This manuscript describes a modeling-measurement comparison of residence time distributions in a PAM-style oxidation flow reactor (OFR). The authors show that under their experimental setup determining the true reactor RTD requires deconvolution of the plumbing external to the reactor. It is shown that for various changes in the gas introduction and exit configuration (single tube, sparger, rings), the RTD is indistinguishable. A CFD simulation shows that despite the RTD suggesting a well-stirred reactor, the flow pattern is quite different with central jetting, recirculation and dead zones. An additional CFD simulation showed that with a cone on the inlet, the flow pattern is similar and not plug-flow. The paper is generally well-written and explores an understudied and important aspect of OFRs which are rapidly becoming more widely used in atmospheric lab and field studies. Therefore, I recommend publication after a few minor-to-moderate revisions described below.

We thank the referee for their time in reading and reviewing this manuscript.

[In reference to: Main Comments]

- The authors seemed to have missed some very relevant recently-published work on RTDs and some of the effects on kinetics and VOC reactions (see details below) which provide additional context for framing this work.

  We thank the referee for pointing this out. Upon review of (Palm et al., 2017, 2018; Peng et al., 2017; Peng and Jimenez, 2017) we restructured our arguments in the ‘Introduction’ section, as well as in the ‘Potential Implications’ section. Please see our responses to the detailed comments, kindly offered by the referee, below.

- The “Potential Impacts” section could use substantial improvement. The OH reactivity (OHRext) usage seems inaccurate and the discussion following is therefore unclear (see details below). Also, this section seems a bit abstract and underdeveloped, in that it doesn’t convey how these issues may actually impact real experiments and applications that people are using OFRs for. I would recommended framing and expanding the points made to discuss how they might affect results for typical applications. I.e. SOA yields or compositions, gas-product formation, aerosol chemical or physicochemical transformation (e.g. hygroscopicity), etc. Given that the manuscript is intended for publication in an atmospheric-focused paper, a stronger connection to how this study will help advance measurements related to the atmosphere is important.

  We thank the referee for suggesting a more concrete point of view for the implications of our work. We have done our best to address this, and with the review of the recent literature, believe the ‘Potential Implications’ section is significantly improved as a result. We have included excerpts, in quotations, of new sections as well as improved wording of the revised manuscript in response to the Detailed Comment section, below.

- Indeed, the experimental setup used in this study requires backing out the substantial delays and smearing of the gas delivery and measurement systems. The authors do a nice job of working out and explaining a method to accurately extract the true OFR RTDs. However, in practice wouldn’t
it be best to minimize the plumbing and/or detection delays using a system with a much faster response time? E.g. use of 1/8” tubing, CO2 gas, and LICOR CO2 detector could achieve response times of probably only a few seconds, couldn’t it? It would be useful to discuss/recommend the best experimental practices to most easily and accurately extract the parameters that other OFR users could then apply to their systems, based on what was learned in this study.

The referee offers a fair, thought-provoking argument. On one hand, an alternate method to minimize plumbing and increase response time may minimize bias in the results (although can still be present). On the other hand, our method entirely removes operation-specific bias, and is conveniently adaptable to multiple inlets and outlets, or any other operation-specific arrangement that may be required given other constraints. We believe there are multiple scenarios in which minimizing plumbing and utilizing on-hand instrumentation, such as the LI-COR LI-820 CO2 Analyzer, may not be feasible or cost-effective. For example, there can be physical/space limitations as to how short plumbing lines can be, there may be a need for peripheral inlets and outlets (e.g., “cNO” idealized configuration in (Peng et al., 2017)) or requirements for additional dilutors, scrubbers, etc.,

Also, novel techniques strive to minimize residence time in OFRs (e.g., Simonen et al., 2016). It is arguable if in exceedingly large OFRs, such as the CPOT (Huang et al., 2016), the spacetime in the lines is so small that any RTD in the plumbing will not affect the overall RTD. However this assumption loses validity as the spacetimes of the tubing and reactor become comparable or non-negligible. The RTD should only apply for fluid moving in the reaction zone – and for OFRs the reaction zone is confined to the zone illuminated by the UV lamps (the OFR itself). Our method also allows for data correction post-experiment, if necessary. While we are hesitant to offer best practice recommendations without quantitative data, we have included the following (lines 454-461 of the revised manuscript):

“We do recognize that OFR (or any environmental chemical reactor) users may have a preference to rapidly obtain an RTD profile perhaps using an improvised setup with very short sample lines and a fast time-response gas analyzer. However, the accuracy to which the profile is obtained should be carefully examined. If the reactor is considerably large, or if it is an OFR to be deployed for low levels of exposure, then the influence of plumbing is minimal. If the reactor of choice is small, the oxidant exposure is high, or the reactor has more than one inlet/outlet or other peripheral components, it would be recommended to use the method described here to obtain the most representative RTD, since all sources of bias are removed.”

[In reference to: Detailed Comments]

- P5, L97: Ortega et al. 2015 should be updated to ACP 2016.

We have updated the citation from the discussion article to the final article.

- P5, L97-104 (and latter part of the intro such as P6, L126-128) seems to be missing some of the recent literature related to measured/modelled RTDs and chemical effects in PAM-type OFRs that
would provide better context of what has/hasn’t been done in terms of modeling/characterizing OFR flow (especially PAM-type most relevant to this work). These include (but may not be limited to): Peng et al. 2015 (which the authors cite earlier) expands substantially on the Li et al paper and discusses how different flow RTD assumptions (plug, laminar, measured) affect OH exposure (see Section 3.5, Figs. 9, 10, S11, S12, S16, Table S1); Ortega et al. ACP 2016 (cited elsewhere) shows FLUENT CFDs of with/without the inlet plate installed (Section 2.2, Fig. S1); Palm et al. ACP 2017 (www.atmos-chem-phys.net/17/5331/2017/) shows RTDs from FLUENT CFDs without the inlet plate installed for the PAM OFR for different particles sizes and compared to the Lambe et al 2011 RTD. (Section 2.2, Fig. S1); Palm et al. ACPD, 2017 (https://doi.org/10.5194/acp-2017-795) shows some modeled chemical differences (in VOC decays) for different RTD flow assumptions (Figs. 1, 2, S6).

Similar to the first comment in the Main Comments section, we thank the reviewer for highlighting this recent work. With reference to L102-112, we included the following in place of the last sentence of the paragraph:

“Following an experimentally determined RTD (Lambe et al., 2011) in a PAM OFR, Peng et al. extend the model developed by Li et al., to include this non-ideal RTD, suggesting model disagreement at high exposures. Ortega et al. employ FLUENT to show that removal of the inlet plate (resulting in a less pronounced aperture to the reactor) significantly decreases recirculation regions; and Palm et al. then extend the simulation to show that the FLUENT-derived RTD (Palm et al., 2017) has a narrower distribution than the experimentally-derived RTD by Lambe et al. Finally, Peng and Jimenez lay an initial framework for the possibility of OFRs investigating NO chemistry (Peng and Jimenez, 2017), where initial sensitivity analysis on RTDs suggest considerable model disagreement at high exposures. The fundamental caveat in this recent work is the reliance on an accurately determined experimental RTD, that provides the basis for error analysis.”

With respect to the latter part of the introduction (L126-128 of the original manuscript pointed out by the referee), we believe to have reviewed the literature appropriately. The intent of this paragraph was to compare experimental methods and experimentally-obtained RTDs, such as those in Lambe et al (2011a), Huang et al. (2016), and Simonen et al. (2016). Literature suggested by the referee employs FLUENT to either model an RTD or takes the compartmental model from Lambe et al. (2011a) to interpret their results, but does not provide an approach to experimentally obtaining RTDs, per se. To clarify this point, the sentence (lines 134-136 in the revised manuscript) now reads:

“We compare this approach to that of previous studies by Lambe et al. (2011a), Huang et al. (2016), and Simonen et al. (2016), which to the best of our knowledge are the only other studies to date that report experimentally-derived RTDs in OFRs.”

Nonetheless, the review of the very recent literature indeed provided better context for our introduction, for which we thank the reviewer as our manuscript is now significantly improved.

- P7, L161: consider reporting SO2 tank concentration.
We added a note here that states 3 ppm SO$_2$ tank concentration.

- **P8, L182**: delete “create” or “allow”

  Similar to Reviewer 2, we thank the referee for pointing this out, and have deleted “allow”.

- **P10, L218**: add hyphen for first-order

  We changed “first order” to “first-order”.

- **P10, L224-225**: What is meant by “however those simulations required significant computer time to resolve mesh sizing”? Do the authors mean to say it would take too much time to run (or justify running) for this study?

  Yes. We have deleted the ambiguous phrase, and added the new sentence below (lines 233-236 of the revised manuscript):

  However, resolving the simulation mesh size to account for these internals significantly extended the computational requirements, to the point that running these simulations was not possible on our computer system and would require a computing cluster to perform.”

- **P18, L395-397**: Again, more detailed modeling work from other publications on effects of differing RTDs and flow assumptions missing here.

  We thank the referee for bringing this to our attention, and have included references from (Palm et al., 2017, 2018; Peng et al., 2015, 2016; Peng and Jimenez, 2017) in this section, with additional discussion suggested by Reviewer 2. We have restructured the paragraph (lines 406-434 in the revised manuscript):

  “Initial PAM modeling work assumed plug flow behavior in OFRs (Li et al., 2015). Li et al. stated that correcting for the non-ideal E-Curve in their OFR would account for ~10% error in their oxidant exposure results, which is less than the overall model uncertainty. However, recent work incorporates the effect of non-ideal RTDs on model outputs (Palm et al., 2017, 2018; Peng et al., 2015, 2016; Peng and Jimenez, 2017). Peng et al. (2015) show that for three OFR operational modes (that is, modes of different oxidant formation mechanisms denoted by ‘OFR185’, ‘OFR254-70’, and ‘OFR254-7’), a comparison between model output for ideal plug flow vs. non-ideal RTDs (using the RTD experimentally obtained by Lambe et al., 2011a) for OH exposure (OH$_{exp}$) generally agree within a factor of 2 for low OH$_{exp}$; the model disagreement exacerbates at high OH$_{exp}$ beyond a factor of ~4. Peng and Jimenez then extend OFR operational modes to include N-containing chemistry (in modes referred to therein as ‘OFR185-iNO’, ‘OFR185-7-iNO’, and ‘OFR185-70-iNO’) where at moderate-to-high OH$_{exp}$, the deviations exacerbate significantly, although the authors argue those conditions represent unrealistic chemical pathways. It is worthwhile noting that the chemistry modeled by Peng and Jimenez may find a workaround by utilizing N$_2$O as NO precursor (Lambe et al., 2017) rather than NO.
itself, potentially minimizing RTD-related errors. Palm et al. (2018) report data from OFR field deployment where the same comparison (ideal plug flow vs. the RTD experimentally obtained by Lambe et al., 2011a) suggests RTD-related errors overpredict (for CO) or underpredict (for toluene and monoterpenes) photochemical age (that is, the ratio of OH$_{\text{exp}}$ to tropospheric average OH number concentrations) in the reactor, generally within a factor of 3 of model error. Considering this work employs the compartmental model RTD described by Lambe et al. (2011a), which for reasons mentioned in the previous section may not be the true PAM RTD, and given that non-ideality in RTDs affects certain OFRs more than others, implementing the method presented here to obtain a more representative reactor RTD can either help constrain error uncertainty in the models, or possibly extend the OH$_{\text{exp}}$ range in which OFRs can be operated, a reportedly nontrivial task (Palm et al., 2018). Considering our results indicate that OFRs like the WU-PAM exhibit an RTD closely matching that of an ideal CSTR, which is more well-mixed than the Lambe et al. RTD, the sensitivity analysis conducted so far could represent a lower bound for error analysis because the Lambe et al. RTD is closer to a PFR-like RTD than a CSTR-like RTD.”

- P18-19: “Potential Implications” section. The use of OH$_{\text{ext}}$ appears to not be accurately used. OHR is not an exclusively intensive property of a compound (as seems to be implied in the text) but rather depends on the concentration and OH rate constants of the compounds present that can react with OH. Also OHR is a measure of the (inverse) OH lifetime, not its reaction partners. Maybe the authors really mean the OH lifetime of different compounds? i.e. $k_{\text{voc OH}} \times [\text{OH}]$. We replaced ‘OH$_{\text{ext}}$’ with ‘lifetime to OH’ and restructured the paragraph (lines 436-451 in the revised manuscript):

“For compounds with low lifetimes to OH, contacting could influence the model results to a greater extent (e.g., field deployment monoterpene decay reported by Palm et al., 2018). By taking a ratio of characteristic reaction time to the characteristic transport time, one can define the Damköhler number (Da$_{\text{d}}$). Considering spacetimes of 52-411 s (as per this study), the value of Da$_{\text{d}}$ can be between 0.52 and 4.11 for a compound with lifetimes of ~100s. Since reaction timescales are on the order of transport timescales, contact patterns may play an important role, as seen in Palm et al. (2018). This could also be the case for heterogenous reactions, diffusion-limited reactions, or semivolatile compound (SVOC) oxidation that exhibit slow gas-particle partitioning. Furthermore, combining a phenomenological model to an associated RTD can impact kinetics (and yields) further. The RTD generated by Lambe et al. (2011a) employed in Li et al. (2015) may lead to greater than 10% error if the 2 PFRs in parallel model suggested by Lambe et al. (2011a) is not applicable. In these scenarios, ensuring a high degree of plug flow can not only maximize exposure, but minimize the distribution of aged compounds (e.g., first or second generation compounds) that are due to different exit ages because of recirculation or stagnation. However, this configuration may not suit a field deployment where trace compounds have short lifetimes to OH and can be easily lost to reactor walls, in which case ensuring a high degree of mixing would be beneficial.”
- P19, L412-16: It’s not clear why compounds that react faster with OH would be more prone to be lost to the reactor walls. It seems that the opposite is stated above. Also not clear how rapid mixing would help that situation.

  We removed this argument from our discussion.

- P19, L406-407. Add “a” before phenomenological or make “model” plural.

  We incorporated “a” in the sentence:

  “Furthermore, combining a phenomenological model to an associated RTD can impact kinetics (and yields) further.”

- P19, L412: Statement: “This configuration would suit a laboratory experiment with slow kinetics, where concentrations can be made high enough to where wall losses aren’t an issue.” This statement may be very misleading. Simply increasing concentrations in many cases does not decrease the relative importance of wall effects since they are often first-order losses and the walls may not necessarily establish equilibrium and relevant timescales. Please revise to precisely state what is meant here, or possibly delete if not relevant.

  Upon re-examination of the sentence, we removed the sentence altogether.

- P20, L442: add “the” or “a” before “focus”

  We incorporated “a” in the sentence:

  “Finally, to obtain accurate experimental RTDs, achieving a functional direct deconvolution code should be a focus of future development.”

Figures:

- Fig. 1: Higher resolution on detailed photos needed. This may have just been the pdf conversion that shouldn’t be an issue if high-resolution pictures provided for final publication. Otherwise, the thorough photographic documentation is a nice inclusion.

  We will work with the editor to ensure high quality images.

- Fig. 1b “internals” photo: black label too hard to read on dark background. Try white or yellow and move to the right.

  We moved “internals” to the center of the insert, and changed the font color to white.

- Fig. 2: all text too small (axes labels, tick label). Also x-axes labels on two plots on left are hiding behind data

  We restructured Fig. 2 accordingly, incorporating requests from Reviewer 2 as well.
- Fig. 4. Units for velocity missing. Also, the colorbar and labels are too small.

Insert (e) represents a vector field for the velocity, so units are not needed. We stated this in the caption for clarification. The legend size cannot be changed as it comes out of OpenFOAM this way.

References


Mitroo et al. introduce a method to deconvolve the measured residence time distribution (RTD) from sampling tubes to get the real RTD inside the Washington University Potential Aerosol Mass (WU-PAM) reactor, which is also validated by computational fluid dynamic (CFD) simulation. The idea of this paper can help improve the understanding of RTD for the oxidative flow reactor (OFR) user community. This paper is well-written and fits the scope of AMT. I suggest for publication after considering the following aspects:

We thank the referee for their time in reading and reviewing this manuscript.

[In reference to: General Comments]

1. I agree with Review #2’s comments about the expansion of Section “5 Potential implication”. My concern is that how your method can be applied to simulation rather than just used to explain RTD. In other words, how does the incorporation of CSTR tank-in-series (TIS) model framework behave when compared with the PFR framework? For example, most of your inversion results indicate that the number of TIS, N, is a little bit larger than 1. Does that mean it is CSTR rather than PFR that can better represent OFR? So to simulate what happens in OFR, we should use CSTR model instead of PFR? Then the question is to what extent the difference will be introduced to the simulated results by shifting from PFR to CSTR. I think the authors should clarify these points in this section.

The referee is correct that given the number of TIS is a little bit larger than 1, the reactor is considered to behave more like a CSTR than as a PFR. We address comments for both referees in the revised manuscript (lines 406-434):

“Initial PAM modeling work assumed plug flow behavior in OFRs (Li et al., 2015). Li et al. stated that correcting for the non-ideal E-Curve in their OFR would account for ~10% error in their oxidant exposure results, which is less than the overall model uncertainty. However, recent work incorporates the effect of non-ideal RTDs on model outputs (Palm et al., 2017, 2018, Peng et al., 2015, 2016; Peng and Jimenez, 2017). Peng et al. (2015) show that for three OFR operational modes (that is, modes of different oxidant formation
mechanisms denoted by ‘OFR185’, ‘OFR254-70’, and ‘OFR254-7’), a comparison between model output for ideal plug flow vs. non-ideal RTDs (using the RTD experimentally obtained by Lambe et al., 2011a) for OH exposure (OH\textsubscript{exp}) generally agree within a factor of 2 for low OH\textsubscript{exp}; the model disagreement exacerbates at high OH\textsubscript{exp} beyond a factor of ~4. Peng and Jimenez then extend OFR operational modes to include \(N\)-containing chemistry (in modes referred to therein as ‘OFR185-iNO’, ‘OFR185-7-iNO’, and ‘OFR185-70-iNO’) where at moderate-to-high OH\textsubscript{exp}, the deviations exacerbate significantly, although the authors argue those conditions represent unrealistic chemical pathways. It is worthwhile noting that the chemistry modeled by Peng and Jimenez may find a workaround by utilizing N\textsubscript{2}O as NO precursor (Lambe et al., 2017) rather than NO itself, potentially minimizing RTD-related errors. Palm et al. (2018) report data from OFR field deployment where the same comparison (ideal plug flow vs. the RTD experimentally obtained by Lambe et al., 2011a) suggests RTD-related errors overpredict (for CO) or underpredict (for toluene and monoterpenes) photochemical age (that is, the ratio of OH\textsubscript{exp} to tropospheric average OH number concentrations) in the reactor, generally within a factor of 3 of model error. Considering this work employs the compartmental model RTD described by Lambe et al. (2011a), which for reasons mentioned in the previous section may not be the true PAM RTD, and given that non-ideality in RTDs affects certain OFRs more than others, implementing the method presented here to obtain a more representative reactor RTD can either help constrain error uncertainty in the models, or possibly extend the OH\textsubscript{exp} range in which OFRs can be operated, a reportedly nontrivial task (Palm et al., 2018). Considering our results indicate that OFRs like the WU-PAM exhibit an RTD closely matching that of an ideal CSTR, which is more well-mixed than the Lambe et al. RTD, the sensitivity analysis conducted so far could represent a lower bound for error analysis because the Lambe et al. RTD is closer to a PFR-like RTD than a CSTR-like RTD.”

2. TIS model can have different forms. The authors assume the same residence time for each CSTR-tank and find the tank number. One can also take the form with a fixed CSTR (or PFR or mixed CSTR/PFR) number but to find each residence time, which looks more reasonable given the CFD simulation. Can the authors discuss this a little bit more? For example: How does the number of TIS, N, depend on the flow rate, or in other words the average residence time? Since the flow rate changes the fluid field, the mixing style could be different at different flow rates (e.g. Fig.3a-c). But I cannot see any trend. Can the author give some explanation for that?

The classic TIS model assumes constant mean residence time across the \(N\) tanks, which is \(\bar{\tau}_i = \bar{\tau}/N\). In this work it is treated as a two-parameter model in which both \(N\) and \(\bar{\tau}\) are scanned to find the optimum value pair that results in the best fit with experimental data. It is found that the calculated mean residence time \(\bar{\tau}\) is similar to the space-time \(\tau\) as expected. Theoretically we can use any well-defined reactor model in place of TIS, such as the axial dispersion model (ADM) (employed by Lambe et al., 2011a in tandem with compartmental modeling) which measures the non-ideality from PFR. Mixed CSTR/PFR is also possible, provided the mathematical derivation is properly carried out. Developing such a new model is out of the scope of the current manuscript, but can be recommended as future work in this field. Whether the reactor model selected is valid to represent the real reactor is subject to validation with experimental measurements, as performed in Figure 3.
In this work we find the TIS model is satisfactory for the PAM reactor according to the close agreement between model prediction and experimental data, stating the caveat that the TIS model is not phenomenological. The reviewer raised the question about unclear trend between $N$ and space-time in Figure 3(a-c), which is interesting to the authors too. Our guess is that under these conditions the reactor behaves so similarly to a single CSTR that the subtle differences are buried in the experimental uncertainties. Perhaps the trend would become more clear as the space-time is further raised, and we predict the trend to be $N$ increasing with space-time. The reason is that the larger the space-time, the slower the flow, thus the weaker the turbulence and back-mixing, which means the further away the reactor is from a single CSTR. This reasoning is backed by Figure 3f, where $N$ is more than doubled at a much higher space-time (although it is also a different configuration).

3. Equations in Appendix B should be carefully checked. For example, in Eq. (B3) it should be $E_i|_{k_c}$ instead of $E_i|_{k_c}$. In addition, try to avoid "$N$", since the number of TIS is also "$N"", which may cause confusion. In Eq. (B8), $A$ is a matrix, which should be listed as $A_{ij}$ not just $A_i$. One more, as a vector, $B$ should be listed as $B_i$ with $i = 1, 2, ..., N - 1$ and $i = N$. About time step $\Delta t$, see following comments for Figure 3.

We thank the referee for pointing out the inconsistent notations in the equations. The misuse of indices can make the equations confusing and even wrong. We rewrote all of the equations in Appendix B with carefully checked syntax. We hope they bring much more clarity now. Please see revised manuscript lines 608-672.

[In reference to: Specific Comments]

1. Line 182: “create allow”, delete either one.

   Similar to Reviewer 1, we thank the referee for pointing this out, and have deleted “allow”.

2. Line 218: “F-curve”, define it here or mention it later

   We restructured the sentences (L226-227 of the revised manuscript):
   “After the simulation, the exit concentration is mixing-cup averaged to output a representative of a cumulative RTD (explained in the next section).”

3. It is unnecessary to list both dimensional and non-dimensional equations at the same time, e.g. EQ. 1-4 and 8-9, since the non-dimensional form has been introduced in detail in Appendix A

   We respect the referee’s point of view, however we choose to represent both dimensional and dimensionless equations in the main text for the audience.

4. Figure 2: Please use higher resolution figures and rearrange the figure locations (too compact, and x-labels are hidden)

   We restructured Fig. 2 accordingly, incorporating requests from Reviewer 1 as well.
5. Figure 3: Why time resolution is different in Panel e? Does $\Delta t$ in Appendix B correspond to the time interval in Figures 3a-f?

We had instrument problems that day, and could not take datapoints as frequently as for all other panels. We have noted it in the figure caption. This doesn’t affect the output of our algorithm based on longer $\Delta t$.

“Lower frequency data for panel e) was due to instrument repair, and temporarily set on longer averages.”

6. Figure 5: Please use an intuitive y-label instead of “F”. Also please specify “N” value in the caption

We relabeled the y-axis with “Normalized Concentration” for easier interpretation. The “N” for the N-CSTR acronym the referee is referring to in the legend is another acronym for the TIS model. We clarify this in the caption, and introduced this acronym along ‘TIS’ in Section 3.2 (lines 313-317):

“We chose to apply the tank-in-series (TIS) model (MacMullin and Weber Jr., 1935), also referred to as N-CSTR model, to the convolution integral since it is a one parameter model that, although not specific to flowtube, tubular, laminar, or plug-flow reactors, gives an idea of where the reactor lies on the spectrum of mixed flow vs. plugged flow based on the value of a parameter, $N$”

References


Assessing the degree of plug flow in oxidation flow reactors (OFRs): a study on a Potential Aerosol Mass (PAM) reactor

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Abstract

Oxidation flow reactors (OFRs) have been developed to achieve high degrees of oxidant exposures over relatively short space times (defined as the ratio of reactor volume to the volumetric flowrate). While, due to their increased use, attention has been paid to their ability to replicate realistic tropospheric reactions by modeling the chemistry inside the reactor, there is a desire to customize flow patterns. This work demonstrates the importance of decoupling tracer signal of the reactor from that of the tubing when experimentally obtaining these flow patterns. We modeled the residence time distributions (RTDs) inside the Washington University Potential Aerosol Mass (WU-PAM) reactor, an OFR, for a simple set of configurations by applying the tank-in-series (TIS) model, a one parameter model, to a deconvolution algorithm. The value of the parameter, $N$, is close to unity for every case except one having the highest space time. Combined, the results suggest that volumetric flowrate affects mixing patterns more than use of our internals. We selected results from the simplest case, at 78s space time with one inlet and one outlet, absent of baffles and spargers, and compared the experimental F-Curve to that of a computational fluid dynamics (CFD) simulation. The F-Curves, which represents the cumulative time spent in the reactor by flowing material, match reasonably well. We value that the use of a small aspect ratio reactor such as the WU-PAM reduces wall interactions, and suggest applying the methodology of tracer testing described in this work to investigate RTDs in OFRs and modify inlets, outlets, and use of internals prior to applications (e.g., field deployment vs. laboratory study).

1 Introduction
Tubular reactors were first introduced to the field of atmospheric science by means of small flow cell reactors developed to study the kinetics of stratospheric reactions (Brune et al., 1983; Howard, 1979; Keyser, 1980; Lamb et al., 1983). Accurate kinetic measurements were possible due to the high pipe aspect ratios, which encouraged a high degree of plug flow behavior (Keyser, 1984). The design of these miniature tubular reactors, with volumes on the order of a few cm$^3$, was different from that of significantly larger, batch-type or semi-continuous type well mixed reactors, with volumes on the order of several m$^3$, built to understand aerosol formation in the troposphere (Crump et al., 1982; Crump and Seinfeld, 1980; Leone et al., 1985). To study aerosol formation and growth chemistry, the dynamics of atmospheric circulation and transport needed to be excluded. It was therefore convenient to mimic the troposphere by treating it as an enormous, well mixed reactor, which led to the development of larger well mixed reactors. The discovery of secondary processes preceding aerosol formation led to significant emphasis on the study of secondary organic aerosol (SOA) formation (Haagen-Smit, 1952, 1963, 1970; Went, 1960). The approach of using large, well mixed batch-style environmental chambers eventually helped elucidate chemical mechanisms for model compounds (Claeys, 2004; Kamens et al., 1982; Kroll et al., 2006; Nozière et al., 1999; Paulson et al., 1990; Pereira et al., 2015; Volkamer et al., 2001), and, with improved instrumentation (Canagaratna et al., 2007; Crounse et al., 2006; de Gouw and Warneke, 2007; Hansel et al., 1995; Jayne et al., 2000; Williams et al., 2006; Zhao et al., 2013), the community gained a better understanding of SOA formation. Unfortunately, low levels of conversion and high wall losses seen in these large reactors did not allow simulated exposures that exceeded a day at most, which is just a short glimpse into the average two week lifespan of an atmospheric aerosol (Seinfeld and Pandis, 2006). Due to such limitations, oxidation flow reactors
(OFRs) with short spacetimes (ratio of reactor volume to the volumetric flowrate) are being developed (Cazorla and Brune, 2010; Ezell et al., 2010; George et al., 2007; Huang et al., 2016; Kang et al., 2007).

OFRs can be viewed as tubular reactors due to their pipe aspect. They have been widely used for over a decade to study heterogeneous reactions on organic aerosol surfaces involving gas-phase oxidants such as hydroxyl radicals and ozone (George et al., 2007; George and Abbatt, 2010; Katrib et al., 2005; Kessler et al., 2010, 2012; Knopf et al., 2005; Kroll et al., 2012; Smith et al., 2009). These reactors are able to generate very high concentrations of hydroxyl (OH) radicals, tens to thousands times higher than typical tropospheric levels, which accelerates the rate of gas-phase oxidation reactions. Within spacetimes of a few minutes, it is possible to achieve integrated oxidant exposures equivalent to multiple days or weeks of atmospheric oxidation. It is important to distinguish OFRs from modern day conventional flow tube reactors, which stem from designs of old flow tube reactors (e.g., Keyser 1984) but employed in the study of gas uptake kinetics on aerosol surfaces rather than homogeneous gas-phase reactions, as described in the previous paragraph. Beyond the original application of heterogeneous oxidation studies, Kang et al. introduced the potential aerosol mass (PAM) OFR which, alongside newer OFR designs, was intended specifically for studies of SOA physicochemical properties (Kang et al., 2007, 2011; Keller and Burtscher, 2012; Lambe et al., 2011b, 2012, 2013; Massoli et al., 2010; Ortega et al., 2013; Slowik et al., 2012). This application therefore altered the study of SOA formation, previously dominated by the traditional large, well mixed reactors (Kroll and Seinfeld, 2008; Rudich et al., 2007; Turpin et al., 2000), by allowing to generate laboratory data beyond first simulated day of exposure. Because the mechanism of exposure between traditional chambers
OFRs was different, validating the OFR concept began by replicating data obtained from traditional chambers (Chhabra et al., 2015; Lambe et al., 2015; Liu et al., 2015), and to assess whether the chemistry was realistic (Li et al., 2015; McNeill et al., 2008; Peng et al., 2015; Renbaum and Smith, 2011). Consequently, much modeling work has focused on pure chemical reactions and comparison of SOA yields between the two (Bruns et al., 2015; Lambe et al., 2015; Li et al., 2015; Ortega et al., 2016; Peng et al., 2015). However, essentially no modeling work has been done on understanding hydrodynamics or flow fields inside OFRs so that the flow patterns can be improved. In a study from Li et al., it appears that residence time distributions (RTDs) that deviate significantly from plug flow in the PAM result only in a ~10% error of reported values such as OH exposure (Li et al., 2015), which is conducive to OFRs being viewed as tubular reactors. Following an experimentally determined RTD (Lambe et al., 2011) in a PAM OFR, Peng et al. extend the model developed by Li et al., to include this non-ideal RTD, suggesting model disagreement at high exposures. Ortega et al. employ FLUENT to show that removal of the inlet plate (resulting in a less pronounced aperture to the reactor) significantly decreases recirculation regions; and Palm et al. then extend the simulation to show that the FLUENT-derived RTD (Palm et al., 2017) has a narrower distribution than the experimentally-derived RTD by Lambe et al. Finally, Peng and Jimenez lay an initial framework for the possibility of OFRs investigating NO chemistry (Peng and Jimenez, 2017), where initial sensitivity analysis on RTDs suggest considerable model disagreement at high exposures. The fundamental caveat in this recent work is the reliance on an accurately determined experimental RTD, that provides the basis for error analysis. It is unknown if the error may trend with external OH reactivity (OHR_{ext}) and become
more significant for slow reacting compounds, although efforts by the Jimenez Group at the
University of Colorado at Boulder are underway.

In both single and multiphase reactors, contact patterns and the degree of mixing determine reactor
performance, e.g., selectivity and yield (Bourne, 2003; Deckwer, 1976; Levenspiel, 1999). This
implies that upon desired contacting, chemical pathways that would be otherwise suppressed can
become more competitive. For example, if during a mixed OH / ozonolysis heterogeneous
reaction, a fresh biomass burning aerosol is introduced in the centerline port of an OFR and ozone
is introduced along a side port, most of the aerosol may travel ballistically through the chamber
having limited contact with ozone or OH, and chemical reaction is less competitive with photolysis
/ photobleaching reactions of the aerosol. RTDs describe the probability of a fluid element’s age
inside the reactor: one can think of those as the probability distribution function (PDF) of a fluid
element in the reactor (Fogler, 2006; Levenspiel, 1999). Tools are available to diagnose or predict
flow behavior. These tools fall in two categories: tracer tests (diagnostics) and computational fluid
dynamics (CFD) simulations (predictions).

We present a technique to assess the degree of plug flow in an OFR, that can be in principle
extended to any vessel. The rigor of the technique is tested by varying use of internals and flowrate
and observing the resulting RTD curves in the Washington University PAM (WU-PAM) reactor.
We begin by introducing an experimental method for obtaining the reactor RTD, which can be
applied to any other OFR, via inert tracer injections. From raw data, we explain how to obtain
PDFs. We chose to run CFD on the simplest design (a base case configuration) of the WU-PAM
reactor to gain hydrodynamics information. Finally, we compare results from tracer tests and CFD
for the base case. We compare this approach to that of previous studies by Lambe et al. (2011a), Huang et al. (2016), and Simonen et al. (2016), which to the best of our knowledge are the only other studies to date that report experimentally-derived RTDs in OFRs. We compare this approach to that of previous studies by Lambe et al. (Lambe et al., 2011a), Huang et al. (Huang et al., 2016), and Simonen et al. (Simonen et al., 2016), to the best of our knowledge, the only other studies on RTDs in OFRs. We do not provide predictive configurations for the PAM reactor because there are many avenues different groups can take depending on their focus, and this study is central to the current design.

2 Methods

The WU-PAM reactor is an iridite-treated aluminum cylinder, 18 inches in length and 8 inches in inner diameter, giving it a total volume of 13 L. It has two 12 inch mercury lamps with peak wavelengths at 185 nm and 254 nm (BHK Inc. Analamp Model No. 82-9304-03) housed in Teflon sheaths, directly opposite each other, along the axial direction. Annular flow of N₂ (Airgas) through the sheaths prevents direct contact with the lamps and purges any outgas products when the lamps are turned on. The mercury lamps are left in place with their housing to mimic simple OFR internals; they have not been turned on during this study. Details of their mode of operations for oxidant formation can be found elsewhere (Li et al., 2015; Peng et al., 2015, 2016). OFRs like the WU-PAM have removable internals, face plates, and peripheral inlets and outlets that allow a wide variety of configurations. For example, Ortega et al. removed the inlet plate of their PAM reactor during a deployment in the Fire Lab at Missoula Experiment (FLAME-3) while keeping the inlet baffle to reduce particle loss, and in doing so observed a reduction in jetting of centerline
flow (Ortega et al., 2013). In a different study, Lambe et al. ran experiments keeping the inlet plate on the PAM coupled with a sparger (a cap with large holes in the side in fixed onto the inlet, so that the flow does not jet into the chamber), because laboratory experiments required a closed system (Lambe et al., 2011a).

In this work, we chose four configurations: I (one inlet, one outlet, two lamp housings as internals), II (one inlet, one outlet, two lamp housings with sparger and baffles as internals), III (multiple inlets, multiple outlets, two lamp housings as internals), and IV (multiple inlets, one outlet, two lamp housings with sparger and baffles as internals). Configuration I at 78 s spacetime was subject to a CFD simulation as a simple scenario where the simulation could capture hydrodynamics accurately.

2.1 Tracer studies

The laboratory setup to determine RTDs experimentally is shown in Fig. 1. N₂ (Airgas) was the carrier fluid and SO₂ (3 ppm; Air Liquide) was the inert tracer. Both flow rates were controlled by mass flow controllers (MFCs) (Pneucleus Technologies, LLC). All experiments began by allowing one hour to achieve a steady state of the carrier gas’ flow profile inside the reactor, after which SO₂ was introduced in a single step-up manner. A tracer flowrate of 100 cm³ min⁻¹ allowed good detection in the measurement and minimized perturbation of the flow field. Analogously, the flow of the carrier fluid was stepped down to maintain a constant desired total volumetric flowrate. SO₂ mixing ratios were determined by a Trace level-Enhanced SO₂ Analyzer (Thermo Scientific Model 43i, Thermo Scientific) via pulsed fluorescence, and the instrument was set to an averaging time
of 10s. This setting was the highest frequency over which the instrument could average the signal.

Obtaining high frequency data simplifies data analysis by avoiding the need for interpolation techniques, as discussed in Sect. S1.

We expected that the tracer would experience an associated spacetime and RTD in places other than the reactor, between the exit of the flow controller and the SO₂ detection chamber in the gas analyzer. We therefore ran two experiments for every WU-PAM reactor configuration. The first incorporated both the reactor and the inlet and outlet plumbing, and the second bypassed the reactor. From these two signals we could extract the actual reactor RTD as described in Sect. 3.2.

Both experiments were operated by allowing the formation of fully developed flow before injecting the tracer stepwise, as mentioned previously. Appendix A describes in detail how we obtained a PDF and a cumulative distribution function (CDF) from raw data.

The WU-PAM reactor has peripheral inlets and outlets to optionally create a ring (annular) flow around the centerline. Ideally, a uniformly distributed flow around the centerline helps stabilize the flow, avoids recirculation, and reduces wall losses. To create ring flow, we formed a three-eighth inch Teflon tube into a circle, and drilled six one-sixteenth inch diameter holes evenly spaced along the side of the tube facing in the direction of flow. A similar Teflon tube circle was created for the outflow. The ring flow setup required additional plumbing internals (Fig. 1b).

Tracer tests were accomplished for configuration I at three different spacetimes (of 52s, 78s, and 152s), for three different configurations (I, II, and III) at a 78s spacetime, and an arbitrary special case for configuration IV at 411s spacetime (configuration and spacetime not commonly used).
2.2 Simulations

While tracer studies are a powerful diagnostic tool and result, if done correctly, in accurate RTDs, they cannot capture the full hydrodynamics details, or the state of mixing in the reactor (i.e., the exchange of mass between the fluid elements). Both hydrodynamics and mixing can significantly influence the reactor performance (Fogler, 2006; Villermaux, 1986). For configuration I at 78s spacetime, we ran a CFD simulation to visualize the hydrodynamics inside the WU-PAM. This comparative analysis seeks to provide validation prior to using the CFD platform as a predictive tool for mixing patterns in OFRs with more complex geometry or internals.

As a solver, we used OpenFOAM, an open source CFD toolbox available at www.openfoam.com or www.openfoam.org. The reactor geometries were constructed on FreeCAD, an open source computer aided design (CAD) software available at www.freecadweb.org, and Onshape, available at www.onshape.com, prior to being exported into OpenFOAM. To discretize the volume elements in the geometry, a mesh was created using the snappyHexMesh tool in OpenFOAM either directly or in the HELYX-OS GUI. By generating mainly hexahedral meshes, this tool can mesh objects of irregular shape. Then, additional layers of different geometry are added to the surface to improve the mesh quality. A figure and details of the mesh can be found in Figure S1 and Table S1, respectively. The hydrodynamics were calculated using simpleFoam, a steady-state solver for single phase incompressible laminar or turbulent flow. We used first-order schemes, and specified the boundary conditions in each simulation case. The outlets had zero gradient for velocity and fixed values for pressure, while the walls had fixed value for velocity and zero gradient for pressure. After the flow field is obtained, a tracer experiment is simulated by
scalarTransportFoam for one of the simulations, which solves the transient convection-diffusion transport equation of a passive scalar (dimensionless tracer concentration in this case). The initial condition is zero concentration, and the boundary condition at the inlet is that the dimensionless tracer concentration is equal to 1. After the simulation, the exit concentration is mixing-cup averaged to output a representative of a cumulative RTD (explained in the next section), an F-Curve. We added a modification to the existing solver to account for turbulent diffusivity, which had a non-negligible effect on mixing in the WU-PAM reactor, particularly at the entrance jet for high flowrates. We found that the turbulent diffusivity was on the same order of magnitude as the molecular diffusivity within the jet region near the inlet, suggesting turbulence in the jet was significant. It is worthwhile to note that the inlet sparger and baffles (i.e., internals present in configuration II and IV) left out of the simulation could significantly affect this outcome. However, resolving the simulation mesh size to account for these internals significantly extended the computational requirements, to the point that running these simulations was not possible on our computer system and would require a computing cluster to perform. However, those simulations required significant computer time to resolve mesh sizing.

3 Results

3.1 The RTD function, \(E(t)\), and the cumulative RTD function, \(F(t)\)

Tracer tests give us fast qualitative information about the reactor, but mathematical manipulation (e.g., normalizing the data and scaling the axes) of the data provide quantitative information and offers a basis for comparing reactor behaviors on a universal scale. The main mathematical
descriptors of a fluid element residing in a chamber are its PDF and its CDF. For a chemical reactor, the PDF is more commonly referred to as the RTD function, \( E(t) \), in the dimensional domain, or \( E(\theta) \) in the dimensionless domain (referred to as E-Curves). Similarly, the CDF is called the cumulative RTD function, \( F(t) \), in the dimensional domain, or \( F(\theta) \) in the dimensionless domain (referred to as F-Curves) (Danckwerts, 1953; MacMullin and Weber Jr., 1935). The relations between E-Curves and F-Curves are derived for the reader in this Appendix A, but are well established and available on the internet and in classical textbooks (Fogler, 2006; Levenspiel, 1999, 2002).

Figure 2 gives an example of how mathematical processing of the data looks. The shape of the curve does not change, but the axes do. Section S1 explains how we obtained a pulse response equivalent of concentration data from stepwise addition of the tracer.

In the WU-PAM, advective flow should be the main form of transport (we do not consider convective effects due to thermal gradients from lamp activity in this work). Modeling real reactors can be challenging, but approximations are possible using ideal reactor concepts (Levenspiel, 2002). The two most common examples of ideal reactors are the plug flow reactor (PFR), where the flow is perfectly plugged or piston-like, and the continuously stirred tank reactor (CSTR), where the flow is perfectly mixed. Mathematically, their E-Curves are represented by Equations 1-4:

\[
E_{PFR}(t) = \delta(t - \bar{t}) \quad (1)
\]
\[
E_{PFR}(\theta) = \delta(\theta - 1) \quad (2)
\]
Examples of how RTDs look like based on compartmental modeling using both ideal reactors are available in chemical engineering textbooks (Fogler, 2006; Levenspiel, 1999) and, although not discussed here, a variety of phenomenological models can be applied to describe or compare OFRs. It is then open to interpretation whether the combination of ideal reactors chosen for an E-Curve (e.g., a PFR and CSTR in series, or two CSTRs in parallel) describes the hydrodynamics of the reactor as well. The RTD of an OFR should be obtained experimentally, if possible, before deciding what model to use to describe it. Development of a phenomenological model to describe the WU-PAM RTD is beyond the scope of this study, whose aim is to develop a robust methodology to assess degree of plug flow in any OFR, however is an avenue that should be pursued in the future. Given our current setup at Washington University, the true reactor RTD is impossible to measure accurately by a single tracer injection. The tubing length, pressure drop inside the filter holder upstream of the SO₂ detector, and location of the SO₂ detector have not been minimized, thus we expect that collectively they could perturb our measurements significantly. We choose not to simply subtract the theoretical space time of the tubing, because non-ideal tracer injection or detection are most likely not represented by a Dirac function of a perfect impulse (or derived from a perfect stepwise injection, represented by the Heaviside function). Therefore we need to deconvolute the RTD signal due to the reactor from the signal due to additional plumbing.

3.2 Tank-in-Series model for indirect deconvolution
Levenspiel describes the convolution integral (Levenspiel, 1999) in his textbook “Chemical Reaction Engineering”, which has been adapted to solve previous problems of decoupling RTD signals (Hamed, 2012; Han, 2007; Mills and Duduković, 1988; Simonen et al., 2016; Sun, 2010).

This integral focuses on packets of the tracer that enter \( t' \) seconds before \( t \), that is \(( t - t' )\), and stay \( t' \) seconds in the reactor:

\[
C_{\text{out}}(t) = \int_0^t C_{\text{in}}(t') \cdot E(t - t') dt'.
\]  

(5)

or

\[
C_{\text{out}}(t) = C_{\text{in}} \ast E
\]

(6)

where \( E \) is the true E-Curve of the reactor, and \( C_{\text{in}} \) and \( C_{\text{out}} \) are the time-dependent concentration profiles of the measured tracer at the injection port and outlet port respectively. This equation is based on assumptions of mass conservation (i.e., no wall loss inside the reactor) and memory loss (i.e., the fluid elements in fast-moving fluid in a region are not bound to behave as fast-moving in another region). We separate two regions in our setup, and identify three E-Curves. These correspond to curves for the reactor, the plumbing (including filters, instrument plumbing, and the instrument detector chamber), and the two together. Respectively, we denote them as \( E_0(t) \), \( E_1(t) \), and \( E_2(t) \). We are able to accurately measure \( E_2(t) \) and \( E_1(t) \), but not \( E_0(t) \). Thus, Eq. (6) now takes the form

\[
E_2(t) = E_0(t) \ast E_1(t),
\]

(7)

and we need to solve for \( E_0(t) \). Details of the deconvolution approach can be found in Appendix B, however direct application of this technique failed to get the solution to converge. It is a robust protocol to accurately determine a numerical RTD, and should be applied whenever a stable solution is available.
What we propose is an indirect application, i.e., to guess $E_0(t)$ so that the convolution integral yields a curve that matches that of $E_2(t)$. This requires a formidable number of guesses and iterations and could be a lengthy process if done numerically. One workaround is to assume a form of $E_0(t)$, ideally with one variable parameter, that can be tuned to give the $E_2(t)$ that best matches the experimental $E_2(t)$ curve. The CSTR and PFR forms should not be considered since they are ideal extremes of reactor behavior. We chose to apply the tank-in-series (TIS) model (MacMullin and Weber Jr., 1935), also referred to as N-CSTR model, to the convolution integral since it is a one parameter model that, although not specific to flowtube, tubular, laminar, or plug-flow reactors, gives an idea of where the reactor lies on the spectrum of mixed flow vs. plugged flow based on the value of a parameter, $N$. $N$ refers to the fictitious number of equivalent CSTRs that, in series, describe the E-Curve for the reactor. This function is

$$E(t) = \frac{t^{N-1} e^{-\frac{(N)\theta}{t}}} {(N-1)! \left(\frac{\theta}{N}\right)^N} \quad (8)$$

$$E(\theta) = \frac{N(N\theta)^{N-1}}{(N-1)!} e^{-N\theta}. \quad (9)$$

For a value of $N = 1$, the E-Curve becomes that of a perfect CSTR; for a value of $N = \infty$, it becomes that of a perfect PFR, as shown in Fig. S2. Using this model, the convolution integral takes the form

$$E_2^*(t) = \int_0^t E_1(t - t') \cdot \frac{t'^{N-1} e^{-\frac{(N)\theta'}{t'}}} {(N-1)! \left(\frac{\theta'}{N}\right)^N} \, dt'.$$  

(10)
where $E_1(t - t')$ is an array of accurate experimental data already obtained, and $E_2^*(t)$ is the output guess. $E_2^*(t)$ is then matched to $E_2(t)$ by varying $N$ in an iterative fashion. Using this form, the algorithm in Appendix B is still valid. We used MATLAB to solve this for all cases. The results are displayed in Fig. 3.

4 Discussion

The small aspect ratio of the WU-PAM limits wall interactions, preventing laminar flow development due to absence of a boundary layer. This suggests the flow field would then depend on inlet/outlet geometries or volumetric flowrate. Though, for a fixed spacetime of 78s, we observed that different configurations had no significant effect on the RTD (Figs. 3b, d, e). Further, for configuration I, different spacetimes also had no significant effect. The only case with a marked change in the signal was for configuration IV at 411s spacetime (Fig. 3f). We attribute this difference to the low volumetric flowrate, implying that advective transport begins to be less dominant than turbulent or molecular diffusivity as mode of transport. Such a low spacetime, while increasing the degree of plug flow, would result in a potentially significant loss of semivolatile or low volatility gases. Additionally, other modes of transport such as convective effects (vertical mixing for non-isothermal conditions) could become more apparent, as revealed by Huang et al. for the Caltech photooxidation flow tube (CPOT) reactor. As mentioned earlier, a detailed phenomenological modeling study of RTDs in the WU-PAM is beyond the scope of this study, however at more conventional spacetimes, it would be helpful to visualize hydrodynamics to assess what contacting patterns and state of mixing the reactor exhibits. We thus chose a simple scenario as a base case for simulation: configuration I at 78s spacetime.
CFD reveals that the hydrodynamics inside the PAM are far from that of a well-mixed reactor (Fig. 4). This is insightful because the F-Curve of the simulation matches reasonably well with that of the experiment (Fig. 5) and alone would imply CSTR-like mixing. This is the caveat associated with interpreting RTDs, and further supports investigation in phenomenological modeling. Snapshots of the simulation displayed in Fig. 4a-c show there is jetting (short-circuiting), recirculation, and dead zones. Jetting leads to fluid elements that have a very short residence time and cause high values of E(t) at t > 0s. Recirculation leads to fluid elements spending more time in the reactor, yielding middle values of E(t) as elements exit at t ~ \bar{t}. Stagnation (dead zones) at the inlet of the reactor cause fluid elements to remain entrained in the reactor for a long time before exiting the reactor at ~ 2-3 times \bar{t} at low values of E(t), leading to a long tail in the E-Curve. These three effects together lead to an E-Curve that looks similar to that of a CSTR, but mixing in CSTRs is dominated by recirculation; meaning that the local concentration of tracer at the exit is identical to all other locations in the reactor (Zwietering, 1959). Therefore, while tracer tests give a general idea about contacting patterns, CFD visualizes the hydrodynamics, and help model the reactor. Plotting the WU-PAM OFR’s E-Curves for this scenario on a semilog plot does not yield different gradients, which would otherwise indicate different volumes for the compartmental modeling of the jetting, recirculation, and dead volumes (Levenspiel, 2002). The limitation to that statement is that the E-Curves in this work have been obtained by fitting a one-parameter model, consequences of which should be the focus of future work in conjunction with phenomenological modeling. Furthermore, our simulations are limited to isothermal conditions, therefore cannot predict buoyancy effects that could explain spread in the RTD at low flowrates (or low Reynolds numbers) (Fig. 3f), as observed by Huang et al. (2016).
Lambe et al. (2011a) modeled the Pennsylvania State University PAM (PSU-PAM) reactor using a compartmental model consisting of two parallel tubular reactors that exhibit Taylor dispersion (Taylor, 1953), suggesting that their reactor (whose geometry is identical to that of the WU-PAM OFR) has two main volumes: an active reactor volume, and another volume with entrainment. The model output matches their experimental data reasonably well, but, they did not decouple the reactor’s E-Curve from that of the setup, implying the match may include phenomena occurring in other pipes of the setup. Lambe et al. describe RTDs for the two volumes using the axial dispersion model (ADM) (Taylor, 1953, 1954a, 1954b), which is based on modeling plug or laminar flow with axial dispersion of material. Generally, as also stated by Huang et al. (2016), the ADM is valid for regions where the radial Péclet number (Pé) is less than ~4 times the aspect ratio (length of reactor divided by its cross sectional area), or if Pé is greater than √48 (Aris, 1956; Taylor, 1954b). Both the PSU-PAM OFR and the WU-PAM OFR meet these requirements under typical flowrates (see SI, Sect. S4). If the reactor could be described by the ADM, CFD would show that the entrance and exit effects would be separate from the main flow in the tube – which is not the case for the simplified geometry of configuration I. We do not know how well they apply to the other configurations. At no point inside the reactor does pipe flow fully develop, so the high aspect ratio concept (Kang et al., 2007) does not allow a velocity profile to become established with the current end caps used. Thus, although Pé appears acceptable, the inlet and outlet regions should be re-engineered to allow formation of fully developed pipe flow in the main cylinder for the ADM to be valid. While the E-Curve for configuration II is similar to that of configuration I at 78s spacetime, it would be helpful to run CFD on that configuration at different spacetimes to observe if, and if so at what spacetime, the sparger and baffles efficiently suppress jetting.
Unfortunately, our CFD mesh could not be refined enough to capture the geometry of those without sacrificing valuable computational time.

Instead, we chose to apply the use of an inlet cone (45° angle, 4.94” length) and outlet peripherals to simulate a more attenuated inlet and exit from sudden aperture. The results are displayed in Fig. 6. While the size of the jet appears to be broader compared to simulations in Fig. 5 (unaltered PAM geometry), it is nonetheless present. Furthermore, recirculation in the form of backmixing is evident towards the front, and stagnation close to the walls and corners persists. From the velocity field (Fig. 6 center figure), a smaller cone angle that follows the contour of the light blue velocity field could prevent backmixing.

5 Potential implications

Initial PAM modeling work assumed plug flow behavior in OFRs (Li et al., 2015). Li et al. stated that correcting for the non-ideal E-Curve in their OFR would account for ~10% error in their oxidant exposure results, which is less than the overall model uncertainty. However, recent work incorporates the effect of non-ideal RTDs on model outputs (Palm et al., 2017, 2018, Peng et al., 2015, 2016; Peng and Jimenez, 2017). Peng et al. (2015) show that for three OFR operational modes (that is, modes of different oxidant formation mechanisms denoted by ‘OFR185’, ‘OFR254-70’, and ‘OFR254-7’), a comparison between model output for ideal plug flow vs. non-ideal RTDs (using the RTD experimentally obtained by Lambe et al., 2011a) for OH exposure \( \text{OH}_{\text{exp}} \) generally agree within a factor of 2 for low \( \text{OH}_{\text{exp}} \); the model disagreement exacerbates at high \( \text{OH}_{\text{exp}} \) beyond a factor of ~4. Peng and Jimenez then extend OFR operational modes to include
N-containing chemistry (in modes referred to therein as ‘OFR185-iNO’, ‘OFR185-7-iNO’, and ‘OFR185-70-iNO’) where at moderate-to-high OH$_{\text{exp}}$, the deviations exacerbate significantly, although the authors argue those conditions represent unrealistic chemical pathways. It is worthwhile noting that the chemistry modeled by Peng and Jimenez may find a workaround by utilizing N$_2$O as NO precursor (Lambe et al., 2017) rather than NO itself, potentially minimizing RTD-related errors. Palm et al. (2018) report data from OFR field deployment where the same comparison (ideal plug flow vs. the RTD experimentally obtained by Lambe et al., 2011a) suggests RTD-related errors overpredict (for CO) or underpredict (for toluene and monoterpenes) photochemical age (that is, the ratio of OH$_{\text{exp}}$ to tropospheric average OH number concentrations) in the reactor, generally within a factor of 3 of model error. Considering this work employs the compartmental model RTD described by Lambe et al. (2011a), which for reasons mentioned in the previous section may not be the true PAM RTD, and given that non-ideality in RTDs affects certain OFRs more than others, implementing the method presented here to obtain a more representative reactor RTD can either help constrain error uncertainty in the models, or possibly extend the OH$_{\text{exp}}$ range in which OFRs can be operated, a reportedly nontrivial task (Palm et al., 2018). Considering our results indicate that OFRs like the WU-PAM exhibit an RTD closely matching that of an ideal CSTR, which is more well-mixed than the Lambe et al. RTD, the sensitivity analysis conducted so far could represent a lower bound for error analysis because the Lambe et al. RTD is closer to a PFR-like RTD than a CSTR-like RTD. Recent modeling work assumes plug-flow behavior in OFRs (Li et al., 2015; Peng et al., 2015, 2016). Li et al. state that correcting for the non-ideal E-Curve in their OFR would account for ~10% error in their results, which is less than the overall model uncertainty.
For compounds with low lifetimes to OH, contacting could influence the model results to a greater extent (e.g., field deployment monoterpene decay reported by Palm et al., 2018). By taking a ratio of characteristic reaction time to the characteristic transport time, one can define the Damköhler number (Da). Considering spacetimes of 52-411s (as per this study), the value of Da can be between 0.52 and 4.11 for a compound with lifetimes of ~100s. Since reaction timescales are on the order of transport timescales, contact patterns may play an important role, as seen in Palm et al. (2018). This could also be the case for heterogenous reactions, diffusion-limited reactions, or semivolatile compound (SVOC) oxidation that exhibit slow gas-particle partitioning. Furthermore, combining a phenomenological model to an associated RTD can impact kinetics (and yields) further. The RTD generated by Lambe et al. (2011a) employed in Li et al. (2015) may lead to greater than 10% error if the 2 PFRs in parallel model suggested by Lambe et al. (2011a) is not applicable. In these scenarios, ensuring a high degree of plug flow can not only maximize exposure, but minimize the distribution of aged compounds (e.g., first or second generation compounds) that are due to different exit ages because of recirculation or stagnation. However, this configuration may not suit a field deployment where trace compounds have short lifetimes to OH and can be easily lost to reactor walls, in which case ensuring a high degree of mixing would be beneficial. However, for compounds with low OHR, contacting could influence the model results to a greater extent. By taking a ratio of characteristic reaction time (e.g., OHR) to the characteristic transport time, one can define the Damköhler number (Da). Considering spacetimes of 52-411s (as per this study), the value of Da can be between 5200 and 41100 for a compound with OHR~100s⁻¹. Since reaction timescales are 10⁴-times faster than transport timescales, contact patterns won’t matter to a large degree. However, the value of Da can be between 5.2 and 41.1 for a compound with OHR~0.1s⁻¹, in which case contacting patterns may play a more
significant role. This could be the case for heterogenous reactions, diffusion limited reactions, or semivolatile compound (SVOC) oxidation that exhibit slow gas-particle partitioning. Furthermore, combining phenomenological model to an associated RTD can impact kinetics (and yields) further. The RTD generated by Lambe et al. (2011) employed in Li et al. (2015) may lead to greater than 10% error if the 2 PFRs in parallel model suggested by Lambe et al. (2011) is not applicable. In these scenarios, ensuring a high degree of plug flow can not only maximize exposure, but minimize the distribution of aged compounds (e.g., first or second generation compounds) that are due to different exit ages because of recirculation or stagnation. This configuration would suit a laboratory experiment with slow kinetics, where concentrations can be made high enough to where wall losses aren’t an issue. However, this configuration may not suit a field deployment where trace compounds have high OHR_{ext} and can be easily lost to reactor walls, in which case ensuring a high degree of mixing would be beneficial.

We do recognize that OFR (or any environmental chemical reactor) users may have a preference to rapidly obtain an RTD profile perhaps using an improvised setup with very short sample lines and a fast time-response gas analyzer. However, the accuracy to which the profile is obtained should be carefully examined. If the reactor is considerably large, or if it is an OFR to be deployed for low levels of exposure, then the influence of plumbing is minimal. If the reactor of choice is small, the oxidant exposure is high, or the reactor has more than one inlet/outlet or other peripheral components, it would be recommended to use the method described here to obtain the most representative RTD, since all sources of bias are removed.

6 Conclusion
The WU-PAM reactor’s hydrodynamics are complex, and even though the E-Curve looks simple, applying a compartmental model (phenomenological modeling) to obtain an analytical E-Curve (rather than the empirically-based TIS E-Curve) can be challenging. Having too sudden an aperture at the entrance zone leads to dead volumes at the inlet corners. We cannot confirm if the sparger design helps reduce dead volume, but tracer tests suggest it doesn’t appear to affect the degree of plug flow under standard operating spacetimes (52-156s). The reactor is described neither by back mixing, plug flow, nor by the ADM in any configuration. However, for configuration IV at 411s spacetime, a noticeable shift towards plug flow behavior is observed, perhaps due to a combined effect of internals and low inlet velocity. We note that the E-Curves we obtain are not as accurate as an E-Curve numerically obtained by direct deconvolution, since we are forcing a closed form solution on our data. We further note the need for phenomenological modeling.

Tapered ends on the inlet and the outlet would help to develop a steady flow profile at the inlet and avoid recirculation at the outlet, however the cone angle should be predetermined by CFD if possible. By improving simulations to include temperature gradients induced when the internal lamps are on, and refining the mesh to capture internals, the ADM should be revisited as a model to describe the PAM reactor. If the ADM satisfactorily describes the PAM reactor’s RTD, kinetics should be easier to obtain, and diffusivity values using the Aris-Taylor relationship (Aris, 1956) can even be obtained. This could help assess whether processes are reaction limited or diffusion limited, arguing the reactor validity in experimental setups. At that point, the reactors would be regulated by only one parameter, their flowrate. This parameter would be adjusted to achieve desired spacetimes depending on OHR_{ext}. Finally, to obtain accurate experimental RTDs,
achieving a functional direct deconvolution code should be a focus of future development. The implementation of this technique can be extended to drift tubes in mass spectrometers, as those are essentially flow tube reactors where ionization efficiency can be strongly influenced by mixing.

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Figures
Figure 1: Experimental setup for tracer studies for a) one inlet and one outlet and b) peripheral inlets and outlets. The main difference is the presence of the ring sparger in b).
Figure 2: Tracer tests at 10 L min\(^{-1}\) (78s spacetime) through the reactor for configuration I. This figure serves as an illustrative example for non-dimensionalizing tracer response curves.
Figure 3: E-Curves for the WU-PAM configuration I at a) 52s b) 78s c) 156s spacetimes, at 78s spacetimes for d) configuration II e) configuration III, and f) for configuration IV at 411s spacetime. Details on the configurations are in the Methods section. Lower frequency data for panel e) was due to instrument repair, and temporarily set on longer averages.
Figure 4: CFD output for configuration I at 78s spacetime: snapshots at a) 1s b) 10s and c) 100s of runtime, and d) pressure field, e) velocity (vector) field, and f) turbulent diffusivity field. Color scales are dimensionless scalar concentration for the tracer (a-c), Bar for the pressure field (d), and cSt for the kinematic viscosity (f).
Figure 5: Comparison of F-Curve output between simulation (CFD) and tracer test (N-CSTR) for configuration I at 78s spacetime. N-CSTR is an acronym (describing ‘N’ CSTRs in series) equivalent to TIS: both refer to the Tank-in-Series model (see Section 3.2).
Figure 6: CFD analysis on the effect of inlet cone and peripheral outlets on fluid flow. All figures represent a visualization of the flow field, with color scales representing (from left to right): kinematic viscosity, velocity, and $\omega$. The 3D representation on the leftmost figure highlights the uniformity of the recirculation region.

Appendix A: The use of E-Curves and F-Curves

To determine RTDs, we injected tracer in a steady stream rather than a single pulse. This prolonged and constant injection, which we call a step input, gave us $F(t)$, from which we can derive $E(t)$ as follows:

$$ F(t) = \frac{v}{m} C_{\text{step}} $$

$$ E(t) = \frac{dF(t)}{dt} $$

where $v$ is the volumetric flowrate in $\text{m}^3\text{s}^{-1}$, $m$ is the molar flowrate of the tracer in $\text{mol s}^{-1}$, and $C_{\text{step}}$ is the concentration of the tracer for a step input in $\text{mol m}^{-3}$. Therefore, $F(t)$ is dimensionless, and $E(t)$ in this example has units of $\text{s}^{-1}$. The area under the E-Curve is unity, representing the PDF of the system:
\[ \int_{0}^{\infty} E(t) dt = 1. \]  \hspace{1cm} (A3)

1125 Similarly, for the dimensionless domain
\[ \int_{0}^{\infty} E(\theta) d\theta = 1. \]  \hspace{1cm} (A4)

1126 And if we take \( \bar{\ell} \) to be the mean residence time of the reactor, then
\[ \theta = \frac{t}{\bar{\ell}} \]  \hspace{1cm} (A5)

1127 The additional utility of the dimensionless domain is that for reactors of different sizes, built to behave the same, the RTD is numerically identical. For example, if PAM OFRs are operated in different ways (e.g., they operate at different flowrates) or are built in different sizes but display the same E-Curve in the dimensionless domain, then their performance will be identical, and their mean residence time will always occur at \( \theta = 1 \). This identity would apply for the F-Curve as well in both domains, where from Eq. (A2) we can see that

\[ F(t) = \int_{0}^{t} E(t) dt \]  \hspace{1cm} (A6)

\[ F(\theta) = \int_{0}^{\theta} E(\theta) d\theta. \]  \hspace{1cm} (A7)

1134 The mathematical properties of interest for PDFs are their moments: These have quantitative meanings in E-Curve analysis. A general equation for the moments of a function \( f(x) \) is
\[ \mu_n = \int_{-\infty}^{\infty} x^n \cdot f(x) dx, \]  \hspace{1cm} (A8)

where \( \mu_n \) is the nth moment of the distribution. If we consider a raw \( C(t) \) dataset from our tracer, we can derive the moments:
\[ \frac{\int_{0}^{\infty} C(t) dt}{\int_{0}^{\infty} C(t) dt} = \int_{0}^{\infty} E(t) dt = 1 = \mu_0 \]  \hspace{1cm} (A9)
\[ \frac{\int_0^\infty t \cdot c(t) dt}{\int_0^\infty c(t) dt} = \int_0^\infty t \cdot E(t) dt = \bar{t} = \mu_1. \quad (A10) \]

Here, we are interested in the first moment, which represents the mean residence time. For higher moments, we use the central moments of the distribution since we are interested in quantities like variance, skewness, and kurtosis around the mean (and not around zero). This alters Eq. (A8) as follows:

\[ \mu_n = \int_{-\infty}^{\infty} (x - a)^n \cdot f(x) dx; \quad n \geq 2, \quad (A11) \]

where \(a\) is a constant, and is generally the mean of the distribution (\(\bar{t}\) in this case). Thus, the second (central) moment of the E-Curve becomes

\[ \frac{\int_0^\infty (t - \bar{t})^2 \cdot c(t) dt}{\int_0^\infty c(t) dt} = \int_0^\infty (t - \bar{t})^2 \cdot E(t) dt = \sigma^2 = \mu_2, \quad (A12) \]

where \(\sigma^2\) has a clear physical meaning, and is the variance around the mean. Higher moments (skewness and kurtosis) can be of use, and require additional math, but are not addressed in this work.

**Appendix B: Algorithm for direct deconvolution**

Here, we perform an inverse operation to Eq. (7) (Sun, 2010) and work towards an output curve:

\[ E_2(t) = \int_0^t E_1(t - t')E_0(t')dt' \quad (B1) \]

where \(E_0\) is the RTD of interest, \(E_1\) is the RTD of another component in series with \(E_0\), and \(E_2\) is the convoluted RTD. The deconvolution task is to solve for \(E_0\) with measured \(E_1\) and \(E_2\). Due to
the unknown function forms of \( E_1 \) and \( E_2 \), the integral is most easily resolved numerically. Thus, the time is discretized into \( t_{i-1} \leq t \leq t_i \), where \( t_i = i \Delta t \), \( i = 0 \ldots \infty \). The time interval \( \Delta t \) is determined by the data acquisition frequency for \( E_1 \) and \( E_2 \), and is small enough to resolve the RTD’s in fine detail. An even smaller \( \Delta t \) is also feasible by interpolating the data on the finer temporal resolution. Eq. (B1) is now rewritten as (B2):

\[
E_2(t_i) = \int_0^{t_i} E_1(t_i - t')E_0(t')dt' = \sum_{j=1}^{i} \int_{t_{j-1}}^{t_j} E_1(t_i - t')E_0(t')dt'
\]

\[(B2)\]

Within the small interval between \( t_{j-1} \) and \( t_j \), we can assume \( E_1 \) and \( E_0 \) to be either constant (0\(^{th}\) order) or linear with time (1\(^{st}\) order). Obviously the 1\(^{st}\) order approximation is more accurate than the 0\(^{th}\) order with a little more complexity in the integration. Both methods have been tested and proven to result in similar deconvoluted RTD, indicating that 0\(^{th}\) order is good enough with sufficiently small \( \Delta t \). Thus the following derivation takes the 0\(^{th}\) order simplification, i.e. for \( t_{j-1} \leq t' \leq t_j \):

\[
E_1(t_i - t') = \frac{1}{2} \left( E_1(t_i - t_{j-1}) + E_1(t_i - t_j) \right) = \frac{1}{2} \left( E_1(t_{i-j} + 1) + E_1(t_{i-j}) \right)
\]

\[
= \frac{1}{2} \left( E_1|_{i-j+1} + E_1|_{i-j} \right)
\]

\[(B3)\]

\[
E_0(t') = \frac{1}{2} \left( E_0(t_{j-1}) + E_0(t_j) \right) = \frac{1}{2} \left( E_0|_{j-1} + E_0|_{j} \right)
\]

\[(B4)\]

which are Eq. (B3) and (B4) with simplified notation (e.g. from \( E_0(t_j) \) to \( E_0|_j \)). Thus Eq. (B5):

\[
\int_{t_{j-1}}^{t_j} E_1(t_i - t')E_0(t')dt' = \frac{1}{4} \left( E_1|_{i-j+1} + E_1|_{i-j} \right) \left( E_0|_{j-1} + E_0|_j \right) \Delta t
\]
Eq. (B2) becomes (B6):

\[ E_2|_i = \sum_{j=1}^{i} \frac{\Delta t}{4} (E_1|_{i-j+1} + E_1|_{i-j})(E_0|_{j-1} + E_0|_j) \]

(B6)

where \( i \) starts at 1 as \( E_2|_0 = E_1|_0 = E_0|_0 = 0 \) (except for RTD of an ideal CSTR). Again, \( E_2 \) and \( E_1 \) are known by measurements, and \( E_0 \) is the unknown to be solved. Let \( x \) be \([E_0|_1, E_0|_2, \ldots, E_0|_n] \), where \( n \) is an integer sufficiently large beyond which \( E_0 \) is considered to have converged to zero. Let

\[ a_{i,j} = \frac{\Delta t}{4} (E_1|_{i-j+1} + E_1|_{i-j}) \]

(B7)

\[ E_2|_1 - a_{1,1}E_0|_0 = a_{1,1}E_0|_1 \]

\[ E_2|_2 - a_{2,1}E_0|_0 = (a_{2,1} + a_{2,2})E_0|_1 + a_{2,2}E_0|_2 \]

\[ E_2|_3 - a_{3,1}E_0|_0 = (a_{3,1} + a_{3,2})E_0|_1 + (a_{3,2} + a_{3,3})E_0|_2 + a_{3,3}E_0|_3 \]

\[ \ldots \]

Therefore, define the coefficient matrix \( A \) in Eq. (B8) where

\[ A_{i,j} = \begin{cases} 
  a_{i,i} & \text{if } j = i \\
  a_{i,j} + a_{i,j+1} & \text{if } j < i \\
  0 & \text{if } j > i 
\end{cases} \]

(B8)

And define the vector \( b \) in Eq. (B9) where

\[ b_i = E_2|_i - a_{i,1}E_0|_0 \]

(B9)
In this way, the integral Eq. (B1) is converted to a linear algebra problem in Eq. (B10):

\[ Ax = b \]  

Therefore, \( E_0 \) can be obtained by solving

\[ x = A^{-1} b \]  

This is called “direct deconvolution” which requires taking inverse of the coefficient matrix \( A \). However, in some cases \( A \) is ill conditioned and numerical inversion method like “inv(A)” in MATLAB does not converge. This non-ideality results primarily from measurement uncertainties.

Thus, instead of directly solving Eq. (B10), it is proposed in this work to first assume a reasonable function form for \( x \), e.g. the tanks-in-series (TIS) model, and then iteratively update the model parameters to minimize the residual of Eq. (B10). This “indirect deconvolution” method always works to yield a stable and accurate solution of \( E_0 \), the accuracy being judged by comparing \( b \) and \( b' = Ax' \), where \( x' \) represents the converged solution. The validity of the “indirect deconvolution” depends on the reactor model being assumed. The TIS model is one of the two mostly used non-ideal reactor models (the other one is the axial dispersion model), which has proven to work well for the PAM reactor under investigation. The model parameter \( N \) (the number of CSTR’s) indicates the non-ideality of the reactor, i.e. the larger \( N \) is than 1, the more differently the reactor behaves from an ideal CSTR. The mathematical form of the TIS model can be found in Section 3.2.
In discrete form, taking a constant time step $\Delta t$, we can take a datapoint at $t^*_i = i \Delta t$,

$$E_{z,N}(t^*_i) = \sum_{i=1}^{N} \int_{t_{i-1}}^{t_i} E_x(t_{N-1} = t') \cdot E_\alpha(t') dt'.$$

(B2)

If we then assume that the functions $E_x(t = t')$ and $E_\alpha(t')$ are constant for the interval $t_{i-1} \leq t' \leq t_i$, we can simplify the integral:

$$E_x(t_{N-1} - t') = \frac{1}{2} (E_x|_{N-1} + E_x|_{N-1+1})$$

(B3)

$$E_\alpha(t') = \frac{1}{2} (E_\alpha|_{i} + E_\alpha|_{i-1})$$

(B4)

$$\int_{t_{i-1}}^{t_i} E_x(t_{N-1} = t') \cdot E_\alpha(t') dt' = \frac{1}{4} (E_x|_{N-1} + E_\alpha|_{i} + E_\alpha|_{i-1}) \Delta t.$$

(B5)

Now, Eq. (B2) becomes

$$E_{z,N}(t^*_i) = \sum_{i=1}^{N} \frac{1}{4} (E_x|_{N-1} + E_x|_{N-1+1})(E_\alpha|_{i} + E_\alpha|_{i-1}) \Delta t.$$

(B6)

From experimental data, we can accurately collect datapoints for $(E_x|_{N-1} + E_x|_{N-1+1})$ as well as $E_x(t^*_i)$, so we need to rearrange for $(E_\alpha|_{i} + E_\alpha|_{i-1})$, which has to be solved numerically in matrix form. Let

$$\alpha_i = \beta_i = \frac{1}{4} (E_x|_{N-1} + E_x|_{N-1+1})$$

(B7)

$$A_{N,i} = \begin{cases} \alpha_i + \beta_{i+1} & i = 1, 2, ..., (N-1) \\ \alpha_N & i = N \end{cases}.$$  

(B8)

Upon the initial condition

$$B_{N} = \frac{E_x(t_{N})}{\Delta t} = \beta_1 E_\alpha|_{i}$$

(B9)

we have that

$$B_{N} = \sum_{i=1}^{N} A_{N,i} E_\alpha|_{i}.$$  

(B10)
Finally,

$$E_0(t) = A - B. \quad (B11)$$

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