Technical Note: Effect of varying the $\lambda = 185$ and 254 nm photon flux ratio on radical generation in oxidation flow reactors

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Abstract.

Oxidation flow reactors (OFRs) complement environmental smog chambers as a portable, low-cost technique for exposing atmospheric compounds to oxidants such as ozone ($O_3$) and hydroxyl (OH) radicals. OH is most commonly generated in OFRs via photolysis of externally added $O_3$ at $\lambda=254$ nm (OFR254), or combined photolysis of $O_2$ and $H_2O$ at $\lambda = 185$ nm plus photolysis of $O_3$ at $\lambda=254$ nm (OFR185) using low-pressure mercury (Hg) lamps. Whereas OFR254 radical generation is influenced by [$O_3$], [$H_2O$], and photon flux at $\lambda=254$ nm ($I_{254}$), OFR185 radical generation is influenced by [$O_2$], [$H_2O$], $I_{185}$, and $I_{254}$. Because the ratio of photon fluxes, $I_{185}/I_{254}$, is OFR-specific, OFR185 performance varies between different systems even when constant $H_2O$ and $I_{254}$ are maintained. Thus, calibrations and models developed for one OFR185 system may not be applicable to another. To investigate these issues, we conducted a series of experiments in which $I_{185}/I_{254}$ emitted by Hg lamps installed in an OFR was systematically varied by fusing multiple segments of lamp quartz together that either transmitted or blocked $\lambda = 185$ nm radiation. Integrated OH exposure ($OH_{exp}$) values achieved for each lamp type were obtained using the tracer decay method as a function of UV intensity, humidity, residence time, and external OH reactivity ($OHR_{ext}$). Following previous related studies, a photochemical box model was used to develop a generalized $OH_{exp}$ estimation equation as a function of [$H_2O$], [$O_3$] and $OHR_{ext}$ that is applicable for $I_{185}/I_{254} \approx 0.001$ to 0.1.

1 Introduction

Hydroxyl (OH) radicals govern the concentrations of most atmospheric organic compounds, including those that lead to secondary organic aerosol (SOA) formation. For decades, environmental chambers and oxidation flow reactors (OFRs) have been used to simulate atmospheric aging processes through the controlled exposure of trace gases and aerosols to OH radicals. Environmental chamber studies are typically conducted over experimental timescales and equivalent atmospheric exposure times of hours up to 1 or 2 days. OFRs with residence times on the order of minutes achieve multiple days of equivalent atmospheric OH exposure ($OH_{exp}$), typically through the reactions
This method is referred to as OFR254, and relies on addition of externally generated O₃ at the OFR inlet. In some cases, OFRs have additionally employed the secondary λ = 185 nm emission line present in low-pressure mercury (Hg) lamps to generate radicals from the following reactions in addition to those listed above that are employed in OFR254:

\[
\begin{align*}
    O_3 + h\nu_{254} &\rightarrow O_2 + O(^1D) \quad \text{(R1)} \\
    O(^1D) + H_2O &\rightarrow 2OH \quad \text{(R2)} \\
    O(^1D) + N_2O &\rightarrow 2NO \quad \text{(R3)}
\end{align*}
\]

This method is referred to as OFR185. Recent modeling studies suggest that OFR185 is less affected by experimental artifacts than OFR254 such as SOA photolysis and unwanted reactions with non-OH oxidants (Peng et al., 2016, 2018, 2019). Additionally, OFR185 is often more practical than OFR254 to apply in field studies because compressed air or O₂ is not required for external O₃ generation. However, because the λ = 185 nm photon flux (I₁₈₅) is influenced by OFR-specific design considerations that are mainly related to the Hg lamps being used, concentrations of O₃, HOₓ = OH + HO₂ and NOₓ = NO + NO₂ generated using OFR185 are potentially variable between different systems even when constant H₂O, N₂O and I₂₅₄ are established. Thus, calibrations and models developed for one OFR185 system may not be applicable to another, making it more difficult to evaluate results or plan experiments. To investigate these issues, we designed a series of experiments in which I₁₈₅:I₂₅₄ was systematically varied over a wide range using multiple novel Hg lamp configurations. Integrated OH\text{exp} values were obtained as a function of OFR185 conditions, and a photochemical box model was used to develop a system of OH\text{exp} estimation equations that are applicable to OFR185 systems with I₁₈₅:I₂₅₄ ≈ 0.001 to 0.1.

2 Experimental

Experiments were conducted using an Aerodyne Potential Aerosol Mass (PAM) OFR, which is a horizontal aluminum cylindrical chamber (46 cm long × 22 cm ID) operated in continuous flow mode (Lambe et al., 2011). A simplified schematic is shown in Figure S1. The H₂O mixing ratio in the OFR was controlled by passing the carrier gas through a Nafion humidifier (Perma Pure LLC) or heated recirculating water bath (Neslab Instruments, Inc.) and then diluting with different levels of dry carrier gas at the OFR inlet. A photodetector (TOCON-C6, sglux Gmbh) and a relative humidity and temperature (RH/T) sensor were mounted in the exit flange of the OFR. Across all experiments, [H₂O] ranged from 0.03% (1% RH at 25.3 °C) to
3.9% (88% RH at 30.9 °C). The O₃ mixing ratio at the exit of the OFR was measured with a UV ozone analyzer (106-M, 2B Technologies).

2.1 HOₓ generation

HOₓ was produced via reactions R1-R2 and R4-R7. Photolysis of H₂O, O₂ and O₃ in the OFR was achieved using two low-pressure Hg fluorescent lamps (Light Sources, Inc.) that were isolated from the sample flow using type 214 quartz sleeves. Nitrogen purge gas was flowed over the lamps to prevent O₃ buildup between the lamps and sleeves. A fluorescent dimming ballast was used to regulate current applied to the lamps. The dimming voltage applied to the ballast ranged from 0.8 to 10 VDC.

Figure 1 shows the Hg fluorescent lamp configurations that were used in this study. Lamp type A is a standard ozone-producing low-pressure Hg germicidal fluorescent lamp (GPH436T5VH/4P, Light Sources Inc.) in which quartz that transmits λ = 185 and 254 nm radiation is present along the entire 356 mm arc length. The relative transmissivity of λ = 185 nm radiation (T₁₈₅) in lamp type A is thus equal to 1. Lamp type B is equivalent to lamp type A with added segments of opaque heat shrink tubing applied to approximately 86% of the arc length (T₁₈₅ ≈ 0.14; see also Fig. S2) to reduce I₁₈₅ and I₂₅₄ to levels below what is achievable using the ballast dimming voltage. A different type of quartz is available that blocks λ = 185 nm and transmits λ = 254 nm radiation (T₁₈₅ = 0). Lamp types C, D, E (GPH436T5L/VH/4P 90/10, GPH436T5L/VH/4P 96/4, GPH436T5L/VH/4P 98.5/1.5; Light Sources, Inc.) fused one segment each of quartz with T₁₈₅ = 0 and T₁₈₅ = 1 to provide reduced I₁₈₅ relative to lamp type A while maintaining constant I₂₅₄. Finally, to evaluate the effect of lamp design at fixed T₁₈₅ and I₂₅₄, lamp types F and G contain the same ratios of T₁₈₅ = 0 and T₁₈₅ = 1 quartz as Types C and D, but with 5 and 13 total segments instead of 2 segments. These different designs isolate the effect of discretized λ = 185 nm irradiation across the entire arc length of the lamp versus having all λ = 185 nm radiation near the entrance of the OFR.

2.2 OH_{exp} characterization studies

OH_{exp}, defined here as the product of the average OH concentration and the mean OFR residence time (τ_{OFR}), was characterized by measuring the decay of carbon monoxide (CO) and/or sulfur dioxide (SO₂) tracers using Thermo 48i and 43i CO and SO₂ analyzers (e.g. Lambe et al. (2011)). Tracer mixing ratios entering the reactor were 6-9 ppmv for CO and 288-629 ppbv for SO₂, each diluted from separate gas mixtures of 0.5% CO or SO₂ in N₂ (Praxair). The corresponding total external OH reactivity (OHR_{ext}), which is the summed product of each tracer mixing ratio and its bimolecular OH rate coefficient, ranged from approximately 9 to 64 s⁻¹. Tracer concentrations were allowed to stabilize before initiating OH_{exp} measurements, during which steady-state levels of CO and/or SO₂ were obtained with the lamps turned off. Then, the lamps were turned on, and tracer concentrations were allowed to equilibrate before being measured at illuminated steady-state conditions.

In most experiments, the mean residence time was τ_{OFR} = 124 s, which was calculated from the ratio of the internal OFR volume (≈ 13 L) and the total sample and makeup flow rate through the OFR (6.4 L min⁻¹). This calculation implicitly assumes plug flow conditions, with associated uncertainty of approximately 10% compared to an explicit residence time distribution measurement (Li et al., 2015b). To characterize the uncertainty in the plug flow approximation in our work, in a subset
of experiments, \( \tau_{\text{OFR}} \approx 63 \) and 251 s were achieved by systematically changing the sample flow rate to 12.5 and 3.1 L min\(^{-1} \).

At \( \tau_{\text{OFR}} = 63, 124, \) and 251 s, we measured integrated OH exposure (\( \text{OH}_{\text{exp}} \)) values of \( 3.3 \times 10^{11}, 7.8 \times 10^{11}, \) and \( 2.0 \times 10^{12} \) molecule cm\(^{-3} \) s, respectively, using the tracer decay method (Sec. 2.2) with the OFR operated at the same humidity and lamp intensity. Thus, perturbing the “plug flow” \( \tau_{\text{OFR}} = 124 \) s by a factor of 2 in either direction changed \( \text{OH}_{\text{exp}} \) by factors of 2.36 and 2.56. Based on these results, an upper-limit estimated uncertainty in \( \tau_{\text{OFR}} \) and corresponding \( \text{OH}_{\text{exp}} \) is approximately 30%.

### 2.3 Photochemical model

We used a photochemical model implemented in MATLAB and Igor Pro to calculate concentrations of radical/oxidant species produced in the reactor (Li et al., 2015b). The KinSim chemical kinetic solver was used to compile the version of the model that was implemented in Igor Pro (Peng and Jimenez, 2019). Model input parameters are shown in Table 1, and reactions and associated kinetic rate coefficients that were included in the model are summarized in Table S1 (Peng and Jimenez, 2020).

For cases where \([\text{H}_2\text{O}] \leq 0.1\% \) and the RH was comparable to the accuracy of the measurement (± 2% RH), \([\text{H}_2\text{O}] \) input to the model was varied between 0.01% and 0.1% to generate better model:measurement \( \text{OH}_{\text{exp}} \) agreement. \( I_{254} \) and \( I_{185} \) values input to the model were adjusted to match the measured \( \text{OH}_{\text{exp}} \) values as best as possible within the following constraints:

1. \( I_{254,\text{max}} = (3.5 \pm 0.7) \times 10^{15} \) photons cm\(^{-2} \) s\(^{-1} \) for two lamps operated at maximum output (Lambe et al., 2019).

2. At reduced lamp output, \( I_{254} \) was calculated by multiplying \( I_{254,\text{max}} \) by the ratio of photodetector-measured irradiance values measured at maximum and reduced lamp output at \( \lambda = 254 \) nm.

3. \( I_{185,\text{max}} : I_{254,\text{max}} \leq 0.10 \) for lamp types A and B only (Spicer, 2013).

4. \( I_{185,\text{max}} : I_{254,\text{max}} \leq 0.01, 0.004, \) and 0.0015 for lamp types C and F, D and G, and E, respectively.

5. At reduced lamp output, \( I_{185} \) was calculated by multiplying \( I_{185,\text{max}} \) by the ratio of \( \text{O}_3 \) mixing ratios measured at maximum and reduced lamp output.

Within these constraints, the mean (± 1\( \sigma \)) ratios of modeled:measured CO and \( \text{SO}_2 \) concentrations remaining at the exit of the OFR were 1.02±0.06 and 0.97±0.17, respectively.

### 3 Results and Discussion

#### 3.1 Influence of \( I_{185} \) on \([\text{O}_3]\) and \( \text{OH}_{\text{exp}} \)

Figure 2 shows \([\text{O}_3]\) measured at the exit of the OFR as a function of \( T_{185} \) with each lamp type operated at maximum UV output. Binned data are shown for conditions where \([\text{H}_2\text{O}] = 0.15\pm0.11\%, 0.98\pm0.08\%, 1.74\pm0.23\%, \) and 3.42±0.30%. At fixed \([\text{H}_2\text{O}], [\text{O}_3] \) increased as a function of \( T_{185} \). For example, \([\text{O}_3]\) increased from 17.8 to 155 ppmv at \([\text{H}_2\text{O}] = 0.15\% \) and from 4.5 to 56 ppmv at \([\text{H}_2\text{O}] = 1.74\% \) as \( T_{185} \) increased from 0.1 to 1. At fixed \( T_{185} \) and \( I_{254}, [\text{O}_3] \) decreased with increasing...
[H$_2$O] due to faster O($^1$D) + H$_2$O reaction rate following O$_3$ photolysis at $\lambda$ = 254 nm. Consequently, as [H$_2$O] increased from 0.15 to 3.42%, [O$_3$] decreased by a factor of 4-5 for lamp types A and C-G, whereas [O$_3$] decreased by a factor of 2 for lamp type B because of its reduced I$_{254}$ (Fig. 1). At [H$_2$O] = 1.74% and $T_{185}$ = 0.04 and 0.1, Figure 2, shows that [O$_3$] generated using lamp types D and G was approximately 1.7 and 1.8 ppmv; here, lamp type D had one 15 mm quartz segments with $T_{185}$ = 1, whereas lamp type G had three 5 mm quartz segments with $T_{185}$ = 1. At the same OFR conditions, [O$_3$] generated using lamp types C and F was 4.5 and 2.7 ppmv; these lamps had one 35 mm and seven 5 mm quartz segments with $T_{185}$ = 1. Despite the discrepancy in measured [O$_3$], corresponding OH$_{\text{exp}}$ obtained with lamp types C and F were $2.5 \times 10^{12}$ and $2.8 \times 10^{12}$ molecules cm$^{-3}$ s$^{-1}$ respectively. Thus, the worse agreement in [O$_3$] measured between lamp types C and F may be associated specifically with O$_3$ measurements from these experiments. We hypothesize that the OFR-volume-averaged I$_{185}$ is sufficient to describe associated HO$_x$ production for these cases.

Figure 3 plots OH$_{\text{exp}}$ as a function of $T_{185}$ at [H$_2$O] = 1.90 ± 0.26%. The corresponding equivalent photochemical age shown on the right y-axis assumes a 24-hour average OH concentration of $1.5 \times 10^6$ molec cm$^{-3}$ (Mao et al., 2009). Results obtained with lamp types D & G and C & F were averaged together at $T_{185}$ = 0.04 and 0.1 respectively due to their similar OH$_{\text{exp}}$ values. Over the range of $T_{185}$ shown in Fig. 3, excluding lamp type B, OH$_{\text{exp}}$ increased by approximately a factor of 5 at I$_{254}$ = (3.7 ± 0.6) $\times 10^{15}$ photons cm$^{-2}$ s$^{-1}$) and a factor of 17 at I$_{254}$ = (2.1 ± 0.3) $\times 10^{14}$ photons cm$^{-2}$ s$^{-1}$. Maximum OH$_{\text{exp}}$ also decreased by about a factor of 5 between lamp types A and B due to reduction in both I$_{254}$ and I$_{185}$ (not shown in Fig. 3). Similar trends were observed for OH$_{\text{exp}}$ measurements at [H$_2$O] = 0.93 ± 0.06% and 3.42 ± 0.30%, but at [H$_2$O] = 0.09 ± 0.07%, the sensitivity of OH$_{\text{exp}}$ to $T_{185}$ was weaker due to suppressed OH production at lower humidity.

### 3.2 $I_{185}$:I$_{254}$ determination and derivation of OH$_{\text{exp}}$ estimation equations

Figure 4 plots $I_{185}$ as a function of I$_{254}$ for the Hg lamps used in this study and a different model of Hg lamps used in an earlier-generation PAM OFR (Li et al., 2015a). As with OH$_{\text{exp}}$ values shown in Fig. 3, $I_{185}$ and I$_{254}$ values obtained with lamp types D & G and C & F were combined together into $T_{185}$ = 0.04 and 0.1 symbols following our hypothesis that the OFR-volume-averaged $I_{185}$ was sufficient to describe HO$_x$ production. Linear fits applied to the data shown in Fig. 4 were used to calculate average $I_{185}$: I$_{254}$ values for lamp types A & B, C & F, D & G, and E. Lamp types A and B (red symbols) had the highest $I_{185}$: I$_{254}$ = 0.0664, whereas lamp type E had the lowest $I_{185}$: I$_{254}$ = 0.00167. $I_{185}$: I$_{254}$ = 0.00561 for lamp types C and F (blue symbols) fell within the envelope of $I_{185}$: I$_{254}$ = 0.004 to 0.012 characterized by Li et al. (2015a), with a lower apparent sensitivity of $I_{185}$: I$_{254}$ to lamp power. This is presumably due to differences in the specific Hg lamps and/or method of dimming used in the two studies.

Previous studies reported empirical OH exposure algebraic estimation equations for use with OFRs (Li et al., 2015a; Peng et al., 2015, 2018; Lambe et al., 2019). These equations parameterize OH$_{\text{exp}}$ as a function of readily-measured experimental parameters, therefore providing a simpler alternative than detailed photochemical models for experimental planning and analysis. Here, we expand on those studies by deriving OH$_{\text{exp}}$ estimation equations for the lamp types that were used in this study.
We adapted the estimation equation format introduced by Li et al. (2015a):

\[
\log[\text{OH}_\text{exp}] = (a + (b + c \times \text{OHR}_\text{ext}^d + e \times \log[O_3 \times \text{OHR}_\text{ext}^e]) \times \log[O_3] + \log[\text{H}_2\text{O}]) + \log \left( \frac{T}{124} \right) \tag{1}
\]

Equation 1 was fit to data obtained from the base case of the model, with CO reacting with OH as a surrogate of OHR

\text{ext}, over the following OFR185 phase space: \( T = 25 \degree C, \tau = 124 \text{ s}, \text{OHR}_\text{ext} = 0.77 \) to 232 \( \text{s}^{-1} \), \([\text{H}_2\text{O}] = 0.1 \) to 3\%., \( I_{254} = 10^{13} \) to \( 10^{16} \) photons \( \text{cm}^{-2} \text{s}^{-1} \), and \( I_{185}:I_{254} = 0.00167, 0.00242, 0.00595, \) and 0.0664. For each \( I_{185}:I_{254} \) value, we explored 10, 15, and 20 logarithmically evenly distributed values in the ranges of \( \text{OHR}_\text{ext}, [\text{H}_2\text{O}], \) and \( I_{254} \), respectively. Figure 5 compares \( \text{OH}_\text{exp} \) estimated from Eq. 1 and calculated from the model for the \( I_{185}:I_{254} = 0.0664 \) case. Almost all of the equation-estimated and model \( \text{OH}_\text{exp} \) values agreed within a factor or 2 or better. The absolute value of the relative deviations increased above \([\text{H}_2\text{O}] \approx 0.5\% \) and was largest at \([\text{H}_2\text{O}] = 3\% \); the mean absolute value of the relative deviations was 28\%. Analogous plots for \( I_{185}:I_{254} = 0.00167, 0.00242, \) and 0.00595 cases are shown in Fig. S3. For these other cases, the mean absolute values of the relative deviations were 20\%, 17\% and 16\%, respectively. Eq. 1 coefficients for lamps with the \( I_{185}:I_{254} \) values reported here are presented in Table 2.

To generalize the results shown in Figs. 5 and S3 to OFR185 systems with other \( I_{185}:I_{254} \) values, Figure 6 plots fit coefficients \( a - f \) as a function of \( I_{185}:I_{254} \). Each of these coefficients changes monotonically as a function of \( I_{185}:I_{254} \), enabling the usage of simple exponential regression functions to parameterize the \( a - f \) values as a continuous function of \( I_{185}:I_{254} \).

Exponential function coefficients for the regression curves shown in Fig. 6 are presented in Table 3. Figure 7 compares the equation-estimated \( \text{OH}_\text{exp} \) (obtained using Eq. 1 with Table 3 fit coefficients) and the measured \( \text{OH}_\text{exp} \) obtained using the tracer decay method. The mean \((\pm 1\sigma)\) ratios of equation-estimated and measured \( \text{OH}_\text{exp} \) values were 0.94\( \pm 0.55, 1.13 \pm 0.48, 1.03 \pm 0.37, \) and 1.32\( \pm 0.71 \) for \( I_{185}:I_{254} = 0.00167, 0.00242, 0.00595, \) and 0.0664.

### 3.3 Influence of \( I_{185} \) on \( \text{HO}_2 \), \( \text{NO}_x \), and UV photolysis of aromatic volatile organic compounds

In addition to \([\text{OH}], [\text{HO}_2] \) and \([\text{NO}_x] \) (with \( \text{N}_2\text{O} \) present) also increase with increasing \( I_{185} \) (Fig. S4). To isolate the effect of \( I_{185} \) on related OFR photochemistry at fixed \( \text{OH}_\text{exp} \), we investigated two OFR185 cases using \( I_{185}:I_{254} = (3.33 \times 10^{12}, 1.96 \times 10^{15}) \) and \((6.65 \times 10^{12}, 1.01 \times 10^{14}) \) photons \( \text{cm}^{-2} \text{s}^{-1} \) that each generate a model-calculated \( \text{OH}_\text{exp} = 5.0 \times 10^{11} \) molecules \( \text{cm}^{-3} \) s \( \) at base case conditions of \([\text{H}_2\text{O}] = 2\% \), \( \tau = 124 \text{ s}, \) and \( \text{OHR}_\text{ext} = 30 \text{ s}^{-1} \). These cases were designated as “low” and “high” \( I_{185}:I_{254} \) cases. Thus, increasing \( I_{185} \) by a factor of 2 enabled lowering \( I_{254} \) by a factor of 20 to achieve equivalent \( \text{OH}_\text{exp} \).

First, we investigated the resilience of each OFR185 case to OH suppression via \( \text{OHR}_\text{ext} \). As \( \text{OHR}_\text{ext} \) was increased from 30 to 300 \( \text{s}^{-1} \), \( \text{OH}_\text{exp} \) decreased from \( 5.0 \times 10^{11} \) to \( 7.9 \times 10^{10} \) \( \text{low} \) \( I_{185}:I_{254} \) and \( 9.0 \times 10^{10} \) \( \text{high} \) \( I_{185}:I_{254} \) molecules \( \text{cm}^{-3} \) \( \text{s} \). Thus, increasing \( I_{185} \) decreased OH suppression by 15\%, primarily due to 30\% higher \([\text{HO}_2] \) in the high \( I_{185}:I_{254} \) case that increased the \( \text{OH} + \text{HO}_2 \) reaction rate and partially buffered the system against increasing \( \text{OHR}_\text{ext} \). Second, we compared the ability of each OFR185 case to generate high-\( \text{NO} \) conditions in the presence of added \( \text{N}_2\text{O} \). For example, at \([\text{N}_2\text{O}] = 2.7\% \), \( \text{NO}:\text{HO}_2 = 1 \) and 0.4 at low and high \( I_{185}:I_{254} \). While increasing \([\text{N}_2\text{O}] \) from 2.7\% to 4.0\% achieved \( \text{NO}:\text{HO}_2 = 1 \) at high \( I_{185}:I_{254} \), \([\text{NO}_2] \) also increased from 50 to 100 ppbv. At higher UV intensity, a similar increase in \([\text{N}_2\text{O}] \) could generate \([\text{NO}_2] \)
> 1 ppm and promote artificially fast RO₂ + NO₂ reactions compared to atmospheric conditions (Peng and Jimenez, 2017). Third, we compared relative timescales for OH oxidation and photolysis of representative aromatic volatile organic compounds (VOCs) that absorb λ = 185 and 254 nm radiation. The fractional VOC loss due to photolysis, \( F_{\text{photolysis}} \), was calculated using Equation 2:

\[
F_{\text{photolysis}} = \frac{\sigma_{185} I_{185} \phi_{185} + \sigma_{254} I_{254} \phi_{254}}{\sigma_{185} I_{185} \times \phi_{185} + \sigma_{254} I_{254} \phi_{254} + k_{\text{OH}}[\text{OH}]} \tag{2}
\]

Where \( \sigma_{185} \) and \( \sigma_{254} \) are the VOC absorption cross sections at λ = 185 and 254 nm, \( \phi_{185} \) and \( \phi_{254} \) are the VOC photolysis quantum yields, and \( k_{\text{OH}} \) is the bimolecular reaction rate coefficient with OH. Assuming upper limit \( \phi_{185} = 1 \) and \( \phi_{254} = 1 \) values, \( F_{\text{photolysis,benzene}} \leq 0.26 \) and 0.07 at low and high \( I_{185}:I_{254} \) (Atkinson, 1986; Dawes et al., 2017). Similarly, \( F_{\text{photolysis,toluene}} \leq 0.07 \) and 0.04 at low and high \( I_{185}:I_{254} \) (Atkinson, 1986; Serralheiro et al., 2015).

4 Conclusions

OFR185 is emerging as one of the most commonly used OFR methods by enabling efficient HOₓ and NOₓ generation over a range of oxidative aging timescales that are relevant to atmospheric processes. Important OFR185 parameters are \( I_{185}, I_{254}, [\text{H}_2\text{O}], [\text{N}_2\text{O}] \) (if NOₓ generation is required), \( \text{OHR}_{\text{ext}} \), and \( \tau_{\text{OFR}} \). However, \( I_{185}:I_{254} \) is specific to the Hg lamp and/or OFR, as are associated calibration and estimation equations. To develop a general framework within which to evaluate and compare different OFR185 systems, we characterized \( \text{OH}_{\text{exp}} \) as a function of \( I_{185}, I_{254}, \text{OHR}_{\text{ext}} \), and [H₂O] values, in the process using several novel low-pressure Hg lamp configurations to extend the range of achievable \( I_{185}:I_{254} \). \( \text{OH}_{\text{exp}} \) estimation equations were developed for the Hg lamp types that were used, and corresponding estimation equation fit coefficients were parameterized as a function of \( I_{185}:I_{254} \) to enable interpolation to other OFR185 systems that were not studied here. \( \text{OHR}_{\text{int}}, \text{HO}_2:\text{OH}, \) and \( F_{\text{photolysis}} \) were improved at higher \( I_{185}:I_{254} \), whereas NO:HO₂ and NO:NO₂ were improved at lower \( I_{185}:I_{254} \). Overall, our results suggest that optimal OFR185 performance is achieved by (1) maximizing \( I_{185}:I_{254} \) (2) reducing \( \text{OH}_{\text{exp}} \) (if needed) through simultaneous reduction in \( I_{185} \) and \( I_{254} \) via electronically or mechanically dimming the lamp output (Fig. S2) (3) increasing [N₂O] to offset higher [HO₂] if high-NO conditions are required, provided that [NO₂] does not exceed \( \approx 1 \) ppm, in which case lower \( I_{185}:I_{254} \) should be used. Future work will investigate the sensitivity of NOₓ-dependent, OH-initiated OVOC and SOA formation processes to \( I_{185}:I_{254} \).

**Code and data availability.** Data and KinSim mechanisms presented in this paper are available upon request. The KinSim kineticsolver is freely available at: https://tinyurl.com/kinsim-cases#permalink=kix.6zu8zdqw2lce.

**Author contributions.** AL conceived and planned the experiments. JR performed the experiments. JR and AL performed the data analysis.

JR, AL, and WB conceived and planned the model simulations, and JR and AL carried out the model simulations. JR, AL and WB contributed to the interpretation of the results. AL took the lead in writing the paper. All authors provided feedback on the paper.
**Competing interests.** The authors declare no competing interests.

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Figure 1. Low-pressure Hg fluorescent lamp types used in this study. Each lamp type contains 356 mm of quartz material that either transmits both $\lambda = 185$ and 254 nm radiation (white, $T_{185} = 1$), blocks $\lambda = 185$ nm and transmits $\lambda = 254$ nm radiation (grey, $T_{185} = 0$), or blocks both $\lambda = 185$ and 254 nm radiation (black, $T_{185} = 0$).
Figure 2. O₃ mixing ratio generated using OFR185 at $I_{254} = (3.5 \pm 0.7) \times 10^{15}$ photons cm⁻² s⁻¹ (lamp types A and C-G) and $I_{254} = 5.8 \times 10^{14}$ photons cm⁻² s⁻¹ (lamp type B) as a function of $T_{185}$ and [H₂O]. Error bars represent ±1σ of replicate O₃ measurements and ± 2 mm uncertainty in lengths of individual $T_{185} = 0$ and 1 segments.

Figure 3. OH_{exp} generated using OFR185 ([H₂O] = 1.90 ± 0.26%) at minimum and maximum $I_{254}$ for each $T_{185}$ value. Corresponding photochemical age shown on right y-axis assuming mean [OH] = $1.5 \times 10^6$ molec cm⁻³ (Mao et al., 2009). Error bars assume ± 30% uncertainty in OH_{exp} and ± 2 mm uncertainty in lengths of individual $T_{185} = 0$ and 1 segments.
Figure 4. Calculated $I_{185}$ and $I_{254}$ values for the lamp types shown in Figure 1. $I_{185}:I_{254}$ values were calculated from linear regression functions and used to derive OH$_{exp}$ estimation equations. $I_{185}$ and $I_{254}$ values obtained by Li et al. (2015a) in an earlier-generation PAM OFR are shown for reference.

Figure 5. OH$_{exp}$ calculated from the estimation equation (Eq. 1) as a function of OH$_{exp}$ calculated from the full OFR185 KinSim mechanism (Table S1) for lamp types A and B. Solid and dashed lines correspond to the 1:1 and the 1:2 and 2:1 lines, respectively. Estimation equation fit coefficients are shown in Table 2.
Figure 6. \( \text{OH}_{\text{exp}} \) estimation equation fit coefficients plotted as a function \( I_{254}:I_{254} \). Trendlines were calculated from exponential regression functions with fit parameters that are presented in Table 3.

Figure 7. \( \text{OH}_{\text{exp}} \) calculated from estimation equation (Eq. 1 and Table 2) as a function of \( \text{OH}_{\text{exp}} \) calculated from tracer decay method for Hg lamp types with \( I_{254}:I_{254} \) values specified in legend.
Table 1. OFR conditions input to photochemical model.

<table>
<thead>
<tr>
<th>P (mbar)</th>
<th>1013</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>22.5-31.9</td>
</tr>
<tr>
<td>Residence time (s)</td>
<td>63, 124, 251</td>
</tr>
<tr>
<td>H₂O (%)</td>
<td>0.03-3.9</td>
</tr>
<tr>
<td>O₃ (ppmv)</td>
<td>0.4-156</td>
</tr>
<tr>
<td>CO (ppmv)</td>
<td>0 or 6-9</td>
</tr>
<tr>
<td>SO₂ (ppbv)</td>
<td>0 or 288-629</td>
</tr>
<tr>
<td>I₁₈₅ (photons cm⁻² s⁻¹)</td>
<td>1.1×10¹²-3.2×10¹⁴</td>
</tr>
<tr>
<td>I₂₅₄ (photons cm⁻² s⁻¹)</td>
<td>6.0×10¹³-4.2×10¹⁵</td>
</tr>
</tbody>
</table>

Table 2. OH_{exp} estimation equation coefficients (±1σ) as defined in Eq. 1.

<table>
<thead>
<tr>
<th>I₁₈₅/I₂₅₄</th>
<th>Coefficient</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00167</td>
<td>16.109 ± 0.321</td>
<td>-0.4734 ± 0.0382</td>
<td>-1.1613 ± 0.0182</td>
<td>0.079284 ± 0.00105</td>
<td>0.99503 ± 0.00195</td>
<td>0.059251 ± 0.00115</td>
<td></td>
</tr>
<tr>
<td>0.00242</td>
<td>15.949 ± 0.347</td>
<td>-0.45692 ± 0.0398</td>
<td>-1.0974 ± 0.0186</td>
<td>0.084855 ± 0.0012</td>
<td>0.99376 ± 0.00206</td>
<td>0.06416 ± 0.00134</td>
<td></td>
</tr>
<tr>
<td>0.00595</td>
<td>12.306 ± 0.42</td>
<td>-0.070275 ± 0.04130</td>
<td>-0.8052 ± 0.0227</td>
<td>0.11347 ± 0.00249</td>
<td>0.062916 ± 0.00233</td>
<td>0.094896 ± 0.00291</td>
<td></td>
</tr>
<tr>
<td>0.0664</td>
<td>10.098 ± 0.576</td>
<td>0.15062 ± 0.0455</td>
<td>-0.44244 ± 0.0329</td>
<td>0.18041 ± 0.00872</td>
<td>0.031146 ± 0.00265</td>
<td>0.1672 ± 0.00953</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Parameterization of Eq. 1 coefficients (±1σ): y₀ + A × exp(I₁₈₅ : I₂₅₄) × invTau.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>y₀</th>
<th>A</th>
<th>invTau</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>10.053 ± 0.593</td>
<td>9.4455 ± 1.52</td>
<td>230.41 ± 71.8</td>
</tr>
<tr>
<td>b</td>
<td>0.15553 ± 0.0641</td>
<td>-0.99468 ± 0.168</td>
<td>237.54 ± 76.9</td>
</tr>
<tr>
<td>c</td>
<td>0.44174 ± 0.0106</td>
<td>-0.95747 ± 0.0223</td>
<td>163.04 ± 8.41</td>
</tr>
<tr>
<td>d</td>
<td>0.18069 ± 0.000904</td>
<td>-0.12054 ± 0.00161</td>
<td>98.577 ± 3.91</td>
</tr>
<tr>
<td>e</td>
<td>0.031037 ± 0.00208</td>
<td>0.094968 ± 0.00462</td>
<td>182.31 ± 18.8</td>
</tr>
<tr>
<td>f</td>
<td>0.16754 ± 0.00167</td>
<td>-0.1287 ± 0.00295</td>
<td>96.245 ± 6.65</td>
</tr>
</tbody>
</table>