Second round review

We thank the Referee #2 again for his review. To facilitate the review process we have copied the reviewer comments in black text. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper (in bold text). Page and line numbers refer to the first revised manuscript.

Referee #2

The authors have largely addressed my concerns in their rebuttal. I am happy that the paper can form the basis of ongoing discussions in the field of OFR deployment and interpretation. I am particularly satisfied with the RTD analysis and its explanation of the deviation from plug flow. I am still slightly concerned by the continued separation of the gaseous and condensed phase processes. I am in full agreement with the authors that "OFR modeling is a subfield in itself, and our group cannot be expected to address every single possible topic". However, where a process can have a substantial influence on the processes that are the subject of a manuscript, then this possibility should be acknowledged.

It can be argued that the two statements in point 2.2 of the authors response:

i) "The presence of aerosols has typically negligible impacts on the gas-phase chemistry" and

ii) "gas-phase species have only limited impacts on OA"

are not demonstrably correct for all conditions in OFRs.

R2.5) To rebut i), consider the typical concentrations in diesel emissions. Concentrations of NOx in raw diesel exhaust are typically between 50 and 1000 ppm depending on running conditions and technology (and can be very much higher during transients and below 17 degrees C when EGR is not mandated). Clearly this is the sort of NOx target regime of the current manuscript. Whilst PM emissions do not respond in the same way as NOx to engine technologies (e.g. EGR generally increases PM whilst decreasing NOx, and only DPF fitted vehicles have significantly reduced PM) or load-speed conditions, typical concentrations from a modern light-duty (EURO5) diesel generally range from between 1 and 30 mg/m^3 in raw exhaust. Assuming 80 nm modal diameter, 1 mg/m^3 will provide a mass transfer rate ("condensation sink") of about 4 s^-1 (using an uptake coefficient of unity); so a lifetime of 0.25 s for such a condensing gas (and 30 mg/m^3 would give a lifetime of less than 0.01 s). A lower uptake coefficient would obviously lead to a longer lifetime (e.g. 1 s for 0.01 at 30 mg/m^3).

Lines 88 to 92 explicitly include OFR conditions where there is a substantial likelihood of such high primary PM mass (an urban tunnel, "where NOx was high enough to be a major OH reactant"... and ... emissions of vehicles, biomass burning, and other combustion sources, "where NO can often be hundreds of ppm"). Looking at the Karjalainen et al., 2016 case presented in Figures 7 and 8, the authors are carrying out calculations under raw, 12 x and 100 x dilution
conditions for gasoline engine emissions. Figure 7 in Karjalainen reported average primary PM values of 0.45 mg/m^3 for parts of the test cycle (assumed raw), rising to more than 10 mg/m^3 including the SOA from a gasoline engine. Similarly, the Link et al., 2016 study of diesel emissions at 45 - 110 dilution employed no primary particle removal technology to emissions from a turbocharged, intercooled, heavy-duty, off-road diesel engine likely to emit massively more than the light-duty levels stated above (in excess of 100 mg/m^3 is readily possible in raw exhaust from such engines). In both these cases the mass transfer of potentially condensing closed shell and radical species to PM could clearly provide very significant sinks of gaseous components that should be considered in a model of OFRs.

We realize that the Referee is not understanding what we intended to communicate with our statements. When we stated that the “gas-phase chemistry” was not significantly perturbed by the presence of particles, we were referring to the gas-phase chemistry that we are modeling, i.e., the radical and NOx-NOy chemistry, as well as the consumption of VOCs and other OH reactants. We did not intend to include the physical partitioning of semivolatile and low volatility species, which clearly is an area of strong interaction of the gas and particle phases (but for the most part does not involve chemistry). We will clarify the language, as described below, to remove this potential source of confusion.

We thank the Referee for providing detailed examples for high condensational sink in combustion exhausts. Nevertheless, even if raw exhausts are injected into the reactor, they still cannot have significant impacts on the major gas-phase oxidants, since VOCs and NOx in raw exhausts, which are also proportionally higher, still dominate total oxidant sink. Dilution of raw exhausts simultaneously lowers condensational sinks and gas-phase reactive oxidant sinks, with their relative importance remaining the same.

We have added a few sentences to clarify this point at the end of the paragraph i) in L151. The modified paragraph now reads:

i) “The presence of aerosols has typically negligible impacts on the gas-phase chemistry of radicals, NOx/NOy, and OH reactants studied here. Condensational sink (CS) of ambient aerosols can rarely exceed 1 s^{-1} even in polluted areas and is usually 1-3 orders of magnitude lower (Donahue et al., 2016; Palm et al., 2016). Thus, even under the assumption of unity uptake coefficient, CS cannot compete with OHR_{ext} (usually on the order of 10 s^{-1} or higher) in OH loss. Uptake of NO onto aerosols only occurs through the reaction with RO2 on particle surface (Richards-Henderson et al., 2015), which is formed very slowly (see below) compared to gas-phase HOx and NOx chemistry. Uptake of HO2, O3, NO3 etc. is even more unlikely to be of importance due to lower uptake coefficients (Moise and Rudich, 2002; Moise et al., 2002; Hearn and Smith, 2004; Lakey et al., 2015). Combustion exhausts can have high aerosol loadings with condensational sinks on the order of 10^2–10^3 s^{-1} (Matti Maricq, 2007). Even if these exhausts are directly injected into the reactor without any pre-treatment, uptake onto the particles still cannot play a major role in the fate of gas-phase radical and NOx species, since VOCs and NOx in raw exhausts, which are
proportionally orders-of-magnitude higher, still dominate the fate of oxidants. Dilution of combustion emissions simultaneously lowers condensational sinks and the sinks of oxidants due to chemical reactions, with their relative importance remaining the same as in undiluted emissions.”

We acknowledge that a strong dilution leads to a lower PM loading than in raw exhausts, which slows down the uptake. But this “lower” PM loading may still be much higher than typical ambient values after dilution. So it may not necessarily be “low PM loading” compared to ambient conditions, as suggested by the Referee below (R2.8).

We have added some text to L566 to acknowledge the PM loading change by dilution:

“Note that a strong dilution lowers aerosol mass loading in vehicle emissions. As a result, condensation of gases onto particles is slower than in raw exhausts. However, condensational sinks after dilution may still be significantly higher than typical ambient values (Matti Maricq, 2007; Donahue et al., 2016).”

R2.6) To address author response 2.2 ii), clearly gas-phase species have a strong impact on OA, being 100% responsible for all SOA. Mass transfer of semi-volatile and low volatility gas-phase species (in the case of exhaust experiments, almost completely due to condensation on existing primary PM) has a determinant effect on PM mass. Gas phase oxidants may have a limited impact on OA chemistry, but gas phase species have a profound effect on OA. Given the paper title relates to modelling the chemistry in OFRs (not modelling the oxidants), it is not solely transfer of radical species between phases that is of concern.

As discussed in response to R2.5, we agree with this and did not intend to say otherwise. However this mostly concerns physics (“mass transfer” in the Referee’s words) and not chemistry. We have modified that paragraph to clarify the fact that physical uptake of semivolatile and low-volatility gas-phase species have a strong impact on PM mass:

ii) “Gas-phase radical and NOx/NOy species only has limited impacts on OA chemistry in this study. Heterogeneous oxidation of OA by OH is generally slow. Significant OA loss due to heterogeneous oxidation can only be seen at equivalent photochemical ages as high as weeks (Hu et al., 2016). The enhancement of heterogeneous oxidation due to NO is remarkable only at OH concentration close to the ambient values but not at typical values in OFR (Richards-Henderson et al., 2015).

It is well known that the aerosol concentration can have a major impact on the physical uptake of semivolatile and low-volatility gas-phase species. However this process is not explicitly modeled in this study.”

Also, we have modified text to L148 for more clarity:

“Also, particle-phase chemistry and physical and chemical interactions of gas-phase species with particles are not considered in this study.”
R2.7) In the context of the above discussion, I do not understand the final paragraph of the authors suggested added text in point 2.2. I think this requires further explanation before inclusion in the paper.

The core idea of that paragraph is that the details of VOC product evolution have a strong influence on the rate of OH loss, but this is highly complex and not well captured even by models as explicit as MCM. We surrogated VOC evolution by SO\textsubscript{2} for simplicity and efficiency and this introduces much more uncertainty on (the temporal variation of) OHR\textsubscript{ext} due to VOC (and hence the radical chemistry) than mass transfer to the particle phase does. Thus, there is no strong need for explicitly including gas-particle mass transfer in the present modeling work.

We have modified that paragraph (L166) below for more clarity:

“As OHR\textsubscript{ext} plays a major and even dominant role in OH loss, it is an important approximation that the real OHR\textsubscript{ext} decay (due to not only primary VOC oxidation and subsequent oxidation of higher generation products, but also wall loss, partitioning to the particle phase, reactive uptake etc.) is surrogated by that of SO\textsubscript{2} (see Fig. S2 of Peng et al. 2015). Gas-phase measurements in literature laboratory studies revealed that there is a large variability of the evolution of total OHR\textsubscript{ext} during oxidation of primary VOCs and subsequent oxidation of their intermediate products, depending on the type of precursors (Nehr et al., 2014; Schwantes et al., 2017). This variability is obviously mainly due to the formation of different types and amounts of oxidation intermediates/products contributing to OHR\textsubscript{ext}. This variation is highly complex due to the large number of possible oxidation intermediates and the limited knowledge of detailed higher-generation mechanisms, and thus is difficult to accurately capture even if modeling with a mechanism as explicit as Master Chemical Mechanism is performed (Schwantes et al., 2017). Therefore, it is justified to use a lumped surrogate to model the OHR\textsubscript{ext} decay for simplicity and efficiency. This approximation is a major contributor to uncertainty of our model. The uncertainties due to both the types of oxidation intermediates/products.”

R2.8) Whilst I do not expect the paper to explicitly address coupling of the gaseous and particulate processes, I would expect the current manuscript to at least acknowledge the interaction between the gas phase chemistry and gaseous losses associated with condensation and the resultant increase in PM mass. The authors should state that their study is completely relevant for low PM loadings in OFRs, but care should be taken when applying it to high ambient PM concentration or direct emission studies (both raw and diluted). Clearly the authors are aware of the necessity to include coupled multiphase processes and should be commended in their work with Jeff Pierce's group on this.

We have acknowledged (see the response to R2.5) that dilution changes PM loadings and hence mass transfer rates, and, when diluted, sources have lower PM loadings in OFRs than in raw emissions. However, we believe that the statement that our study is only valid to low PM loadings is incorrect, as discussed in detail in our response to R2.5. Thus no changes have been made in response to this point.
References


Modeling of the chemistry in oxidation flow reactors with high initial NO

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Abstract. Oxidation flow reactors (OFRs) are increasingly employed in atmospheric chemistry research because of their high efficiency of OH radical production from low-pressure Hg lamp emissions at both 185 and 254 nm (OFR185) or 254 nm only (OFR254). OFRs have been thought to be limited to studying low-NO chemistry (where peroxy radicals (RO\textsubscript{2}) react preferentially with HO\textsubscript{2}) because NO is very rapidly oxidized by the high concentrations of O\textsubscript{3}, HO\textsubscript{2}, and OH in OFRs. However, many groups are performing experiments aging combustion exhaust with high NO levels, or adding NO in the hopes of simulating high-NO chemistry (where RO\textsubscript{2} + NO dominates). This work systematically explores the chemistry in OFRs with high initial NO. Using box modeling, we investigate the interconversion of N-containing species and the uncertainties due to kinetic parameters. Simple initial injection of NO in OFR185 can result in more RO\textsubscript{2} reacted with NO than with HO\textsubscript{2} and minor non-tropospheric photolysis, but only under a very narrow set of conditions (high water mixing ratio, low UV intensity, low external OH reactivity (OHR\textsubscript{ext}), and initial NO concentration (NO\textsuperscript{i}) of tens to hundreds of ppb) that account for a very small fraction of the input parameter space. These conditions are generally far away from experimental conditions of published OFR studies with high initial NO. In particular, studies of aerosol formation from vehicle emissions in OFR often used OHR\textsubscript{ext} and NO\textsuperscript{i} several orders of magnitude higher. Due to extremely high OHR\textsubscript{ext} and NO\textsuperscript{i}, some studies may have resulted in substantial non-tropospheric photolysis, strong delay to RO\textsubscript{2} chemistry due to peroxynitrate formation, VOC reactions with NO\textsubscript{3} dominating over those with OH, and faster reactions of OH-aromatic adducts with NO\textsubscript{2} than those with O\textsubscript{3}, all of which are irrelevant to ambient VOC photooxidation chemistry. Some of the negative effects are worst for alkene and aromatic precursors. To avoid undesired chemistry, vehicle emissions generally need to be diluted by a factor of >100 before being injected into OFR. However, sufficiently diluted vehicle emissions generally do not lead to high-NO chemistry in OFR, but are rather dominated by the low-NO RO\textsubscript{2}+HO\textsubscript{2} pathway. To ensure high-NO conditions without substantial atmospherically irrelevant chemistry in a more controlled fashion, new techniques are needed.
1 Introduction

The oxidation of gases that are emitted into the atmosphere, in particular volatile organic compounds (VOCs), is one of the most important atmospheric chemistry processes (Haagen-Smit, 1952; Chameides et al., 1988). VOC oxidation is closely related to radical production and consumption (Levy II, 1971), O₃ production, and formation of secondary aerosols (Odum et al., 1996; Hoffmann et al., 1997; Volkamer et al., 2006; Hallquist et al., 2009), which have impacts on air quality and climate (Lippmann, 1991; Nel, 2005; Stocker et al., 2014).

Chemical reactors are critical tools for research of VOC oxidation. Oxidation reactions of interest often have typical timescales of hours to weeks. Studying these processes in ambient air can be confounded by dispersion and changes in ambient conditions, which often occur on similar timescales. Chemical reactors allow for decoupling of these two types of processes. Also, they should be able to simulate the different regimes of reactions occurring in the atmosphere, e.g., VOC oxidation under low and high-NO conditions (peroxy radical fate dominated by reaction with HO₂ or with NO) representing remote and urban areas, respectively (Orlando and Tyndall, 2012).

Large environmental chambers are a commonly used reactor type (Carter et al., 2005; Wang et al., 2011). They typically employ actinic wavelength (>300 nm) light sources (e.g., outdoor solar radiation and UV blacklights) to produce oxidants and radicals and have large volumes (on the order of several cubic meters or larger). However, the capability of generating sustained elevated levels of OH, the most important tropospheric oxidant, is usually limited in chambers, resulting in OH concentrations similar to those in the atmosphere (10⁶–10⁷ molecules cm⁻³; Mao et al., 2009; Ng et al., 2010), and consequently, long simulation times (typically hours) to reach OH equivalent ages of atmospheric relevance (George et al., 2007; Kang et al., 2007; Carlton et al., 2009; Seakins, 2010; Wang et al., 2011). The partitioning of gases and aerosols to chamber walls (usually made of Teflon) in timescales of tens of minutes to hours makes it difficult to conduct very long experiments that simulate high atmospherically-relevant photochemical ages (Cocker et al., 2001; Matsunaga and Ziemann, 2010; Zhang et al., 2014; Krechmer et al., 2016). In addition, the long simulation times and large size of chambers and auxiliary equipment are logistically difficult for field deployment, and their cost limits the number of laboratories equipped with them.

Given the limitations of environmental chambers, a growing number of experimenters have instead employed oxidation flow reactors (OFRs). OFRs have a much smaller size (of the order of 10 L), efficiently generate OH via photolysis of H₂O and/or O₃ by more energetic 185 and 254 nm photons from low-pressure Hg lamps, and overcome the abovementioned shortcomings of chambers due to a much shorter residence time (George et al., 2007; Kang et al., 2007, 2011; Lambe et al., 2011). Moreover, OFRs are able to rapidly explore a wide range of OH equivalent ages within a short period (~2 hr), during which significant changes of ambient conditions can usually be avoided in the case of field deployment (Ortega et al., 2016; Palm et al., 2016, 2017). Because of these advantages, OFRs have recently been widely used to study atmospheric chemistry, in particular secondary organic aerosol (SOA) formation and aging, in both the laboratory and the field (Kang et al., 2011; Li et al., 2013; Ortega et al., 2013,
In addition to experimental studies using OFRs, there has also been some progress in the characterization of OFR chemistry by modeling. Li et al. (2015) and Peng et al. (2015) developed a box model for OFR HO\textsubscript{x} chemistry that predicts measurable quantities [e.g., OH exposure [OH\textsubscript{ex}], in molecules cm\textsuperscript{-3} s\textsuperscript{-1} and O\textsubscript{3} concentration (abbr. O\textsubscript{3} hereinafter, in ppm)] in good agreement with experiments. This model has been used to characterize HO\textsubscript{x} chemistry as a function of H\textsubscript{2}O mixing ratio (abbr. H\textsubscript{2}O hereinafter, unitless), UV light intensity (abbr. UV hereinafter, in photons cm\textsuperscript{-2} s\textsuperscript{-1}), and external OH reactivity [in s\textsuperscript{-1}, OHR\textsubscript{ext}=\sum k_i c_i, i.e., the sum of the products of concentrations of externally introduced OH-consuming species (c) and rate constants of their reactions with OH (k)]. Based on this characterization, Peng et al. (2015) found that OH suppression, i.e., reduction of OH concentration caused by OHR\textsubscript{ext}, is a common feature under many typical OFR operation conditions. Peng et al. (2016) systematically examined the relative importance of non-OH/non-tropospheric reactants on the fate of VOCs over a wide range of conditions, and provided guidelines for OFR operation to avoid non-tropospheric VOC photolysis, i.e., VOC photolysis at 185 and 254 nm.

In previous OFR modeling studies, NO\textsubscript{x} chemistry was not investigated in detail, since in such in typical OFR experiments with large amounts of oxidants (e.g., OH, HO\textsubscript{2}, and O\textsubscript{3}), NO would be very rapidly oxidized and thus unable to compete with HO\textsubscript{2} for reaction with peroxy radicals (RO\textsubscript{2}). Li et al. (2015) estimated an NO (NO\textsubscript{2}) lifetime of ~0.5 (~1.5) s under a typical OFR condition. From these estimates, OFRs processing ambient air or laboratory air without large addition of NO\textsubscript{x} were assumed to be not suitable for studying oxidation mechanisms relevant to polluted conditions under higher NO\textsubscript{x} concentrations. OFRs have recently been used to conduct laboratory experiments with very high initial NO\textsubscript{x} levels (Liu et al., 2015) and deployed to an urban tunnel, where NO\textsubscript{x} was high enough to be a major OH reactant (Tkacik et al., 2014). The former study reported evidence for the incorporation of nitrogen into SOA. Besides, OFRs have been increasingly employed to process emissions of vehicles, biomass burning, and other combustion sources (Table 1), where NO can often be hundreds of ppm (Ortega et al., 2013; Martinsson et al., 2015; Karjalainen et al., 2016; Link et al., 2016; Schill et al., 2016; Alanen et al., 2017; Simonen et al., 2017). It can be expected that such a high NO input together with very high VOC concentrations would cause a substantial deviation from good OFR operation conditions identified in Peng et al. (2016). Very recently, N\textsubscript{2}O injection has been proposed by Lambe et al. (2017) as a way to study oxidation of VOCs under high NO\textsubscript{x} conditions in OFR. As more OFR studies at high NO\textsubscript{x} level are conducted, there is growing need to understand the chemistry of N-containing species in OFRs and whether it proceeds along atmospherically-relevant channels.

In this study, we present the first comprehensive model of OFR NO\textsubscript{x} chemistry. We extend the model of Li et al. (2015) and Peng et al. (2015) by including a scheme for NO\textsubscript{x} species. Then this model is used to investigate i) if an OFR with initial NO injection results in NO significantly reacting with RO\textsubscript{2} under any conditions, ii) if previously published OFR experiments with high initial NO concentrations led to RO\textsubscript{2}+NO being dominant in VOC oxidation without negative side effects (e.g., non-tropospheric reactions), iii) how to avoid undesired chemistry in future studies. The results can provide insights into...
the design and interpretation of future OH-oxidation OFR experiments with large amounts of NO2 injection.

2 Methods

The physical design of the OFR modeled in the present work, the chemical kinetics box model, and the method of propagating and analyzing the parametric uncertainties on the model have already been introduced previously (Kang et al., 2007; Li et al., 2015; Peng et al., 2015). We only provide brief descriptions for them below.

2.1 Potential Aerosol Mass flow reactor

The OFR modeled in this study is the “Potential Aerosol Mass” (PAM) flow reactor, firstly introduced by Kang et al. (2007). The PAM OFR is a cylindrical vessel with a volume of ~13 L, equipped with low-pressure Hg lamps (model no. 82-9304-03, BHK Inc.) to generate 185 and 254 nm UV light. This popular design is being used by many atmospheric chemistry research groups, particularly those studying SOA (Lambe and Jimenez, 2017 and references therein). When the lamps are mounted inside Teflon sleeves, photons at both wavelengths are transmitted and contribute to OH production (“OFR185 mode”). In OFR185, H2O photolyzed at 185 nm produces OH and HO2, while O3 photolyzed at the same wavelengths results in O3 formation. O(3P) is produced via O3 photolysis at 254 nm and generates additional OH through its reaction with H2O. 185 nm lamp emissions can be filtered by mounting the lamps inside quartz sleeves, leaving only 254 nm photons to produce OH (“OFR254 mode”). In this mode, injection of externally formed O3 is necessary to ensure OH production. As the amount of O3 injected is a key parameter under some conditions (Peng et al., 2015), we adopt the notation OFR254-X to denote OFR254 experiments with X ppm initial O3 (O3). In this study, we investigate OFR experiments with NO injected and thus utilize “OFR185-NO” to describe the OFR185 mode of operation with initially (at the reactor entrance) injected NO. The same terminology is used for the OFR254 mode. For instance, the initial NO injection into OFR254-7 is denoted as OFR254-7-NO.

2.2 Model description

The basic framework of the box model used in this study, a standard chemical kinetics model, is the same as in Peng et al. (2015). Plug flow is assumed in the model, since approximately taking residence time distribution into account leads to similar results under most conditions but at much higher computational expense (Peng et al., 2015). In addition to the reactions in the model of Peng et al. (2015), including all HOx reactions available in the JPL Chemical Kinetic Data Evaluation (Sander et al., 2011), all gas-phase NOx reactions available in the JPL database except those of organic nitrates and peroxyxinitriles are also considered in the current reaction scheme. An updated JPL evaluation was published recently (Burkholder et al., 2015), with slightly different (~20%) rate constants for NOx+HOx=M→HO2+NOy+M and NOy+NOy→N2Oy. The updated rate constants only result in changes of ~10–20% of the concentrations of the species directly consumed/produced by these reactions. These changes are smaller than the parametric uncertainties of the model (see Section 3.1.3). For other species, concentration changes are negligible. HO2NOy+M→HO2+NOy+M and N2Oy+M→NOy+NOy+M, are also included in the scheme, with kinetic parameters from the IUPAC Task Group on Atmospheric
Chemical Kinetic Data Evaluation (Ammann et al., 2016). As in Peng et al. (2015, 2016), SO2 is used as a surrogate of external OH reactants (e.g., VOCs). NOx species, although also external OH reactants, are explicitly treated in the model and not counted in OHRext in this work. Therefore, OHRext stands for non-NOx OHRext only hereinafter, unless otherwise stated.

Also, particle-phase chemistry and physical and chemical interactions of gas-phase species with particles are not considered in this study. We have made this assumption because:

1. The presence of aerosols has typically negligible impacts on the gas-phase chemistry of radicals, NOx/NOy, and OH reactants studied here. Condensational sink (CS) of ambient aerosols can rarely exceed 1 s\(^{-1}\) even in polluted areas and is usually 1-3 orders of magnitude lower (Donahue et al., 2016; Palm et al., 2016). Thus, even under the assumption of unity uptake coefficient, CS cannot compete with OHRext (usually on the order of 10 s\(^{-1}\) or higher) in OH loss.

2. Uptake of NO onto aerosols only occurs through the reaction with ROx on particle surface (Richards-Henderson et al., 2015), which is formed very slowly (see below) compared to gas-phase HOx and NOx chemistry. Uptake of HOy, Oy, NOy etc. is even more unlikely to be of importance due to lower uptake coefficients (Moise and Rudich, 2002; Moise et al., 2002; Hearn and Smith, 2004; Lakey et al., 2015). Combustion exhausts can have high aerosol loadings with condensational sinks on the order of 10\(^{-3}\)-10\(^{-1}\) s\(^{-1}\) (Matti Maricq, 2007). Even if these exhausts are directly injected into the reactor without any pre-treatment, uptake onto the particles still cannot play a major role in the fate of gas-phase radical and NOx species, since VOCs and NOx in raw exhausts, which are proportionally orders-of-magnitude higher, still dominate the fate of oxidants. Dilution of combustion emissions simultaneously lowers condensational sinks and the sinks of oxidants due to chemical reactions, with their relative importance remaining the same as in undiluted emissions.

3. Gas-phase radical and NOx/NOy species only has limited impacts on OA chemistry in this study. Heterogeneous oxidation of OA by OH is generally slow. Significant OA loss due to heterogeneous oxidation can only be seen at photochemical ages as high as weeks (Hu et al., 2016). The enhancement of heterogeneous oxidation due to NO is remarkable only at OH concentration close to the ambient values but not at typical values in OFR (Richards-Henderson et al., 2015).

It is well known that the aerosol concentration can have a major impact on the physical uptake of semivolatile and low-volatility gas-phase species. However this process is not explicitly modeled in this study.

As OHRext plays a major and even dominant role in OH loss, it is an important approximation that the real OHRext decay (due to not only primary VOC oxidation and subsequent oxidation of higher generation products, but also wall loss, partitioning to the particle phase, reactive uptake etc.) is surrogated by that of SO2 (see Fig. S2 of Peng et al. 2015). Gas-phase measurements in literature laboratory studies revealed that there is a large variability of the evolution of total OHRext during oxidation of primary VOCs and subsequent oxidation of their intermediate products, depending on the...
type of precursors (Nehr et al., 2014; Schwantes et al., 2017). This variability is obviously mainly due to
the formation of different types and amounts of oxidation intermediates/products contributing to
OHR_{exp}. This variation is highly complex due to the large number of possible oxidation intermediates and
the limited knowledge of detailed higher-generation mechanisms, and thus is difficult to accurately
capture even if modeling with a mechanism as explicit as Master Chemical Mechanism is performed
(Schwantes et al., 2017). Therefore, it is justified to use a lumped surrogate to model the OHR_{exp} decay
for simplicity and efficiency. This approximation is a major contributor to uncertainty of our model. The
uncertainties due to both the types of oxidation intermediates/products,

A residence time of 180 s and typical temperature (295 K) and atmospheric pressure (835 mbar)
in Boulder, CO, USA are assumed for all model cases. The lower-than-sea level pressure only leads to
minor differences in the outputs (Li et al., 2015). We explore physical input cases evenly spaced in a
logarithmic scale over very wide ranges: H_2O of 0.07%–2.3%, i.e., relative humidity (RH) of 2–71% at
295 K; 185 nm UV of 1.0x10^{13}–1.0x10^{14} and 254 nm UV of 4.2x10^{13}–8.5x10^{13} photons cm^{-2} s^{-1}; OHR_{exp} of
1–16000 s^{-1}; O_{2,exp} of 2.2–70 ppm for OFR254; initial NO mixing ratio (NO') from 10 ppt to 40 ppm.
Besides, conditions with OHR_{exp}=0 are also explored. UV at 254 nm is estimated from that at 185 nm
according to the relationship determined by Li et al. (2015). Several typical cases within this range as
well as their corresponding 4 or 2-character labels (e.g., MM0V and HL) are defined in Table 2. Literature
studies are modeled by adopting all reported parameters (e.g., residence time, H_2O, and O_{2,exp}) and
estimating any others that may be needed (e.g., UV) from the information provided in the papers.

In this study, OH equivalent ages are calculated under the assumption of an ambient OH
concentration of 1.5x10^9 molecules cm^{-3} (Mao et al., 2009). Conditions leading to a ratio of RO_{2} reacted
with NO over the entire residence time [r(RO_{2}+NO)] to that with HO_{2} [r(RO_{2}+HO_{2})] larger than 1 are
regarded as ”high NO” (under the assumption of constant OHR_{exp} from VOCs, see Section S1 for more
details), where [r(X)] is the total reactive flux for reaction X over the entire residence time. F185_{exp}/OH_{exp}
and F254_{exp}/OH_{exp} are used as measures of the relative importance of VOC photolysis at 185 and 254
nm to their reactions with OH, respectively [F185_{exp} (F254_{exp}) are 185 (254) nm photon flux exposure,
i.e., product of 185 (254) nm photon flux and time]. Readers may refer to Figs. 1 and 2 of Peng et al.
(2016) for the determination of the relative importance of non-tropospheric (185 and 254 nm) 
photolysis of individual VOCs. Although the relative importance of non-tropospheric photolysis depends
on individual VOCs, in the present work, we set criteria on F185_{exp}/OH_{exp}>3x10^5 cm/s and
F254_{exp}/OH_{exp}>4x10^5 cm/s to define “good” conditions and F185_{exp}/OH_{exp}<1x10^5 cm/s and
F254_{exp}/OH_{exp}<1x10^5 cm/s (excluding good conditions) to define “risky” conditions. Conditions with
higher F185_{exp}/OH_{exp} or F254_{exp}/OH_{exp} are defined as “bad”. Under good conditions, photolysis of most
VOCs has a relative contribution <20% to their fate; under bad conditions, non-tropospheric photolysis
is likely to be significant in all OFR experiments, since it can hardly be avoided for oxidation
intermediates, even if the precursor(s) does not photolyze at all. Under risky conditions, some species
photolysing slowly and/or reacting with OH rapidly (e.g., alkanes, aldehydes, and most biogenics) still
have a relative contribution of photolysis <20% to their fates, while species photolyzing more rapidly
and/or reacting with OH more slowly (e.g., aromatics and other highly conjugated species and some saturated carbonyls) will undergo substantial non-tropospheric photolysis. Note that these definitions are slightly different than in Peng et al. (2016). All definitions of the types of conditions are summarized in Table 3.

2.3 Uncertainty analysis

We apply the same method as in Peng et al. (2014, 2015) to calculate and analyze the output uncertainties due to uncertain kinetic parameters in the model. Random samples following log-normal distributions are generated for all rate constants and photoabsorption cross sections in the model using uncertainty data available in the JPL database (Sander et al., 2011) or estimated based on IUPAC data (Ammann et al., 2016). Then, Monte Carlo Uncertainty Propagation (BIPM et al., 2008) is performed for these samples through the model to obtain the distributions of outputs. Finally, we compute squared correlation coefficients between corresponding input and output samples and apportion the relative contributions of individual kinetic parameters to the output uncertainties based on these coefficients (Saltelli et al., 2005).

3 Results and discussion

In this section, we study the NOy chemistry in OFR while considering relevant experimental issues. Based on these results, we propose some guidelines for OFR operation for high-NO OH oxidation of VOCs.

3.1 NOy chemistry in typical OFR cases with initial NO injection

NO was thought to be unimportant (i.e., unable to significantly react with RO2) in OFRs with initial NO injection (OFR-iNO) based on the argument that its lifetime is too short due to large amounts of O3, OH, and HO2 to compete with RO2+HO2 (Li et al., 2015). We evaluate this issue below by calculating NO effective lifetime ($\tau_{NO}$, in s), defined as NO exposure ($NO_{exp}$, in molecules cm$^{-3}$ s) divided by initial NO concentration, under various conditions. This definition cannot effectively capture the true NO average lifetime if it is close to or longer than the residence time. In this case, $\tau_{NO}$ close to the residence time will be obtained, which is still long enough for our characterization purposes.

3.1.1 OFR185-iNO

In OFR185-iNO, NO is not oxidized extremely quickly under all conditions. For instance, under a typical condition in the midrange of the phase space shown in Fig. 1a, $\tau_{NO}$ $\sim$13 s. This lifetime is much shorter than the residence time, but long enough for OH$_{exp}$ to reach $\sim$3x10$^{12}$ molecules cm$^{-3}$ s, which is equivalent to an OH equivalent age of $\sim$6 hrs. Such an OH equivalent age is already sufficient to allow some VOC processing and even SOA formation to occur (Lambe et al., 2011; Ortega et al., 2016). Within $\tau_{NO}$, NO suppresses HO2 through the reaction NO+HO2 $\rightarrow$ NO2+OH, leading to NO$_{exp}$/HO2$_{exp}$ of $\sim$700 during this period, high enough for RO2 to dominantly react with NO. Meanwhile, NO+HO2 $\rightarrow$ NO2+OH enhances OH production, which helps OH$_{exp}$ build up in a relatively short period. In addition, non-tropospheric photolysis of VOCs at 185 and 254 nm is minor ($F_{185\text{exp}}$/OH$_{exp}$ $\sim$ 600 cm/s, Fig. 1a), because of enhanced OH production and moderate UV. Therefore, such an OFR condition may be of some interest for high-NO VOC oxidation. We thus analyze the NOy chemistry in OFR185-iNO in more detail below, by taking
the case shown in Fig. 1a as a representative example.

In OFR185-iNO, NO \textsubscript{x} concentrations are orders-of-magnitude higher than in the atmosphere while the amount of O\textsubscript{3} produced is relatively small during the first several seconds after the flow enters the reactor. As a result, NO is not oxidized almost exclusively by O\textsubscript{3} as in the troposphere, but also by OH and HO\textsubscript{2} to form HONO and NO\textsubscript{2}, respectively (Fig. 1a). The large concentration of OH present then oxidizes HONO to NO\textsubscript{2}, and NO\textsubscript{2} to HNO\textsubscript{2}. Photolysis only plays a negligible role in the fate of HONO and NO\textsubscript{2} in OFRs, in contrast to the troposphere, where it is the main fate of these species. This is because the reactions of HONO and NO\textsubscript{2} with OH are greatly accelerated in OFR compared to those in the troposphere, while photolysis not (Peng et al., 2016). The interconversion between NO\textsubscript{2} and HO\textsubscript{2}NO\textsubscript{2} is also greatly accelerated (Fig. 1a), since a large amount of HO\textsubscript{2} promotes the formation of HO\textsubscript{2}NO\textsubscript{2}

whose thermal decomposition and reaction with OH in turn enhance the recycling of NO\textsubscript{2}. Though not explicitly modeled in this study, RO\textsubscript{2} are expected to undergo similar reactions with NO\textsubscript{2} to form reservoir species, i.e., peroxy-nitrates (Orlando and Tyndall, 2012). Peroxynitrates that decompose on timescales considerably longer than OFR residence times may serve as effectively permanent NO\textsubscript{y} sinks in OFRs (see Section 3.4.1).

Interestingly but not surprisingly, the NO\textsubscript{y} chemistry shown in Fig. 1a is far from temporally uniform during the OFR residence time (Fig. S1a). Within \(\tau\)\textsubscript{NO}, NO undergoes an e-fold decay as it is rapidly converted into NO\textsubscript{2} and HONO, whose concentrations reach maxima around that time. After most NO is consumed, HONO and NO\textsubscript{2} also start to decrease, but significantly more slowly than NO, since they do not have as many and efficient loss pathways as NO. The reaction of OH with HONO, the dominant fate of HONO, is slower than that with NO (Fig. 1a). The net rate of the NO\textsubscript{2}-to-HO\textsubscript{2}NO\textsubscript{2} conversion becomes low because of the relatively fast reverse reaction (Fig. 1a). Besides, the total loss of NO\textsubscript{2} is partially offset by the production from HONO. The generally stable concentrations of HONO and NO\textsubscript{2} (Fig. S1a) result in their respective reaction rates with OH that are comparable during and after \(\tau\)\textsubscript{NO} (Fig. 1a), as OH variation is also relatively small during the entire residence time (Fig. S1b). However, the NO\textsubscript{2}-to-HO\textsubscript{2}NO\textsubscript{2} conversion after \(\tau\)\textsubscript{NO} is much faster than during it (Fig. 1a), resulting from substantially decreased NO and HO\textsubscript{2} concomitantly increasing \(\sim1\) order of magnitude after \(\tau\)\textsubscript{NO} (Fig. S1a,b). HNO\textsubscript{3} and HO\textsubscript{2}NO\textsubscript{2} which are substantially produced only after NO\textsubscript{2} is built up, have much higher concentrations later than within \(\tau\)\textsubscript{NO}.

Under other OFR185-iNO conditions than in Fig. 1a, the major reactions interconverting NO\textsubscript{y} species are generally the same, although their relative importance may vary. At lower NO\textsubscript{y}, the perturbation of HO\textsubscript{x} chemistry caused by NO\textsubscript{y} species is smaller. Effects of NO\textsubscript{y} less than 1 ppb (e.g., typical non-urban ambient concentrations) are generally negligible regarding HO\textsubscript{x} chemistry. Regarding NO\textsubscript{y} species, the pathways in Fig. 1a are still important under those conditions. At higher NO\textsubscript{y} (e.g., >1 ppm), one might expect NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} to play a role (as in OFR254-iNO; see Section 3.1.2 below), since high NO\textsubscript{y} concentrations might enhance self/cross reactions of NO\textsubscript{y}. However, this would not occur unless OH production is high, since relatively low O\textsubscript{3} concentrations in OFR185-iNO cannot oxidize NO\textsubscript{2} to NO\textsubscript{3} rapidly. Also, a large amount of NO\textsubscript{y} can lead to significant OH suppression. That would in turn
slow down the NO₂ production from HNO₂ by OH. This is especially true when an OFR is used to oxidize
the output of highly concentrated sources (e.g., from vehicle exhausts). When sources corresponding
to OHRₓₓ of thousands of s⁻¹ and NO₁₀ of tens of ppm are injected into OFR185 (Fig. 1b), they essentially
inhibit active chemistry except NO consumption, as all subsequent products are much less abundant
compared to remaining NO (Fig. 51c).

3.1.2 OFR254-INO

The ppm-level O₁ₓₓ used in the OFR254-INO mode of operation has a strong impact on its NOₓ chemistry. An O₁ₓₓ of 2.2 ppm (lowest in this study) is already enough to shorten τₑₓₓ to ~1 s, preventing
NO from playing a role in the chemistry under most explored conditions. The reaction fluxes under a
typical O₁ₓₓ of 7 ppm are shown in Fig. 1c. A reactive flux from NO+O₂→NO₂ makes the reaction of NO
with other oxidants (OH, HO₂, etc.) negligible. The HNO₂ production pathway from NO₂ is similar to that
in OFR185-INO. The interconversion between NO₂ and HO₂NO₂ is also fast over the residence time, and
even faster than in OFR185-INO during τₑₓₓ, since a high concentration of O₂ also controls the OH-HO₂
interconversion and makes HO₂ more resilient against suppression due to high NO (Fig. S1f; Peng et al.,
2015). A major difference in the NOₓ chemistry in OFR254-INO (Fig. 1c) compared to OFR185-INO (Fig.
1a) is significant NO₂/N₂O₅ chemistry due to high O₂ in OFR254-INO, which accelerates the oxidation of
NO₂ to NOₓ. Interconversion between NOₓ+NO and N₂O₅ also occurs to a significant extent because of
high NO₂. Under the conditions of Fig. 1c, NOₓ can also be significantly consumed by HO₂. Unlike
OFR185-INO, OFR254-INO can substantially form NOₓ from HNO₂ under conditions that are not on the
extremes of the explored physical condition space, e.g., at higher UV and lower NO₁₀ (e.g., Fig. S2). In
the case of very high NO₁₀ (equal to or higher than O₂), all O₂ can be rapidly destroyed by NO. As a
consequence, OH production is shut down and these cases are of little practical interest (Fig. S3h).

3.1.3 Uncertainty analysis

The results of uncertainty propagation confirm that the output uncertainties due to uncertain
kinetic parameters are relatively low compared to other factors (e.g., non-plug flow in OFR; Peng et al.,
2015) and the overall model accuracy compared to experimental data (a factor of 2–3; Li et al., 2015).
For OFR185-INO, NO, NOₓ, and OH exposures have relative uncertainties of ~0–20%, ~40–70%, and ~15–
40%, respectively. The uncertainties in OH exposure are very similar to those in the cases without NOₓ
(Peng et al., 2015). The contribution of NOₓ reactions to OHₓₓ uncertainty is negligible, except for some
contribution of OH+NO→HONO in a few cases with high NO₁₀ (Fig. 2). The uncertainties on NOₓₓ are
dominated by the reactions producing HO₂ and Oₓₓ, i.e., the major consumers of NO. For NOₓ exposure,
a few major production and loss pathways (e.g., NOₓ+NO→N₂Oₓ, N₂Oₓ→NOₓ+NO, and
HOₓₓ+NO→OH+NOₓ+O₂) dominate its uncertainties. OFR254-INO has a simpler picture of parametric
uncertainties in terms of composition. O₂ controls the NO oxidation under most conditions and this
reaction contributes most of output uncertainties for NO exposures. HOₓₓ+NO→OH+NOₓ+O₂ dominates
the uncertainty on NOₓ exposure. The levels of those uncertainties are lower than in OFR185-INO (~2%)
for NO exposure; <60% in all cases and <25% in most cases for NOₓ exposure). Thus, model uncertainties
in OFR254-INO are not shown in detail.
Different conditions types

Having illustrated the main NO\textsubscript{x} chemical pathways for typical cases, we present the results of the exploration of the entire physical parameter space (see Section 2.2). Note that the explored space is indeed very large and gridded logarithmically uniformly in every dimension. Therefore, the statistics of the exploration results can be useful to determine the relative importance of the conditions types defined in Section 2.2 and Table 3.

It has been shown that during $\tau_{\text{NO}}$, RO\textsubscript{2} can react dominantly with NO (Section 3.1.1), while to determine if a condition is high-NO (see Table 3), the entire residence time is considered. This is done because for VOC oxidation systems of interest, there will be significant oxidation of the initial VOC and its products under low-NO conditions, if $\tau_{\text{NO}}$ is shorter than the reactor residence time. After most NO is consumed, the longer the remaining residence time, the more RO\textsubscript{2} will react with HO\textsubscript{2} and the more likely that an input condition is classified as low-NO. For a condition to be high-NO, a significantly long $\tau_{\text{NO}}$ is required.

Figure 3 shows the fractional occurrence distribution of good/risky/bad conditions in the entire explored condition space over logarithm of $r(\text{RO}_2+\text{NO})/r(\text{RO}_2+\text{HO}_2)$, which distinguishes high- and low-NO conditions. In OFR254-iNO, $\tau_{\text{NO}}$ is so short that no good high-NO condition is found in the explored range in this study (Fig. 3a). A fraction of explored conditions are bad high-NO. These conditions result from a full consumption of O\textsubscript{3} by NO. Then very little HO\textsubscript{2} is produced (right panels in Fig. S3h), but the fate of any RO\textsubscript{2} formed is dominated by RO\textsubscript{2}+NO (right panels in Fig. S3i). However, also due to negligibly low OH concentration, little RO\textsubscript{2} is produced and non-tropospheric photolysis of VOCs is also substantial compared to their reaction with OH under these conditions, classifying all of them as “bad” (Fig. 3a).

In OFR185-iNO, in addition to the typical case shown in Fig. 1a, many other cases have a $\tau_{\text{NO}}$ of ~10 s or longer (Figs. S3b and S4), which allow the possibility of high-NO conditions. Indeed, ~1/3 of explored conditions in OFR185-iNO with a residence time of 3 min are high-NO (Fig. 3b). Most of these high-NO conditions are also classified as bad, similar with those in OFR254-iNO. More importantly, in contrast to OFR254-iNO, good and risky high-NO conditions also comprise an appreciable fraction of the OFR185-iNO conditions. It is easily expected that very high OHR\textsubscript{ext} and NO\textsubscript{in} lead to bad high-NO conditions (all panels in Fig. 4), since they strongly suppress HO\textsubscript{2}, which yields bad conditions and in turn keep NO destruction relatively low. Besides, the occurrence of bad high-NO conditions is reduced at high UV (bottom panels in Fig. 4), which can be explained by lowered NO due to high O\textsubscript{3} production and fast OH reactant loss due to high OH production. Good high-NO conditions are rare in the explored space. They are only 1.1% of total explored conditions (Fig. 3b) and present under very specific conditions, i.e., higher H\textsubscript{2}O, lower UV, lower OHR\textsubscript{ext}, and NO\textsubscript{in} of tens to hundreds of ppb (Figs. 4 and 5). Since a very high NO can suppress OH, to obtain both a significant NO level and a good conditions, NO\textsubscript{in} can only be tens to hundreds of ppb. As NO\textsubscript{in} is lower and OH is higher than under bad high-NO conditions, UV should be lower than bad high-NO conditions to keep a sufficiently long presence of NO.

Thus, UV at 185 nm for good high-NO conditions are generally lower than $10^{15}$ photons cm\textsuperscript{-2} s\textsuperscript{-1} (Fig. 5). In addition, a low OHR\textsubscript{ext} (generally <50 s\textsuperscript{-1}) and a higher H\textsubscript{2}O (the higher the better, although there is...
no apparent threshold) are also required for good high-NO conditions (Fig. S5), as Peng et al. (2016) pointed out. Risky high-NO conditions often occur between good and bad high-NO conditions, e.g., at lower NO\textsubscript{y} than bad conditions (e.g., Cases ML, MM, HL, and HM in Fig. 4, see Table 2 for the typical case label code), at higher OH\textsubscript{tot} and/or NO\textsubscript{y} than good conditions (e.g., Cases ML and MM), and at lower H\textsubscript{2}O than good conditions (e.g., Case LL).

The trend of the distributions of good, risky, and bad low-NO conditions is generally in line with the analysis in Peng et al. (2016). For low-NO conditions, NO\textsubscript{y} species can be simply regarded as external OH reactants, as in Peng et al. (2016). As H\textsubscript{2}O decreases and/or OHR\textsubscript{ext} or NO\textsubscript{y} increases, a low-NO condition becomes worse (good→risky→bad) (Figs. 4 and 5). In OFR185-iNO, increasing UV generally makes a low-NO condition better because of an OH production enhancement (Fig. 4); while in OFR254-iNO, increasing UV generally makes a low-NO condition worse (Fig. 5), since at a higher UV, more O\textsubscript{3} is destroyed and the resilience of OH to suppression is reduced.

As discussed above, the fraction of high-NO conditions also depends on OFR residence time. A shorter residence time is expected to generally lead to a larger fraction of high-NO conditions, since the time spent in the reaction for \( t > \tau \) is significantly smaller. Thus, we also investigate an OFR185-iNO case with a residence time of 30 s. In Fig. 3b, compared to the case with a residence time of 3 min, the distributions of all condition types (good/risky/bad) of the 30 s residence time case shift toward higher \( \frac{r(RO_2+NO)}{r(RO_2+HO_2)} \). Nevertheless, shortening the residence time also removes the period when the condition is better (i.e., less non-tropospheric photolysis), when external OH reactants have been partially consumed and OH suppression due to OH\textsubscript{tot} has been reduced later in the residence time. As a result, the fractions of good and risky conditions decrease (Fig. 3b). With the two effects (higher \( \frac{r(RO_2+NO)}{r(RO_2+HO_2)} \) and more significant non-tropospheric photolysis) combined, the fraction of good high-NO conditions increases by a factor of \(<3\). An even shorter residence time does not result in a larger good high-NO fraction, since the effect of enhancing non-tropospheric photolysis is even more apparent.

3.3 Effect of non-plug flow

We performed model runs where the only change with respect to our box model introduced in Section 2.2 is that the plug-flow assumption is replaced by the residence time distribution (RTD) measured by Lambe et al. (2011) (also see Fig. S8 of Peng et al. (2015)). The chemistry of different air parcels with different residence times is simulated by our box model and outputs are averaged over the RTD. Lateral diffusion between different air parcels is neglected in these simulations.

\( \text{OH}_{\text{exp}} \) calculated from the mode with RTD (\( \text{OH}_{\text{exp,RTD}} \)) is higher than that calculated from the plug-flow model (\( \text{OH}_{\text{exp,PF}} \)) in both OFR185-iNO and OFR254-iNO (Table 4 and Fig. S6). Under most explored conditions deviations are relatively small, which leads to an overall positive deviation of \( \text{OH}_{\text{exp,RTD}} \) from \( \text{OH}_{\text{exp,PF}} \) by \(<2\) (within the uncertainties of the model and its application to real experimental systems).

For OFR185-iNO, most conditions (~90%) in the explored space lead to \(<3\) differences between \( \text{OH}_{\text{exp,PF}} \) and \( \text{OH}_{\text{exp,RTD}} \), while for a small fraction of cases the differences can be larger (Fig. S6). The larger deviations are mainly present at high UV, OH\textsubscript{tot}, and NO\textsubscript{y}, where conditions are generally “bad” and in...
which experiments are of little atmospheric relevance. Under these specific conditions, external OH reactants and NO can be substantially destroyed for the air parcels with residence times longer than the average, while this is not the case for the average residence time. This feature was already described by Peng et al. (2015) (see Fig. S10 of that study). Although only non-NO external OH reactants were considered in that study, the results are the same. In the present study, a higher upper limit of the explored OHR range (compared to Peng et al., 2015, due to trying to simulate extremely high OHR used in some recent literature studies) large amounts of NO and cause somewhat larger deviations. In OFR254-INO, OH is less suppressed at high OHR and NO than in OFR185-INO because of high O (Peng et al., 2015). OH, deviations from OH are also smaller (Table 4).

Based on the outputs of the model with RTD, similar mapping of the physical input space as Figs. 4 and 5 can be done (Figs. S7 and S8). Overall, the mapping of the RTD model results is very similar with that of the plug-flow model. The conditions appear to be only slightly better in a few places of the explored space than those from the plug-flow model, which can be easily explained by the discussions above. Besides, the mapping in Figs. S7 and S8 also appear to be slightly more low-NO, for the same reasons discussed above. After NO is destroyed at long residence times, HO, suppressed by NO, also recovers as OH. r(RO2+NO)/r(RO2+HO2) is obviously expected to be smaller than in the plug-flow model in general.

Note that most conditions that appear to be better in the RTD model results are already identified as bad by the plug-flow model. Those conditions look slightly better only because of their better RTD-averaged F185/ and F254/ deviations. However, each of those cases is actually composed of both a better part at longer residence times and also a worse part at shorter residence times. Under those conditions, the reactor simultaneously works in two distinct regimes, one of which is bad due to heavy OH suppression. Such conditions are obviously not desirable for OFR operation.

3.4 Possible issues related to high-NOx levels

In the discussion above, we focused on obtaining high-NO conditions and considered only one experimental issue (non-tropospheric photolysis) that had been previously investigated in Peng et al. (2016) and is not specific for experiments with high NO injection. We discuss additional potential reasons why the OFR-INO chemistry can deviate strongly from tropospheric conditions, as specifically related to high-NO level in this subsection.

3.4.1 NOx

NOx reacts with RO2 to form peroxynitrates, generally regarded as reservoir species in the atmosphere as most of them thermally decompose very quickly compared to atmospheric time scales. However, in OFRs, with residence times on the order of minutes, some peroxynitrates may no longer be considered as fast decomposing. This is especially true for acylperoxy nitrates, whose lifetimes can be hours at room temperature (Orlando and Tyndall, 2012). Acrlyperoxy nitrates are essentially sinks instead of reservoirs in OFRs for both NOx and RO2. RO2 is estimated to be as high as several ppb in OFRs by our model (e.g., ~6 ppb RO2 in OFR185 at H2O=1%, UV at 185 nm=1x10^13 photons cm^-2 s^-1, OHRext=1000 s^-1, and NO^=0), while high-NO experiments can yield far higher NO2. If all RO2 were acylperoxy, the RO2
chemistry could be rapidly shut down by NO\textsubscript{2}, as rate constants of these RO\textsubscript{2} + NO\textsubscript{2} reactions are around \(10^{12}\) cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} (Orlando and Tyndall, 2012). Nevertheless, acyloperoxy nitrates are not expected to typically be the dominant component of peroxy nitrates, since acyl radicals are not a direct oxidation product of most common VOCs and can only be formed after several steps of oxidation (Atkinson and Arey, 2003; Ziemann and Atkinson, 2012). Most acyloperoxy nitrates retain their short-lived reservoir characteristics in OFRs due to their relatively short thermal decomposition time scales (on the order of 0.1 s; Orlando and Tyndall, 2012). Even so, OFR experiments can be seriously hampered at extremely high NO\textsubscript{2}. If NO\textsubscript{2} reaches ppm levels, the equilibrium between RO\textsubscript{2}+NO\textsubscript{2} and acyloperoxy nitrate \((\text{RO}_{2}\text{+NO}_{2} \leftrightarrow \text{RO}_2\text{NO}_{2})\) is greatly shifted toward the acyloperoxy nitrate side, as the forward and reverse rate constants are on the order of \(10^{12}\) cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} and 1 s\textsuperscript{-1}, respectively (Orlando and Tyndall, 2012). This results in a substantial decrease in effective RO\textsubscript{2} concentration, or in other words, a substantial slow-down of RO\textsubscript{2} chemistry.

Parts per million levels of NO\textsubscript{2} may impose an additional experimental artifact in the oxidation chemistry of aromatic precursors. OH-aromatic adducts, i.e., the immediate products of aromatic oxidation by OH, undergo addition of O\textsubscript{2} and NO\textsubscript{2} at comparable rates under ppm levels of NO\textsubscript{2} (rate constants of the additions of O\textsubscript{2} and NO\textsubscript{2} are on the order of \(10^{16}\) and \(10^{11}\) molecules cm\textsuperscript{-3} s\textsuperscript{-1}, respectively; Atkinson and Arey, 2003). However, only the former addition is atmospherically relevant (Calvert et al., 2002). Liu et al. (2015) performed OFR254-INO experiments with toluene over a range of NO\textsubscript{2} of 2.5–10 ppm, encompassing the NO concentration range at which the reactions of OH-toluene adduct with O\textsubscript{2} and with NO\textsubscript{2} are of equal importance (~5 ppm; Atkinson and Arey, 2003). This suggests that nitroaromatics, whose formation was reported in the study of Liu et al. (2015), might have been formed in substantial amounts in that study through the addition of NO\textsubscript{2} to the OH-toluene adduct.

### 3.4.2 NO\textsubscript{3}

As discussed in Section 3.1, NO\textsubscript{3} can be formed in significant amounts in OFRs with high NO injection. Although NO\textsubscript{3} is also present in the atmosphere, especially during nighttime, significant VOC oxidation by both OH and NO\textsubscript{3} results in more complex chemistry that may complicate the interpretation of experimental results. NO\textsubscript{3} oxidation-only OFR has been previously realized experimentally via thermal dissociation of injected N\textsubscript{2}O\textsubscript{5} (Palm et al., 2017). We discuss below how to avoid significant VOC oxidation by NO\textsubscript{3} and achieve OH-dominated VOC oxidation in OFRs with high NO injection.

If NO\textsubscript{3exp}/OH\textsubscript{exp} > 0.1, NO\textsubscript{3} can be a competitive reactant for biogenic alkenes and dihydrofurans, which have a C=C bond for NO\textsubscript{3} addition, and phenols, which have activated hydroxyl for fast hydrogen abstraction by NO\textsubscript{3} (Atkinson and Arey, 2003), while for lower NO\textsubscript{3exp}/OH\textsubscript{exp}, OH is expected to dominate the oxidation of all VOCs, as shown in Fig. 6. Oxidation for VOCs without alkene C=C bonds and phenol hydroxyl (such as alkanes and (alkyl)benzenes) is dominated by OH unless NO\textsubscript{3exp}/OH\textsubscript{exp} > 1000. Despite its double bond, ethene reacts as slowly with NO\textsubscript{3} as alkanes, likely due to lack of alkyl groups enriching electron density on the C=C bond, which slows NO\textsubscript{3} addition. We calculate NO\textsubscript{3exp}/OH\textsubscript{exp} for OFR185-INO and OFR254-INO and plot histograms of this ratio in Fig. 6. Many experimental conditions lead to
high enough NO\textsubscript{react}/OH\textsubscript{react} that NO\textsubscript{3} is a competitive sink for alkenes, while only under very extreme conditions can NO\textsubscript{3} be a competitive sink for species without C-C bonds. High-NO conditions in OFR\textsubscript{185-INO} have lower NO\textsubscript{react}/OH\textsubscript{react} (~10\textsuperscript{-3}–10\textsuperscript{-4}) than in OFR\textsubscript{254-INO} (~10\textsuperscript{-4}–10\textsuperscript{-5}) (Figs. 6 and S3d,g,j). This difference in NO\textsubscript{react}/OH\textsubscript{react} is due to the different levels of O\textsubscript{3} in the two modes, as high O\textsubscript{3} promotes NO\textsubscript{2}-to-NO\textsubscript{3} oxidation. Note that low-NO conditions in both OFR\textsubscript{185-INO} and OFR\textsubscript{254-INO} can also reach high NO\textsubscript{react}/OH\textsubscript{react} as some high-NO conditions have. This is because in OFR\textsubscript{185-INO} a large part of NO\textsubscript{3} is formed by OH oxidation, resulting in NO\textsubscript{react}/OH\textsubscript{react} being largely influenced by NO\textsuperscript{3} but not by other factors mainly governing OH (Fig. S3d); and under low-NO conditions in OFR\textsubscript{254-INO}, NO\textsubscript{3} can form rapidly from NO\textsubscript{2}+O\textsubscript{3}, while OH can be heavily suppressed by high OHR\textsubscript{react} (Fig. S3g,j).

Most of the species shown in Fig. 6 are primary VOCs, except phenols and a dihydrofuran, which can be intermediates of the atmospheric oxidation of (alkyl)benzenes (Atkinson and Arey, 2003) and long-chain alkanes (Aimanant and Ziemann, 2013; Strollo and Ziemann, 2013; Ranney and Ziemann, 2016), respectively. Nevertheless, only the phenol production may occur in high-NO OFR\textsubscript{s}, as the particle-phase reaction in the photochemical formation of dihydrofurans from alkanes is too slow compared to typical OFR residence times (Ranney and Ziemann, 2016). Therefore, the impact of NO\textsubscript{3} oxidation on VOC fate needs to be considered only if the OFR input flow contains high NO mixed with biogenics and/or aromatics [(alkyl)benzenes and/or phenols]. However, (alkyl)benzenes were likely to be major SOA precursors in, to our knowledge, the only few literature OFR studies with high NO levels (Ortega et al., 2013; Tkacik et al., 2014; Liu et al., 2015). In the study of the air in a traffic tunnel (OFR\textsubscript{185-INO mode; Tkacik et al., 2014}), where toluene is usually a major anthropogenic SOA precursor as in other urban environments (Dzepina et al., 2009; Borbon et al., 2013; Hayes et al., 2015; Jathar et al., 2015), NO\textsubscript{3} was several hundreds of ppb. This resulted in an estimated NO\textsubscript{react}/OH\textsubscript{react} range of 0.1–1, where up to ~30% of cresols (intermediates of toluene oxidation) may have been consumed by NO\textsubscript{3}.

Dihydrofurans may also have formed in the tunnel air (but outside the OFR) in the presence of NO\textsubscript{3} (Aimanant and Ziemann, 2013; Strollo and Ziemann, 2013) and, after entering the OFR, they would have been substantially (up to ~50%) consumed by NO\textsubscript{3} in the laboratory experiment of Liu et al. (2015) with toluene, the injection of as much as 10 ppm NO elevated NO\textsubscript{react}/OH\textsubscript{react} to ~100, where cresols from toluene oxidation reacted almost exclusively with NO\textsubscript{3} in addition to being photolysed.

### 3.4.3 A case study

We use a case study of an OFR\textsubscript{254-13-INO} laboratory experiment with a large amount of toluene (5 ppm) and NO\textsuperscript{3} (10 ppm) to illustrate how very high VOC and NO concentrations cause multiple types of atmospherically irrelevant reactions in OFR. Due to very high OHR\textsubscript{react} and NO\textsuperscript{3} photolysis of toluene at 254 nm may have been important (Peng et al., 2016). In case of a high (close to 1) quantum yield, up to ~80% of the consumed toluene in their experiments could have been photolysed (Scheme 1). Of the rest of reacted toluene, ~10% undergoes H-abstraction by OH from the methyl group in the model, leading to an RO\textsubscript{2} similar to alkyl RO\textsubscript{2} and likely proceeding with normal RO\textsubscript{2} chemistry. ~90% of the toluene formed an OH-adduct (Calvert et al., 2002). As discussed above, 70% of this adduct (depending on NO\textsuperscript{3}) is predicted to recombine with NO\textsubscript{3} producing nitroaromatics because of the ppm-level NO\textsubscript{3}. 


The adduct could also react with O\textsubscript{3} via two types of pathways, of which one was addition forming a special category of RO\textsubscript{2} (OH-toluene-\textsubscript{2}) adducts potentially undergoing ring-opening (Atkinson and Arey, 2003; Orlando and Tyndall, 2012; Ziemann and Atkinson, 2012), the other H-elimination by O\textsubscript{3} producing cresols. Again, like toluene, cresols may have been substantially photolyzed. As a result of NO<sub>1exp</sub>/OH<sub>exp</sub> ≈100, only a minor portion of cresol could have undergone OH addition and then H-elimination again. This pathway leads to the formation of methylhydroxybenzenes and other OH-oxidation products (Atkinson and Arey, 2003). The rest of cresols may have formed methylphenoxyl radicals, nevertheless, dominantly via H-abstraction by NO<sub>2</sub>, since H-abstraction by OH was even a minor pathway compared to the OH-addition one (Atkinson et al., 1992). In summary, the model results suggest that there were two possible routes leading to nitroaromatic formation. However, one of them (recombination of OH-aromatic adducts with NO<sub>2</sub>) is likely of little atmospheric relevance due to very high NO<sub>2</sub> needed, and the other (H-abstraction from cresol) occurs in the atmosphere but is not a major fate of aromatics (Calvert et al., 2002).

### 3.5 Implications for OFR experiments with combustion emissions as input

Emissions from combustion sources, e.g., vehicles and biomass burning, usually contain VOCs and NO\textsubscript{x} at very high concentrations (Table 1). An injection of this type of emissions (typically with OHR\textsubscript{exp} of thousands of s<sup>-1</sup> or larger and NO\textsubscript{x} of tens of ppm or larger) in OFRs without any pretreatment is likely to cause all experimental issues discussed in Peng et al. (2016) and this paper, i.e., strong OH suppression, substantial non-tropospheric photolysis, strong RO\textsubscript{2} suppression by NO\textsubscript{2} whether RO\textsubscript{2} is acyl RO<sub>2</sub> or not, fast reactions of NO\textsubscript{2} with OH-aromatic hydrocarbon adducts, substantial NO\textsubscript{2} contribution to VOC fate, and even a near-total inhibition of OFR chemistry due to complete titration of O\textsubscript{3} by NO in the case of OFR254. We take the study of Karjalainen et al. (2016), who used an OFR to oxidize diluted car exhaust in real-time, as an example to investigate the extent to which these issues may affect typical combustion source studies and to explore approaches to mitigate the problems.

During the first 200 s of their experiment (defined as the “cold start” period when the catalyst is cold and emissions are high), NO and total hydrocarbon in the emissions of the test vehicle reached ~400 and ~600 ppm, respectively. We first simulate the oxidation of those emissions without any dilution (even though x12 dilution was used in their experiments) to explore the most extreme conditions. Our model simulation indicates that such an extremely concentrated source would generally lead to bad high- or low-NO\textsubscript{x} conditions (depending on NO\textsubscript{x} concentration) in their OFR (Fig. 7), even though it was run at relatively high H\textsubscript{2}O and UV. OH suppression can be as high as 3 orders of magnitude; VOC fates by non-tropospheric photolysis and reactions of alkenes and phenols with NO\textsubscript{x} can be nearly 100%; up to ~1/3 of OH-toluene adduct may be recombined with NO\textsubscript{2} instead of forming an adduct with O\textsubscript{3}. After the test vehicle entered the “hot stabilized” stage (200–1000 s), its VOC emissions (on the order of ppm) were still too high for an undiluted OFR to yield a good condition (Fig. 59). OH suppression can still reach 2 orders of magnitude; non-tropospheric photolysis, and sometimes reactions with NO\textsubscript{2} can still dominate over reactions with OH in VOC fates; reactions of OH-toluene adduct with NO\textsubscript{2} can still be substantial at some small NO emissions spikes. Moreover, although NO emissions were roughly
at ppm level even during the hot stabilized period, NO effective lifetime may be very short during that period, leading to low-NO conditions in their OFR. As suggested in Peng et al. (2016) for low-NO OFR, dilution of sources can also mitigate strong deviations on OFR-iNO chemistry vs. atmospherically-relevant conditions. A dilution by a factor of 12, as actually used by Karjalainen et al. (2016), appears to be sufficient to bring most of the hot stabilized period under good conditions (Fig. 59). However, most VOC, or in other words, most SOA formation potential, was emitted during the cold start period, when risky and bad conditions still prevailed (Figs. 7 and 8). Even if the emissions are diluted by x100, the cold-start emission peak (Fig. 7) is still under risky conditions. Although bad conditions are eliminated and good condition is present during most of time, this emission peak under risky condition may contribute >50% to total SOA formation potential (Fig. 8). For SOA formed under good condition to be dominant, a dilution factor >400 would be needed. Note that a strong dilution lowers aerosol mass loading in vehicle emissions. As a result, condensation of gases onto particles is slower than in raw exhausts. However, condensational sinks after dilution may still be significantly higher than typical ambient values (Matti Maricq, 2007; Donahue et al., 2016).

Note that the emissions of the test vehicle of Karjalainen et al. (2016) are rather clean compared to the typical 2013 US on-road fleet (i.e., all at the hot stabilized stage) measured by Bishop and Stedman (2013) (Figs. 9 and S10). For emissions of an average on-road fleet, a dilution by a factor of 100 or larger would be necessary to ensure that most emissions would be processed in OFR185 under good conditions at the highest H2O and UV in this study (Figs. 9b and S10b,e,h). In the case of lower H2O and/or UV, an even larger dilution factor would be required.

Conducting OFR185-iNO experiments at high UV lowers the dilution factor needed for good conditions. However, it also renders good high-NO condition impossible (see Section 3.2 and Fig. 54). If one wants to oxidize vehicle exhausts in a high-NO environment in OFR, as in an urban atmosphere, OFR185 at low UV is necessary. Consequently, a much stronger dilution is in turn necessary to keep the operation condition still good. Nevertheless, not all vehicle emissions can be moved into good high-NO region through a simple dilution (Figs. 9c and S10c,f,i). Furthermore, a low UV would seriously limit the highest OH\textsubscript{eq} that OFR can achieve (~3x10\textsuperscript{11} molecules cm\textsuperscript{-3} s for modeled good high-NO conditions in this study), while a much higher OH\textsubscript{eq} would be desirable to fully convert SOA formation potential into measurable SOA mass. If both good high-NO condition and high OH\textsubscript{eq} are required, new techniques (e.g., injection of N\textsubscript{2}O at percent level proposed by Lambe et al. (2017)) may be necessary.

4 Conclusions

In this study, OFR chemistry involving NO\textsubscript{x} species was systematically investigated over a wide range of conditions. NO initially injected into the OFR was found to be rapidly oxidized under most conditions. In particular, due to high O\textsubscript{2} concentrations, NO lifetime in OFR254-iNO was too short to result in a significant RO\textsubscript{2} consumption by NO compared to that by HO\textsubscript{2} under all conditions with active chemistry. Nevertheless, it is not completely impossible for OFR185-iNO to have a significant RO\textsubscript{2} fate by NO and minor non-tropospheric photolysis at the same time (“good high-NO conditions”). According to our simulations, these conditions are most likely present at high H\textsubscript{2}O, low UV, low OHR\textsubscript{eq}, and NO\textsuperscript{a}
of tens to hundreds of ppb.

However, many past OFR studies with high NO injection were conducted under conditions remarkably different from the abovementioned very narrow range. NO\textsuperscript{a} and/or OHR\textsubscript{ext} in those studies were often much higher than good high-NO conditions require (particularly, >3 orders of magnitude in some OFR studies using combustion emissions as input). In addition to non-tropospheric organic photolysis, OFR oxidation of highly concentrated sources can cause multiple large deviations from tropospheric OH oxidation, i.e., RO\textsubscript{2} suppression by high NO\textsubscript{2}, substantial nitroaromatic formation from the recombination of NO\textsubscript{2} and OH-aromatic adducts, and fast reactions of VOCs with NO\textsubscript{3} compared to those with OH.

Working at lower NO\textsubscript{x} (sub-ppm level) and VOC concentrations or dilution can mitigate these experimental problems. In general, a strong dilution (by a factor of >100) is needed for OFR that process typical on-road vehicle emissions. Humidification can also make good conditions more likely. By these measures, good conditions can be guaranteed, as long as NO and/or precursor concentrations are sufficiently low, while high-NO conditions cannot be ensured. To aid design and interpretation of OFR experiments with high NO injection, we provide our detailed modeling results in a visualized form (Fig. S3). For OFR users in need for both high OH\textsuperscript{exp} and high NO, simple NO injection is not a good option.

New techniques (e.g., injection of N\textsubscript{2}O proposed by Lambe et al. (2017) or other innovations) may be necessary to meet this need.

Acknowledgements

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Lambe, A., Massoli, P., Zhang, X., Canagaratna, M., Nowak, J., Daube, C., Yan, C., Nie, W., Onasch, T., Jayne, J., Kolb, C., Davidovits, P., Worsnop, D. and Brune, W.: Controlled nitric oxide production via O(3P)+N&lr;sup;1&lr;sup;2&lr;sub;O(1D) + N&lr;sub;2&lr;sub;O;...


Schwantes, R. H., Schilling, K. A., McVay, R. C., Lignell, H., Coggon, M. M., Zhang, X., Wennberg, P. O. and...


Figure 1. Schematics of main N-containing species and their major interconversion pathways under typical input conditions for (a) OFR185-iNO with NO\textsubscript{in}=150 ppb, (b) OFR254-7-iNO with NO\textsubscript{in}=150 ppb, and (c) OFR185-iNO with NO\textsubscript{in}=30 ppm. Species average concentrations (in molecules cm\textsuperscript{-3}) are shown in black beside species names. Arrows denote directions of the conversions. Average reaction fluxes (in units of 10\textsuperscript{9} molecules cm\textsuperscript{-3} s\textsuperscript{-1}) are calculated according to the production rate, and shown on or beside the corresponding arrows and in the same color. Within each schematic, the thickness of the arrows is a measure of their corresponding species flux. Multiple arrows in the same color and pointing to the same species should be counted only once for reaction flux on a species. Note that all values in these schematics are average ones over the residence time, except for those in square brackets in panels a and b, which are average values within approximate NO effective lifetime (\(\tau_{\text{NO}}\), or more accurately, an integer multiple of the model's output time step closest to NO effective lifetime). All concentrations and fluxes have two significant digits.
Figure 2. Relative variances (left axes)/uncertainties (right axes) of several outputs (i.e., NO, NO$_3$, and OH exposures) of Monte Carlo uncertainty propagation, and relative contributions of key reactions to these relative variances in several typical cases (denoted in 4-character labels, see Table 2 for the typical case label code) in OFR185-INO. Relative variances are shown in linear scales (left axis), while corresponding relative uncertainties, equal to relative variances’ square roots, are indicated by the non-linear right axis. Only the reactions with a contribution of no less than 0.04 to at least one relative variance are shown.
Figure 3. Frequency occurrence distributions of good, risky, and bad conditions (see Table 3) over logarithm of the ratio between \( RO_2 \) reacted with NO and with \( HO_2 \) (see Section S1 for more detail) for (a) OFR254-iNO (only the case with a residence time of 180 s) and (b) OFR185-iNO (including two cases with residence times of 180 and 30 s). Low and high-NO regions (see Table 3) are colored in light blue and grey, respectively.
Increasing UV

Increasing H₂O

Case LL

Case LM

Case LH

Case ML

Case MM

Case MH

Case HL

Case HM

Case HH
Figure 4. Image plots of the condition types defined in Table 3 vs. external OH reactivity (excluding N-containing species) and initial NO for several typical cases in OFR185-INO (see Table 2 for the case label code).
Increasing UV

Increasing H₂O

Case LL

Case LM

Case LH

Case ML

Case MM

Case MH

Case HL

Case HM

Case HH
Figure 5. Same format as Fig. 4, but for OFR254-22-INO.
Figure 6. Fractional importance of the reaction rate of several species of interest with NO$_3$ vs. that with OH, as a function of the ratio of exposure to NO$_3$ and OH. The curves of biogenics and phenols are highlighted by solid dots and squares, respectively. The turquoise and orange markers show the ranges of modeled exposure ratios between NO$_3$ and OH.
and OH of a source study in an urban tunnel (Tkacik et al., 2014) and a laboratory study (Liu et al., 2015) using OFR, respectively. In the upper part of the figure, the modeled frequency distributions of ratios of NO exposure to OH exposure under good/risky/bad high/low-NO conditions for OFR185-iNO and OFR254-iNO are also shown. See Table 3 for the definitions of the three types of conditions. All curves, markers, and histograms in this figure share the same abscissa.
Figure 7. (left) NO and total hydrocarbon during the first 200 s of the test of Karjalainen et al. (2016) in the cases of no dilution, dilution by a factor of 12 (as actually done in that study), and dilution by a factor of 100. Different periods of time are colored according to corresponding emissions (i.e., input conditions for OFR), classified as good/risky/bad high/low-NO. (right) OH exposure/percentage of remaining OH after suppression, relative importance of non-OH fate of benzene, exposure ratio of NOx to OH, NO effective lifetime, and relative importance of reaction of OH-toluene adduct with NOx in the fate of this adduct in the OFR of Karjalainen et al. (2016) during the first 200 s of their test in the cases of no dilution, dilution by a factor of 12, and dilution by a factor of 100. Horizontal orange and red dashed lines in the middle right panel denote “risky” and “bad” regions for exposure ratio of NOx to OH, respectively. Above the orange (red) dashed line, reaction with NOx contributes >20% to the fate of phenol (isoprene).
Figure 8. Secondary organic aerosol (SOA) potential (estimated from the total hydrocarbon measurement) in the OFR of Karjalainen et al. (2016) formed during periods of time in the OFR corresponding to good/risky/bad high/low-NO conditions, as a function of dilution factor. Vertical lines denoting dilution factors of 1, 12 (as actually used in that study), and 100 are also shown.
(a) No dilution (background: Case HH)

(b) Dilution by a factor of 100 (background: Case HH)
Figure 9. Location of individual 1 s datapoints vs. OFR185-iNO reaction conditions. Datapoints are shown from the test vehicle of Karjalainen et al. (2016), as well as average exhaust from gasoline vehicle on-road emissions measured by Bishop and Stedman (2013). On-road emissions are classified by vehicle year and the distribution of each category is shown as a cross representing 1 standard deviation (with log-normal distribution assumed). The X and Y axes are NO and external OH reactivity (excluding N-containing species) due to vehicle emissions in OFR in the cases of (a) no dilution and (b,c) dilution by a factor of 100. The Karjalainen et al. (2016) points are classified as cold start (during first 200 s) and hot stabilized (during 200–1000 s). In addition, the same image plots as the panels of Cases HH (high H₂O and high UV, see Table 2 for the case label code) and HL in Fig. 4 (OFR185-iNO) are shown as background for comparison.
Scheme 1. Possible major reactions in an OFR254-13-iNO with 5 ppm toluene and 10 ppm initial NO. Branching ratios in red are estimated by the model and/or according to Calvert et al. (2002), Atkinson and Arey (2003), Ziemann and Atkinson (2012), and Peng et al. (2016). Note that addition/substitution on the aromatic ring may occur at other positions. Intermediates/products shown here are the isomers that are most likely to form. Branching ratios shown in red are not overall but from immediate reactant.
Table 1. Experimental conditions of several OFR studies with high NO injection.

<table>
<thead>
<tr>
<th>Study</th>
<th>Source type</th>
<th>Temperature (K)</th>
<th>Relative humidity (%)</th>
<th>Dilution factor</th>
<th>External OH reactivity of undiluted source (s⁻¹)</th>
<th>Source NOₓ concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Link et al. (2016)</td>
<td>Diesel vehicle emission</td>
<td>50</td>
<td>45–110</td>
<td>~5000</td>
<td>~5000</td>
<td>436</td>
</tr>
<tr>
<td>Martinsson et al. (2015)</td>
<td>Biomass burning emission</td>
<td>1700</td>
<td>45–110</td>
<td>156400</td>
<td>156400</td>
<td>154</td>
</tr>
<tr>
<td>Karjalainen et al. (2016)</td>
<td>Gasoline vehicle emission</td>
<td>295</td>
<td>60</td>
<td>12</td>
<td>~73000*2,a</td>
<td>~400*1,b</td>
</tr>
<tr>
<td>Liu et al. (2015)</td>
<td>Purified gas</td>
<td>293</td>
<td>13</td>
<td>1</td>
<td>~1400*2,a</td>
<td>10</td>
</tr>
<tr>
<td>Tkacik et al. (2014)</td>
<td>Tunnel air</td>
<td>293</td>
<td>42</td>
<td>1</td>
<td>~60*2,a</td>
<td>~0.8</td>
</tr>
<tr>
<td>Ortega et al. (2013)</td>
<td>Biomass burning emission</td>
<td>290</td>
<td>30</td>
<td>~500</td>
<td>~15-500</td>
<td>~0.2</td>
</tr>
</tbody>
</table>

*1 maximum value in the study
*2 value at the moment of maximum NO emission
*a NO species excluded
*b NO only
Table 2. Code of the labels of typical cases. A case label can be composed of four characters denoting the water mixing ratio, the photon flux, the external OH reactivity excluding N-containing species, and the initial NO mixing ratio, respectively. A case label can also be composed of two characters denoting the water mixing ratio and the photon flux.

<table>
<thead>
<tr>
<th>Water mixing ratio</th>
<th>Photon flux</th>
<th>External OH reactivity (no ON)</th>
<th>Initial NO mixing ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>L=low (0.07%)</td>
<td>L=low (10^{12} photons cm^{-2} s^{-1} at 185 nm; 4.2x10^{11} photons cm^{-2} s^{-1} at 254 nm)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>M=medium (1%)</td>
<td>M=medium (10^{7} photons cm^{-2} s^{-1} at 185 nm; 1.4x10^{5} photons cm^{-2} s^{-1} at 254 nm)</td>
<td>L=low (10 s^{-1})</td>
<td>L=low (10 ppb)</td>
</tr>
<tr>
<td>H=high (2.3%)</td>
<td>H=high (10^{4} photons cm^{-2} s^{-1} at 185 nm; 8.5x10^{3} photons cm^{-2} s^{-1} at 254 nm)</td>
<td>H=high (100 s^{-1})</td>
<td>H=high (316 ppb)</td>
</tr>
<tr>
<td>V=very high (1000 s^{-1})</td>
<td>V=very high (1000 s^{-1})</td>
<td>V=very high (10 ppm)</td>
<td>V=very high (10 ppm)</td>
</tr>
</tbody>
</table>

Example:

- LH0V: low water mixing ratio, high photon flux, no external OH reactivity (excluding ON), very high initial NO mixing ratio
- ML: medium water mixing ratio, low photon flux
<table>
<thead>
<tr>
<th>Condition</th>
<th>Good</th>
<th>Risky</th>
<th>Bad</th>
</tr>
</thead>
<tbody>
<tr>
<td>Criterion</td>
<td>$F_{185 \text{exp}}/OH_{\text{exp}} &lt; 3 \times 10^3 \text{ cm s}^{-1}$ and $F_{254 \text{exp}}/OH_{\text{exp}} &lt; 4 \times 10^5 \text{ cm s}^{-1}$</td>
<td>$F_{185 \text{exp}}/OH_{\text{exp}} &lt; 1 \times 10^7 \text{ cm s}^{-1}$ and $F_{254 \text{exp}}/OH_{\text{exp}} &lt; 1 \times 10^7 \text{ cm s}^{-1}$ (excluding good conditions)</td>
<td>$F_{185 \text{exp}}/OH_{\text{exp}} \geq 1 \times 10^7 \text{ cm s}^{-1}$ or $F_{254 \text{exp}}/OH_{\text{exp}} \geq 1 \times 10^7 \text{ cm s}^{-1}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Condition</th>
<th>High-NO</th>
<th>Low-NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Criterion</td>
<td>$r(\text{RO}_2 + \text{NO}) &gt; 1$</td>
<td>$r(\text{RO}_2 + \text{NO}) \leq 1$</td>
</tr>
</tbody>
</table>

* See Section S1 for detail.
<table>
<thead>
<tr>
<th></th>
<th>Geometric mean</th>
<th>Uncertainty factor</th>
<th>Outlier cases (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OFR185-iNO</td>
<td>1.91</td>
<td>1.64</td>
<td>11</td>
</tr>
<tr>
<td>OFR254-7-iNO</td>
<td>1.59</td>
<td>1.51</td>
<td>7</td>
</tr>
<tr>
<td>OFR254-70-iNO</td>
<td>1.48</td>
<td>1.29</td>
<td>3</td>
</tr>
</tbody>
</table>