



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.

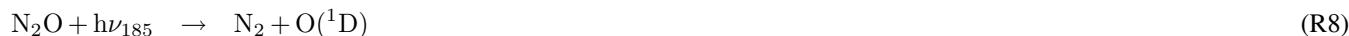
Oxidation flow reactors (OFRs) complement environmental smog chambers as a portable, low-cost technique for exposing atmospheric compounds to oxidants such as ozone (O_3) and hydroxyl (OH) radicals. OH is most commonly generated in OFRs via photolysis of externally added O_3 at $\lambda=254$ nm (OFR254), 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



25 This method is referred to as OFR254, and relies on addition of externally generated O_3 at the OFR inlet. In some cases, OFRs have additionally employed the secondary $\lambda = 185$ 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:



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).
35 Additionally, OFR185 is often more practical than OFR254 to apply in field studies because compressed air or O_2 is not required for external O_3 generation. However, because the $\lambda = 185$ nm photon flux (I_{185}) is influenced by OFR-specific design considerations that are mainly related to the Hg lamps being used, concentrations of O_3 , $\text{HO}_x = \text{OH} + \text{HO}_2$ and $\text{NO}_x = \text{NO} + \text{NO}_2$ generated using OFR185 are potentially variable between different systems even when constant H_2O , N_2O and I_{254} are established. Thus, calibrations and models developed for one OFR185 system may not be applicable to another, making it
40 more difficult to evaluate results or plan experiments. To investigate these issues, we designed a series of experiments in which $I_{185}:I_{254}$ was systematically varied over a wide range using multiple novel Hg lamp configurations. Integrated OH_{exp} values were obtained as a function of OFR185 conditions, and a photochemical box model was used to develop a system of OH_{exp} estimation equations that are applicable to OFR185 systems with $I_{185}:I_{254} \approx 0.001$ to 0.1.

2 Experimental

45 Experiments were conducted using an Aerodyne Potential Aerosol Mass (PAM) OFR, which is a horizontal aluminum cylindrical chamber (46 cm long \times 22 cm ID) operated in continuous flow mode (Lambe et al., 2011). A simplified schematic is shown in Figure S1. The H_2O 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)
50 sensor were mounted in the exit flange of the OFR. Across all experiments, $[\text{H}_2\text{O}]$ 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 HO_x generation

HO_x was produced via reactions R1-R2 and R4-R7. Photolysis of H₂O, O₂ and O₃ in the OFR was achieved using two low-
55 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-
60 producing low-pressure Hg germicidal fluorescent lamp (GPH436T5VH/4P, Light Sources Inc.) in which quartz that transmits $\lambda = 185$ and 254 nm radiation is present along the entire 356 mm arc length. The relative transmissivity of $\lambda = 185$ nm radiation (T_{185}) 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 ($T_{185} \approx 0.14$; see also Fig. S2) to reduce I_{185} and I_{254} to levels below what is achievable using the ballast dimming voltage. A different type of quartz is available that blocks $\lambda = 185$
65 nm and transmits $\lambda = 254$ nm radiation ($T_{185} = 0$). 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 $T_{185} = 0$ and $T_{185} = 1$ to provide reduced I_{185} relative to lamp type A while maintaining constant I_{254} . Finally, to evaluate the effect of lamp design at fixed
70 T_{185} and I_{254} , lamp types F and G contain the same ratios of $T_{185} = 0$ and $T_{185} = 1$ 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 $\lambda = 185$ nm irradiation across the entire arc length of the lamp versus having all $\lambda = 185$ 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 character-
ized 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
75 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.

80 In most experiments, the mean residence time was $\tau_{\text{OFR}} = 124$ 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.
85 At $\tau_{\text{OFR}} = 63, 124,$ and 251 s, we measured integrated OH exposure (OH_{exp}) values of $3.3 \times 10^{11}, 7.8 \times 10^{11},$ and 2.0×10^{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 OH_{exp} by factors of 2.36
and 2.56. Based on these results, an upper-limit estimated uncertainty in τ_{OFR} and corresponding OH_{exp} is approximately
30%.

90 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).
95 For cases where $[\text{H}_2\text{O}] \leq 0.1\%$ and the RH was comparable to the accuracy of the measurement ($\pm 2\%$ RH), $[\text{H}_2\text{O}]$ input to
the model was varied between 0.01% and 0.1% to generate better model:measurement OH_{exp} agreement. I_{254} and I_{185} values
input to the model were adjusted to match the measured OH_{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
100 values measured at maximum and reduced lamp output at $\lambda = 254$ nm.
 3. $I_{185,\text{max}} \cdot I_{254,\text{max}} \lesssim 0.10$ for lamp types A and B only (Spicer, 2013).
 4. $I_{185,\text{max}} \cdot I_{254,\text{max}} \lesssim 0.01, 0.004,$ 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 O₃ mixing ratios measured at
maximum and reduced lamp output.
- 105 Within these constraints, the mean ($\pm 1\sigma$) ratios of modeled:measured CO and SO₂ 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 OH_{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
110 output. Binned data are shown for conditions where $[\text{H}_2\text{O}] = 0.15 \pm 0.11\%, 0.98 \pm 0.08\%, 1.74 \pm 0.23\%,$ and $3.42 \pm 0.30\%$. 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



[H₂O] due to faster O(¹D) + H₂O reaction rate following O₃ photolysis at λ = 254 nm. Consequently, as [H₂O] increased from 0.15 to 3.42%, [O₃] decreased by a factor of 4-5 for lamp types A and C-G, whereas [O₃] decreased by a factor of 2 for lamp type B because of its reduced I₂₅₄ (Fig. 1). At [H₂O] = 1.74% and T₁₈₅ = 0.04 and 0.1, Figure 2, shows that [O₃] 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 T₁₈₅ = 1, whereas lamp type G had three 5 mm quartz segments with T₁₈₅ = 1. At the same OFR conditions, [O₃] 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 T₁₈₅ = 1. Despite the discrepancy in measured [O₃], corresponding OH_{exp} obtained with lamp types C and F were 2.5 × 10¹² and 2.8 × 10¹² molecules cm⁻³ s respectively. Thus, the worse agreement in [O₃] measured between lamp types C and F may be associated specifically with O₃ measurements from these experiments. We hypothesize that the OFR-volume-averaged I₁₈₅ is sufficient to describe associated HO_x production for these cases.

Figure 3 plots OH_{exp} as a function of T₁₈₅ at [H₂O] = 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 × 10⁶ molec cm⁻³ (Mao et al., 2009). Results obtained with lamp types D & G and C & F were averaged together at T₁₈₅ = 0.04 and 0.1 respectively due to their similar OH_{exp} values. Over the range of T₁₈₅ shown in Fig. 3, excluding lamp type B, OH_{exp} increased by approximately a factor of 5 at I₂₅₄ = (3.7 ± 0.6) × 10¹⁵ photons cm⁻² s⁻¹ and a factor of 17 at I₂₅₄ = (2.1 ± 0.3) × 10¹⁴ photons cm⁻² s⁻¹. Maximum OH_{exp} also decreased by about a factor of 5 between lamp types A and B due to reduction in both I₂₅₄ and I₁₈₅ (not shown in Fig. 3). Similar trends were observed for OH_{exp} measurements at [H₂O] = 0.93 ± 0.06% and 3.42 ± 0.30%, but at [H₂O] = 0.09 ± 0.07%, the sensitivity of OH_{exp} to T₁₈₅ was weaker due to suppressed OH production at lower humidity.

3.2 I₁₈₅:I₂₅₄ determination and derivation of OH_{exp} estimation equations

Figure 4 plots I₁₈₅ as a function of I₂₅₄ 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_{exp} values shown in Fig. 3, I₁₈₅ and I₂₅₄ values obtained with lamp types D & G and C & F were combined together into T₁₈₅ = 0.04 and 0.1 symbols following our hypothesis that the OFR-volume-averaged I₁₈₅ was sufficient to describe HO_x production. Linear fits applied to the data shown in Fig. 4 were used to calculate average I₁₈₅: I₂₅₄ values for lamp types A & B, C & F, D & G, and E. Lamp types A and B (red symbols) had the highest I₁₈₅: I₂₅₄ = 0.0664, whereas lamp type E had the lowest I₁₈₅: I₂₅₄ = 0.00167. I₁₈₅: I₂₅₄ = 0.00561 for lamp types C and F (blue symbols) fell within the envelope of I₁₈₅: I₂₅₄ = 0.004 to 0.012 characterized by Li et al. (2015a), with a lower apparent sensitivity of I₁₈₅: I₂₅₄ 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_{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_{exp} estimation equations for the lamp types that were used in this study.



145 We adapted the estimation equation format introduced by Li et al. (2015a):

$$\log[\text{OH}_{\text{exp}}] = \left(a + (b + c \times \text{OHR}_{\text{ext}}^{\text{d}} + e \times \log[\text{O}_3 \times \text{OHR}_{\text{ext}}^{\text{f}}]) \times \log[\text{O}_3] + \log[\text{H}_2\text{O}] \right) + \log\left(\frac{\tau}{124}\right) \quad (1)$$

Equation 1 was fit to data obtained from the base case of the model, with CO reacting with OH as a surrogate of OHR_{ext} , over the following OFR185 phase space: $T = 25^\circ\text{C}$, $\tau = 124$ s, $\text{OHR}_{\text{ext}} = 0.77$ to 232 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
150 20 logarithmically evenly distributed values in the ranges of OHR_{ext} , $[\text{H}_2\text{O}]$, and I_{254} , respectively. Figure 5 compares OH_{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 OH_{exp} values agreed within a factor of 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
155 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 $I_{185}:I_{254}$.
160 Exponential function coefficients for the regression curves shown in Fig. 6 are presented in Table 3. Figure 7 compares the equation-estimated OH_{exp} (obtained using Eq. 1 with Table 3 fit coefficients) and the measured OH_{exp} obtained using the tracer decay method. The mean ($\pm 1\sigma$) ratios of equation-estimated and measured OH_{exp} values were $0.94 \pm 0.55, 1.13 \pm 0.48, 1.03 \pm 0.37,$ and 1.32 ± 0.71 for $I_{185}:I_{254} = 0.00167, 0.00242, 0.00595,$ and 0.0664 .

3.3 Influence of I_{185} on HO_2 , NO_x , and UV photolysis of aromatic volatile organic compounds

165 In addition to $[\text{OH}]$, $[\text{HO}_2]$ and $[\text{NO}_x]$ (with N_2O present) also increase with increasing I_{185} (Fig. S4). To isolate the effect of I_{185} on related OFR photochemistry at fixed OH_{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 $\text{cm}^{-3} \text{s}$ at base case conditions of $[\text{H}_2\text{O}] = 2\%$, $\tau = 124$ 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
170 OH_{exp} .

First, we investigated the resilience of each OFR185 case to OH suppression via OHR_{ext} . As OHR_{ext} was increased from 30 to 300 s^{-1} , OH_{exp} decreased from 5.0×10^{11} to 7.9×10^{10} (low $I_{185}:I_{254}$) and 9.0×10^{10} (high $I_{185}:I_{254}$) molecules $\text{cm}^{-3} \text{s}^{-1}$. 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 OHR_{ext} . Second, we compared the
175 ability of each OFR185 case to generate high-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_{photolysis}, was calculated using Equation 2:

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

Where σ₁₈₅ and σ₂₅₄ are the VOC absorption cross sections at λ = 185 and 254 nm, φ₁₈₅ and φ₂₅₄ are the VOC photolysis quantum yields, and k_{OH} is the bimolecular reaction rate coefficient with OH. Assuming upper limit φ₁₈₅ = 1 and φ₂₅₄ = 1 values, F_{photolysis,benzene} ≤ 0.26 and 0.07 at low and high I₁₈₅:I₂₅₄ (Atkinson, 1986; Dawes et al., 2017). Similarly, F_{photolysis,toluene} ≤ 0.07 and 0.04 at low and high I₁₈₅:I₂₅₄ (Atkinson, 1986; Serralheiro et al., 2015).

4 Conclusions

OFR185 is emerging as one of the most commonly used OFR methods by enabling efficient HO_x and NO_x generation over a range of oxidative aging timescales that are relevant to atmospheric processes. Important OFR185 parameters are I₁₈₅, I₂₅₄, [H₂O], [N₂O] (if NO_x generation is required), OHR_{ext}, and τ_{OFR}. However, I₁₈₅:I₂₅₄ 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 OH_{exp} as a function of I₁₈₅, I₂₅₄, OHR_{ext}, and [H₂O] values, in the process using several novel low-pressure Hg lamp configurations to extend the range of achievable I₁₈₅:I₂₅₄. OH_{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 I₁₈₅:I₂₅₄ to enable interpolation to other OFR185 systems that were not studied here. OHR_{int}, HO₂:OH, and F_{photolysis} were improved at higher I₁₈₅:I₂₅₄, whereas NO:HO₂ and NO:NO₂ were improved at lower I₁₈₅:I₂₅₄. Overall, our results suggest that optimal OFR185 performance is achieved by (1) maximizing I₁₈₅:I₂₅₄ (2) reducing OH_{exp} (if needed) through simultaneous reduction in I₁₈₅ and I₂₅₄ 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 ≈ 1 ppm, in which case lower I₁₈₅:I₂₅₄ should be used. Future work will investigate the sensitivity of NO_x-dependent, OH-initiated OVOC and SOA formation processes to I₁₈₅:I₂₅₄.

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#bookmark=kix.6zu8zdwq2lce>.

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.



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210 References

- Atkinson, R.: Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions, *Chemical Reviews*, 86, 69–201, 1986.
- Dawes, A., Pascual, N., Hoffmann, S. V., Jones, N. C., and Mason, N. J.: Vacuum ultraviolet photoabsorption spectroscopy of crystalline and amorphous benzene, *Phys. Chem. Chem. Phys.*, 19, 27 544–27 555, <http://dx.doi.org/10.1039/C7CP05319C>, 2017.
- 215 Lambe, A. T., Ahern, A. T., Williams, L. R., Slowik, J. G., Wong, J. P. S., Abbatt, J. P. D., Brune, W. H., Ng, N. L., Wright, J. P., Croasdale, D. R., Worsnop, D. R., Davidovits, P., and Onasch, T. B.: Characterization of aerosol photooxidation flow reactors: heterogeneous oxidation, secondary organic aerosol formation and cloud condensation nuclei activity measurements, *Atmospheric Measurement Techniques*, 4, 445–461, 2011.
- Lambe, A. T., Krechmer, J. E., Peng, Z., Casar, J. R., Carrasquillo, A. J., Raff, J. D., Jimenez, J. L., and Worsnop, D. R.: HO_x and NO_x
220 production in oxidation flow reactors via photolysis of isopropyl nitrite, isopropyl nitrite-d₇, and 1,3-propyl dinitrite at λ = 254, 350, and 369 nm, *Atmospheric Measurement Techniques*, 12, 299–311, <https://doi.org/10.5194/amt-12-299-2019>, 2019.
- Li, R., Palm, B. B., Ortega, A. M., Hlywiak, J., Hu, W., Peng, Z., Day, D. A., Knote, C., Brune, W. H., De Gouw, J. A., and Jimenez, J. L.: Modeling the Radical Chemistry in an Oxidation Flow Reactor: Radical Formation and Recycling, Sensitivities, and the OH Exposure Estimation Equation, *The Journal of Physical Chemistry A*, 119, 150406123535 006, 2015a.
- 225 Li, R., Palm, B. B., Ortega, A. M., Hlywiak, J., Hu, W., Peng, Z., Day, D. A., Knote, C., Brune, W. H., De Gouw, J. A., and Jimenez, J. L.: Modeling the Radical Chemistry in an Oxidation Flow Reactor: Radical Formation and Recycling, Sensitivities, and the OH Exposure Estimation Equation, *The Journal of Physical Chemistry A*, 119, 4418–4432, 2015b.
- Mao, J., Ren, X., Brune, W., Olson, J., Crawford, J., Fried, A., Huey, L., Cohen, R., Heikes, B., and Singh, H.: Airborne measurement of OH reactivity during INTEX-B, *Atmospheric Chemistry and Physics*, 9, 163–173, 2009.
- 230 Peng, Z. and Jimenez, J. L.: Modeling of the chemistry in oxidation flow reactors with high initial NO, *Atmospheric Chemistry and Physics*, 17, 11 991–12 010, <https://doi.org/10.5194/acp-17-11991-2017>, 2017.
- Peng, Z. and Jimenez, J. L.: KinSim: A Research-Grade, User-Friendly, Visual Kinetics Simulator for Chemical-Kinetics and Environmental-Chemistry Teaching, *J. Chem. Educ.*, 96, 806–811, <https://doi.org/10.1021/acs.jchemed.9b00033>, 2019.
- Peng, Z. and Jimenez, J. L.: Radical chemistry in oxidation flow reactors for atmospheric chemistry research, *Chem. Soc. Rev.*, <http://dx.doi.org/10.1039/C9CS00766K>, 2020.
- 235 Peng, Z., Day, D. A., Stark, H., Li, R., Lee-Taylor, J., Palm, B. B., Brune, W. H., and Jimenez, J. L.: HO_x radical chemistry in oxidation flow reactors with low-pressure mercury lamps systematically examined by modeling, *Atmospheric Measurement Techniques*, 8, 4863–4890, 2015.
- Peng, Z., Day, D. A., Ortega, A. M., Palm, B. B., Hu, W., Stark, H., Li, R., Tsigaridis, K., Brune, W. H., and Jimenez, J. L.: Non-OH chemistry
240 in oxidation flow reactors for the study of atmospheric chemistry systematically examined by modeling, *Atmospheric Chemistry and Physics*, 16, 4283–4305, <https://doi.org/10.5194/acp-16-4283-2016>, <http://www.atmos-chem-phys.net/16/4283/2016/>, 2016.
- Peng, Z., Palm, B. B., Day, D. A., Talukdar, R. K., Hu, W., Lambe, A. T., Brune, W. H., and Jimenez, J. L.: Model Evaluation of New Techniques for Maintaining High-NO Conditions in Oxidation Flow Reactors for the Study of OH-Initiated Atmospheric Chemistry, *ACS Earth Space Chem.*, 2, 72–86, <https://doi.org/10.1021/acsearthspacechem.7b00070>, 2018.



- 245 Peng, Z., Lee-Taylor, J., Orlando, J. J., Tyndall, G. S., and Jimenez, J. L.: Organic peroxy radical chemistry in oxidation flow reactors and environmental chambers and their atmospheric relevance, *Atmospheric Chemistry and Physics*, 19, 813–834, <https://doi.org/10.5194/acp-19-813-2019>, 2019.
- Serralheiro, C., Duflot, D., da Silva, F. F., Hoffmann, S. V., Jones, N. C., Mason, N. J., Mendes, B., and Limão-Vieira, P.: Toluene Valence and Rydberg Excitations as Studied by ab initio Calculations and Vacuum Ultraviolet (VUV) Synchrotron Radiation, *J. Phys. Chem. A*, 119, 9059–9069, <https://doi.org/10.1021/acs.jpca.5b05080>, <https://doi.org/10.1021/acs.jpca.5b05080>, 2015.
- 250 Spicer, D.: Germicidal Lamp Basics, https://www.light-sources.com/wp-content/uploads/2015/05/Germicidal_Lamp_Basics_-_2013.pdf, 2013.

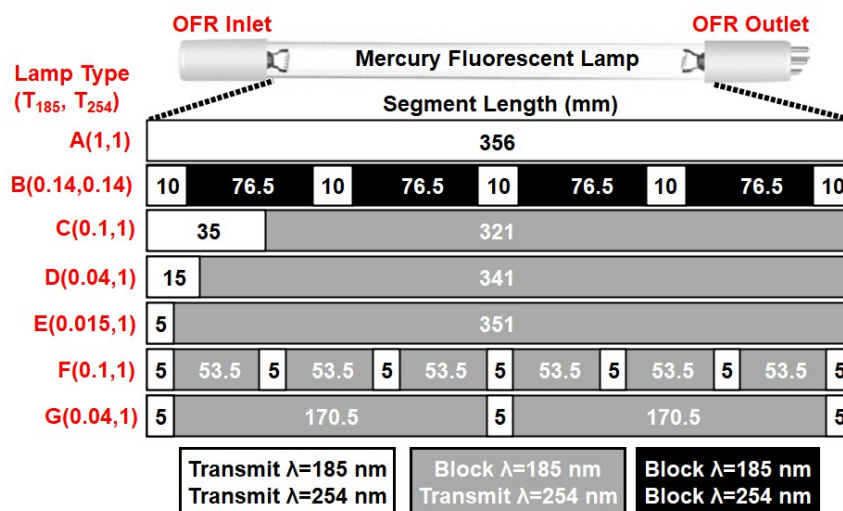


Figure 1. Low-pressure Hg fluorescent lamp types used in this study. Each lamp type contains 356 mm of quartz material that either transmits both $\lambda = 185$ and 254 nm radiation (white, $T_{185} = 1$), blocks $\lambda = 185$ nm and transmits $\lambda = 254$ nm radiation (grey, $T_{185} = 0$), or blocks both $\lambda = 185$ and 254 nm radiation (black, $T_{185} = 0$).

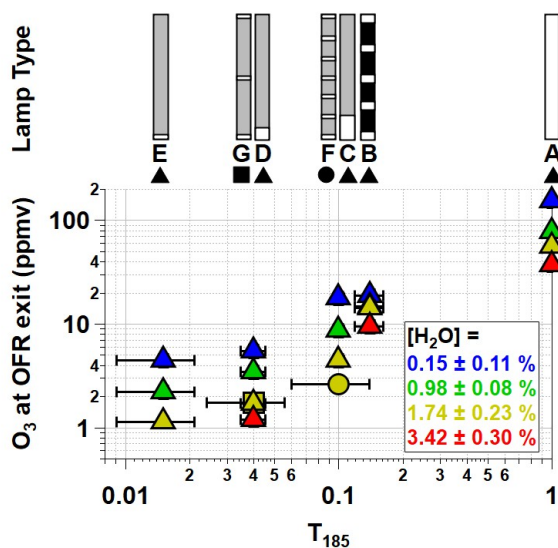


Figure 2. O₃ mixing ratio generated using OFR185 at $I_{254} = (3.5 \pm 0.7) \times 10^{15}$ photons cm⁻² s⁻¹ (lamp types A and C-G) and $I_{254} = 5.8 \times 10^{14}$ photons cm⁻² s⁻¹ (lamp type B) as a function of T₁₈₅ and [H₂O]. Error bars represent ±1σ of replicate O₃ measurements and ± 2 mm uncertainty in lengths of individual T₁₈₅ = 0 and 1 segments.

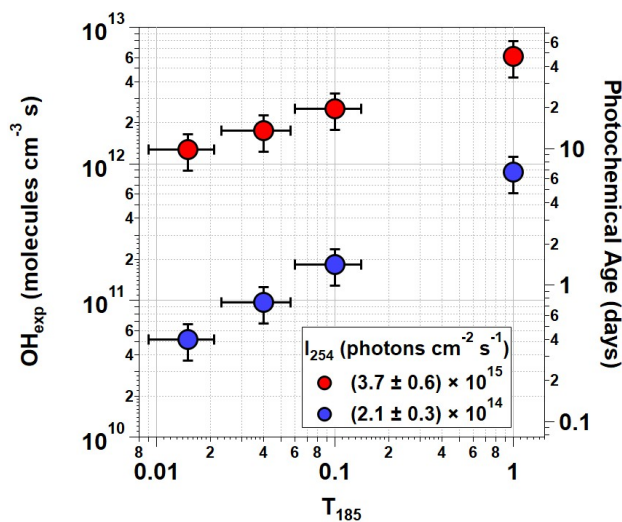


Figure 3. OH_{exp} generated using OFR185 ([H₂O] = 1.90 ± 0.26%) at minimum and maximum I₂₅₄ for each T₁₈₅ value. Corresponding photochemical age shown on right y-axis assuming mean [OH] = 1.5 × 10⁶ molec cm⁻³ (Mao et al., 2009). Error bars assume ± 30% uncertainty in OH_{exp} and ± 2 mm uncertainty in lengths of individual T₁₈₅ = 0 and 1 segments.

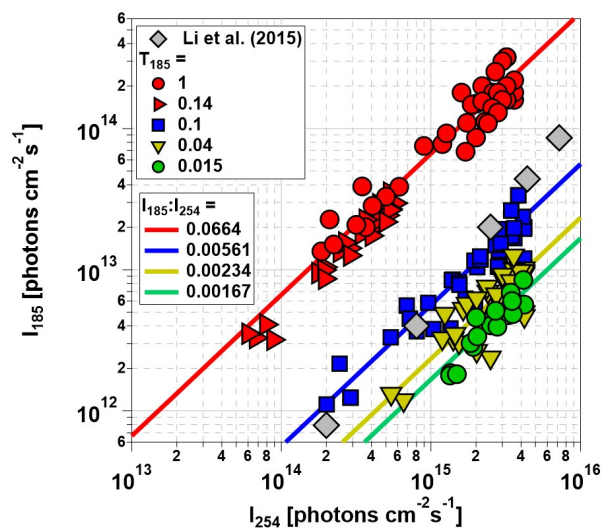


Figure 4. Calculated I_{185} and I_{254} values for the lamp types shown in Figure 1. $I_{185}:I_{254}$ values were calculated from linear regression functions and used to derive OH_{exp} estimation equations. I_{185} and I_{254} values obtained by Li et al. (2015a) in an earlier-generation PAM OFR are shown for reference.

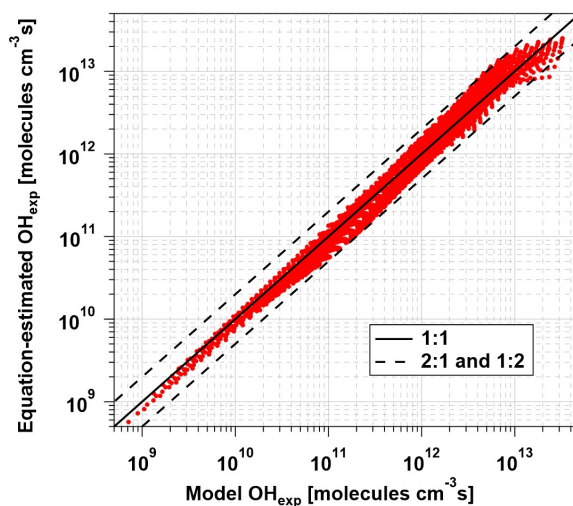


Figure 5. OH_{exp} calculated from the estimation equation (Eq. 1) as a function of OH_{exp} calculated from the full OFR185 KinSim mechanism (Table S1) for lamp types A and B. Solid and dashed lines correspond to the 1:1 and the 1:2 and 2:1 lines, respectively. Estimation equation fit coefficients are shown in Table 2.

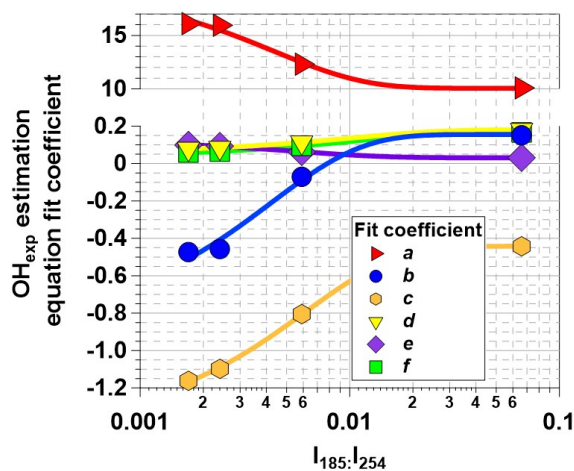


Figure 6. OH_{exp} estimation equation fit coefficients plotted as a function $I_{254}:I_{185}$. Trendlines were calculated from exponential regression functions with fit parameters that are presented in Table 3.

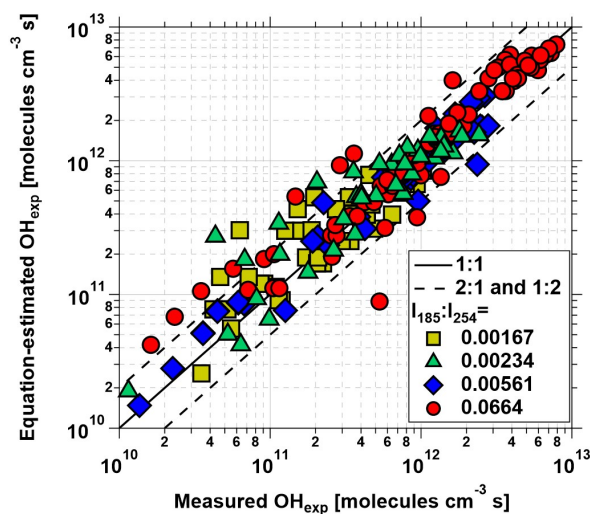


Figure 7. OH_{exp} calculated from estimation equation (Eq. 1 and Table 2) as a function of OH_{exp} calculated from tracer decay method for Hg lamp types with $I_{254}:I_{185}$ values specified in legend.



Table 1. OFR conditions input to photochemical model.

P (mbar)	1013
T (°C)	22.5-31.9
Residence time (s)	63, 124, 251
H ₂ O (%)	0.03-3.9
O ₃ (ppmv)	0.4-156
CO (ppmv)	0 or 6-9
SO ₂ (ppbv)	0 or 288-629
I ₁₈₅ (photons cm ⁻² s ⁻¹)	1.1 × 10 ¹² -3.2 × 10 ¹⁴
I ₂₅₄ (photons cm ⁻² s ⁻¹)	6.0 × 10 ¹³ -4.2 × 10 ¹⁵

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

I ₁₈₅ :I ₂₅₄	Coefficient					
	a	b	c	d	e	f
0.00167	16.109 ± 0.321	-0.4734 ± 0.0382	-1.1613 ± 0.0182	0.079284 ± 0.00105	0.99503 ± 0.00195	0.059251 ± 0.00115
0.00242	15.949 ± 0.347	-0.45692 ± 0.0398	-1.0974 ± 0.0186	0.084855 ± 0.0012	0.093976 ± 0.00206	0.064116 ± 0.00134
0.00595	12.306 ± 0.42	-0.070275 ± 0.04130	-0.8052 ± 0.0227	0.11347 ± 0.00249	0.062916 ± 0.00233	0.094896 ± 0.00291
0.0664	10.098 ± 0.576	0.15062 ± 0.0455	-0.44244 ± 0.0329	0.18041 ± 0.00872	0.031146 ± 0.00265	0.1672 ± 0.00953

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

Coefficient	y ₀	A	invTau
a	10.053 ± 0.593	9.4455 ± 1.52	230.41 ± 71.8
b	0.15553 ± 0.0641	-0.99468 ± 0.168	237.54 ± 76.9
c	0.44174 ± 0.0106	-0.95747 ± 0.0223	163.04 ± 8.41
d	0.18069 ± 0.000904	-0.12054 ± 0.00161	98.577 ± 3.91
e	0.031037 ± 0.00208	0.094968 ± 0.00462	182.31 ± 18.8
f	0.16754 ± 0.00167	-0.1287 ± 0.00295	96.245 ± 6.65