption will be relaxed subsequently. To evaluate the effect of reactor temperature gradients, the COMSOL laminar flow package was coupled to the convective and diffusive heat transfer interface. To visualize fluid flow through the reactor, transient simulations were performed using the COMSOL dilute species transport package. This model, when coupled to the Navier-Stokes equations, enables one to track convection and diffusion of a tracer species, as described in Section 4. After first generating the steady-state laminar flow profile, a 30 s rectangular pulse of a  $0.1 \text{ mol m}^{-3}$  tracer was introduced numerically into the reactor at the entrance to the static mixer to generate the RTD. No wall uptake of gases or particles was assumed in this computation. Molecular or Brownian diffusivity can be varied over several orders of magnitude to represent that of vapor molecules and particles. The simulation was run for 80 min with data output every 15 s (consistent with the data acquisition of the instruments, e.g.  $\text{O}_3$  monitor and CPC). Simulations were performed for a variety of different inlet geometries, flow rates, and reactor temperature gradients. These simulations served to evaluate the design against alternative configurations and also demonstrate the sensitivity of fluid field to various flow conditions.

## 2.6 Photochemical Model



While the CFD simulation serves as a comprehensive method to understand the fluid dynamics, it is not efficient to solve a complex chemical kinetic system within this framework. A simplified 1D axial-dispersion photochemical model based on the RTD measurement is built here to evaluate the oxidation level. The mechanism presented here is that in the absence of  $\text{NO}_x$ . The oxidation of 100 ppb  $\text{SO}_2$  by the OH radical is studied.  $\text{H}_2\text{O}_2$  at 1 ppm serves as the OH precursor. The three types of UV lamps are considered, sequentially, to investigate the effect of the radiation source on OH exposure. Each simulation is carried out at  $\text{RH} = 5\%$  and  $T = 295 \text{ K}$  (corresponding to  $[\text{H}_2\text{O}] = 1500 \text{ ppm}$ ). The case in the absence of  $\text{H}_2\text{O}_2$  input is also simulated to check the background OH level. Reactions of the full mechanisms and the rate coefficients including photolysis rate under different lamps that are necessary for the chemical kinetic modeling are listed in Appendix B.

The AD-PFR model setup is used in the present study and described in Appendix C. The Danckwerts boundary condition is employed to ensure the flux continuity at both the inlet and outlet (Davis and Davis, 2003). This model system is solved in MATLAB (R2015b) by a boundary value problem solver `bvp4c`. The PFR model is run simultaneously as a comparison. No wall interaction and new particle formation are considered in the models. The result will be discussed in Section 6.

### 3 Design of the Flow Tube Reactor

Essential elements of the design of a flow tube reactor are: (1) the manner by which reactants are introduced into the reactor; (2) the nature of the flow inside the reactor; (3) the type and location of the radiation source relative to the reactor itself; and (4) the management of heat generation owing to the radiation source. The first two correspond to the inlet section design, while the latter two address the problem of possible non-isothermal conditions in the reaction section.

#### 3.1 Injection Method

A number of possible arrangements exist to introduce material into a flow tube reactor (Fig. 4). The nature of the injection manifold has the potential to profoundly affect the flow profile in the subsequent reaction section. In the case of a laminar flow reactor, it is desirable to minimize such "end effects" in order to establish parabolic flow quickly within the reaction section; otherwise, phenomena such as jetting and recirculation have the potential to impact flow patterns throughout the entire reactor. Figure 4A depicts the simplest injection method, by which vapor and particles are introduced into the reaction section through a short injection tube. While a benefit of this design is its simplicity, with this mode of injection, it is challenging to distribute reactant mixtures evenly across the reactor cross section. We tested this inlet method on a cylindrical Pyrex glass tube and visualized the flow pattern by the injection of smoke (Fig. 4A). With flow controlled by a vacuum line attached to the exit section, the gas-particle mixture is pulled into the reaction tube at a rate that is dictated by mass conservation. Smoke visualization studies illustrate that the mixture concentrates in a plug at the center of the reactor. This "fire hose" effect arises from the enhanced velocity at the exit of the injection tube ( $U_{\text{avg, injection}}$ ). Such flow behavior is typical for that occurring with a sudden expansion (Bird et al., 2007).

Some flow tube designs address inlet issues using flow management devices, e.g. a spoked-hub/showerhead disk inlet (Bonn et al., 2002; Ezell et al., 2010) that distributes the reactants evenly about the reactor cross-section and provides sufficient mixing (Fig. 4B). Even when reactants are introduced gently into the tube, an axial distance is still required for the flow to develop to the characteristic parabolic laminar flow profile. This entrance length,  $L_{\text{entr}}$ , is estimated to be  $0.035 D \text{Re}$  (Bird et al., 2007). The inlet section should be designed with a sufficient entrance length  $L_{\text{entr}}$  to ensure the development of the laminar profile prior to the reaction section.

In the CPOT, reactants are injected via a conical diffuser (Fig. 4C) which has the advantage of gradually decreasing the velocity, thereby assisting with the formation of the laminar parabolic profile. The employment of a diffuser cone essentially replaces  $L_{\text{entr}}$ , and a parabolic profile is fully developed when the reactants reach the reaction section.

In addition to the flow field inside the reactor introduced by the inlet design, the transmission of different reactants (i.e. gas-phase species and particles) in the inlet system should also be considered (Karjalainen et al., 2016; Ortega et al., 2013, 2016; Palm et al., 2016; Simonen et al., 2016; Tkacik et al., 2014). Generally, a larger surface area means more interaction between the reactants and the walls, especially for "sticky" molecules. The effect of static mixer on the transmission of gas-phase species will be investigated in Section 5.1.

### 3.2 Angle of the Diffuser

A key consideration in designing a diffuser is avoiding flow separation that occurs when streamlines detach from the diffuser wall. Separation may be characterized by two flow patterns: stall and jetting flow. In stall, an asymmetrical flow pattern develops due to an adverse pressure gradient. Fluid is accelerated along one wall of the diffuser and recirculates slowly back along the other wall to the point of streamline detachment (Tavoularis, 2005). As demonstrated in Fig 4A, jetting flow is characterized by a symmetric flow pattern where the fluid is accelerated at the center of the diffuser and recirculates slowly along the walls. Recirculation introduces non-ideality since it accelerates gases and particles down the reactor, thereby affecting the residence time distribution (RTD) and leading to uncertain reaction times.

Diffusers are routinely applied in larger systems such as wind tunnels and turbines; therefore, most literature on diffuser design focuses on flow patterns at high Re ( $Re > 5000$ , e.g. Mehta and Bradshaw, 1979; Seltsam, 1995; Tavoularis, 2005; Prakash et al., 2014). As a rule of thumb for high Re systems, flow separation can be suppressed if the diffuser half-angle is  $\leq 5^\circ$ ; however, smaller angles are needed if the area ratio between the diffuser inlet and reactor section is much greater than 5 (Mehta and Bradshaw, 1979). We are unaware of studies that report diffuser performance at modest Re ( $< 500$ ). Fried and Idelchik (1989) recommend that diffusers be designed with an angle of divergence  $< 7^\circ$  to avoid flow separation; alternatively, White (2008) recommends an angle  $< 15^\circ$ . Sparrow et al. (2009) modeled the flow of fluid through diffuser cones at various Re. For further discussion about flow separation within diffusers, see Tavoularis (2005).

Under a typical working flow rate ( $2 \text{ L min}^{-1}$ ), the value of Re at the entrance of the conical diffuser is  $\sim 200$ . Figure 5 shows simulated flow profiles for a range of diffuser angles. The red traces represent streamlines, whereas the blue surface illustrates points where flow recirculation occurs, that is, where the axial velocity  $< 0 \text{ cm s}^{-1}$ . Collectively, these traces provide a visualization of the recirculation zone. We present flow profiles in the presence and absence of a static mixer since swirling flow has been shown to improve diffuser performance for systems with appreciable separation (McDonald et al., 1971).

As the diffuser angle increases, separation becomes more appreciable, and the recirculation zone penetrates farther into the reaction section ( $\Delta z > 0$ ). At the most extreme angle we considered ( $\theta = 37^\circ$ ), the simulation predicts that the first 46 cm of the reaction section is impacted by recirculation. For reference, the extreme of a sudden expansion ( $\theta = 90^\circ$ ) exhibits recirculation that penetrates nearly halfway through the reactor ( $\Delta z = 110 \text{ cm}$ ). For flow tube systems operated at similar Re as here, if a parabolic flow profile is desired, it is recommended that one utilizes a diffuser with  $\theta < 20^\circ$  in order to minimize laminar flow disturbance within the reaction section.

The presence of a static mixer tends to quell separation at moderate diffuser angles. The recirculation zone appears to propagate into the reaction section only at diffuser angles  $> 30^\circ$ ; however, the extent of this recirculation is substantially reduced compared to simulations in the absence of a static mixer. Furthermore, the recirculation zone is predicted to be symmetric; fluid from the static mixer is directed radially towards the walls of the diffuser and recirculates back towards the center. In contrast, the recirculation zone in diffusers without static mixers is predicted to be asymmetric (Fig. 5), with flow recirculating at one wall of the diffuser. With flow introduced via a sudden expansion, the presence of a static mixer does little to minimize recirculation. The improvement in diffuser performance with swirling flow at the inlet is consistent with observations at high

Re (McDonald et al., 1971), suggesting that the addition of a static mixer may help to mitigate moderate separation in systems employing wide-angled diffusers.

Figure 6 further illustrates the CFD-modeled velocity profiles for the actual CPOT design, with a  $15^\circ$  diffuser cone coupled to a static mixer, in the region of the reactor extending from the inlet cone to the first 10 cm of the reaction section. We refer to this section of the reactor as the "inlet-affected" region, since axial positions farther downstream exhibit fully-developed laminar profiles. Figure 6A visualizes the entire velocity field along select cross-sections within the inlet-affected region, whereas Fig. 6B presents 1D velocity profiles at various axial positions. Note that Fig. 6A presents the velocity magnitude, whereas Fig. 6B illustrates the axial velocity component (i.e., flow in the  $z$ -direction) to facilitate identification of regions impacted by flow recirculation. In general, the simulation predicts the absence of recirculation within the reactor under isothermal conditions. As demonstrated by Fig. 6B, the simulated axial velocity profile immediately downstream of the static mixer exhibits two jets with a maximum axial velocity of  $31 \text{ cm s}^{-1}$ . The jets quickly dissipate as the flow develops through the diffuser cone. At the exit of the diffuser cone, the flow is nearly parabolic, and the maximum velocity slows to  $0.5 \text{ cm s}^{-1}$ . Within 10 cm of the diffuser exit, the flow becomes parabolic with a maximum centerline velocity of  $0.4 \text{ cm s}^{-1}$ . We also simulated the fluid field under higher flow rates (e.g.  $4$  and  $6 \text{ L min}^{-1}$ ) and found no separation of flow within the diffuser. These results demonstrate that the CPOT inlet is within the design limits for a diffuser with non-separated flows and that the presence of a static mixer has little effect on the parabolic profile in an isothermal reaction section. However, the presence of the static mixer does have an impact on the residence time of the reactants. Fig. 6C shows the corresponding residence time at the three positions for both vapor molecules and monodisperse particles, both of which are a  $30 \text{ s}$  square wave input. Section 4.3 addresses RTD.

### 3.3 Non-isothermal Effect

Precise control of temperature is crucial in maintaining as well-characterized a laminar flow as possible in the reaction section (Khalizov et al., 2006; Jonsson et al., 2008). In one class of flow tube design, the radiation source is positioned within the flow tube reactor itself, and the reactor walls are constructed of a UV blocking material. In that design, the effect of the internal heat source on the flow must be taken into account. In the present design, with the reaction tube suspended at the center of the chamber and the lights positioned on the outside of the tube, an exterior water jacket provides a heat transfer medium, while allowing penetration of UV radiation to the reactor. If water recirculation in the jacket is sufficiently rapid, axial temperature gradients in the cooling jacket can be minimized. Any jacket temperature maintained appreciably below or above that in the reactor itself will lead to temperature gradients that may induce secondary flows in the reactor.

Although the CPOT is equipped with a temperature control system (Section 2.3), maintaining a target temperature under UV irradiation is challenging. The measured rise in coolant temperature at steady state under full irradiation conditions is  $\leq 0.2 \text{ K}$ . Given the absence of heat sources within the reactor itself, the increase in coolant temperature is a result of the absorption of heat generated by the exterior UV lamps. Temperature gradients along the reactor wall have the potential to induce recirculation from changes in density. The establishment of radial temperature gradients near the wall induces recirculation cells as density variations force the flow to stratify.

The dimensionless group that characterizes the effect of free convection on flow is the Richardson number, which relates the strength of buoyancy forces to that of convective forces. The Richardson number (Holman, 2010),  $Ri$ , can be expressed as the ratio of the Grashof number,  $Gr$ , to the square of the Reynolds number,  $Re$ :

$$Ri = \frac{Gr}{Re^2} = \frac{g\beta D^3 \Delta T / \nu^2}{(\rho U_{avg} D / \mu)^2} \sim \frac{gD}{T U_{avg}^2} \Delta T \quad (1)$$

- 5 where  $g$  is the gravitational acceleration,  $\beta$  is the thermal expansion coefficient of air ( $\frac{1}{T}$  for ideal gases),  $U_{avg}$  is the average fluid velocity,  $\nu$  is the kinematic viscosity of air ( $\frac{\mu}{\rho}$ ), and  $\Delta T$  is a characteristic temperature difference between the tube wall and centerline. When  $Ri < 0.1$ , convective forces dominate, and effects of buoyancy on the flow are small. When  $Ri > 10$ , buoyancy forces may lead to flow bifurcation and recirculation. Under typical CPOT operating conditions, a radial temperature gradient between the fluid and wall of  $\sim 0.007$  K is required to maintain  $Ri < 10$ . Because this is a very small temperature  
10 difference, modest inequalities in temperature are anticipated to affect flow patterns within the reactor.

To investigate the effect of wall temperature differences on flow within the reaction section, we performed COMSOL simulations, assuming a non-isothermal reactor wall. The COMSOL laminar flow package was coupled to the convective and diffusive heat transfer interface. Since water is assumed to flow uniformly through the annular water jacket cross section from the exit to the entrance, we apply an axial temperature gradient to the simulation. A schematic illustration of the simulation  
15 setup is shown in Fig. 3C. At the exit of the reaction section, the temperature of the reactor wall is set to that of water entering the cooling jacket ( $T_{in}$ ). At the entrance to the reaction section, we assume that the wall temperature is that of the water exiting the cooling jacket ( $T_{out} = T_{in} + \Delta T$ ). The wall temperature is assumed to change linearly between the entrance and exit. The diffuser cone is prescribed at a constant temperature equivalent to the cooling jacket temperature  $T_{out}$ , whereas the exit cone is prescribed a constant temperature of  $T_{in}$ . In the following discussion, we focus on results with  $T_{in} = 23^\circ\text{C}$ , which is the typical  
20 room temperature in the Caltech laboratory. Note that this model setup is a simplified case, since in actual experiments the entrance and exit cones should be kept at the same temperature (i.e.,  $T_{in}$ ); this will introduce temperature discontinuity between the entrance cone and the reaction tube. Nonetheless, this idealized model provides insight into the temperature difference induced flow perturbation within the flow tube reactor.

Figure 7 demonstrates the simulated effect of an axial temperature gradient ( $\Delta T$ ) on flow profiles within the reactor. Figure  
25 7A illustrates 2D velocity profiles at various axial positions and a blue isosurface where the axial velocity  $< 0$  cm s $^{-1}$ . Figure 7B illustrates 1D velocity profiles at the midpoint of the reactor. As the temperature gradient within the reactor increases, the velocity profiles skew owing to the buoyancy of the warm air. This bifurcation induces recirculation and is predicted to affect the entire reactor region. For a temperature gradient of 0.2 K (equivalent to that actually measured), the recirculation zone exhibits a maximum velocity of  $-0.15$  cm s $^{-1}$ .

- 30 The simulations demonstrate the sensitivity of the velocity profile in the reactor to small temperature gradients within the reaction section. Such disturbances will manifest in shorter, broader residence times due to induced recirculating flow. As demonstrated in Fig. 7, a critical temperature difference exists at which recirculation becomes important. At a volumetric flow of 2 L min $^{-1}$ , this critical temperature difference between the exit and the entrance is estimated to be  $\sim 0.08$  K. The  $Ri$  number criterion indicates that higher flow rates reduce the reactor sensitivity to temperature gradients. We find the critical

temperature differences at  $4 \text{ L min}^{-1}$  and  $6 \text{ L min}^{-1}$  are 0.18 K and 0.3 K, respectively. Even at higher flow rates, relatively small temperature gradients along the walls of the reactor can have potential consequences on reactor flow patterns.

## 4 Behavior of Gaseous and Particulate Species in a Laminar Flow Tube Reactor

### 4.1 Fluid Field in the Reaction Section

- 5 At the typical operating flow rate ( $2 \text{ L min}^{-1}$ ), flow within the reaction section is laminar ( $\text{Re} \cong 20$ ), under which the axial fluid velocity is given by the parabolic distribution,

$$v_z(r) = U_{\max} \left[ 1 - \left( \frac{r}{R} \right)^2 \right] \quad (2)$$

- where  $U_{\max}$  is the centerline velocity,  $r$  is the radial coordinate in the tube, and  $R$  is the tube radius. The residence time of fluid elements in laminar flow differs along streamlines, for which the average residence time of fluid elements is precisely  
10 calculated. Owing to the sensitivity to small temperature difference, as noted above, the actual velocity profile in the reactor under non-isothermal condition will not adhere to an ideal parabolic distribution.

### 4.2 Penetration Efficiency ( $\eta$ )

- The penetration efficiency  $\eta$  is defined as the fraction of material entering the reactor that leaves in the absence of chemical reaction. If no removal occurs during flow through the reactor, then  $\eta = 1$ . Diffusional loss in a laminar cylindrical tube is  
15 addressed in Appendix D. The mass conservation Eqs. (D2) to (D5) can be solved either numerically or analytically (Davis, 2008) to determine the penetration efficiency  $\eta$ , given a first-order loss rate to the wall,  $k_{wi}$ . For the case of complete removal of species  $i$  at the wall, in which  $k_w \rightarrow \infty$ , corresponding to the boundary condition  $c_i = 0$  at the wall, the analytical solution for  $\eta$  is (Fuchs, 1964):

$$\eta = 0.8191 \exp(-3.657\xi) + 0.0975 \exp(-22.3\xi) + 0.0325 \exp(-57\xi) + \dots \quad (3)$$

- 20 where  $\xi$  is the dimensionless length ( $\frac{\pi \mathcal{D} L_{\text{cylid}}}{Q}$ ),  $\mathcal{D}$  is the diffusivity of the species,  $L_{\text{cylid}}$  is the length of the cylindrical tube, and  $Q$  is the volumetric flow rate. For small  $\xi$ , i.e.  $< 0.02$ , an alternative equation is available (Gormley and Kennedy, 1948):

$$\eta = 1 - 2.56\xi^{2/3} + 1.2\xi + 0.177\xi^{4/3} \quad (4)$$

The penetration efficiency for particles is size dependent, i.e.  $\eta(D_p)$ . We will address the RTD of particles in Section 4.3.2 and Appendix F.

### 25 4.3 Residence Time Distribution (RTD)

In a laminar flow field, idealized non-diffusing vapor or non-diffusing and non-settling particles, introduced as a pulse at the entrance of the tube, will first emerge as a pulse at the residence time of the centerline, followed by a decaying curve as the

material on the slower streamlines reaches the exit. Under actual conditions, vapor molecules undergo molecular diffusion in both the radial and axial directions, and particles are subject to Brownian diffusion and gravitational settling.

#### 4.3.1 Vapor Molecule RTD

Vapor molecules in laminar flow in a tube undergo molecular diffusion in both the radial and axial directions. With molecular diffusion coefficient  $\mathcal{D}_i$ , the characteristic diffusion time in the radial direction is  $\tau_{c,\mathcal{D}_i} = \frac{R^2}{\mathcal{D}_i}$ . To assess the importance of radial diffusion as a mechanism for smearing vapor molecules across the tube cross-section during convection down the tube, one can compare the characteristic timescale for radial diffusion with the characteristic residence time in the cylindrical tube,  $\tau_{c,\text{cyl}} = \frac{L_{\text{cyl}}}{U_{\text{avg}}}$ . If  $\tau_{c,\mathcal{D}_i} \ll \tau_{c,\text{cyl}}$ , for example, the vapor molecules will diffuse more or less uniformly across the tube radius in the time it takes for the fluid to flow to the tube exit. Likewise, if  $\tau_{c,\mathcal{D}_i} \gg \tau_{c,\text{cyl}}$ , each vapor molecule will effectively remain on the streamline upon which it entered. Vapor molecules also diffuse in the axial direction; this process is represented by the axial diffusion term,  $\mathcal{D}_i \frac{\partial^2 c_i}{\partial z^2}$ , on the right hand side of Eq. (D1). As noted earlier, for flow velocities of the magnitude of those here, the effect of this axial diffusion is negligible when compared with axial convection. However, an apparent axial diffusion can arise from the interaction of radial molecular diffusion and the laminar flow, a process known as Taylor dispersion (Taylor, 1953; Bird et al., 2007). Under the criterion,  $\tau_{c,\text{cyl}} \gg \frac{\tau_{c,\mathcal{D}_i}}{3.83^2}$ , the concentration becomes approximately uniform over the cross-section of the tube. Appendix E presents a discussion of the application of Taylor dispersion based RTDs with respect to different initial conditions.

In the PAM reactor (Lambe et al., 2011a), the Taylor dispersion criteria do not strictly meet the working conditions, however, the two flow regime fitting results suggest that two types of flow may exist in the reactor: a direct flow with minor dispersion and a secondary recirculation flow with significant dispersion. Under the current flow rate of  $2 \text{ L min}^{-1}$  and characteristic vapor molecular diffusivity  $\sim 1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ ,  $\tau_{c,\text{cyl}} = 1290 \text{ s} \gg \frac{\tau_{c,\mathcal{D}_i}}{3.83^2} = 50 \text{ s}$ ; therefore, the Taylor dispersion approximation for the gas-molecule RTD applies, and Taylor dispersion can be expected to be important. Note that the presence of the static mixer and conical diffuser in the inlet section alters the input distribution of vapor molecules and particles at the entrance of the reaction section (Fig. 6C) from an idealized uniform initial condition, and Eq. (E3) will not hold exactly for the fitting of the results from actual pulse RTD experiments. The convolution (Eq. (E6)) of the skewed input shape must be numerically calculated. The actual RTD of the reactor should also include the RTDs in the exit cone and sample line.

#### 4.3.2 Particle RTD

For the behavior of particles in the reactor, in general, the following processes need to be accounted for: (1) advection; (2) Brownian diffusion; (3) gravitational settling; (4) growth/shrinkage owing to mass transfer from or to the gas phase; and (5) coagulation. The particle number concentration distribution as a function of particle diameter  $D_p$  is denoted  $n(D_p, r, z)$ . Processes (1) - (4) are related to the penetration efficiency, while the total mass of particles are conserved during the coagulation process with the size distribution being shifted. To discuss the penetration efficiency, coagulation is not included here, which will be further discussed in Section 5.1.2

In general, particles undergo both Brownian diffusion in the flow as well as settling under the influence of gravity. Collectively, these processes give rise to particle loss by deposition on the wall during transit through a laminar flow tube reactor. The Brownian diffusion coefficient of a 80 nm diameter particle is approximately four orders of magnitude smaller than that of a typical vapor molecule. Consequently, for typical particle sizes and residence times in the reactor, the Brownian diffusion of particles can be neglected, except in the region very close to the wall, wherein particle uptake at the wall because of diffusion can occur. Gravitational settling of particles in a horizontal tubular flow reactor occurs as particles fall across streamlines and deposit on the lower half of the tube. To assess the effect of gravitational settling of particles, one needs to compare the characteristic settling distance during transit through the reactor,  $v_s \tau_{c,cyl}$ , with the tube radius,  $R$ , where  $v_s$  is the particle settling velocity. Figure 8 shows the size-dependent settling velocity and particle diffusivity for spherical particles. Under typical operating conditions, particles introduced uniformly across the entrance will tend to settle somewhat during transit down the reactor, so this process needs to be accounted for in analyzing particle RTDs. The full equation describing the motion of particles in the horizontal tubular laminar flow under simultaneous diffusion and settling cannot be easily solved. As suggested by the particle-size dependence of settling velocity and diffusivity in Fig. 8, consideration of the two separate regimes, i.e., diffusion and settling, respectively, can simplify the problem. Here we define the diffusion regime as that for particles with diameter  $\leq 80$  nm and otherwise for the settling regime. In each regime, we will consider only one process, i.e. either diffusion or settling.

A discussion of the motion of particles in the settling regime is presented in Appendix F. The corresponding RTD (Eq. (F4)) can be calculated based on the particle trajectories. In the diffusion regime, the settling velocity can be ignored, and Taylor dispersion is not applicable. The RTD of a pulse input can be approximated by the residence time along each streamline (Eq. (F7)). Since actual particles undergo some degree of radial Brownian diffusion, which is not considered in Eq. (F7), the full RTD should exhibit a broader and smoother profile than that predicted by Eq. (F7) (as simulated by COMSOL, see Section 5.2.2).

The penetration efficiency ( $\eta$ ) for mono-disperse particles can be calculated in their respective regimes. In the settling regime, Equation (F6) calculates the size dependent  $\eta$ . The behavior of particles in the diffusion regime can be calculated by Eqs. (3) and (4), where removal of particles at the wall is assumed. This is consistent with the boundary condition of the particles in the settling regime.

## 5 Results and Discussion

### 5.1 Experimental Evaluation of Penetration Efficiency

The penetration efficiency ( $\eta$ ) was determined by using a constant input of either gas-phase species ( $\text{SO}_2$ ,  $\text{O}_3$ , and  $\text{H}_2\text{O}_2$ ) or polydisperse ammonium sulfate particles through the static mixer or through the flow tube. The relative humidity (RH)-dependent penetration efficiency is investigated for both gas-phase species and particles. The results are shown in Fig. 9.

### 5.1.1 Vapor Molecules



The  $\eta$  of  $O_3$  in both the static mixer and the flow tube is constant ( $\eta \sim 98\%$ ) over a wide RH range.  $SO_2$  shows no removal by the static mixer, while  $H_2O_2$  exhibits a loss of 20% to 40% in the static mixer. The measured  $\eta$  values in the flow tube of all the gas-phase species ( $O_3$ ,  $SO_2$ , and  $H_2O_2$ ) are essentially 100 % under dry conditions ( $RH < 5\%$ ). In the flow tube, the  $\eta$  values of both  $SO_2$  and  $H_2O_2$  decrease with RH. At  $RH = 42\%$ , about 70% of  $H_2O_2$  is lost, while at this RH about 20% of  $SO_2$  is lost. These results show the complexity of the  $\eta$  of gas-phase species. The extent of wall deposition of organic vapors in the flow tube reactor requires a comprehensive study and will be addressed in a future publication.

### 5.1.2 Particles

The  $\eta$  values for polydisperse ammonium sulfate particles are also investigated at different RH. No RH-dependence was found for  $RH < 50\%$ , which is below the deliquescence RH of ammonium sulfate (results not shown). Figures 9C and D show the measured size distributions before and after the static mixer and the flow tube, as well as the size-dependent penetration efficiency obtained as a ratio. Figure 9C indicates that about half of the small particles ( $< 50$  nm) are lost in the static mixer, while large particles ( $> 100$  nm) penetrate essentially entirely through the static mixer. This is reasonable since the flow inside the static mixer is laminar ( $Re = 150$ ). The smaller particles diffuse to the static mixer, while the larger ones follow the flow streamline.

The theoretical particle  $\eta$  curves under the influence of loss by gravitational settling and diffusion have also been calculated by applying the relevant parameters to Eqs. (4) and (F6) (Fig. 9D). Only the reaction sections were considered in this theoretical calculation (i.e. the inlet and exit cones are excluded). We consider this calculation as a qualitative guideline for  $\eta$ . Settling velocity and diffusivity of particles are size-dependent (Fig. 8), resulting in reduced transmission for very small and large particles, due to diffusion loss and gravitational settling, respectively. Both measurements and theory indicate that  $\eta$  is maximized at a particle diameter of approximately 100 nm. The measured maximum penetration efficiency is  $\sim 80\%$ , indicating a loss of particles, which is likely caused by secondary flow that actively conveys particles closer to the wall. This secondary flow will be discussed in Section 5.3. Also, the behavior of particles in the exit cone is difficult to predict and may reflect a certain extent of particle loss.



A numerical coagulation model is used to check the influence of coagulation on particle size distribution. This model uses a PFR framework with an average residence time of 1520 s, which is the measured particle average residence time (Section 5.2.2). A unity coagulation efficiency is assumed and no wall deposition of particles. The result is shown in Fig. 10. The comparison indicates that the coagulation process lowers the small particle number, accounting for about half of the missing small particles. The total particle number concentration and average residence time are the two key parameters that impact the coagulation process. Coagulation will have a negligible influence in the case of smaller particle number and shorter residence time. The CPOT typically uses particle number and surface concentrations in the order of magnitude of  $10^4 \text{ cm}^{-3}$  and  $10^3 \mu\text{m}^2 \text{ cm}^{-3}$ . Note that coagulation process itself has an impact only on the size distribution not the total particle mass. However, the presence of coagulation may enhance the gravitational settling effect owing to the production of larger particles.

## 5.2 Experimental Evaluation of RTD

We present here the results of experimental evaluation of the RTD for both vapor molecules and particles. The RTD profiles were determined by introducing a 30 s pulse of O<sub>3</sub> or polydisperse ammonium sulfate particles into the reactor under dry conditions (RH < 5%). All experiments were performed at the typical operating flow rate of 2 L min<sup>-1</sup> in at least triplicate.

5 The average residence time ( $\tau_{\text{avg}}$ ) was obtained from each RTD profile according to:

$$\tau_{\text{avg}} = \frac{\sum I_j t_j}{\sum I_j}, \quad (5)$$

where  $I_i$  is the signal recorded at each time step  $t_j$ .

### 5.2.1 Vapor Molecules

As noted earlier, a typical value of diffusivity,  $1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ , is used in COMSOL to predict the gas-phase RTD. Measured and predicted gas-phase RTDs are shown in Fig. 11A. A large discrepancy is observed between the measured and theoretical RTD under presumed isothermal conditions. The predicted gas-phase RTD exhibits a symmetrical distribution centered at approximately 27 min. However, the measured RTD of gas-phase O<sub>3</sub> exhibits an asymmetrical feature, somewhat similar to the particle RTD (Fig. 11B). The  $\tau_{\text{avg}}$  values obtained from the O<sub>3</sub> pulse experiments and simulations are also summarized in Fig. 11A. The measured  $\tau_{\text{avg}}$  value of O<sub>3</sub> is shorter than predicted by 1.5 min. Potential explanations for measured RTDs are discussed in Section 5.3.

### 5.2.2 Particles

A typical value of particle diffusivity,  $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , corresponding to that of a  $\sim 100 \text{ nm}$  diameter particle, is used in COMSOL to predict the RTD. Figure 11B compares the measured RTD of polydisperse ammonium sulfate particles to that of the COMSOL simulation. Under isothermal conditions, the particle RTD exhibits a zigzag feature which is likely due to the static mixer that may distribute particles somewhat unevenly across streamlines, as can be seen in the velocity profile in Fig. 6A. As laminar flow develops in the reaction section, particles follow their respective streamlines until the exit cone, appearing as the zigzag pattern on the RTD profile. This zigzag feature is absent in the vapor molecule RTD, likely due to the larger diffusivity of vapor molecules. The theoretical RTD of particles in an idealized laminar flow reactor exhibits a sharp peak when the center line first arrives at the exit (Eq. F7). The experimental RTD observed exhibits a rather gradual rise instead of a sharp pulse likely due to the method of introduction (Fig. 6C). Figure 11B shows that, under isothermal conditions, the modeled RTD reproduces the shape and the peak time of the observed RTD, and the  $\tau_{\text{avg}}$  values also show excellent agreement. However, the modeled RTD appears narrower than that observed. This indicates that particles arrive earlier and remain for a longer time than COMSOL predicts.

Overall, the experimental RTD results of both gas-phase species and particles in the CPOT are essentially comparable to those of present flow reactors (Lambe et al., 2011a), given the arrival time and the width of the peak. This discrepancy of the RTDs between the theoretical laminar flow and the real flow indicates the presence of non-ideal flow in the reactor.

### 5.3 Non-ideal Flow in the Reactor

The discrepancy between isothermal laminar flow theory and the experimental results can be attributed in part to non-isothermal conditions in the reactor. As noted earlier, the Richardson number (Eq. (1)) criterion indicates that a small temperature difference ( $\sim 0.007$  K) between the bulk and the wall can induce recirculation flows. The measured particle RTDs under isothermal conditions are compared to that obtained under maximum UVA radiation in Fig. 11B. A pronounced difference is that the RTD curve under radiation appears much smoother. The  $\tau_{\text{avg}}$  value under irradiation is shortened by 1.5 min compared to that under isothermal conditions. Given the close agreement between the two RTD profiles, it is unlikely that a recirculation within the tube exists; more likely, the slight non-isothermal condition has created secondary flows that act to mix the tracers both radially and axially.

To further investigate non-isothermal effects, the temperature of the water jacket was raised in a step-wise manner to approach a significant temperature difference between the bulk flow and the wall. The experiments were conducted in the absence of UV radiation. The injected air was at room temperature (approximately  $23^\circ\text{C}$ ), so a higher water jacket temperature exacerbates the deviation from isothermal conditions. The results of these experiments are shown in Fig. 12. The RTD at each temperature is the average of 3 to 4 replicates. As shown in Fig. 12A, the RTD at  $25^\circ\text{C}$  appears indistinguishable from that at quasi-isothermal conditions (the dashed line, we use "quasi-isothermal" here to distinguish from strict isothermal conditions in the model). Particles arrive at the exit cone earlier at higher water jacket temperatures, mirroring the observed discrepancy between the modeled and observed RTD profiles. This trend is clearly illustrated by Fig. 12B, where the arrival time of particles in each experiment is shown as a function of the water jacket temperature. This observation is consistent with the hypothesis that a difference in temperature between the wall and the inlet flow leads to the non-ideal conditions.

Consider that the wall of the reactor is at a constant room temperature as slightly cooler air is introduced into the reactor. Two orthogonal forces interact with each other in the horizontal flow tube when they are of similar orders of magnitude: forced convection by the pressure gradient (horizontal) and buoyancy-induced free convection (vertical). The actual velocity field in this situation is challenging to simulate (Iqbal and Stachiewicz, 1966; Mori and Futagami, 1967; Faris and Viskanta, 1969; Siegwarth et al., 1969). Generally, to satisfy mass conservation, the air close to the wall is warmed and rises along the side wall, inducing a downward flow in the center of the tube, forming two symmetric vortices. Superposition of the primary forced convective and the secondary free convective flows convert the vertical recirculation into spiral motions along the tube. The spiral flow developed in the reaction section plays a similar role as the static mixer in the inlet section. The spiral flow is more easily established if there are hot spots inside, which can be likely, as the sample ports on the reaction sections are not heat-insulated by the water jacket. To quantitatively represent this effect, one can introduce an enhanced isotropic eddy-like diffusivity ( $\mathcal{D}_e$ ), a statistical fluid field related property.

To verify the presence of the spiral secondary flow in the CPOT, we systematically increased the diffusivity used in the COMSOL simulations. The agreement between simulated and observed RTD improves, as the value of  $\mathcal{D}_e$  is increased in the COMSOL simulation, with the optimal agreement achieved when  $\mathcal{D}_e = 4.5 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  and  $6.0 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  for  $\text{O}_3$  and particles, respectively (Fig. 13). These  $\mathcal{D}_e$  values are, respectively, 45 and  $6 \times 10^5$  times the diffusivity of vapor molecules

and particles from the strictly parabolic flow base case (Fig. 11). The vapor molecule RTD (Fig. 13A) no longer exhibits the symmetrical feature of the base case, due to the enhanced Taylor dispersion. The particle RTD (Fig. 13B) is also substantially broadened compared to the base case and exhibits close agreement with the observations. The optimal  $\mathcal{D}_e$  values for vapor molecules and particles are similar, suggesting that the molecular diffusion in the CPOT is dominated by the secondary flows.

5 This offers an explanation for the similarity in the observed RTD profiles of  $O_3$  and particles, despite orders of magnitude difference in their inherent diffusivity.

To further evaluate the  $\mathcal{D}_e$  values determined from the COMSOL simulations and the hypothesis of secondary flows, one can adopt a separate approach to examine  $\mathcal{D}_e$ . Given the mixing provided by the static mixer and the conical diffuser, the optimal values of  $\mathcal{D}_e$  can be applied in Eq. (E5). The values of  $U_{\text{avg,fit}}$  and  $\tau_{c,\text{cyl,d,fit}}$  are adjusted to find the best match between Eq.

10 (E5) and the observed RTD profiles. The optimal fitting results are shown in Fig. 13. The fitted average flow velocity ( $U_{\text{avg,fit}}$ ) is  $2.1 \times 10^{-3} \text{ m s}^{-1}$ , which results in a characteristic residence time  $\tau_{c,\text{cyl,d,fit}}$  of 1360 s. This  $U_{\text{avg,fit}}$  value agrees well with the designed average velocity ( $2.0 \times 10^{-3} \text{ m s}^{-1}$ ). This observation again suggests that the non-isothermal secondary flow induced eddy-like diffusion dominates the mass transport process in the tube.

Overall, these results highlight the importance of temperature effects in approaching an ideal flow condition in a gas-phase  
15 laminar flow reactor. Even a small temperature deviation can likely create secondary flows in the flow field that affect both the RTD and the  $\tau_{\text{avg}}$  of tracers. It is to be noted that these secondary flows occurring at  $\text{Re} \cong 20$  should be distinguished from the classic turbulent flow.

## 6 Photochemical Model



The fitted parameters in Section 5.3 have been used in the simulation of the photochemical reactions, and the results are shown  
20 in Fig. 14. The absorption cross section of  $H_2O_2$  increases exponentially towards shorter wavelengths; hence, the Hg vapor lamp (Fig. 2) is highly efficient in photolyzing  $H_2O_2$ , whereas the efficiency drops substantially when UVB and UVA lamps are employed (Fig. 14A). The decay of  $SO_2$  (Fig. 14B) and the steady-state concentration of the OH radical (Fig. 14C) follow the photolysis rates of  $H_2O_2$  under each type of radiation. The model simulation also confirms that the OH radical reaches a steady state immediately, with its steady-state concentration, ranging from  $\sim 10^6$  to  $\sim 10^9$  molecules  $\text{cm}^{-3}$ , staying uniform  
25 along the entire tube in the presence of a high mixing ratio of  $H_2O_2$ .

As mentioned in Section 2.2, a small amount of the 185 nm radiation is present in the CPOT when Hg vapor lamps are equipped. Radiation at 185 nm generates additional OH radicals via photolysis of  $O_2$  and subsequent reaction between  $O(^1D)$  and  $H_2O$ . We have performed control simulations to investigate the relative contribution of the OH radical generated from this pathway. No OH was generated in the absence of photolysis of  $O_2$  that happens only in the presence of the 185 nm radiation  
30 (data not shown). With the full Hg vapor emission, even at an RH as low as 5%, a significant amount of the OH radical was generated in the absence of  $H_2O_2$ . The  $SO_2$  decay without  $H_2O_2$  was approximately half that with  $H_2O_2$  (Fig. 14B). The OH concentration at the end of the reactor reached the same level as the case in which  $H_2O_2$  is added (Fig. 14C) but a major

difference was observed in the concentration profile of the OH radical along the tube. Without  $\text{H}_2\text{O}_2$ , the OH concentration increases along the tube, and consequently, the decay profiles of  $\text{SO}_2$  do not follow that of a first-order decay.

Discrepancies were observed in the  $\text{H}_2\text{O}_2$  and  $\text{SO}_2$  concentration profiles near the inlet and exit of the CPOT between the PFR and AD-PFR models (Fig. 14A and B). These discrepancies arise from the necessary Danckwerts boundary condition, which is more significant at higher oxidation levels. The profiles indicate the effect from the axial dispersion, which arises from the axial mixing induced by secondary flow inside the reactor. The axial dispersion always acts to lower the conversion of the reactant by smoothing the concentration gradient caused by reactions.

The OH exposure ( $\text{OH}_{\text{exp}}$ ) is commonly obtained based on the PFR assumption, using the initial and final concentrations of  $\text{SO}_2$ , i.e.  $[\text{SO}_2]_0$  and  $[\text{SO}_2]_\tau$ :

$$\text{OH}_{\text{exp}} = \int [\text{OH}](t) dt = \frac{1}{k_{\text{SO}_2+\text{OH}}^{II}} \ln \frac{[\text{SO}_2]_0}{[\text{SO}_2]_\tau} \quad (6)$$

However, to use the PFR assumption, the effect of radial and axial dispersion need to be addressed. Under the PFR framework, the radial diffusion is considered to be rapid, and the concentration is uniform within the cross section. This assumption can be justified by comparing the radial diffusion time scale ( $\frac{R^2}{\mathcal{D}}$ ) with the axial convection time scale ( $\frac{L}{U}$ ), i.e.  $\frac{R}{L} \text{Pe}$ , where  $\text{Pe}$  is the Péclet number. A ratio of  $\sim 0.01$  with the fitted parameters indicates that radial diffusion is approximately 100 times faster than convection and that a uniform cross-section concentration can be expected in the absence of any chemical reactions. The dimensionless number that relates the reaction rate to the diffusion rate is the Damköhler number ( $\text{Da} = \frac{k^I R^2}{\mathcal{D}}$ , where  $k^I$  is a first-order reaction rate). In the case of the oxidation of  $\text{SO}_2$  by OH,  $k^I = k_{\text{SO}_2+\text{OH}}^{II} [\text{OH}]$ . If  $\text{Da} \ll 1$ , the radial diffusion rate overwhelms the reaction rate, and a uniform cross-section concentration can be expected. In the current chemical system, even with the Hg vapor lamps (the largest  $j_{\text{H}_2\text{O}_2}$  and therefore the most rapid  $k_{\text{SO}_2+\text{OH}}^{II}$ ), the  $\text{Da}$  value is  $0.011 \ll 1$ . We conclude that the radial diffusion always dominates in the reactor and that the simplified 1D model framework employed in the current work is valid.

On the other hand, the effect of axial dispersion should be counted in interpreting experimental data (Donahue et al., 1996; Howard, 1979). For the first-order reaction system, Howard (1979) showed that the axial dispersion lowers the effective rate constant of a first-order reaction by the factor  $(1 - \frac{\mathcal{D}k^I}{U^2})$ . Thus, for the pseudo-first-order reaction in which OH is effectively constant, the  $\text{OH}_{\text{exp}}$  in Eq. (6) is modified as:

$$\text{OH}_{\text{exp}} = \frac{1}{(1 - \frac{\mathcal{D}k^I}{U^2}) k_{\text{SO}_2+\text{OH}}^{II}} \ln \frac{[\text{SO}_2]_0}{[\text{SO}_2]_\tau} \quad (7)$$

According to Eq. 7, the effect of axial dispersion is enhanced when the OH oxidation proceeds more rapidly (i.e. at higher  $k^I$  values) or the axial dispersion is stronger. There are several ways to estimate the OH exposure in the axially-dispersed flow system. Li et al. (2015) calculate the residence time dependent  $\text{OH}_{\text{exp}}$  first and then couple this relationship with the RTD. Because of the uniform OH concentration along the tube, the method by Li et al. (2015) and Eq. (6) give the same  $\text{OH}_{\text{exp}}$ . In this work, we employ Eq. (7) for the AD-PFR model and compare the results with those calculated by Eq. (6) for the PFR model. The simulated  $\text{OH}_{\text{exp}}$  results are summarized in Table 1, along with their atmospheric equivalent time scale. The results

show that the PFR model always gives a higher  $\text{OH}_{\text{exp}}$  value and there is about an 8 ~ 10% difference between the values calculated by the PFR and AD-PFR models, indicating the effect from axial dispersion. Peng et al. (2015) have performed a detailed comparison of  $\text{OH}_{\text{exp}}$  calculated with the PFR model, the coupling of RTD with PFR model, and the experimental tracer decay method. The authors have recommended using the experimental tracer decay method. For a non-ideal flow reactor, we suggest to use Eq. (7) to account for axial dispersion in the evaluation of  $\text{OH}_{\text{exp}}$ .

Overall, the current photochemical model indicates that with  $\text{H}_2\text{O}_2$  as the OH precursor in the absence of  $\text{NO}_x$ , the CPOT can achieve a wide range of steady-state OH concentrations and  $\text{OH}_{\text{exp}}$  that are comparable to the PAM system (Lambe et al., 2011a; Li et al., 2015).

## 7 Conclusions



We report the development of a laminar flow tube reactor for studies of atmospheric VOC oxidation and formation of secondary organic aerosol. The flow tube reactor has been designed to achieve a relatively well-defined flow environment for interpretation of reaction conditions. As has been recognized in existing flow tube reactors, inlet design plays a significant role in establishing the fluid dynamic environment in the reactor. The current design comprises a static mixer followed by a conical diffuser. Computational fluid dynamics (CFD) simulations demonstrate that this injection scheme introduces flow into the reaction section that avoids flow separation from the wall, assisting a rapid transition to a parabolic profile under idealized, isothermal conditions. Some loss of reactive species,  $\text{H}_2\text{O}_2$ , used as an OH precursor, occurs in the static mixer; however, this loss can be compensated by an increased feed concentration designed to generate the desired OH level in the reactor.

The fluid dynamics in the reactor was examined experimentally by comparing the penetration efficiency ( $\eta$ ) and residence time distribution (RTD) of vapor molecules and particles to those predicted under ideal laminar flow conditions.  $\text{O}_3$  and  $\text{SO}_2$  molecules exhibit ~ 100% transmission in the static mixer.  $\text{H}_2\text{O}_2$  losses in the static mixer are 20% to 40%, increasing as RH increases. Small particles are lost at ~ 50% in the static mixer. The penetration efficiency of polydisperse ammonium sulfate particles under dry conditions was measured and compared with theoretical predictions accounting for diffusional deposition and gravitational sedimentation in laminar flow. The penetration efficiency calculated with this theory captures the trend in the two regimes, i.e. in the diffusion regime the smaller the particles, the more loss they exhibit, while in the settling regime the larger the particles the more the deposition. A simple coagulation model calculation suggests that the coagulation process accounts for half of the particle number loss over the small size range.

As has been noted in prior studies of flow regime behavior in flow tube reactors, comparison of theoretically predicted and observed RTDs of vapors and particles reveal the importance of small temperature gradients in inducing a departure from the ideal laminar flow. Despite the presence of a temperature-controlled water jacket, the RTD profiles are affected by slightly non-isothermal conditions in the reactor that lead to secondary flows. This conclusion is supported by substantially improved agreement between observed and predicted RTDs when an enhanced eddy-like diffusivity ( $\mathcal{D}_e$ ) is employed in the CFD simulations. The best-fit ( $\mathcal{D}_e$ ) values,  $4.5 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  and  $6.0 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  for  $\text{O}_3$  and particles, respectively, are sufficiently large to indicate that the transport of tracers is likely dominated by secondary flow.

Despite these flow non-idealities, the observations and simulations demonstrate that the combination of the static mixer/conical diffuser allows a radially uniform and axially dispersed flow system to develop within the reactor, useful for quantitative kinetics studies. A 1D photochemical model is formulated correspondingly. When  $\text{H}_2\text{O}_2$  is employed as the OH precursor, the model predicts that the OH concentration is uniform along the whole tube. The extent to which this uniformity depends on the external OH reactivity, i.e.  $[\text{tracer}]k_{\text{tracer}+\text{OH}}$ , will be evaluated in future work. The system can produce a wide range of  $\text{OH}_{\text{exp}}$  under different radiation conditions for specific scientific objectives. Future work will focus on detailed studies of secondary organic aerosol formation, with particular attention given to wall interactions of gases and particles.

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## Appendix A: Determination of Photon Fluxes

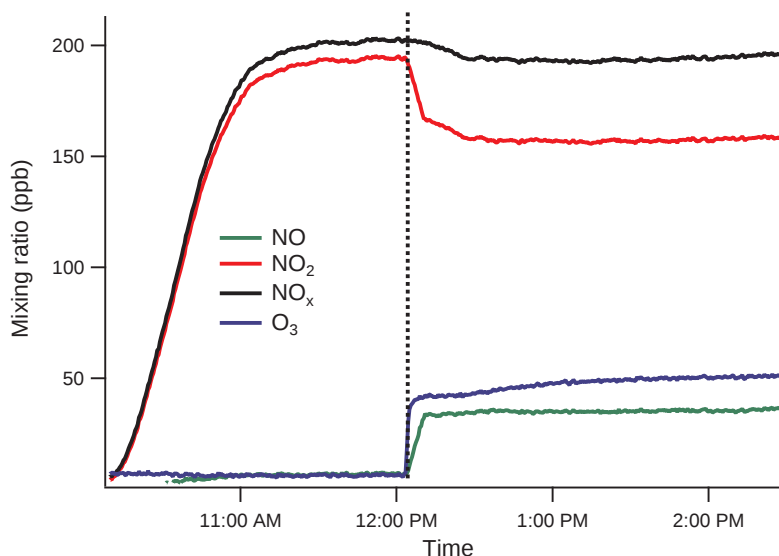


The irradiance of the three types of lamps from 190 to 850 nm ( $E_{e,\lambda}$ ) was recorded using an Ocean Optics fiber optic spectroradiometer (HR2000CG-UV-NIR). The unit is pre-calibrated by the manufacturer and is equipped with a 20 cm long fiber optic cable which can be inserted into the CPOT through one of the sampling ports so that the recorded spectra reflect those inside the CPOT.

The  $j_{\text{NO}_2}$  values were determined by photolyzing 200 ppb of  $\text{NO}_2$  that is continuously supplied to the reactor. Mixing ratios of  $\text{NO}_2$ ,  $\text{NO}$  and  $\text{O}_3$  were monitored at the exit cone. Experimental results employing the UVA lamps are shown in Fig. A.1. A fraction of  $\text{NO}_2$  is photolyzed, forming an equivalent amount of  $\text{NO}$  and  $\text{O}_3$ . The  $j_{\text{NO}_2}$  value can be obtained using the photo-stationary state assumption (Seinfeld and Pandis, 2016):

$$j_{\text{NO}_2} = \frac{k_{\text{NO}+\text{O}_3} [\text{O}_3] [\text{NO}]}{[\text{NO}_2]} \quad (\text{A1})$$

where  $[\text{O}_3]$ ,  $[\text{NO}_2]$  and  $[\text{NO}]$  are the concentrations of these three species at photo-stationary state, respectively.  $k_{\text{NO}+\text{O}_3}$  is the rate coefficient of the reaction  $\text{NO} + \text{O}_3$ , and a value of  $1.9 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  (298 K) is used here (Seinfeld and Pandis, 2016). The  $j_{\text{NO}_2}$  value obtained from this experiment is  $5.36 \times 10^{-3} \text{ s}^{-1}$ . The validity of the photo-stationary phase was confirmed by solving a simple kinetic model of relevant species (i.e. the mixing ratios of the three species did not further change within the CPOT run time).



**Figure A.1.** The temporal profiles of  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{NO}_x$  and  $\text{O}_3$  at the end of the CPOT during a  $\text{NO}_2$  photolysis experiment. The lamps were turned on at the time indicated by the dashed line.

The UVA flux was adjusted until we obtained a light intensity  $I(\lambda)$  that best represents the observed  $j_{\text{NO}_2}$ . The photolysis rate of species  $i$ ,  $j_i$ , can be obtained as the integral of its quantum yield ( $\phi_i(\lambda)$ ), absorption cross section ( $\sigma_i(\lambda)$ ) and the photon

flux ( $I(\lambda)$ ) over wavelengths  $\lambda_1$  to  $\lambda_2$ :

$$j_i = \int_{\lambda_1}^{\lambda_2} \phi_i(\lambda) \sigma_i(\lambda) I(\lambda) d\lambda \quad (\text{A2})$$

Determination of  $j_{\text{NO}_2}$  under the Hg vapor lamps and UVB lamps, however, was difficult because photolysis of  $\text{NO}_2$  leads to a net loss of  $\text{NO}_x$  when these lamps were used (i.e. the photo-stationary state was not achieved). We suspect the reason is

5 that light with shorter wavelengths created an excess amount of  $\text{O}(^1\text{D})$ .

Alternatively, we determined the fluxes of the Hg vapor lamp and the UVB lamp by relating the signal strength obtained from these two types of lamp to that from the UVA lamp. We fixed the fiber optics probe at the same position while changing the type of lamps surrounding the CPOT. By doing this, we assume that the ratio between the recorded spectra represents the ratio of their photon fluxes.

10 The Hg vapor lamp emits wavelength at 185 nm at an intensity typically less than 1 % of that at 254 nm (Li et al., 2015).

Direct quantification of 185 nm light in the CPOT is difficult because the fiber optic spectrometer cannot record radiation with wavelengths shorter than 190 nm. Instead, the intensity of the 185 nm light can be roughly estimated from  $\text{O}_3$  formation. Under full emission of the Hg vapor lamp with  $2 \text{ L min}^{-1}$  of clean air flowing through, we observe 60 ppb of  $\text{O}_3$  at the exit cone. Assuming all of  $\text{O}_3$  has arisen from  $\text{O}_2$  photolysis, the radiation intensity at 185 nm can be evaluated based on the Chapman  
15 mechanism (Seinfeld and Pandis, 2016) with an average residence time of 1520 s (Section 5.2.2). The intensity of the 185 nm band is estimated to be  $10^{-5}$  that of the 254 nm band, the majority of which is likely absorbed by the water jacket.

## Appendix B: Photochemical Reactions



**Table B1.** Photolysis reactions in OH generation

| # | Reaction                                                          | Photolysis Rate              | Photolysis Rate               | Photolysis Rate               |
|---|-------------------------------------------------------------------|------------------------------|-------------------------------|-------------------------------|
|   |                                                                   | @ Hg Lamps[s <sup>-1</sup> ] | @ UVB Lamps[s <sup>-1</sup> ] | @ UVA Lamps[s <sup>-1</sup> ] |
| 1 | $\text{H}_2\text{O}_2 \xrightarrow{h\nu} 2\text{OH}$              | $5.48 \times 10^{-4}$        | $3.54 \times 10^{-5}$         | $4.44 \times 10^{-6}$         |
| 2 | $\text{O}_2 \xrightarrow{h\nu} 2\text{O}$                         | $1.97 \times 10^{-11}$       | 0                             | 0                             |
| 3 | $\text{O}_3 \xrightarrow{h\nu} \text{O}_2 + \text{O}(^1\text{D})$ | $7.64 \times 10^{-2}$        | $1.94 \times 10^{-3}$         | $1.53 \times 10^{-5}$         |
| 4 | $\text{O}_3 \xrightarrow{h\nu} \text{O}_2 + \text{O}$             | $8.50 \times 10^{-3}$        | $3.22 \times 10^{-4}$         | $2.61 \times 10^{-5}$         |
| 5 | $\text{H}_2\text{O} \xrightarrow{h\nu} \text{OH} + \text{H}$      | $5.79 \times 10^{-10}$       | 0                             | 0                             |
| 6 | $\text{HO}_2 \xrightarrow{h\nu} \text{OH} + \text{O}(^1\text{D})$ | $2.60 \times 10^{-3}$        | $3.86 \times 10^{-5}$         | $1.76 \times 10^{-7}$         |

Absorption cross sections and quantum yields come from Burkholder et al. (2015) and IUPAC (<http://iupac.pole-ether.fr/>). The photon flux was measured in the current study conducted in Caltech. O refers to  $\text{O}(^3\text{P})$ . All lamps are at full emission.

**Table B2.** Reactions in OH generation and SO<sub>2</sub> oxidation

| #  | Reaction                                                                   | Rate Constant                                                              | Low-pressure limit                   | High-pressure limit                  |
|----|----------------------------------------------------------------------------|----------------------------------------------------------------------------|--------------------------------------|--------------------------------------|
|    |                                                                            | [(cm <sup>3</sup> /molecule) <sup>n-1</sup> s <sup>-1</sup> ] <sup>a</sup> | rate constant (k <sub>0</sub> )      | rate constant (k <sub>∞</sub> )      |
| 1  | $\text{O}^b + \text{O}_2 + \text{M} \longrightarrow \text{O}_3 + \text{M}$ | $6.0 \times 10^{-34} M(300/T)^{2.4}$                                       |                                      |                                      |
| 2  | $\text{O} + \text{O}_3 \longrightarrow 2\text{O}_2$                        | $8.0 \times 10^{-12} \exp(-2060/T)$                                        |                                      |                                      |
| 3  | $\text{H} + \text{HO}_2 \longrightarrow \text{H}_2 + \text{O}_2$           | $6.9 \times 10^{-12}$                                                      |                                      |                                      |
| 4  | $\text{H} + \text{HO}_2 \longrightarrow 2\text{OH}$                        | $7.2 \times 10^{-11}$                                                      |                                      |                                      |
| 5  | $\text{H} + \text{HO}_2 \longrightarrow \text{H}_2\text{O} + \text{O}$     | $1.6 \times 10^{-12}$                                                      |                                      |                                      |
| 6  | $\text{H} + \text{O}_2 + \text{M} \longrightarrow \text{HO}_2 + \text{M}$  | Eq(1) <sup>c</sup>                                                         | $4.4 \times 10^{-32} M(300/T)^{1.3}$ | $7.5 \times 10^{-11} (300/T)^{-0.2}$ |
| 7  | $\text{H} + \text{O}_3 \longrightarrow \text{OH} + \text{O}_2$             | $1.4 \times 10^{-10} \exp(-470/T)$                                         |                                      |                                      |
| 8  | $\text{O} + \text{OH} \longrightarrow \text{O}_2 + \text{H}$               | $1.8 \times 10^{-11} \exp(180/T)$                                          |                                      |                                      |
| 9  | $\text{O} + \text{HO}_2 \longrightarrow \text{OH} + \text{O}_2$            | $3.0 \times 10^{-11} \exp(200/T)$                                          |                                      |                                      |
| 10 | $\text{O} + \text{H}_2\text{O}_2 \longrightarrow \text{OH} + \text{HO}_2$  | $1.4 \times 10^{-12} \exp(-2000/T)$                                        |                                      |                                      |

**Table B2.** Reactions in OH generation and SO<sub>2</sub> oxidation (continued)

| #  | Reaction                                                                                       | Rate Constant                                                                                        | Low-pressure limit                  | High-pressure limit                 |
|----|------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|-------------------------------------|-------------------------------------|
|    |                                                                                                | $[(\text{cm}^3/\text{molecule})^n \text{s}^{-1}]$                                                    | rate constant ( $k_0$ )             | rate constant ( $k_\infty$ )        |
| 11 | $\text{OH} + \text{H}_2 \longrightarrow \text{H}_2\text{O} + \text{H}$                         | $2.8 \times 10^{-12} \exp(-1800/T)$                                                                  |                                     |                                     |
| 12 | $2\text{OH} \longrightarrow \text{H}_2\text{O} + \text{O}$                                     | $1.8 \times 10^{-12}$                                                                                |                                     |                                     |
| 13 | $2\text{OH} + \text{M} \longrightarrow \text{H}_2\text{O}_2 + \text{M}$                        | Eq(1)                                                                                                | $6.9 \times 10^{-31} (300/T)$       | $2.6 \times 10^{-11}$               |
| 14 | $\text{OH} + \text{HO}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$                      | $4.8 \times 10^{-11} \exp(250/T)$                                                                    |                                     |                                     |
| 15 | $\text{OH} + \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{HO}_2$            | $1.8 \times 10^{-12}$                                                                                |                                     |                                     |
| 16 | $\text{OH} + \text{O}_3 \longrightarrow \text{HO}_2 + \text{O}_2$                              | $1.7 \times 10^{-12} \exp(-940/T)$<br>$(3.0 \times 10^{-13} \exp(460/T)$                             |                                     |                                     |
| 17 | $\text{HO}_2 + \text{HO}_2 \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2$                  | $+2.1 \times 10^{-33} \exp(920/T))$<br>$(1 + 1.4 \times 10^{-21} [\text{H}_2\text{O}] \exp(2200/T))$ |                                     |                                     |
| 18 | $\text{HO}_2 + \text{O}_3 \longrightarrow \text{OH} + \text{O}_2 + \text{O}_2$                 | $1.0 \times 10^{-14} \exp(-490/T)$                                                                   |                                     |                                     |
| 19 | $\text{O}(^1\text{D}) + \text{O}_2 \longrightarrow \text{O} + \text{O}_2$                      | $3.3 \times 10^{-11} \exp(55/T)$                                                                     |                                     |                                     |
| 20 | $\text{O}(^1\text{D}) + \text{N}_2 \longrightarrow \text{O} + \text{N}_2$                      | $2.15 \times 10^{-11} \exp(110/T)$                                                                   |                                     |                                     |
| 21 | $\text{O}(^1\text{D}) + \text{O}_3 \longrightarrow 2\text{O}_2$                                | $1.2 \times 10^{-10}$                                                                                |                                     |                                     |
| 22 | $\text{O}(^1\text{D}) + \text{O}_3 \longrightarrow \text{O}_2 + 2\text{O}$                     | $1.2 \times 10^{-10}$                                                                                |                                     |                                     |
| 23 | $\text{O}(^1\text{D}) + \text{H}_2 \longrightarrow \text{OH} + \text{H}$                       | $1.2 \times 10^{-10}$                                                                                |                                     |                                     |
| 24 | $\text{O}(^1\text{D}) + \text{H}_2\text{O} \longrightarrow 2\text{OH}$                         | $1.63 \times 10^{-10} \exp(60/T)$                                                                    |                                     |                                     |
| 25 | $\text{O} + \text{SO}_2 + \text{M} \longrightarrow \text{SO}_3 + \text{M}$                     | Eq(1)                                                                                                | $5.3 \times 10^{-29} (300/T)^{4.4}$ | $1.9 \times 10^{-11} (300/T)^{1.8}$ |
| 26 | $\text{OH} + \text{SO}_2 + \text{M} \longrightarrow \text{HOSO}_2 + \text{M}$                  | Eq(1)                                                                                                | $3.3 \times 10^{-31} (300/T)^{4.3}$ | $1.6 \times 10^{-12}$               |
| 27 | $\text{SO}_3 + 2\text{H}_2\text{O} \longrightarrow \text{H}_2\text{O} + \text{H}_2\text{SO}_4$ | $8.5 \times 10^{-41} \exp(6540/T) [\text{H}_2\text{O}]^2$                                            |                                     |                                     |
| 28 | $\text{HOSO}_2 + \text{O}_2 \longrightarrow \text{HO}_2 + \text{SO}_3$                         | $1.3 \times 10^{-12} \exp(-330/T)$                                                                   |                                     |                                     |

Rate constants from Burkholder et al. (2015) and IUPAC (<http://iupac.pole-ether.fr/>).

<sup>a</sup>Note that  $n$  represents the reaction order *not* including the effects of the bath gas M. The bath gas is already considered in the calculation of each rate constant.

<sup>b</sup>Without any specific indication, O refers to O(<sup>3</sup>P).

$$\text{Eq(1): } k(M, T) = \frac{k_0 M}{1 + k_0 M / k_\infty} 0.6^{\{1 + [\log_{10}(k_0 M / k_\infty)]\}^{-1}}$$

## Appendix C: Danckwerts Boundary Condition



At steady state, the simplified 1D governing equation is:

$$\mathcal{D}_e \frac{d^2 c_i}{dz^2} - U_{\text{avg,fit}} \frac{dc_i}{dz} + \sum_i R_i = 0 \quad (\text{C1})$$

The first term is the axial diffusion, the second term is the convection, and the third term contains all the sources and sinks.

- 5 Equation (C1) has incorporated the Taylor dispersion derived RTD information. Thus we can solve it as a RTD coupled transport problem. We also employ the Danckwerts boundary condition, which ensures the continuity of the flux:

$$U_{\text{avg,fit}} c_i \Big|_{0-} = \left[ U_{\text{avg,fit}} c_i - \mathcal{D}_e \frac{dc_i}{dz} \right] \Big|_{0+} \quad (\text{C2})$$

$$\frac{dc_i}{dz} \Big|_{L-} = 0 \quad (\text{C3})$$

- 10 In Eq. (C2),  $c_i \Big|_{0-}$  is the input concentration, while  $c_i \Big|_{0+}$  is unknown and should be solved. It is this form that determines the discontinuity of the concentration at the inlet. With all the known reactions (Appendix B), one can solve Eqs. (C1) to (C3) numerically. If one wants to add the wall loss terms, assuming a first-order wall loss rate,  $k_{wi}$ , the surface-to-volume ratio ( $\frac{S}{V}$ ) of the reactor should be added, i.e.  $\frac{S}{V} k_{wi} c_i$ . The  $k_{wi}$  value can be preset if we are interested in the output, or be determined as long as we know the output. The parameters used in these equations are:  $\mathcal{D}_e = 4.5 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ ,  $U_{\text{avg,fit}} = 2.1 \times 10^{-3} \text{ m s}^{-1}$ ,  $\tau_{\text{c,cyl,fit}} = 1360 \text{ s}$ , and  $L = U_{\text{avg,fit}} \tau_{\text{c,cyl,fit}}$ . As a comparison, a plug flow reactor model runs at the same time, with the only parameter as  $\tau_{\text{avg}} = 1520 \text{ s}$ .

## Appendix D: Diffusional Loss in A Laminar Cylindrical Tube

The full conservation equation for gas-phase species  $i$ ,  $c_i(t, r, z)$ , is

$$\frac{\partial c_i}{\partial t} + v_z(r) \frac{\partial c_i}{\partial z} = \mathcal{D}_i \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c_i}{\partial r} \right) + \frac{\partial^2 c_i}{\partial z^2} \right] + P_i - S_i \quad (\text{D1})$$

where  $\mathcal{D}_i$  is the molecular diffusivity of species  $i$  in air, and  $P_i$  and  $S_i$  are the rates of generation and consumption of species  $i$ , by chemical reaction and gas-particle partitioning, respectively. A typical order of magnitude estimate of the molecular diffusion coefficient for vapor molecules in air is  $\sim 10^{-5} \text{ m}^2 \text{ s}^{-1}$ . Under conditions typical of the operation of the flow tube reactor, the magnitude of the axial molecular diffusion term in Eq. (D1) is small relative to that of the other terms in the equation and may be neglected. Davis (2008) gives a thorough discussion on the analytical solution for this system that is at steady state. Without any generation and consumption of species  $i$ , Eq. (D1) becomes:

$$v_z(r) \frac{\partial c_i}{\partial z} = \mathcal{D}_i \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c_i}{\partial r} \right) \right] \quad (\text{D2})$$

Equation D2 is subject to a boundary condition at the reactor entrance,  $z = 0$ :

$$c_i(r, 0) = c_{i0} \quad (\text{D3})$$

where a uniform concentration  $c_{i0}$  is assumed at the inlet of the reactor, and the symmetry condition at the centerline of the reactor,  $r = 0$ :

$$\frac{\partial c_i}{\partial r}(0, z) = 0 \quad (\text{D4})$$

A general boundary condition at the reactor wall allows for the possible deposition of species  $i$  on the wall, is

$$\mathcal{D}_i \frac{\partial c_i}{\partial r}(R, z) = -k_{wi} c_i \quad (\text{D5})$$

where  $k_{wi}$  is a first-order wall deposition coefficient for species  $i$ .  $k_{wi}$  can be expressed in terms of the uptake coefficient for species  $i$ ,  $\gamma_i$ , as  $k_{wi} = \frac{1}{4} \gamma_i \omega_i$ , where  $\omega_i$  is the mean molecular speed of species  $i$ . Either  $k_{wi}$  or  $\gamma_i$  must be determined

experimentally. If no uptake of species  $i$  occurs at the wall, then  $k_{wi} = 0$ .

## Appendix E: Taylor Dispersion-Based RTD

By cross-section averaging of Eq. (D1) (without sources and sinks), the average concentration at any cross section obeys:

$$\frac{\partial \langle c_i \rangle}{\partial t} + U_{\text{avg}} \frac{\partial \langle c_i \rangle}{\partial z} = \mathcal{D}_{\text{eff},i} \frac{\partial^2 \langle c_i \rangle}{\partial z^2} \quad (\text{E1})$$

where  $\mathcal{D}_{\text{eff},i} = \mathcal{D}_i \left( 1 + \frac{\text{Pe}^2}{192} \right)$  which accounts for the convective enhancement in diffusivity (Aris, 1956), where Pe, the Péclet number, is  $\frac{2RU_{\text{avg}}}{\mathcal{D}_i}$ .

The solution of Eq. (E1) for a pulse input at the entrance to the reactor, of  $N_0$  moles over the cross section area  $A$  of the tube, is:

$$\langle c_i \rangle(t, z) = \frac{1}{\sqrt{4\pi\mathcal{D}_{\text{eff},i}t}} \frac{N_0}{A} \exp \left[ -\frac{(z - U_{\text{avg}}t)^2}{4\mathcal{D}_{\text{eff},i}t} \right] \quad (\text{E2})$$

The RTD of the diffusive species in the flow tube, i.e. at  $z = L_{\text{cylid}}$ , is:

$$\langle c_i \rangle(t, L_{\text{cylid}}) = \frac{1}{\sqrt{4\pi\tilde{\mathcal{D}}_{\text{eff},i}\tilde{t}}} \frac{N_0}{V} \exp \left[ -\frac{(1 - \tilde{t})^2}{4\tilde{\mathcal{D}}_{\text{eff},i}\tilde{t}} \right] \quad (\text{E3})$$

where  $V$  is the volume of the tube,  $\tilde{\mathcal{D}}_{\text{eff},i} = \frac{\mathcal{D}_{\text{eff},i}}{\tau_{c,\text{cylid}}U_{\text{avg}}^2}$ , and  $\tilde{t} = \frac{t}{\tau_{c,\text{cylid}}}$ .

For a pulse input, of finite duration  $t_0$ ,

$$\langle c_i \rangle(t, z = 0) = \begin{cases} \frac{N_0}{AU_{\text{avg}}t_0} & 0 \leq t \leq t_0 \\ 0 & t > t_0 \end{cases} \quad (\text{E4})$$

The RTD at  $z = L_{\text{cylid}}$  is:

$$\langle c_i \rangle(t, L_{\text{cylid}}) = \frac{N_0}{2V} \left[ \text{erf} \left( \frac{1 - \tilde{t}}{\sqrt{4\tilde{\mathcal{D}}_{\text{eff},i}\tilde{t}}} \right) - \text{erf} \left( \frac{1 - \tilde{t} - \tilde{t}_0}{\sqrt{4\tilde{\mathcal{D}}_{\text{eff},i}\tilde{t}}} \right) \right] \quad (\text{E5})$$

where  $\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-\eta^2) d\eta$  and  $\tilde{t}_0 = \frac{t_0}{\tau_{c,\text{cylid}}}$ . More generally, by transforming  $t = -\frac{z}{U_{\text{avg}}} = -\frac{z}{L_{\text{cylid}}} \frac{L_{\text{cylid}}}{U_{\text{avg}}} = -\tilde{z}\tau_{c,\text{cylid}}$ ,

where  $\tilde{z} = \frac{z}{L_{\text{cylid}}}$ , the RTD for a non-ideal pulse input  $f(t)$  (e.g. the solid profile in Fig. 6C) is in the form of:

$$\langle c_i \rangle(t, L_{\text{cylid}}) = \frac{1}{\sqrt{4\pi\tilde{\mathcal{D}}_{\text{eff},i}\tilde{t}}} \frac{N_0}{V} \int_{-\infty}^{+\infty} f(-\tilde{z}\tau_{c,\text{cylid}}) \exp \left[ -\frac{(1 - \tilde{t} - \tilde{z})^2}{4\tilde{\mathcal{D}}_{\text{eff},i}\tilde{t}} \right] d\tilde{z} \quad (\text{E6})$$

where  $\tilde{\mathcal{D}}_{\text{eff},i}$  and  $\tilde{t}$  are defined as in Eqs. (E3) and (E5).

## Appendix F: Particle Size Dependent RTDs

Figure 8 can be used to define two separate regimes of particle behavior, i.e. settling regime (diameter larger than 80 nm) and diffusion regime (otherwise).

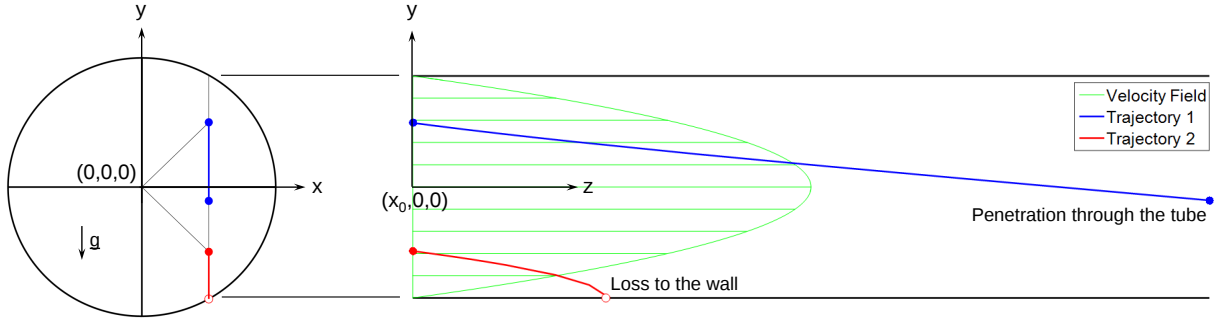
While cylindrical coordinates are usually employed in a flow tube reactor, it will prove to be advantageous to use a Cartesian coordinate framework for the numerical simulation of particle settling in horizontal laminar flow in a tubular geometry. In the settling regime, particle motion in a horizontal tubular laminar flow is governed by the following differential equations for particle position,  $(x(t), y(t), z(t))$ , in a Cartesian coordinate system (with origin at the center of the tube at  $t = 0$ , as shown in Fig. F.1):

$$\frac{dx}{dt} = 0 \quad (F1)$$

$$\frac{dy}{dt} = -v_y(D_p) = -v_s(D_p) \quad (F2)$$

$$\frac{dz}{dt} = v_z(x, y) = U_{\max} \left( 1 - \frac{x^2 + y^2}{R^2} \right) \quad (F3)$$

Given an initial particle position,  $x(0) = x_0$ ,  $y(0) = y_0$ ,  $z(0) = z_0$ , this set of equations can be solved either numerically or analytically. Examples of the numerical simulation of particle trajectories are shown in Fig. F.1.



**Figure F.1.** Particle trajectories in a vertical plane in a laminar flow tube. Particles are of the same size and are subject to gravitational settling and fluid advection. The Cartesian coordinate framework is indicated. Two different cases are shown: blue particles are those that can successfully penetrate through the tube, while red particles eventually deposit on the tube wall.

The analytical solution of Eqs. (F1) – (F3) for the time  $\tau$  that a particle resides in the flow is:

$$\tilde{t}^3 - 2\tilde{y}\tilde{t}^2 - (1 - \tilde{x}^2 - \tilde{y}^2)\tilde{t} + t_1/t_2 = 0 \quad (F4)$$

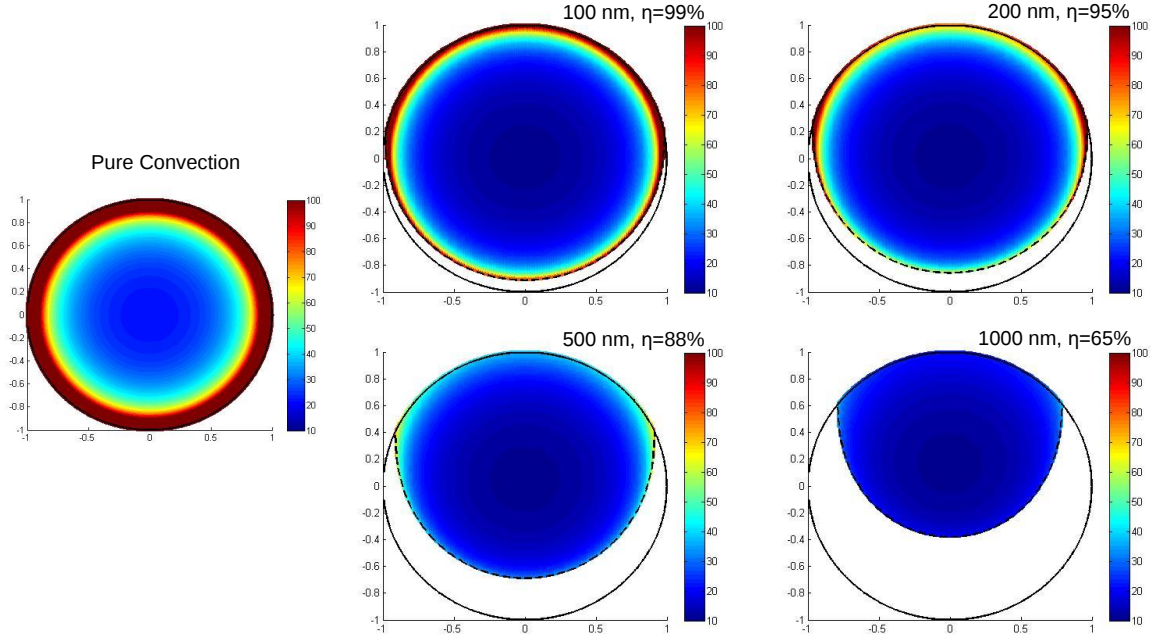
where  $\tilde{x} = x_0/R$ ,  $\tilde{y} = y_0/R$ ,  $t_1 = L_{\text{cyl}}/U_{\max}$ ,  $t_2 = R/v_s$ , and  $\tilde{t} = t/t_2$ .  $\tilde{x}$  and  $\tilde{y}$  are subject to the condition:

$$\tilde{y}(1 - \tilde{x}^2) - \frac{1}{3}\tilde{y}^3 - \frac{t_1}{t_2} + \frac{2}{3}(1 - \tilde{x}^2)^{3/2} \leq \tilde{x}^2 + \tilde{y}^2 \leq 1 \quad (F5)$$

The integral over this closed space leads to the penetration efficiency  $\eta$  for non-diffusive monodisperse particles:

$$\eta = \frac{2}{\pi} (-2\epsilon\sqrt{1-\epsilon^{2/3}} + \epsilon^{1/3}\sqrt{1-\epsilon^{2/3}} + \arcsin\sqrt{1-\epsilon^{2/3}}) \quad (\text{F6})$$

where  $\epsilon = \frac{3t_1}{4t_2}$  and the implicit condition here is that  $\epsilon \leq 1$ , i.e.  $v_s \leq \frac{4R}{3L_{\text{cylid}}}U_{\text{max}}$ , otherwise  $\eta = 0$ . Calculated theoretical RTD and  $\eta$  are shown in Fig. F.2.



**Figure F.2.** Theoretical residence time distribution (Eq. (F4)) and penetration efficiency (Eq. (F6)) of particles with different diameters in a horizontal flow tube. Only gravitational settling and convection are considered. The simulation assumes a uniform distribution of monodisperse particles at the entrance of a well-developed laminar flow with no interaction between particles. Each point corresponds to the residence time and the initial position of the particle. The color bar indicates the residence time (min). The open space between the dashed curve and the tube wall indicates the region in which particles have deposited on the tube wall ( $\eta = 0\%$ ). The residence time of purely convective, **non-diffusing** particles (Eq. (F7)) is shown for reference.

5 The RTD of non-diffusing materials along each streamline for a pulse input is:

$$\langle n \rangle(t, L_{\text{cylid}}) = \begin{cases} 0 & 0 \leq t < t_1 \\ \frac{2N_0 t_1^2}{AU_{\text{avg}} t^3} & t \geq t_1 \end{cases} \quad (\text{F7})$$

where  $N_0$  is the total input quantity of the pulse, the same as defined in Appendix E.

## Appendix G: List of Symbols

| Symbol              | Meaning                                  | unit                                 |
|---------------------|------------------------------------------|--------------------------------------|
| $A$                 | cross section of the reactor             | $\text{m}^2$                         |
| $c$                 | concentration                            | $\text{mol m}^{-3}$                  |
| $D$                 | reactor diameter                         | $\text{m}$                           |
| $D_p$               | particle diameter                        | $\text{nm}$                          |
| $\mathcal{D}$       | diffusivity                              | $\text{m}^2 \text{s}^{-1}$           |
| $g$                 | gravitational acceleration               | $\text{m s}^{-2}$                    |
| $k_w$               | mass transport coefficient to the wall   | $\text{m s}^{-1}$                    |
| $L$                 | length of the reactor                    | $\text{m}$                           |
| $n$                 | particle number concentration            | $\text{cm}^{-3}$                     |
| $N_0$               | total moles or number of the pulse input | mole or number                       |
| $P$                 | generation rate of species               | $\text{molec cm}^{-3} \text{s}^{-1}$ |
| $R$                 | radius of the reactor                    | $\text{m}$                           |
| $S$                 | consumption rate of species              | $\text{molec cm}^{-3} \text{s}^{-1}$ |
| $t_0$               | duration                                 | $\text{s}$                           |
| $T$                 | temperature                              | $\text{K}$                           |
| $U$                 | characteristic velocity of the fluid     | $\text{m s}^{-1}$                    |
| $v$                 | velocity                                 | $\text{m s}^{-1}$                    |
| $V$                 | volume of the reactor                    | $\text{m}^3$                         |
| $Q$                 | volumetric flow rate                     | $\text{m}^3 \text{s}^{-1}$           |
| <b><i>Greek</i></b> |                                          |                                      |
| $\beta$             | thermal expansion coefficient of fluid   | $\text{K}^{-1}$                      |
| $\mu$               | viscosity of the fluid                   | $\text{kg m}^{-1} \text{s}^{-1}$     |
| $\nu$               | kinematic viscosity                      | $\text{m}^2 \text{s}^{-1}$           |
| $\rho$              | density of fluid                         | $\text{kg m}^{-3}$                   |
| $\theta$            | angle of the cone                        | $^\circ$                             |
| $\tau$              | residence time                           | $\text{s}$                           |
| $\omega$            | mean molecular speed                     | $\text{m s}^{-1}$                    |

Note: Some of the symbols appear in Appendix D - F.

**Appendix H: List of Dimensionless Numbers and Subscripts**

| Symbol                             | Name                                                  | Expression                              |
|------------------------------------|-------------------------------------------------------|-----------------------------------------|
| <b><i>Greek</i></b>                |                                                       |                                         |
| $\gamma$                           | uptake coefficient                                    |                                         |
| $\eta$                             | penetration efficiency                                |                                         |
| $\epsilon$                         | ratio of time scale of convection to that of settling | $3L_{\text{cyl d}}v_s/4RU_{\text{max}}$ |
| $\xi$                              | dimensionless length                                  | $\pi\mathcal{D}L_{\text{cyl d}}/Q$      |
| <b><i>Dimensionless groups</i></b> |                                                       |                                         |
| Gr                                 | Grashof number                                        | $g\beta D^3\Delta T/\nu^2$              |
| Pe                                 | Péclet number                                         | $2RU_{\text{avg}}/\mathcal{D}_i$        |
| Re                                 | Reynolds number                                       | $\rho U_{\text{avg}}D/\mu$              |
| Ri                                 | Richardson number                                     | $\text{Gr} / \text{Re}^2$               |
| <b><i>Subscripts</i></b>           |                                                       |                                         |
| c                                  | characteristic value                                  |                                         |
| cyl d                              | cylindrical tube                                      |                                         |
| e                                  | eddy-like                                             |                                         |
| fit                                | fitted result                                         |                                         |
| $i$                                | species                                               |                                         |
| $j$                                | time step                                             |                                         |
| s                                  | settling                                              |                                         |
| avg                                | average value                                         |                                         |
| eff                                | effective value                                       |                                         |
| entr                               | entrance                                              |                                         |
| in                                 | inlet                                                 |                                         |
| max                                | maximum value                                         |                                         |
| out                                | outlet                                                |                                         |
| $r$                                | $r$ -component in cylindrical framework               |                                         |
| $x$                                | $x$ -component in Cartesian framework                 |                                         |
| $y$                                | $y$ -component in Cartesian framework                 |                                         |
| $z$                                | $z$ -component in Cartesian or cylindrical framework  |                                         |
| <b><i>Superscripts</i></b>         |                                                       |                                         |
| $I$                                | first-order reaction rate                             |                                         |
| $II$                               | second-order reaction rate                            |                                         |
| <b><i>overbar</i></b>              |                                                       |                                         |
| $\sim$                             | nondimensionalized variable                           |                                         |

Note: Some of the symbols appear in Appendix D - F.

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**Table 1.** Simulated OH exposure under full light emission

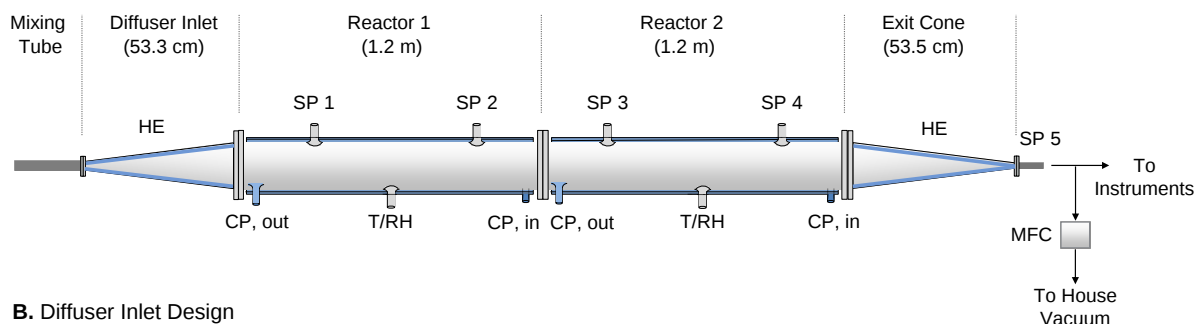
| Lamp type | OH <sub>exp</sub> <sup>a</sup> |                                     | Atmos. Equiv. <sup>b</sup> |                        |
|-----------|--------------------------------|-------------------------------------|----------------------------|------------------------|
|           | (molecules cm <sup>-3</sup> s) |                                     | (h)                        |                        |
|           | PFR                            | AD-PFR <sub>corr</sub> <sup>c</sup> | PFR                        | AD-PFR <sub>corr</sub> |
| Hg vapor  | 8.0 × 10 <sup>11</sup>         | 7.3 × 10 <sup>11</sup>              | 222                        | 203                    |
| UVB       | 5.4 × 10 <sup>10</sup>         | 4.9 × 10 <sup>10</sup>              | 15                         | 13.6                   |
| UVA       | 6.0 × 10 <sup>9</sup>          | 5.4 × 10 <sup>9</sup>               | 1.7                        | 1.5                    |

<sup>a</sup> Input of OH exposure (OH<sub>exp</sub>) simulation: 1 ppm H<sub>2</sub>O<sub>2</sub> and 100 ppb SO<sub>2</sub> at RH = 5% and T = 295 K ([H<sub>2</sub>O] = 1500 ppm).

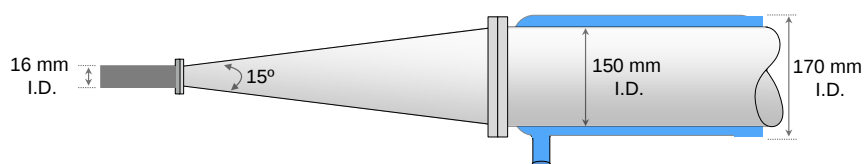
<sup>b</sup> Atmospheric equivalent (Atmos. Equiv.) OH<sub>exp</sub> values are converted to their equivalent hours of OH exposure in the ambient atmosphere, assuming a typical ambient OH concentration of 1 × 10<sup>6</sup> molecules cm<sup>-3</sup>.

<sup>c</sup> PFR and AD-PFR<sub>corr</sub> are calculated by Eqs. (6) and (7), respectively.

### A. System Overview



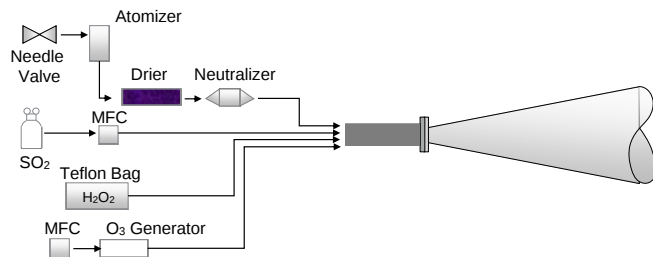
### B. Diffuser Inlet Design



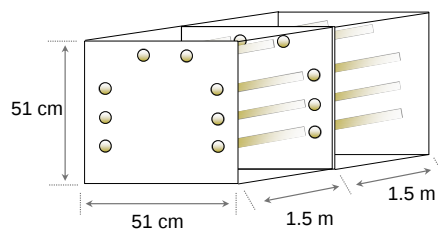
### Legend

|       |                                   |
|-------|-----------------------------------|
| CP:   | Coolant Port                      |
| SP:   | Sample Port                       |
| MFC:  | Mass Flow Controller              |
| T/RH: | Temperature/<br>Relative Humidity |
| HE:   | Heat Exchanger                    |

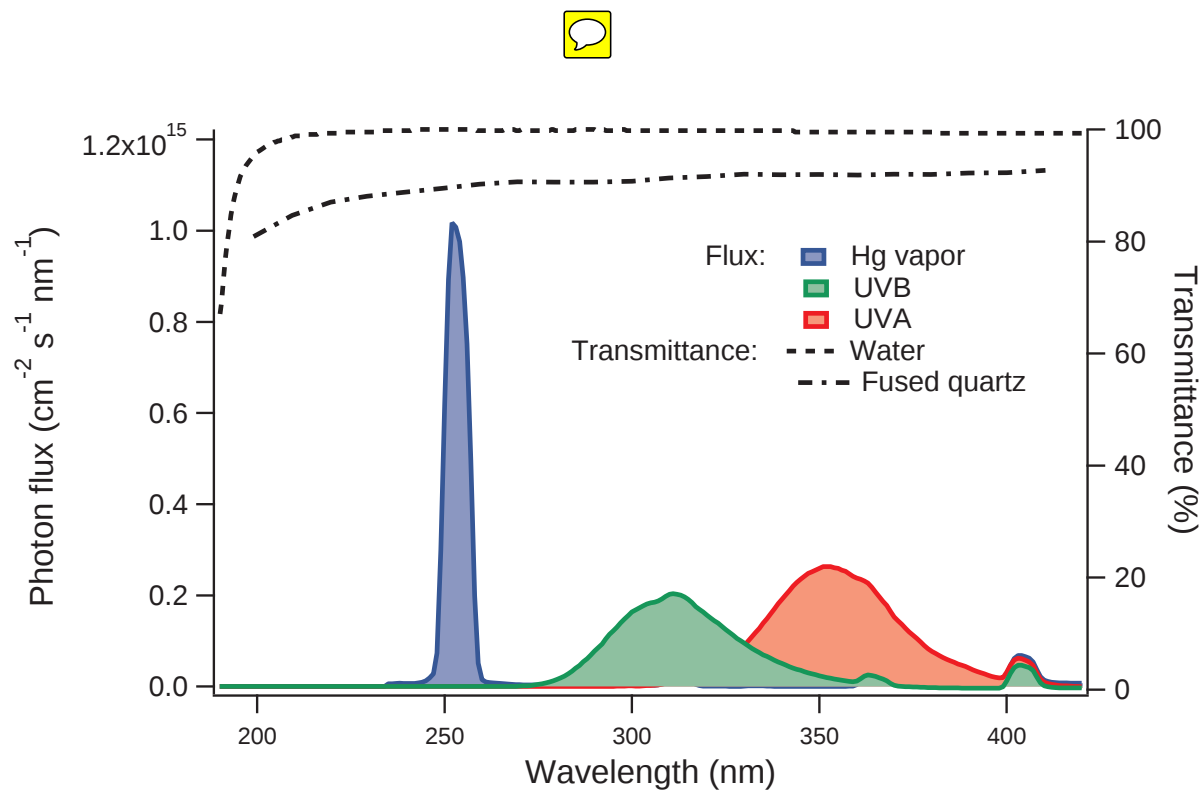
### C. Injection Scheme



### D. UV Light Housing

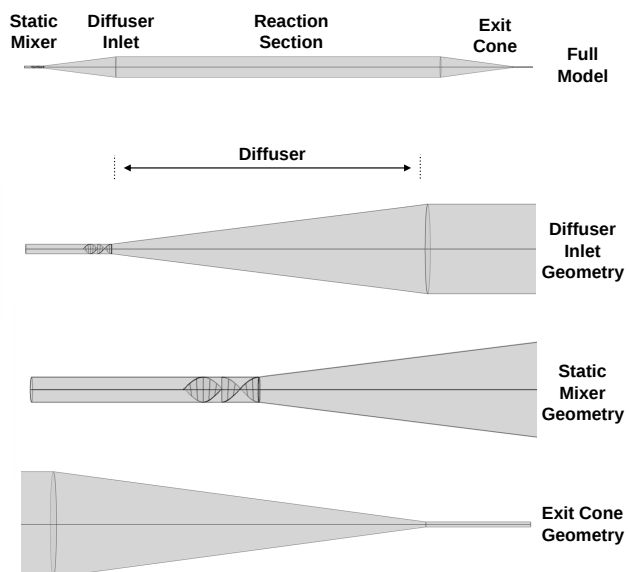


**Figure 1.** Overall schematic of the Caltech PhotoOxidation flow Tube (CPOT). (A) The inlet design. (B) The injection scheme. (C) Schematic for the housing chamber. (D) UV lamps.

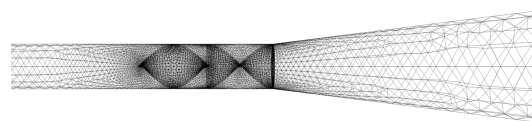


**Figure 2.** Photon fluxes inside the reactor, as well as the transmittance of water and fused quartz (Beder et al., 1971).

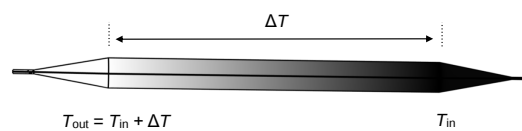
### A. COMSOL Geometry



### B. Inlet Meshing

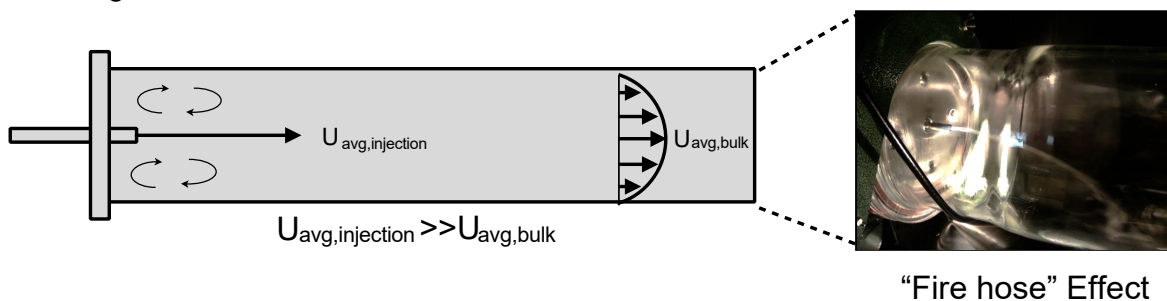


### C. Non-isothermal Surface Temperature

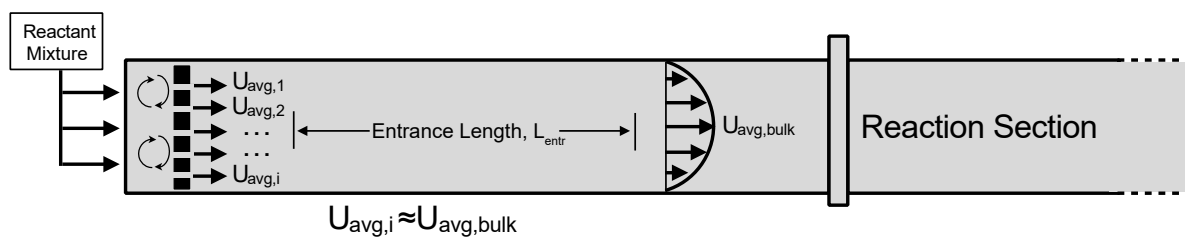


**Figure 3.** (A) Overview of the geometry used to simulate flow and species transport within the CPOT. (B) Inlet meshing for static mixer. (C) Schematic illustration of the temperature gradient used in non-isothermal simulations.

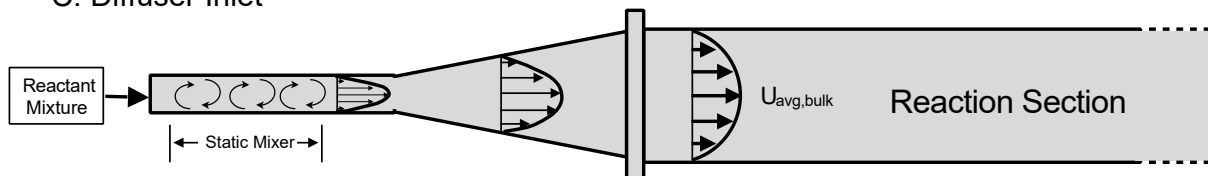
### A. Straight Tube Inlet



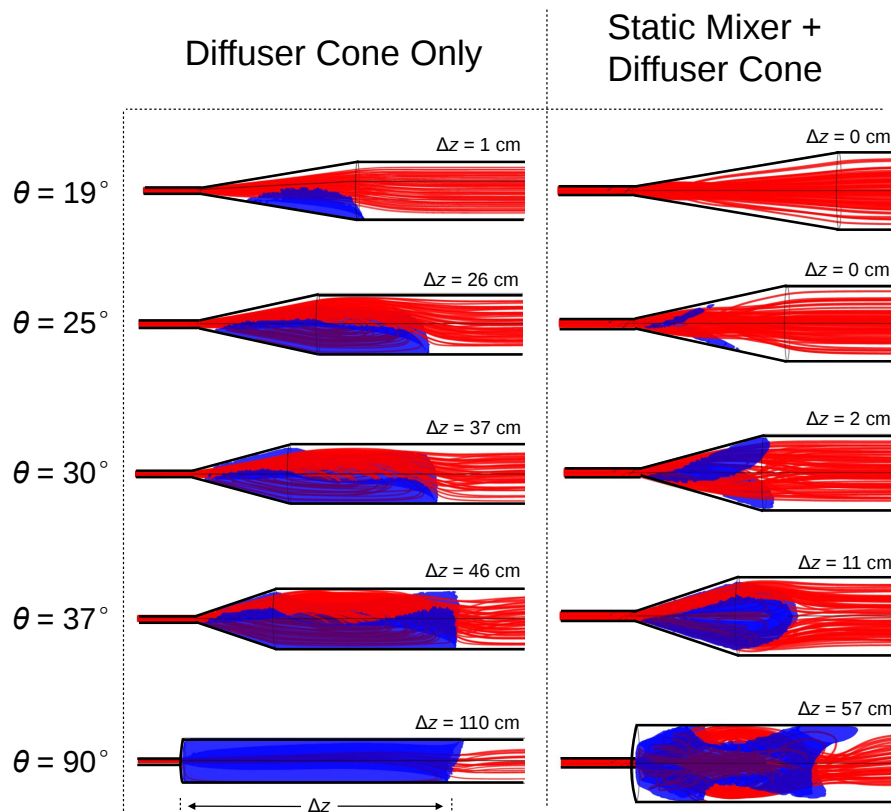
### B. Showerhead Inlet



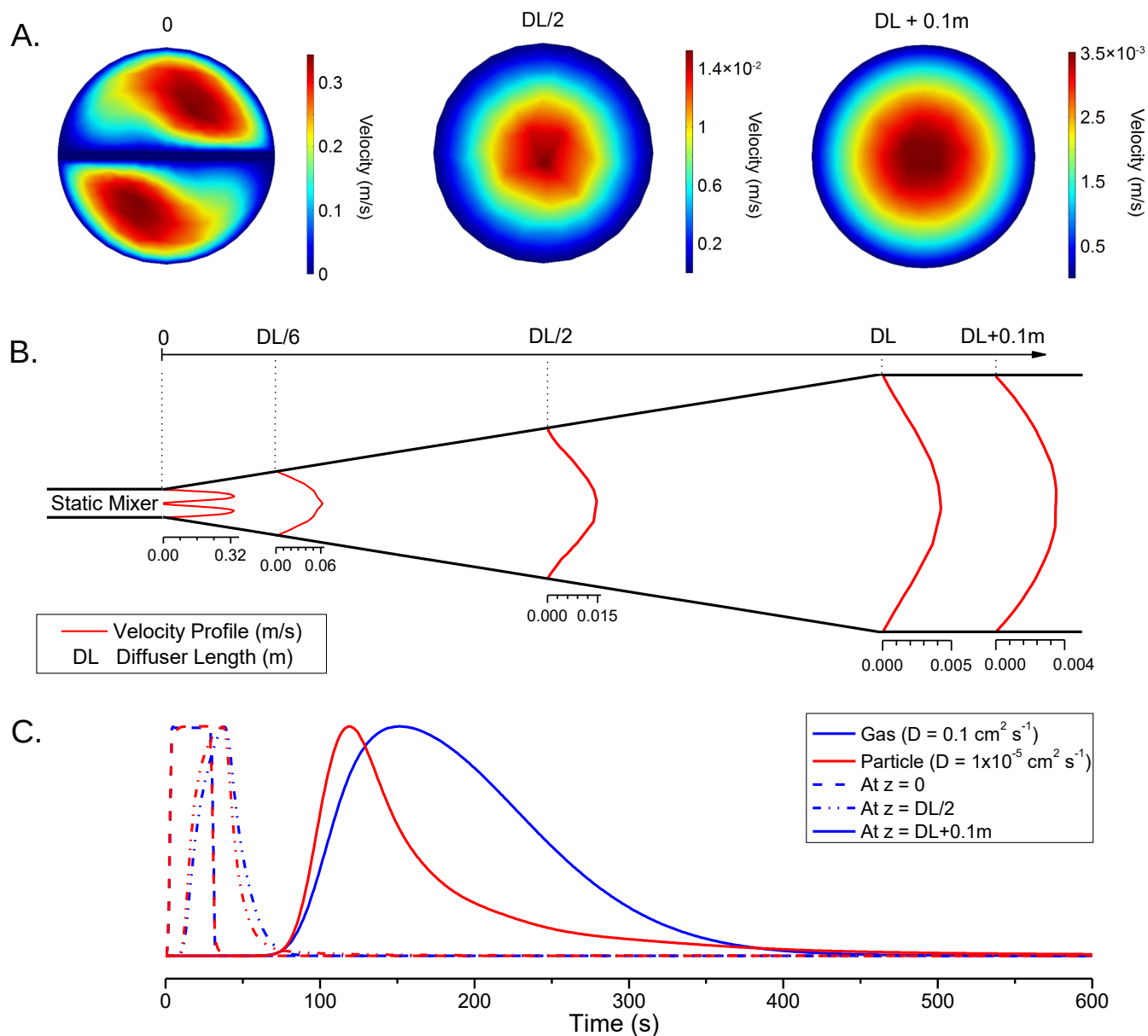
### C. Diffuser Inlet



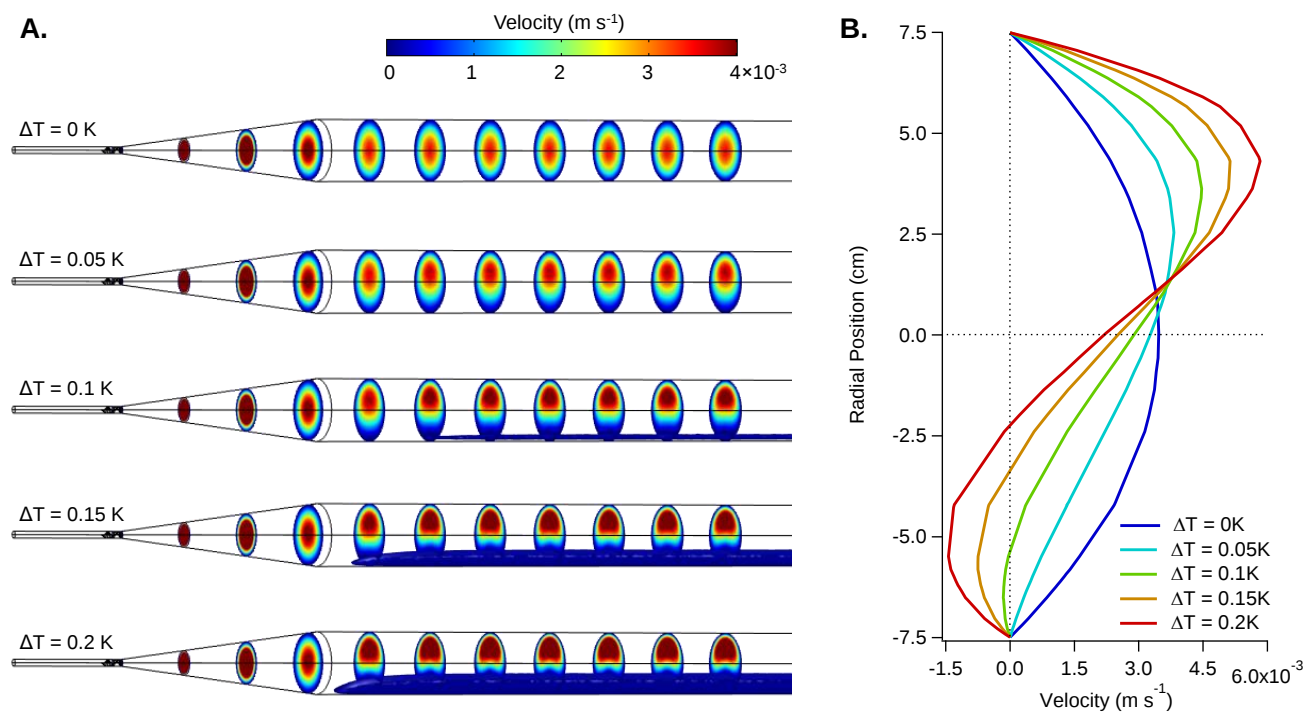
**Figure 4.** Inlet designs exemplified by (A) straight tube injection, (B) showerhead injection, and (C) diffuser injection.  $U_{avg,injection}$ ,  $U_{avg,bulk}$ , and  $U_{avg,i}$  values denote the average velocities at the inlet, in the bulk reaction section, and at the exit of a showerhead hole, respectively. Inlet (A) also illustrates the "fire hose" effect, as demonstrated by the visualization of smoke in a Pyrex glass tube.



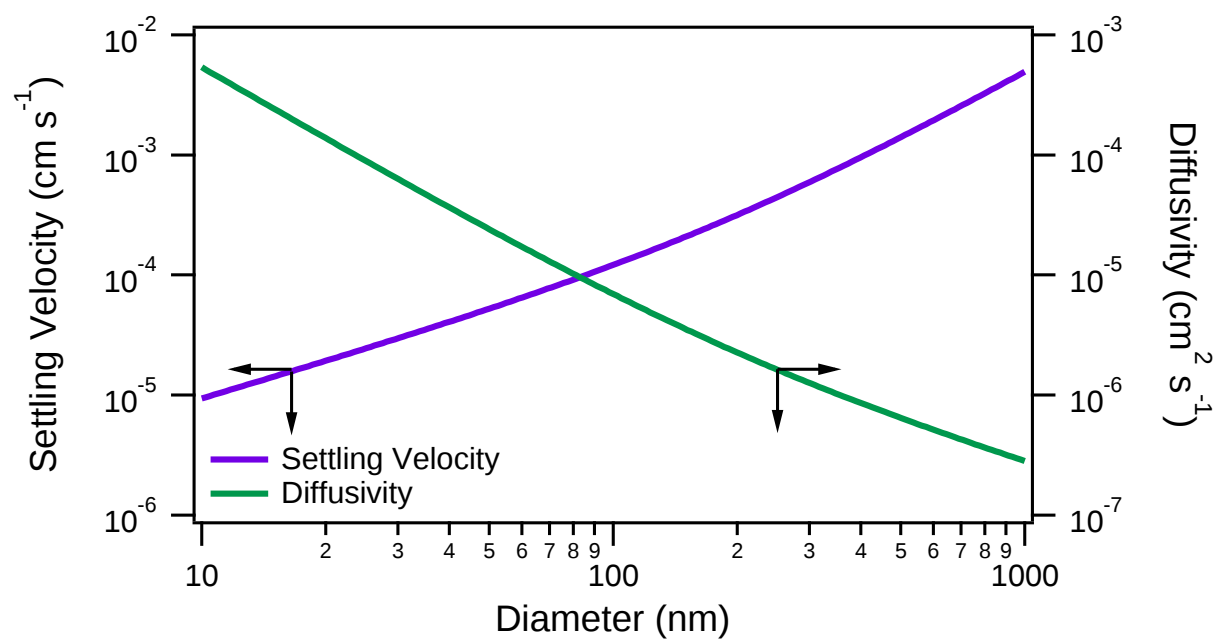
**Figure 5.** COMSOL simulation results for a suite of diffuser angles assuming isothermal conditions. Images in the left column are from simulations conducted in the absence of a static mixer. Images in the right column are from simulations employing a 2-element static mixer upstream of the diffuser cone. The red traces are streamlines demonstrating the flow pattern of fluid introduced upstream of the static mixer. The blue surfaces illustrate regions where the axial velocity  $< 0 \text{ m s}^{-1}$ . Together, these traces illustrate the recirculation zone.  $\Delta z$  is the length that the recirculation zone penetrates into the reaction section. All simulations were performed for a volumetric reactor flow of  $2 \text{ L min}^{-1}$ .



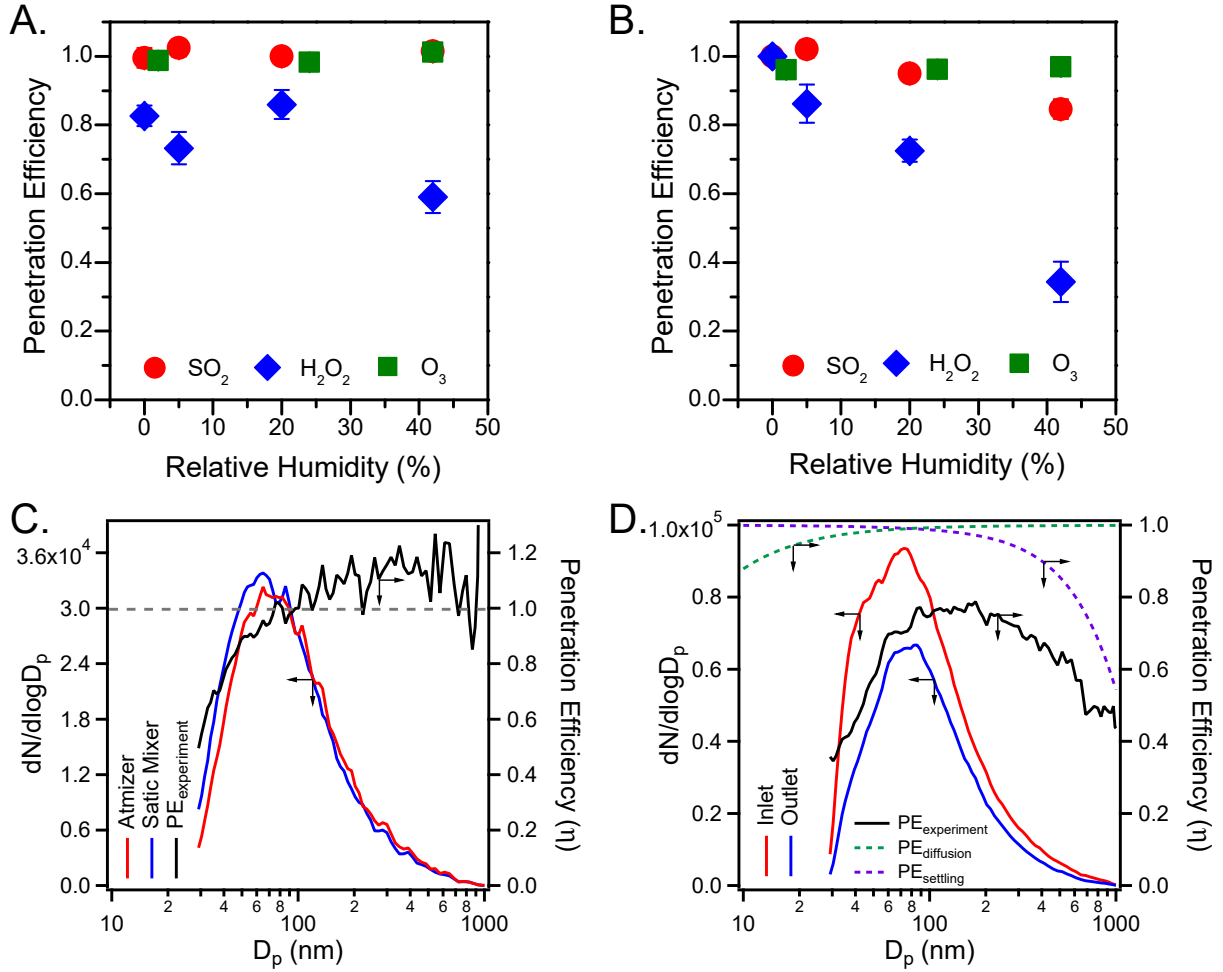
**Figure 6.** COMSOL simulated velocity field at the reactor inlet under isothermal conditions. Simulations were performed for the actual CPOT design: a  $15^\circ$  diffuser cone coupled to a static mixer. The velocity magnitude at various axial positions is shown in (A), and 1D axial velocity profiles within the "inlet-affected" region are shown in (B). The velocity magnitude in (B) is presented on the axis below each velocity profile. Note that DL = Diffuser Length (53.3 cm). (C) shows the normalized residence time of vapor molecules and monodisperse particles at various axial positions. A 30 s square wave pulse is used as the input.



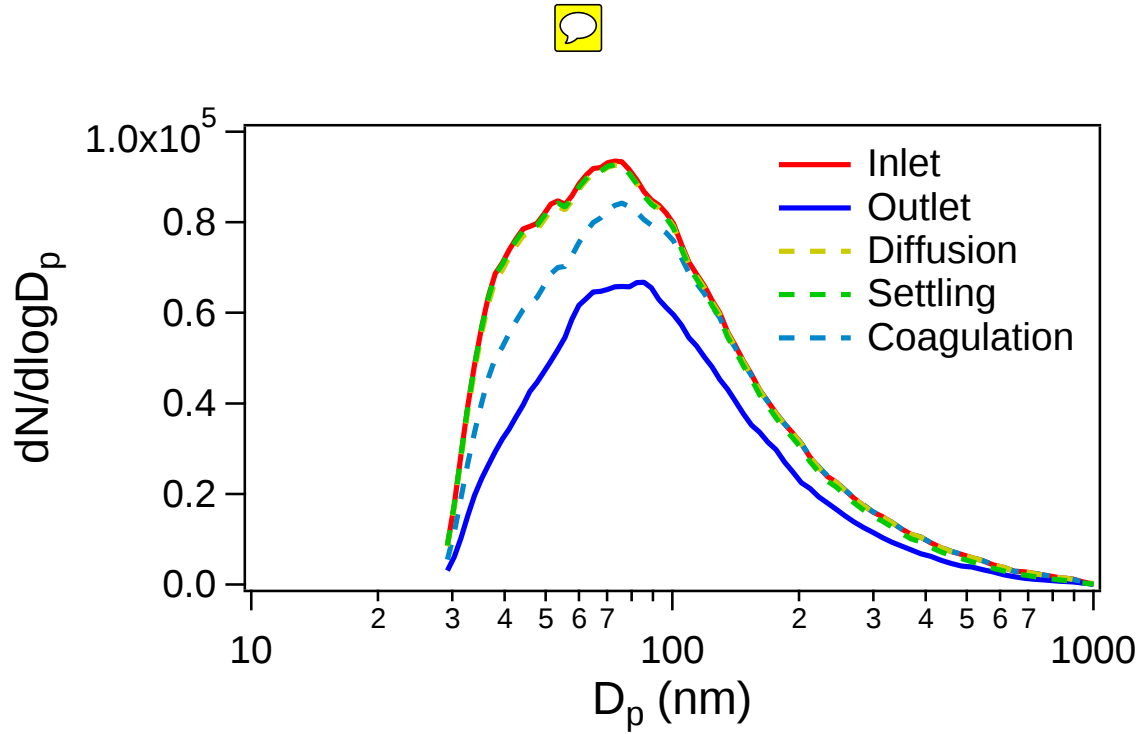
**Figure 7.** COMSOL simulated flow profiles as a function of reactor wall temperature gradient  $\Delta T$ . (A) 3D simulation results demonstrating cross-sectional velocity profiles and consequential recirculation zones (blue isosurface). (B) 1D velocity profiles at axial position  $z = 150$  cm.



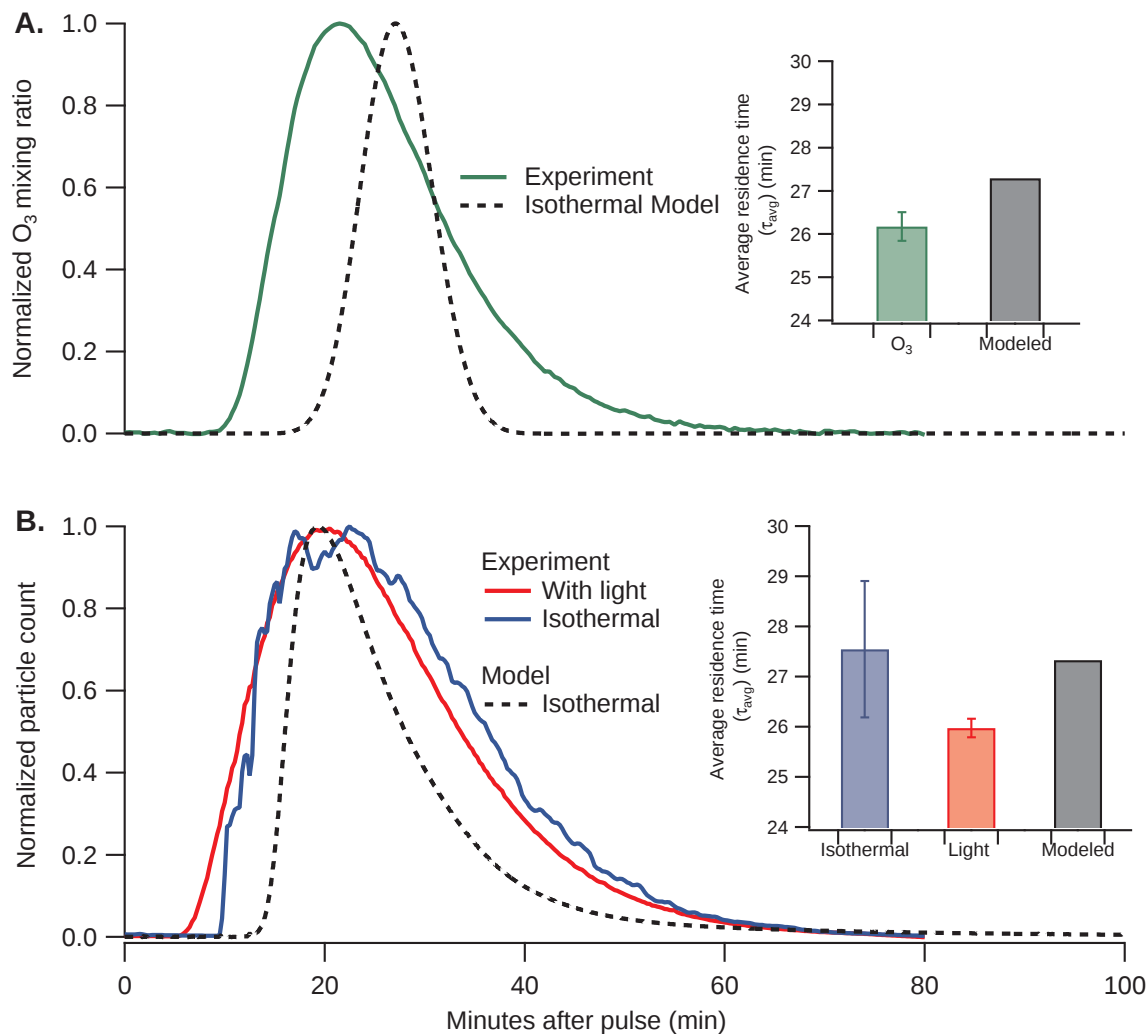
**Figure 8.** Particle settling velocity and Brownian diffusivity for spherical particles of unit density as a function of particle diameter (Seinfeld and Pandis, 2016).



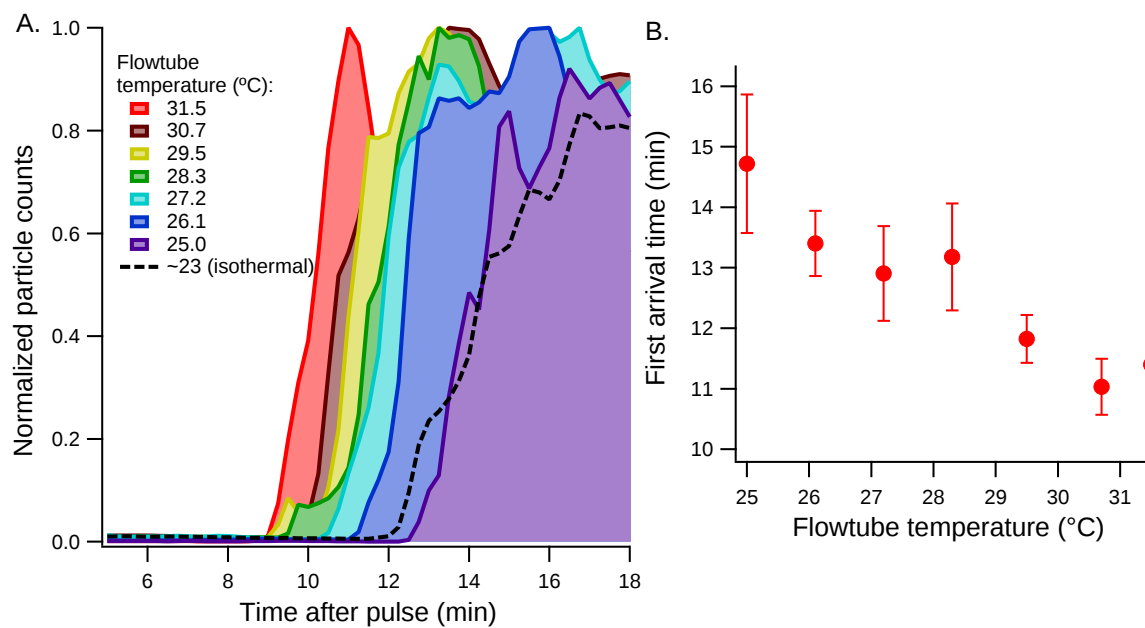
**Figure 9.** Penetration efficiency ( $\eta$ ) of gases and particles in the static mixer and the flow tube. (A) Relative humidity (RH) dependent  $\eta$  of  $\text{SO}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{O}_3$  in the static mixer. (B) RH dependent  $\eta$  of  $\text{SO}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{O}_3$  in the flow tube. Error bar indicates the measured uncertainty. (C) Measured ammonium sulfate particle size distributions before and after the static mixer, as well as the  $\eta$  derived from these measurements. The gray dashed line indicates  $\eta = 1$ , i.e. no particle loss. (D) Measured ammonium sulfate particle size distributions at the inlet and outlet of the flow tube, as well as the  $\eta$  derived from these measurements. The calculated  $\eta$  with respect to particle diffusion loss (Eq. (4)) and gravitational settling (Eq. (F6)) are indicated by the dashed lines.



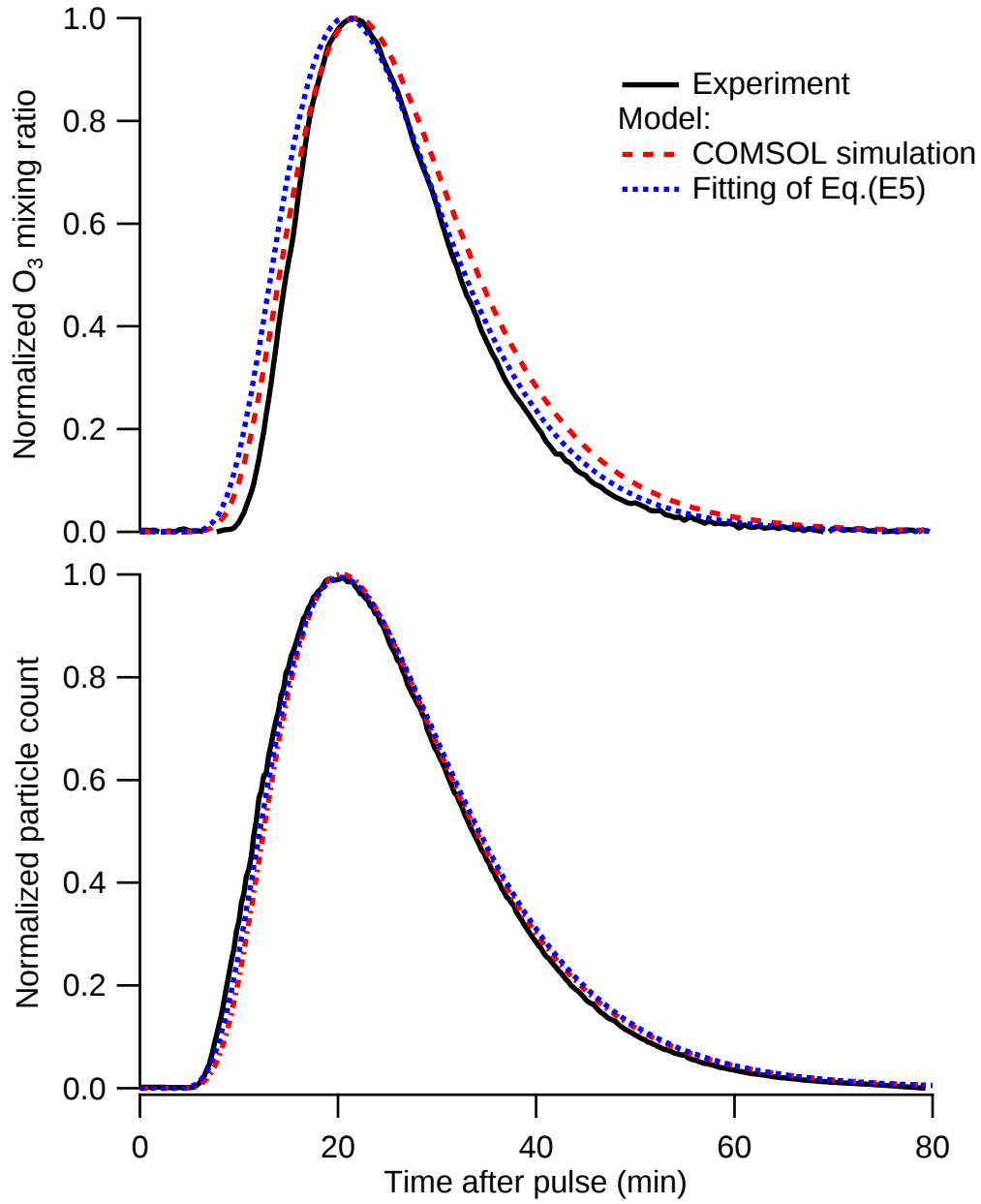
**Figure 10.** Particle size distributions at the outlet when diffusion, gravitational settling, and coagulation processes are coupled separately with the size distribution at the inlet. The measured size distribution at the outlet is plotted as a reference. The coupling of diffusion and gravitational settling with the inlet size distribution is the product of dashed lines and the red line in Fig. 9D. The coagulation process is calculated in a coagulation model, which uses a PFR model with an average residence time of 1520 s by assuming a unity coagulation efficiency and no wall deposition. The coagulation model input is the size distribution at the inlet.



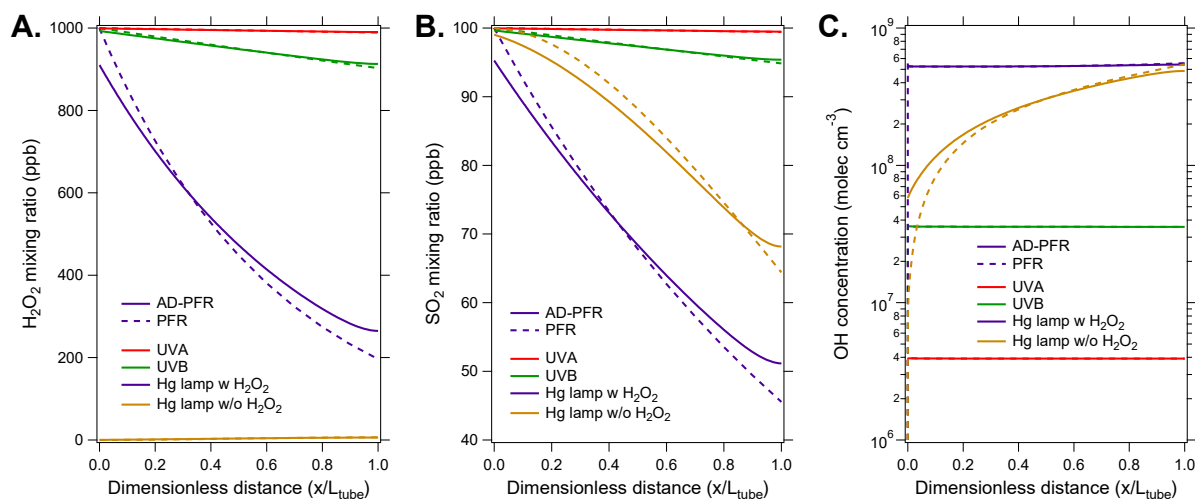
**Figure 11.** Experimental and COMSOL simulated residence time distributions of (A)  $O_3$  vapor molecules and (B) polydisperse ammonium sulfate particles. The diffusivity used in COMSOL for  $O_3$  is that for a generic gas-phase species  $1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  and for particles is  $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  corresponding to a particle size of  $\sim 100 \text{ nm}$ . The average residence time in each case is compared in the insets as reference.



**Figure 12.** Non-isothermal effects on particle RTD. The water jacket temperature was raised systematically against the room temperature ( $\sim 23$  °C). (A) Normalized ammonium sulfate particle counts recorded at the exit are plotted against time after a pulse is introduced at the inlet. The experiment at each temperature is repeated 3 to 4 times. The results from a set of isothermal experiments are also included (dashed line) for reference. (B) Arrival times of the first major peak of each experiment.



**Figure 13.** Comparison of experimentally determined RTD of (A) O<sub>3</sub> vapor molecules and (B) polydisperse ammonium sulfate particles to optimized simulation results employing an eddy-like diffusivity ( $\mathcal{D}_e$ ) in the Taylor dispersion model. The COMSOL simulation employs an optimal  $\mathcal{D}_e$  values of  $4.5 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  for O<sub>3</sub> and  $6.0 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  for particles. The fittings of Eq. (E5) employs the same optimal  $\mathcal{D}_e$ , as well as an optimal average velocity ( $U_{\text{avg,fit}}$ ) of  $2.1 \times 10^{-3} \text{ m s}^{-1}$  and an optimal characteristic residence time ( $\tau_{e,\text{cyl,fit}}$ ) of 1360 s.



**Figure 14.** 1D photochemical model using axially-dispersed assumption (AD-PFR, solid line) and plug flow assumption (PFR, dashed line). 1 ppm  $\text{H}_2\text{O}_2$  and 100 ppb  $\text{SO}_2$  at  $\text{RH} = 5\%$  and  $T = 295 \text{ K}$  is used in the simulation. Hg vapor (purple), UVB (green), and UVA (red) lamps at full emission are used to drive the photochemical reactions. (A) Axial profile of  $\text{H}_2\text{O}_2$ , (B) Axial profile of  $\text{SO}_2$ , and (C) Axial profile of OH.