Atmospheric Oxidation in the Presence of Clouds during the Deep Convective Clouds and Chemistry (DC3) Study

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Abstract. Deep convective clouds are critically important to the distribution of atmospheric constituents throughout the troposphere but are difficult environments to study. The Deep Convective Clouds and Chemistry (DC3) study provided the environment, platforms, and instrumentation to test oxidation chemistry around deep convective clouds and their impacts downwind. Measurements on the NASA DC-8 aircraft included those of hydroxyl (OH), hydroperoxyl (HO$_2$), OH reactivity, and more than 100 other chemical species and atmospheric properties. OH, HO$_2$, and OH reactivity were compared to photochemical models, some with and some without simplified heterogeneous chemistry, to test the understanding of atmospheric oxidation as encoded in the model. In general, the agreement between the observed and modeled OH, HO$_2$, and OH reactivity were all well within the combined uncertainties for both the model without heterogeneous chemistry and the model that includes heterogeneous chemistry with small OH and HO$_2$ uptake consistent with laboratory studies. This agreement is generally independent of the altitude, ozone photolysis rate, nitric oxide and ozone abundances, modeled OH reactivity, and

aerosol and ice surface area. For a sunrise to midday flight downwind of a nighttime mesoscale convective system, the observed ozone increase is consistent with the calculated ozone production rate. Even with some observed-to-modeled discrepancies, these results provide evidence that current photochemical models, properly constrained with measurements, can generally simulate observed atmospheric oxidation processes even around clouds.

1 Introduction

Deep convective clouds alter the chemical composition of the middle and upper troposphere (Chatfield and Crutzen, 1984). At its base, a cloud ingests air containing volatile organic compounds (VOCs) and anthropogenic pollutants emitted into the atmospheric boundary layer, lifts it to the upper troposphere where it spreads into the anvil and is eventually mixed with the
10 surrounding air, including some from the lower stratosphere. Inside the convective cloud, the chemical composition is transformed: boundary layer air is diluted with cleaner mid-latitude air; water soluble chemical species are scrubbed by contact with cloud particles; and nitrogen oxides are added by lightning. At the same time, shading in the cloud core extends the lifetime of certain photochemically active compounds. This transformed chemical composition profoundly alters the atmospheric oxidation in the upper troposphere.

Atmospheric oxidation is driven primarily by hydroxyl (OH), whose concentration is strongly dependent on ozone (O_3), especially in the upper troposphere (Logan et al., 1981). Ozone is a source of OH through its destruction by solar ultraviolet radiation, which produces an excited state oxygen atom that can react with water vapor to produce OH. Hydroxyl reactions with methane (CH_4) and VOCs produce oxygenated volatile organic compounds (OVOCs), and in the presence of nitrogen
20 oxide (NO), organic peroxyl (RO_2, where R = CH_3, C_2H_5, …) and hydroperoxyl (HO_2). At the same time, OH reacts with carbon monoxide to produce HO_2. The reaction of these peroxyls with NO creates new nitrogen dioxide (NO_2), which then absorbs solar radiation to produce NO and $O(^3P)$, resulting in new ozone. In the absence of nitrogen oxides (NO_x = $NO+NO_2$), the formation of OH and HO_2 acts to destroy ozone. Thus, atmospheric oxidation is strongly dependent on the chemical composition of the air exiting deep convective clouds.

Deep convective clouds transform the chemical composition of the upper troposphere in several ways (Barth et al., 2015, and references therein). NO_x produced by lightning can have mixing ratios of several parts per billion (ppbv) in the anvil downwind of convection (Ridley et al., 1996; Schumann & Huntrieser, 2007; Pollack et al., 2016; Nault et al., 2017). In addition to long-lived chemical species such CH_4, carbon monoxide (CO), and alkanes, short-lived chemical species such as isoprene and its
30 reaction products or those found in fire plumes can be rapidly transported from the planetary boundary layer (PBL) by convection into the upper troposphere (Apel et al., 2012; Apel et al., 2015). Convection also provides cloud particle liquid and solid surfaces, which can interact with gas-phase chemical species such as peroxides, potentially scrubbing some chemical

species from the gas-phase, thereby altering the gas-phase chemistry and its products (Jacob, 2000; Barth et al., 2016). The mixture of organics and nitrogen oxides forms organic nitrates, which act as sinks for both organic and hydrogen radicals and nitrogen oxides (Nault et al., 2016). This mixture of organic and hydrogen peroxyl and nitrogen oxides enables enhanced upper tropospheric O_3 production that can be in the range of a 2-15 ppbv day^{-1} (Pickering et al., 1990; Ren et al., 2008; Apel et al., 2012; Olson et al., 2012). Upper tropospheric OH and HO_2 are produced by the photolysis of oxygenated chemical species such as formaldehyde (CH_2O) and peroxides, which are products of organic chemical species that were lofted into the upper troposphere (Jaeglé et al., 1997; Wennberg et al., 1998; Ren et al., 2008).

Aircraft observations of tropospheric OH and HO_2 have been compared to photochemical box models constrained by other simultaneous measurements (Stone et al., 2012). In the planetary boundary layer, measurements of HO_2 (Fuchs et al., 2011) and, in some instruments, measurements of OH (Mao et al., 2012) are affected by interferences due predominantly to high abundances of alkenes and aromatics. In the free troposphere where the abundances of these chemical species are much lower, measured and modeled OH and/or HO_2 often agreed to within their combined uncertainties, which are similar to those for ground-based studies (Chen et al., 2012; Christian et al., 2017), but in most of these studies, either modeled and measured OH or HO_2 inexplicably disagreed beyond combined model and measurement uncertainty for certain altitudes or chemical compositions (Mauldin et al., 1998; Faloona et al., 2000; Tan et al., 2001; Olson et al., 2004; Olson et al., 2006; Ren et al., 2008; Stone et al., 2010; Kubisin et al., 2010; Olson et al., 2012; Regelin et al., 2013).

Only a few studies included OH and HO_2 measurements to test the impact of deep convective clouds on atmospheric oxidation in the upper troposphere. During the First Aerosol Characterization Experiment (ACE-1), modeled OH was 40% greater than measured OH in clouds, possibly due to uptake of OH or HO_2 on the cloud particles (Mauldin et al., 1998). In another study over the western Pacific, the observed-to-modeled HO_2 during cloud penetrations was on average only 0.65, compared to 0.83 outside of clouds, and this difference depended upon both the duration of the cloud penetration and the liquid water content (Olson et al., 2006). In a different study, downwind of persistent deep convective clouds over the United States, the ratio of measured-to-modeled HO_2 increased from approximately 1 below 8 km altitude to 3 at 11 km altitude, suggesting an unknown source of HO_x (= OH+HO_2) coming from the nearby convection (Ren et al., 2008).

Heterogeneous chemistry on aerosol can impact OH and HO_2 abundances (Burkholder et al.,2015 and references therein). Typical OH and HO_2 accommodation coefficients used in global models are 0.2 on aerosol particles and 0.4-1.0 on ice. Results from a study over the north Atlantic Ocean indicated that the lower observed-than-modeled HO_2 could be resolved by including heterogeneous HO_2 loss (Jaeglé et al., 2000), but this did not resolve the same difference in clear air. This result differs from an analysis of in-cloud measurements over the western Pacific, which provide evidence that uptake in ice clouds has little impact on HO_2 (Olson et al., 2004). The uptake in liquid clouds using a simple heterogeneous chemistry scheme reduces

modeled HO_2 too much in liquid clouds, while outside of the clouds, the reduction of HO_2 is only a few percent at altitudes above the planetary boundary layer (PBL) outside of clouds (Olson et al., 2004).

Laboratory studies show that HO_2 uptake on moist aerosol particles includes metal catalyzed chemical reactions in the aqueous phase, which reduces the effective uptake coefficient to less than 0.2 (Thornton et al., 2008). Laboratory studies on other surfaces find similar low uptake coefficients (Lakey et al., 2015; Lakey et al., 2016). On ice surfaces, the OH uptake coefficient is at least 0.1 and probably larger (Burkholder et al., 2016). In global models, metal catalyzed HO_2 destruction on aerosol particles can reduce global HO_2 in a way that is more consistent with observed OH and HO_2 (Mao et al., 2010). More recently, a global sensitivity analysis shows that modeled HO_2 is most sensitive to aerosol uptake at high latitudes (Christian et al. 2016), consistent with the conclusion of Mao et al. (2010).

In this paper, we focus on the comparison of measured and modeled OH and HO_2 near deep convective clouds and the implications of this comparison. Our goal is to test the understanding of atmospheric oxidation around deep convective clouds and in the cloud anvils. One possible effect is heterogeneous uptake of OH, HO_2, and RO_2 around and in these clouds, which could alter OH and HO_2. The data for this analysis were collected during the Deep Convective Clouds and Chemistry (DC3) study in 2012.

2 Measurement and modelling methods

2.1 The DC3 Study

Barth et al. (2015) provide a detailed description of the objectives, strategy, locations, instrument payloads, and modeling for DC3. DC3 was designed to quantify the link between the properties of deep convective clouds and changes in chemical composition in the troposphere. This section provides information on the aspects of DC3 that relate most directly to the measured and modeled OH, HO_2, and OH reactivity.

DC3 involved several heavily instrumented aircraft, ground-based dual Doppler radar, lightning mapping arrays, and satellites (Barth et al., 2015). Studies were generally focused on areas in Colorado, Texas/Oklahoma, and Alabama that had dual Doppler radar coverage to quantify cloud properties. The field study took place in May through June, 2012. The aircraft were based in Salina, Kansas, which was central to the three main target regions in Colorado, Texas/Oklahoma, and Alabama. The NASA DC-8 sampled deep convection six times in Colorado, four times in Texas/Oklahoma, and three times in Alabama. Typically working with the NSF G-V aircraft, the DC-8 would sample the inflow region to a growing cumulus cloud and then after it formed, spiral up to the anvil height (~8-12 km) and join the NSF G-V in sampling the outflow region of the same convection.

In addition, during the night before 21 June, the outflow from a mesoscale convective system in the Midwest spread over Iowa and Missouri and then into Illinois and Tennessee. The southern 2/3 of the first three legs was in a thin cirrus cloud and the rest was clear.

5 Most DC3 flights began late morning in order to be in position to sample near active deep convection occurring in late afternoon and concluded near dusk for safety. About 90% of the flight time occurred when the solar zenith angle was less than 85°. Only the photochemical evolution flight on 21 June began before dawn.

The NASA DC-8 aircraft was the only aircraft that had an instrument to measure OH and HO_2. The DC-8 payload was quite
10 comprehensive, thus providing detailed chemical composition, particle characteristics, and meteorological parameters to constrain the photochemical box model that is used to compare observed and modeled OH and HO_2. Direct comparison between observed and modeled OH and HO_2 is valid because the lifetimes of OH and HO_2 are short, a few seconds or less for OH and a few 10's of seconds for HO_2. Thus, the analyses in this paper uses only measurements from the DC-8.

2.2 Measurement of Hydroxyl (OH) and Hydroperoxyl (HO_2)

15 OH and HO_2 were measured with the Penn State Airborne Tropospheric Hydrogen Oxides Sensor (ATHOS), which uses laser induced fluorescence (LIF) in lower pressure detection cells (Hard et al., 1984). ATHOS is described by Faloona et al. (2004). Sampled air is pulled through a 1.5 mm pinhole into a tube that leads to two detection axes. The pressure varies from 12 hPa at low altitudes to 3 hPa aloft. The laser beam is passed 32 times through the detection region with a multipass cell set at right angles to the gated microchannel plate detector. As the air passes through a laser beam, OH absorbs the laser radiation (3 kHz
20 repetition rate, 20 ns pulse length) and fluoresces. In the first 100 ns, the signal contains fluorescence as well as scattering from the walls, Rayleigh scattering, and clouds drops. OH fluorescence is detected from 150 ns to 700 ns after each laser pulse. OH is detected in the first axis; reagent nitric oxide (NO) is added before the second axis to convert HO_2 to OH, which is then detected by LIF. The laser wavelength is tuned on-resonance with an OH transition for 15 seconds and off-resonance for 5 seconds, resulting in a measurement time resolution of 20 seconds. The OH fluorescence signal is the difference between on-
25 resonance and off-resonance signals. The ATHOS nacelle inlet is attached below a nadir plate of the forward cargo bay of the DC-8 and the lasers, electronics, and vacuum pumps were inside the forward cargo bay.

In clouds, it is possible for cloud particles to be pulled into the detection system and remain intact enough to cause large, short scattering signals in the fluorescence channels randomly during on-resonance and off-resonance periods. Differencing these
30 signals to find OH creates large positive and negative noise. When the background signal due to these cloud particles exceeded the average background signal by four standard deviations, the on-line and off-line data were removed from the data set before the analyses were performed.

The instrument was calibrated on the ground both in the laboratory and during the field campaign. Different sizes of pinholes were used in the calibration to produce different detection cell pressures to mimic different altitudes. Monitoring laser power, Rayleigh scattering, and laser linewidth maintained this calibration in flight. For the calibration, OH and HO_2 were produced through water vapor photolysis by UV light at 184.9 nm. Absolute OH and HO_2 mixing ratios were calculated by knowing the

5   184.9 nm photon flux, which was determined with a Cs-I phototube referenced to a NIST-calibrated photomultiplier tube, the H_2O absorption cross section, the H_2O mixing ratio, and the exposure time of the H_2O to the 184.9 nm light. The absolute uncertainty was estimated to be ±16% for both OH and HO_2 at a 1σ confidence level. The 1σ precision for a one-minute integration time during this campaign was about 0.01 parts per trillion by volume (pptv, equivalent to pmol mol^{-1}) for OH and 0.1 pptv for HO_2. Further details about the calibration process may be found in Faloona et al. (2004).

For environments with substantial amounts of alkenes and aromatics, ATHOS has interferences for both OH (Mao et al., 2012) and HO_2 (Fuchs et al., 2011). New ATHOS measurement strategies have minimized these interferences, but these strategies were not fully developed in time for DC3. However, recent missions have shown that the OH and HO_2 interferences are significant only just above forests or cities and are negligible above the planetary boundary layer. For OH, we will factor in

15   the likelihood that the OH has an interference in the planetary boundary layer above forests in the discussion comparing observed and modeled OH. For HO_2, we can estimate the interference using modeled RO_2. In relation to HO_2, the relative average detection sensitivity of RO_2 is 0.6±0.2 of HO_2 for this ATHOS configuration (Ren et al, 2012). Applying this value to RO_2 from alkenes and aromatics, but not CH_3O_2 for which we saw no interference in the laboratory, reduces observed HO_2 by 10%, on average, with an estimated uncertainty of a factor of two. This correction has been applied to the HO_2 measurements,

20   which increases the absolute uncertainty from ±16% to ±20%, 1σ confidence.

2.3 Measurement of OH Reactivity

The OH reactivity is the sum of the product of OH reactants and their reaction rate coefficients with OH. It is the inverse of the OH lifetime. The OH reactivity can be determined from the equation

$$k_{OH} = -\frac{ln\left([OH]/[OH]_0\right)}{\Delta t} - k_{wall}\qquad(1)$$

where $[OH]_0$ is the initial OH concentration, $[OH]$ is the [OH] concentration after a reaction time Δt between OH and its reactants, and k_{wall} is the OH wall loss.

The OH reactivity is measured with the OH Reactivity instrument (OHR), which sits in a rack in the DC-8 forward cargo (Mao et al., 2009). Ambient air is forced into a flow tube (10 cm dia.) at a velocity of 0.3-0.7 m s^{-1}, flows past the pinhole of an OH

detection system similar to the one used for ATHOS, and then is expelled out of the aircraft. In a movable wand in the center of the flow tube, OH is produced by the photolysis of water vapor by 185 nm radiation and then injected into the flow tube, mixing with the ambient air flow. As the wand is pulled back, the distance between the injected OH and the OH reactants in the air increases, resulting in the OH decay. The distance divided by the measured velocity gives the reaction time. The wand

5   moves 10 cm in 12 s and then returns to the starting position, measuring a decay every 20 s.

The OHR calibration was checked in the laboratory before and after DC3 using several different known amounts of different chemical species. During a semi-formal OHR Intercomparison in Juelich Germany in October 2015, the OHR instrument was combined with a different laser, wand drive, and electronics, and despite the difficulties encountered, it was found to produce

10   accurate OH reactivity measurements (Fuchs et al., 2017).

The uncertainty in the OH reactivity measurement consists of an absolute uncertainty and the uncertainty associated with the wall loss subtraction. Changes in the OHR instrument between ARCTAS and DC3 result in slightly different instrument operation, wall loss, and measurement uncertainties between this paper and Mao et al. (2009). The pressure dependence of the

15   OH wall loss was measured in the laboratory using ultra zero air (99.999% pure) and was found to between 2 s^{-1} and 4 s^{-1} over the range pressures equivalent to 0 to 12 km altitude. The flow tube wall is untreated aluminium so that every OH collision with the wall results in complete OH loss no matter the environment or altitude. Mao et al. (2009) confirm the zero found in the laboratory agrees with the zero found in flight. From these laboratory calibrations, the estimated uncertainty in the wall loss correction is ±0.5 s^{-1} (1σ confidence). When the OH reactivity is 1 s^{-1}, the combined uncertainty from the absolute

20   uncertainty and the zero decay is ±0.6 s^{-1}, 1σ confidence, which suggests that 90% of the measurements should be within ±1.2 s^{-1} of the mean value.

Air entering the OHR flow tube was warmed from ~5ºC at altitudes below 2 km to as much at 75ºC at 12 km. The flow tube pressure was 50 hPa greater than ambient due to the ram force pushing air through the flow tube. These temperature and

25   pressure differences can affect the reaction rate coefficients for some OH reactants and thus change the OH reactivity. In order to compare observed and model-calculated OH reactivity, the model was run for both ambient conditions and for the OHR flow tube pressure and temperature, but the observed and model-calculated OH reactivity will be compared for the OHR flow tube pressure and temperature.

2.4 Measurement of other chemical species, photolysis frequencies, and other environmental variables

30   Accurate measurements of other chemical species and environmental variables are critical for this comparison of measured and modeled OH, HO$_2$, and OH reactivity. The photolysis frequency measurements are particularly critical for DC3 because of all the time spent flying around clouds and in the deep convection anvil. A list of these measurements is summarized in Barth et al. (2015) and uncertainties for some of these instruments is provided by Barth et al. (2016) and Pollack et al. (2016).

2.5 Photochemical Box Model

The photochemical box model used in this study is based on the Matlab-based modeling framework, the Framework for Zero-Dimensional Atmospheric Modeling (F0AM), which was developed and made freely available by Glenn Wolfe (Wolfe et al., 2016). The gas-phase photochemical mechanism was Master Chemical Mechanism v3.3.1 (MCMv331) (Saunders et al., 2003; Jenkin et al., 2003). This model was constrained by all simultaneous measurements of chemical species, photolysis frequencies, and meteorological variables (Table S1) and then run to calculate OH, HO_2, and all reaction products that were not measured, such as organic peroxy radicals. Pernitric acid (HO_2NO_2) was measured but was not used to constrain the model because few measurements were reported below 4 km. Measured and modeled HO_2NO_2 agree to within ~25% from 5 to 9 km, and modeled HO_2NO_2 is 1.7 times that measured above 8 km. This difference between using modeled and observed HO_2NO_2 made only a few percent difference in modeled OH and HO_2.

A publically available merge file provided the constraining measurements for the photochemical model (DC3 Data, 2017). We chose the one-minute merge as a compromise between higher frequency measurements that needed to be averaged into one-minute bins and lower frequency measurements that needed to be interpolated between one-minute bins. OH and HO_2 measurements, made every 20 seconds, where averaged into the one-minute bins.

Heterogeneous chemistry was added to the model for some model runs. While many chemical species undergo heterogeneous chemistry, most of the chemical species that strongly influence OH and HO_2 were measured so that their heterogeneous chemistry can be ignored in these comparisons between observed and modelled OH and HO_2. However, organic peroxyl radicals were not measured and their heterogeneous chemistry could have a large influence on OH and HO_2. Thus, heterogeneous chemistry is implemented in the model for OH, HO_2, and RO_2, even though the uptake of RO_2 is thought to be small.

The common types of particles encountered with convection are humidified sub-micron aerosol particles all around and in the convection, liquid drops in lower altitude clouds, and ice particles in the deep convective cloud anvil. The effective uptake of OH, HO_2, and RO_2 onto these surfaces was found from

$$\frac{1}{\gamma_{eff}} = \left(\gamma_{surface} + \left(\frac{1}{\alpha} + \frac{1}{\gamma_{sol} + \gamma_{rxn}} \right)^{-1} \right)^{-1} + \frac{0.75 + 0.286\, Kn}{Kn\,(Kn+1)} \qquad (2)$$

where γ_{eff} is the effective uptake coefficient, $\gamma_{surface}$ is surface reaction uptake, α is the accommodation coefficient, γ_{sol} is uptake due to diffusion through the liquid, γ_{rxn} is uptake due to aqueous-phase reactions, and the last term is the inverse of the gas-phase diffusion in terms of the Knudsen number, Kn (Burkholder et al., 2016; Tang et al., 2014). The first term on the right-

hand side is the total uptake coefficient, γ_{total}. The gas-phase molecular diffusion of chemical species to the particle surface can limit the uptake, especially for large accommodation coefficients and large particles.

The total uptake coefficient for OH and HO_2 depends on the particle chemical composition, phase, and size (Burkholder et al.,
5   2015). While some particle properties were measured in DC3, there are unknowns in particle composition and uncertainties in trying to calculate the uptake coefficient for each one-minute time step. The goal of including heterogeneous chemistry in the model is to determine if heterogeneous chemistry has a substantial impact on the comparison between the observed and modeled OH and HO_2. Thus, we will run the model with fixed values for the total uptake; if the impact on the modeled OH and HO_2 is substantial, then we will have to improve the parameterization of the total uptake.

For aerosol particles, the dry aerosol particle radius is multiplied by the growth factor and then the area-weighted median ambient aerosol radius is determined. The surface area is found by summing the surface area in each bin, multiplied by the bin width, and then corrected by the square of the growth factor for each minute. Ice particles are assumed to be spherical and their size distribution is used to determine the median particle radius. The surface area concentration is determined by summing the
15   surface area concentration times the bin width, which were provided in the merge file for each minute.

The model is then run for three primary different cases: gas-phase with no heterogeneous chemistry (called "no-het"), heterogeneous chemistry (called "het") with $\alpha_{aer} = 0.2$ (which is consistent with the value used in some global models) and α_{ice} = 1.0 for OH, HO_2, and RO_2, and maximum heterogeneous chemistry (called "hetmax") with $\alpha_{aer} = 1.0$ and $\alpha_{ice} = 1.0$. The
20   observed and modeled OH and HO_2 are compared for these three cases.

OH reactivity was also modeled for comparison to observed OH reactivity. Modeled OH reactivity was calculated from only the measured chemical species or from the measured chemical species plus OH reactants that were not measured but are produced by the photochemical model. Examples of these additional OH reactants are organic peroxy, organic peroxides, and
25   unmeasured aldehydes. Uncertainty in the modeled OH reactivity is estimated to be ±10%, 1σ confidence (Kovacs et al., 2001)

Uncertainty in the photochemical box model can be assessed with Monte Carlo methods in which model constraints are varied randomly over their uncertainty ranges and then the widths of the resulting distributions for OH and HO_2 abundances are used to determine the model uncertainties. If just reaction rate coefficients, photolysis frequencies, and reaction products are varied,
30   the typical OH and HO_2 uncertainties at the 1σ confidence level are typically ±(10-15)% (Thompson and Stewart, 1991; Kubison et al., 2010; Olson et al., 2012; Regelin et al., 2013). When uncertainties in the measurements used to constrain the model are included, uncertainties at the 1σ confidence level are typically ±20% or more for both local and global models (Chen et al., 2012; Christian et al., 2016). We use ±20% uncertainty at the 1σ confidence level for the model uncertainty in this paper, which can be combined with the measurement uncertainty of about ±20% uncertainty at the 1σ confidence level.

We note that the observed-to-modeled difference for statistical significance lies approximately at the sum of the standard deviations of the mean for the observations and model. As a result, the factors of 1.4 and 1/1.4 serve as indicators for agreement between observed and modeled OH, HO_2, and OH reactivity.

5   We decided to make the comparisons between observations for all the DC3 results, including transits from Salina KS to the deep convection region. Using all the data gives a more robust comparison and was found to give comparison results identical to that using data sets restricted to the radar-enhanced sites in Colorado, Texas/Oklahoma, and Alabama near vicinity of convection. The direct impact of deep convection is also tested by examining the observed-to-modeled comparison as a function of the ice surface area concentration. This analysis achieves the goals laid out in the introduction.

10 **3 Results**

The DC3 chemical environments dictate the OH and HO_2 abundances. Using all the flight data, altitude profiles of NO, CO, O_3, and particle surface area were collected into 0.5 km altitude bins and the median values were found (Fig. 1). The radar altitude is used for these comparisons because the surface elevations and thus planetary boundary layer (PBL) is at different pressure altitudes for the Colorado, Texas/Oklahoma, and Alabama regions.

Median NO exhibits a "C"-shaped profile with median values near 50 pptv in the planetary boundary layer, a minimum of 10 pptv at 5 km altitude, and a maximum value of 0.5 ppbv above 10 km. NO in the PBL was largely due to anthropogenic pollution; NO aloft was mainly due to a combination of lightning and stratospheric NO_x. Median CO slightly decreased from ~120 ppbv near the surface to ~80 ppbv at 12 km. Median O_3 was 50 ppbv in the PBL and then increased to as much as 100

20 ppbv near 12 km, likely due to stratospheric ozone influence. The surface area concentration of aerosol was 10^{-6} cm^2cm^{-3} in the PBL, but was about 3×10^{-7} cm^2cm^{-3} above that. Median ice surface area was as much as 2×10^{-5} cm^2cm^{-3}, with high variability spanning a factor of 100.

3.1 Comparing HO_x Observations with the no-het Model

Observations will be compared to the no-het model, which should be considered as the base case; the heterogeneous cases will

25 be considered later.

Median observed OH was about 2×10^6 cm^{-3} from ~3 km to 10 km altitude, but was greater than 3×10^6 cm^{-3} below 3 km and just above 10 km (Fig. 2). This profile is consistent with the NO profile; for the NO amounts measured in DC3, increased NO shifts more HO_x to OH. The median observed-to-modeled ratio for the no-het case is close to 1.0 at 0-4 km, is 1.2-1.3 between

30 5 km and 9 km and 0.8-0.9 above 10 km. Generally, the observed-to-modeled ratio is within the estimated combined uncertainties described previously. The statistics from scatter plots using a fitting routine that considered uncertainty in both

the observations and the model (York et al., 2004) indicate generally good agreement between observed and modeled OH, with the model explaining 84% of the OH variance (Table 1, Fig. S1).

Median observed HO_2 was 10-22 pptv below 2 km altitude and decreased almost linearly to 3 pptv at 12 km (Fig. 3). This profile is consistent the altitude distribution of HO_x sources, which are greater near the surface, and even with convective uplift of oxygenated chemical species such as HCHO, are still much less than at the surface. Again, the observed-to-modeled ratio is within the estimated combined uncertainties. In addition, the statistics from scatter plots indicate generally good agreement between observed and modeled HO_2, with the model explaining 75% of the HO_2 variance (Table 1, Fig. S1). However, the median observed-to-modeled ratio for the no-het case is 1.3 at 1 km altitude, decreases to ~1 at 5 km and remains near 1 above 5 km. Error in our assumptions for the RO_2 interference in the HO_2 measurement is a possible cause of the greater observed-to-modeled HO_2 below 3 km, but this difference is still well within the combined uncertainty limits.

An indicator of the HO_x cycling between OH and HO_2 is the HO_2/OH ratio. If the primary HO_x production rate is smaller than the OH-HO_2 cycling rate, the HO_2/OH ratio approximately equals the total OH loss frequency that cycles OH into HO_2 divided by the reaction frequency of HO_2 reactions that cycle HO_2 to OH, primarily HO_2 reactions with NO and O_3.

$$\frac{[HO_2]}{[OH]} = \frac{k'_{OH}}{k_{HO2+NO}[NO] + k_{HO2+O3}[O_3]} \tag{3}$$

where k'_{OH} is the loss frequency of OH for reactions that lead to HO_2 production and the two terms in the denominator are loss frequencies for HO_2 with NO and O_3.

This ratio is ~140 below 2 km altitude and falls to less than 10 at 12 km (Fig. S2). This profile comes from the greater amount of OH reactants at lower altitudes, which increases the ratio, as opposed to the greater NO amount aloft, which decreases the HO_2/OH ratio. The observed-to-modeled ratio is well within the approximate uncertainty limits.

Another good test of the model photochemistry is the comparison of measured and modeled OH and HO_2 as a function of controlling variables (Fig. 4). The photolysis frequency for O_3 producing an excited state O atom, $JO(^1D)$, and O_3 are both involved in the production of OH. O_3 and NO cycle HO_2 to OH, while modeled OH reactivity cycles OH back to HO_2. In general, measured and model OH and HO_2 agree well over a factor of 600 for $JO(^1D)$, a factor of 100 for NO, a factor of 5 for O_3, and a factor of 10 for modeled OH reactivity. One exception is OH for NO greater than 1 ppbv, but there are few data points defining the median OH values in this case. It is possible that the behavior as a function of controlling variables is also a function of altitude. However, with the exception of low values of $JO(^1D)$, the median observed-to-modeled OH and observed-to-modeled HO_2 are generally independent of both the controlling variables and altitude (Fig. S3). The observed-to-

modeled OH and HO$_2$ are also independent of whether the measurements were made in Colorado, Texas/Oklahoma, or Alabama (Fig. S4), although the ratios for some altitudes vary widely due to fewer data points in the altitude medians.

3.2 Comparing OH Reactivity Observations with the no-het Model

The measured OH reactivity was as much as 30 s^{-1} in the PBL but fell off to less than 1 s^{-1} at 12 km altitude (Fig. 5). Observed
5 and modeled OH reactivity are in reasonable agreement when considered in the context of the typical limit-of-detection for OH reactivity (Fuchs et al., 2017). The modeled OH reactivity for the OHR flow tube temperature and pressure is greater than the modeled OH reactivity for ambient temperature and pressure by about 0.3 s^{-1} below 2 km and by about 0.2 s^{-1} above 10 km (Fig. 5). This difference is negligible below 2 km, but grows to a factor of 1.7 at 10 km where the ambient OH reactivity is just 0.2-0.3 s^{-1}, but for the entire altitude, the difference between the observed and modeled OH reactivity looks quite similar
10 for either modeled values. The median observed OH reactivity is 1-3 s^{-1} greater than the modeled OH reactivity below 3 km, and this difference could be evidence of missing OH reactivity.

The percent error between the OH reactivity calculated with modeled chemical species and that calculated from only the measured OH reactants is, on average, less than 4%. In the PBL over Alabama, the OH reactivity calculated from the model
15 after one day of integration was on average 10% larger than that calculated from measurements. In the Colorado and Texas PBL, the average difference was less than 4%. Thus, for much of DC3, the OH reactivity calculated from the DC3 measurements almost completely comprises the measured OH reactivity.

3.3 Comparing OH Production and OH Loss

Another critical test of OH photochemistry is the balance between OH production and loss (Fig. 6). The OH lifetime is typically
20 tenths of a second or less in the PBL and a few seconds at high altitude. Thus, for one-minute averages, OH production and loss should essentially be in balance to within the uncertainty estimates from a propagation of error analysis. These uncertainty estimates were obtained by assuming that OH production is dominated by HO$_2$+NO→OH+NO$_2$ and ozone photolysis followed by reaction of excited state oxygen atoms with water vapor and the OH loss is given by the OH reactivity multiplied by the OH concentration. The largest contributor to the uncertainty is the zero offset for the OH reactivity instrument. The observed
25 OH loss is the observed OH multiplied by the observed OH reactivity, which was corrected for the difference between ambient and OHR flow tube conditions. While this analysis cannot preclude missing or additional OH production and loss of 10^6 cm^{-3} s^{-1} or less, the OH production and loss that are calculated mostly from observations agree to within uncertainties.

3.4 Comparing HO$_x$ Observations with Models Containing Heterogeneous Chemistry

Ample aerosol and ice during DC3 provide tests for possible effects of heterogeneous chemistry on OH and HO$_2$. We look
30 first at the impact that adding heterogeneous chemistry (het, $\alpha_{ice} = 1.0$; $\alpha_{aer} = 0.2$), and maximum heterogeneous chemistry (hetmax, $\alpha_{ice} = 1.0$; $\alpha_{aer} = 1.0$) to the model has on the comparison of median observed and modeled OH and HO$_2$.

In Figures 2-4 and S5-S6 and Tables 1 and S1, the no-het and het models agree with the observed OH and HO_2 to within the combined uncertainties, with the exception of the het model for HO_2 when the aerosol surface area concentration was greater than 10^{-6} cm^2 cm^{-3}. In that case, the ratio of the observed-to-modeled HO_2 was too large, indicating that the het model was

5   reducing HO_2 too much. On the other hand, the hetmax model gives OH and HO_2 values that are substantially different from the observations in almost every comparison. When the OH observed-to-modeled ratio is plotted as a function of aerosol surface area (Fig. 7), the no-het model gives a better agreement with the observations as a function of surface area than the het model does. For HO_2, the het model is substantially above observations when the aerosol surface area concentration exceeds 10^{-6} cm^2cm^{-3}.

For heterogeneous uptake on ice, the observed-to-modeled comparisons of OH and HO_2 are roughly independent of ice surface area (Fig. S7). Comparing the model with HO_2 uptake on ice equalling 1 to a model with HO_2 uptake on ice set to zero decreases OH and HO_2 by only 10% for the largest ice surface area concentration of $7x10^{-5}$ cm^2 cm^{-3}. Thus, HO_2 uptake on ice causes at most a few percent decrease in HO_2.

The addition of RO_2 heterogeneous chemistry on aerosol and ice did reduce the modeled RO_2 by 10% on average for the het model, but did not reduce either OH or HO_2 by more than 1%, on average. Thus, including RO_2 uptake along with OH and HO_2 uptake had only a small impact on the heterogeneous effects on OH and HO_2.

3.5 Evolution of OH and HO_2 Downwind of a Nighttime Mesoscale Convective System (MCS)

20   The quasi-Lagrangian tracking of convective outflow on 21 June provided an opportunity to test the photochemical evolution of OH and HO_2 in the morning of 21 June (Fig. S8). The flight legs perpendicular to the wind were approximately advected downwind. Initially, observed and modeled OH and HO_2 were close to 0 (Fig. 8). However, both modeled OH and HO_2 soon grew to exceed measured OH and HO_2 by about 20%-50% until about 8 am local time. For the remainder of the flight, observed and modeled OH is in substantial agreement for all three models, which are essentially identical except between 9:30 and 11:00

25   when the aerosol surface area concentration was the greatest. For HO_2, observed HO_2 exceeds modelled by a factor of ~1.5 after 9 (CST). In this time period, the observations agree best with the no-het and het models. Thus, the basic observed behavior of OH and HO_2 is captured by the no-het and het models although there is quantitative disagreement between the model and observations of OH and HO_2 for local solar time between 5:45 and 8:15 (CST) and of HO_2 after 9 (CST).

30   Even though more than half of the first three legs were in an ice cloud, the scaled surface area for aerosol particles (top panel) and ice (bottom panel) do not correlate with the differences between observed and modeled OH and HO_2.

As a test of the photochemistry, OH can be calculated from the observed decay of OH reactants. Nault et al. (2016) showed that the observed decay of ethane, ethyne, and toluene were consistent with an average measured OH of 9.5×10^6 cm^{-3} for times from 7:35 to 9:50 local time. An ATHOS recalibration since the publication of Nault et al. (2016) brings the mean number for this time interval down to 8.8×10^6 cm^{-3}. This median revised observed OH concentration is consistent with the mean modeled

5   OH concentration of 9.6×10^6 cm^{-3}. These results agree well within uncertainties and support the observed OH.

Another good test of the photochemistry is a comparison between the observed O$_3$ change and the accumulated calculated O$_3$ production rate (Fig. 9). The actual O$_3$ change is actually slightly larger than the observed O$_3$ because some of the new O$_3$ is partitioned into NO$_2$, so that the quantity of interest is the change in O$_3$ plus the change in NO$_2$. The ozone production rate,

10   $P(O_3)$, can be calculated with the equation

$$P(O_3) = k_{NO+HO2}[NO][HO_2] + \sum_i k_{NO+RO2i}[NO][RO_{2i}] - L(O_3) \qquad (3)$$

where k is a reaction rate coefficient and $L(O_3)$ is the loss terms for ozone. In this case, the loss term was only a few tenths

15   ppbv hr^{-1} (Fig. S9) and can be neglected. These rates are calculated in ppbv min^{-1} and then accumulated at times from 5:45 to 11:15, in order to match the time period over which the DC-8 was sampling the MCS plume. This accumulated ozone production was calculated for the observed HO$_2$ plus modeled RO$_2$ and for the modeled HO$_2$ plus modeled RO$_2$. HO$_2$ accounts for a little more than half the total O$_3$ production. In order to compare the observed O$_3$ change to that accumulated from calculated O$_3$ production, an ozone offset of 53.4 ppbv was added to the accumulated O$_3$ production at 6:00 local solar time,

20   which is when the ozone production commenced.

Ozone varied by 5-7 ppbv over the legs, which were a few hundred km long and was higher on one end of the leg than the other. These variations are smoothed using a 180-minute filter. During the 5 hours from 6:00 to 11:00, the observed O$_3$ change was 14 ppbv. For the same time period, the ozone production calculated from modeled HO$_2$ was 14 ppbv, and the ozone

25   production calculated from observed HO$_2$ was 14 ppbv. These three methods for determining O$_3$ production agree to well within their uncertainties and provide additional confirmation on the observed and modeled HO$_2$ and the modeled RO$_2$.

4 Discussion

These comparisons between median observed and modeled OH, HO$_2$, and OH reactivity display an agreement that is well within the combined uncertainties of the observations and model. This agreement within uncertainties generally holds in scatter

30   plots and associated statistics and as a function of altitude, JO(^{1}D), NO, CO, and the modeled OH reactivity. It also holds for the wide range of environments encountered during DC3 – different altitudes, cloudiness, and sunlight over roughly one third of the continental United States.

A closer look at the figures shows seemingly random differences between observed and modeled OH and HO$_2$. While most observed and modeled OH, HO$_2$, and OH reactivity one-minute data are within the combined uncertainties (1σ confidence) of each other (57%), there are sometimes persistent unexplained differences. An example is from the 21 June flight over Missouri and Illinois (Fig. 8). For both OH and HO$_2$ are periods when the modeled OH and HO$_2$ are higher than the measurements, lower than the measurements, and equal to the measurements. At the same time, the measured OH reactivity is sometimes greater than the modeled OH reactivity and sometimes equal to it. These types of discrepancies are proving to be hard to resolve. A simple correlation analysis, in which correlation coefficients are found for the observed-to-modeled ratio or difference with every model output variable, produced no large correlation coefficients. Employing more sophisticated methods in future work may be more productive.

4.1 Comparing DC3 to Previous Studies

All previous aircraft studies that included measurements of OH and HO$_2$ have compared these measurements to calculated values from constrained photochemical box model. There is uncertainty in comparing the results from one study to another because often the instruments, their calibrations, and models are different or have evolved over time. Comparing results from very different environments amplifies this problem. Thus, the comparisons here are restricted to previous studies in air that was heavily influenced by convection.

NO, CO, O$_3$, and JO(^{1}D) from DC3 are remarkably similar to those observed in INTEX-A in 2004 during flights over the central and eastern US (Ren et al., 2008) and to those observed from only 7 km to 10 km during HOOVER 2 in summer 2007 during flights over central Europe (Regelin et al., 2013). As in DC3, observed and modeled OH agree to within uncertainties for INTEX-A and HOOVER 2 over their altitude ranges. On the other hand, observed and modeled HO$_2$ agree to within uncertainties for DC3, HOOVER 2, and INTEX-A up to 8 km, but then observed HO$_2$ grows to exceed modeled HO$_2$ by a factor of 3 at 11 km for INTEX-A, in contrast with both DC3 and HOOVER 2 where observed and modeled HO$_2$ agree to within the combined uncertainties.

One explanation could be the treatment of HO$_2$NO$_2$ formation rate in the model. MCMv3.3.1 uses a reaction rate coefficient that takes the much lower low-temperature reaction rate coefficient of the laboratory study of Bacak et al. (2011) into account, while the JPL evaluation (Burkholder et al., 2015) does not. For DC3, using the MCMv3.3.1 rate coefficient, observed-to-modeled OH and HO$_2$ are 0.85-0.9 at altitudes above 10 km altitude, and modeled HO$_2$NO$_2$ is 1.9 times measured, but if the JPL recommended rate is used, then modeled OH and HO$_2$ both increase by a factor of 1.5 at altitudes above 10 km, shifting the observed-to-modeled ratios to 1.3-1.4, while increasing modeled HO$_2$NO$_2$ to 5-10 times that measured (Fig. S10). The JPL recommended reaction rate coefficient was used in the model for INTEX-A, which could explain some of the difference with DC3, except that observed-to-modeled OH ratio should also be a factor of 3 for INTEX-A. We are left to conclude that either

the INTEX-A HO$_2$ calibration at low pressure was in error or that either the measurements used to constrain the model or the model rate coefficients at low temperature and pressure had errors.

The production rates of HO$_x$ (Fig. S11) and O$_3$ (Fig. S9) are comparable to those found in previous studies (Ren et al., 2008; Olson et al., 2012). Modeled HO$_x$ production is dominated by O$_3$ photolysis below 8 km, as has been previously observed (Regelin et al., 2013), but HCHO photolysis dominates above 10 km. The calculated O$_3$ production rates are also comparable to these other studies, which find production rates of a few ppbv hr^{-1} in the PBL and above 10 km with a small loss at mid-altitude (Fig. S11). A spike in excess of 5 ppbv hr^{-1} was found in a fire plume, where abundances of both VOCs and NO$_x$ were enhanced.

4.2 Effects of Heterogeneous Chemistry on OH and HO$_2$

These DC3 results indicate that a total uptake coefficient is much less than 1 for aerosol. They also suggest that a total uptake coefficient of 0.2 is probably also too high because the model calculates HO$_2$ values that are much lower than observed HO$_2$ when the aerosol surface area concentration was greater than 10^{-6} cm^2 cm^{-3}. In the DC3 environment, HO$_x$ has substantial gas-phase loss pathways, making it difficult for heterogeneous chemistry to be dominant when the model uses an uptake coefficient consistent with laboratory studies, except at the largest aerosol surface area concentrations. For the case with a total uptake coefficient of 0.2, HO$_x$ loss including heterogeneous loss is 1.4 times the gas-phase only loss when the aerosol surface area concentration is 5x10^{-7} cm^{2}cm^{-3}, but grows to 1.5 at 1x10^{-6} cm^{2}cm^{-3} and 2.5 for the few one-minute data points when it is greater than 3x10^{-6} cm^{2}cm^{-3}. This increase in HO$_x$ loss translates into decrease in the modeled HO$_x$, with the decrease changing roughly as the square root of the increase in the HO$_x$ loss.

The DC results can also be compared to other studies of heterogeneous effects on HO$_2$ and OH. In Mauldin et al. (1998), a large difference between the observed and modeled OH was found, but this difference may have been due to the lack of photolysis frequency measurements, which are crucial to test photochemistry in a cloudy environment. In the mountaintop cloud measurements by Whalley et al. (2015), the observed an HO$_2$ uptake in liquid clouds that was much more significant than the HO$_2$ uptake on ice observed for DC3. This difference could be due to the surface area concentrations being up to 100 times larger in their study and the drops being liquid and not ice. Also, they appear to have not considered the substantial decrease in the effective uptake coefficient due to large particle size (Tang et al., 2014). On the other hand, these DC3 results of small cloud impacts on HO$_2$ are consistent with the previous results for the western Pacific Ocean (Olson et al., 2004; Olson et al., 2006).

In other cleaner environments or dirtier environments with much high aerosol surface area concentrations, heterogeneous chemistry can be a substantial fraction of the entire HO$_x$ loss and thus strongly affect HO$_2$ and OH abundances. Measuring OH and HO$_2$ in these environments will provide a better test of the understanding of HO$_2$ heterogeneous chemistry than DC3 did.

5 Conclusions

The general agreement between the observed and modeled OH and HO_2 for the complex DC3 environment is encouraging. It suggests that a photochemical box model can simulate the observed OH and HO_2 to well within combined uncertainties, if properly constrained with measurements of other chemical species, photolysis frequencies, and environmental conditions. On the other hand, it is difficult to explain the unexpected deviations between observed and modeled OH and HO_2, such as is observed in Fig. 8. Neither heterogeneous chemistry nor organic peroxyl chemistry are able to explain these deviations.

There are other possible causes for these discrepancies. First, it can be difficult to maintain instrument calibrations for not only OH and HO_2 but also for all the other measurements that were used to constrain the model to calculate OH and HO_2. Second, the simultaneous measurements need to be properly conditioned so that they can be used as model constraints. This process includes filling in isolated missing values because, if this was not done, the constraining data set would be sparse. For DC3, using the merged data set with no interpolation is less than 10% of the full data set, but the observed and modeled OH and HO_2 have essentially the same relationships as with the interpolated data set (Table S2). Third the model parameters, such as integration times and time intervals, must be set up so that the model calculations represent the observations and their variations. For DC3, the one-minute data are adequate for the timescale of variations for most cases, except in small fire plumes and spikes in lightning NO_x in the anvil. Fourth, multiple methods are needed to determine if differences between observations and model are significant. For DC3, the comparisons between observations and models are robust despite the method of comparison. Thus, none of these appear to be the cause of the unexplained deviations between observed and modeled OH and HO_2.

For DC3 and all previous studies, improvements in the measurements and models would enable better testing of the understanding of atmospheric oxidation chemistry that the model should represent and therefore ultimately improve that understanding. Even with these observed-to-modeled discrepancies, these results provide strong evidence that current photochemical models can generally simulate observed atmospheric oxidation processes even around clouds.

Code Availability

The Matlab code used for the zero-dimensional photochemical box modelling with the MCMv3.3.1 mechanism can be downloaded from the website https://sites.google.com/site/wolfegm/models. The manuscript describing this model is Wolfe, G.M, M.R. Marvin, S.J. Roberts, K.R. Travis, and J. Liao, The Framework for 0-D Atmospheric Modeling (F0AM) v3.1, *Geoscientific Model Development*, 9, 3309-3319, doi: 10.5194/gmd-9-3309-2016, 2016.

Data Availability

The merge file for the DC3 DC-8 data and the updated OH, HO₂, and OH reactivity numbers can be accessed from http://data. eol.ucar.edu/ or http://www-air.larc.nasa.gov/cgi-bin/ArcView/dc3-seac4rs, doi:10.5067/Aircraft/DC3/DC8/Aerosol-TraceGas

5   Author Contribution

All authors contributed DC3 measurements that are critical for the modeling and comparison of modeled and measured OH and HO₂ in this manuscript. W. Brune wrote the manuscript and made edits provided by the co-authors before submitting the manuscript.

Competing Interests

10 The authors declare that they have no conflicts of interest.

Acknowledgments

The Deep Convective Clouds and Chemistry (DC3) experiment is sponsored by the U.S. National Science Foundation (NSF), the National Aeronautics and Space Administration (NASA), the National Oceanic and Atmospheric Administration (NOAA), and the Deutsches Zentrum fuer Luftund Raumfahrt (DLR). Archived field data can be accessed from http://data. eol.ucar.edu/
15 or http://www-air.larc. nasa.gov/cgi-bin/ArcView/dc3-seac4rs. Data provided by NCAR/EOL are supported by the National Science Foundation. Acetone/propanal measurements aboard the DC-8 during DC3 were supported by the Austrian Federal Ministry for Transport, Innovation, and Technology (BMVIT) through the Austrian Space Applications Programme (ASAP) of the Austrian Research Promotion Agency (FFG). Support for ATHOS and OHR measurements aboard the NASA DC-8 during DC3 comes from NASA grant NNX12AB84G. We thank NASA management, pilots, and operations personnel for the
20 opportunity to gather these observations, the people of Salina, KS for hosting us and providing excellent facilities, G. Wolfe for his publically available F0AM model framework, and the University of Leeds for the publically available MCMv3.3.1 photochemical model. We also thank J. Thornton for his insights into HO₂ heterogeneous chemistry, and P. Lawson, P. Wennberg, J. Crounse, and J. St. Clair for the use of their measurements.

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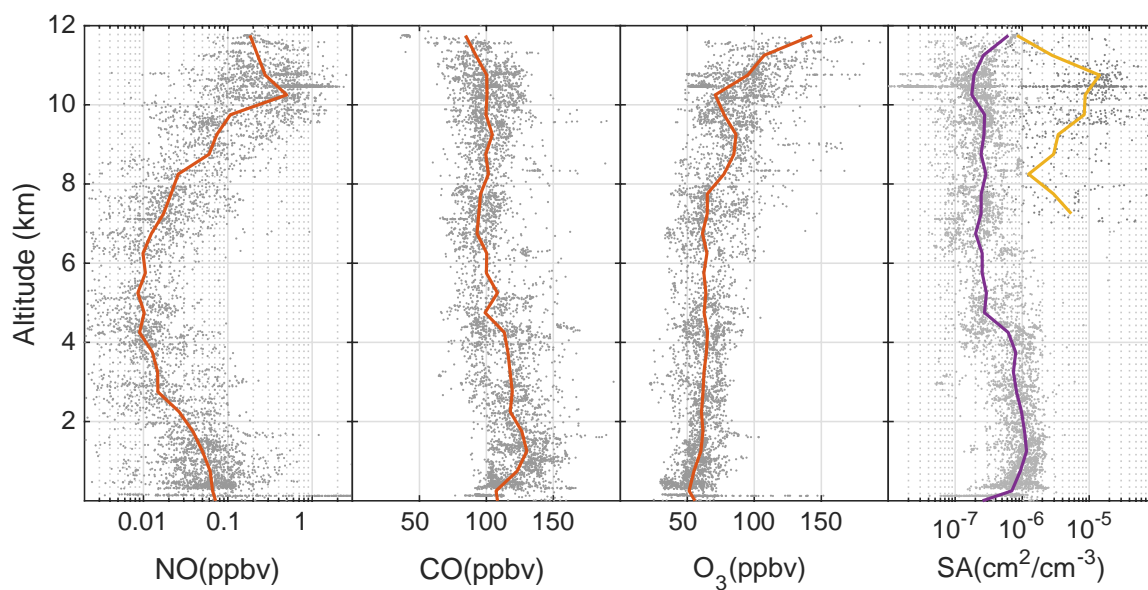
Figure 1. Altitude profiles of median NO, CO, O₃, and aerosol (purple) and ice (yellow) surface area (SA). Grey points are individual one-minute data, while median values are represented by the lines. These data are for the entire DC3 study.
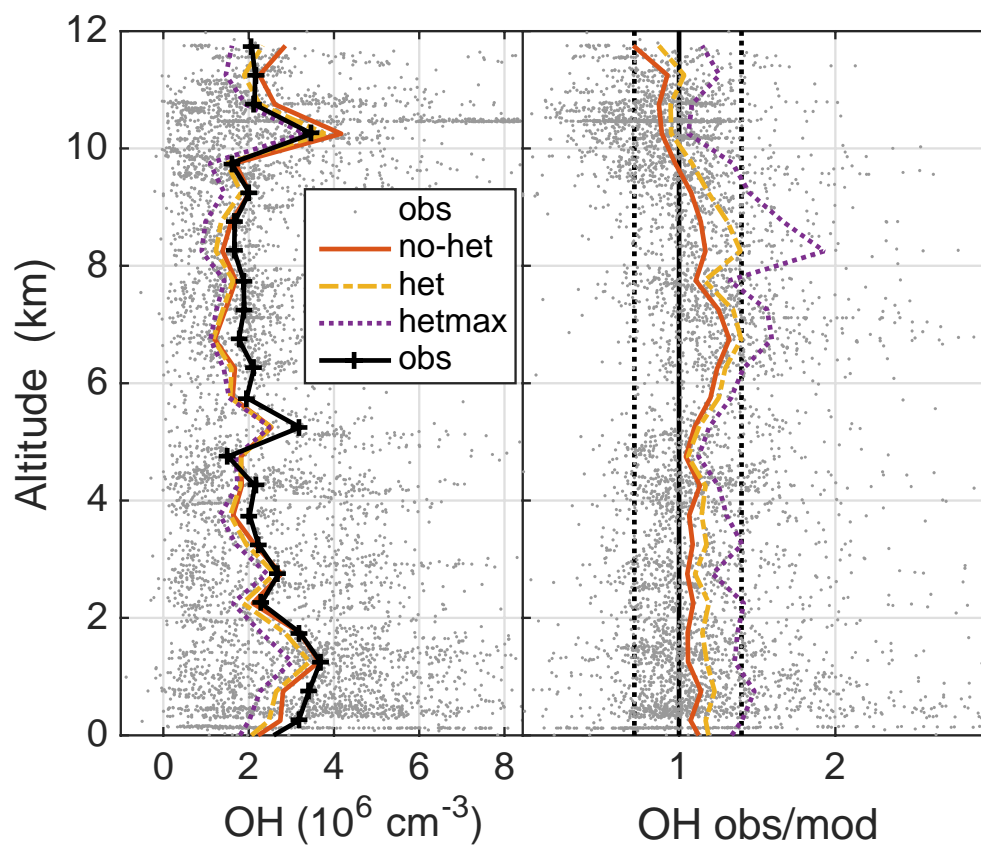
Figure 2. Median measured and modeled OH as a function of altitude (left); median ratio of observed-to-modeled OH as a function of altitude (right) for the three models. Gray points are individual 1-minute OH observations and ratios of observed-to-no-heterogeneous modeled OH. Dotted vertical black lines on right (1/1.4, 1.4) are approximate indicators of measurement-model agreement.
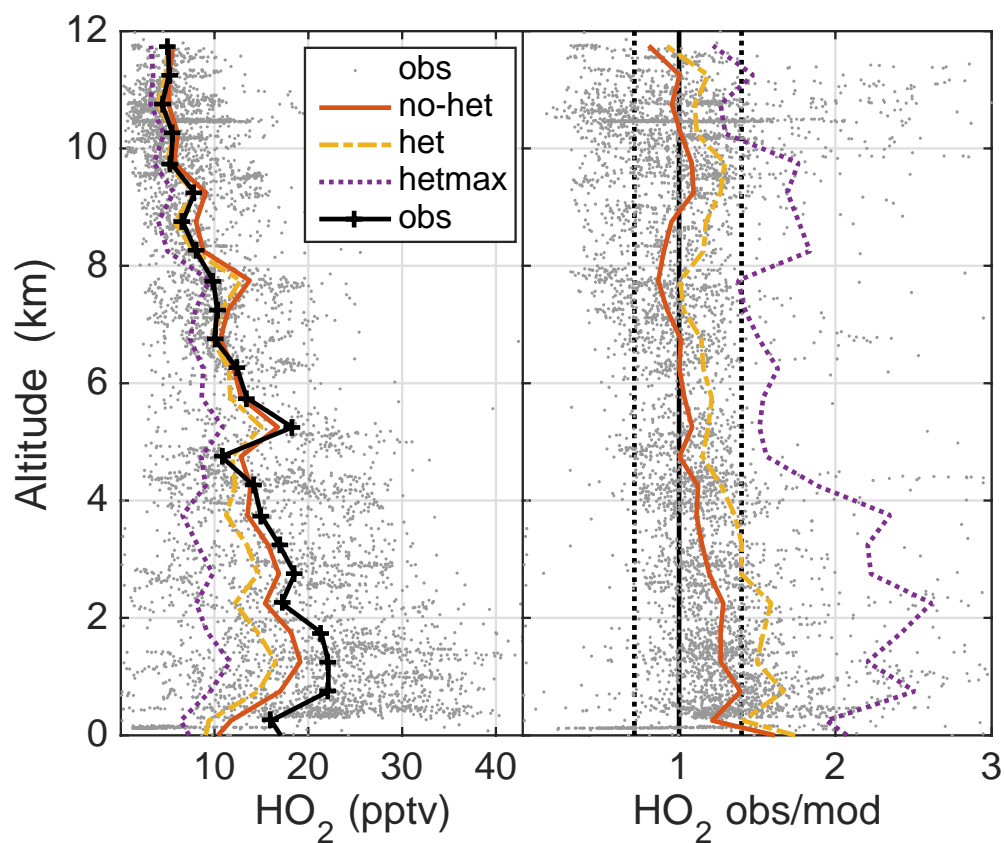
Figure 3. Median measured and modeled HO$_2$ as a function of altitude (left); median ratio of observed-to-modeled HO$_2$ as a function of altitude (right) for the three models. Gray points are individual 1-minute OH observations and ratios of observed-to-no-heterogeneous modeled OH. Dotted vertical black lines on right (1/1.4, 1.4) are approximate indicators of measurement-model agreement.
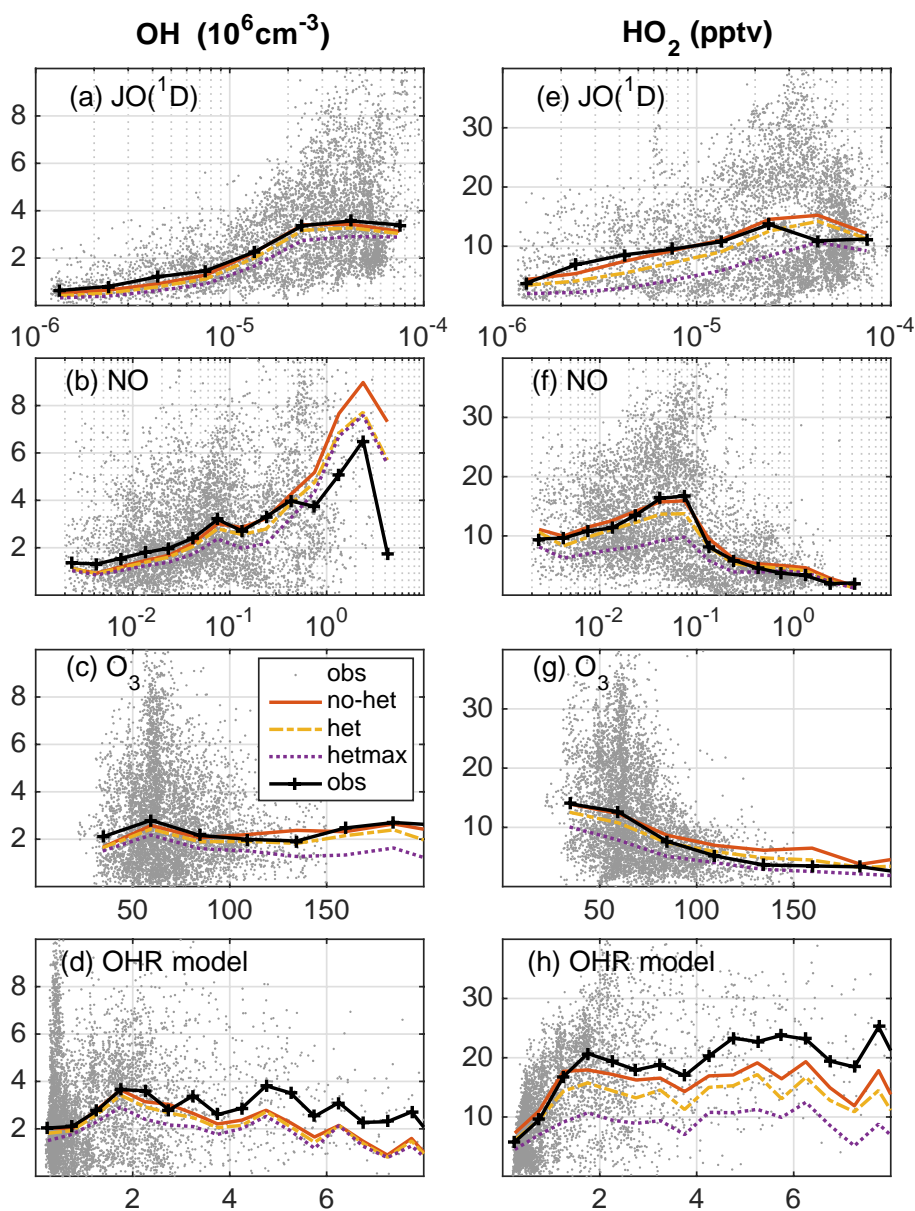
Figure 4. Measured and modeled OH (left) and HO₂ (right) as a function of controlling variables: JO(¹D) in s⁻¹, NO in ppbv, O₃ in ppbv, and modeled OH reactivity in s⁻¹. On the left, OH is in units of 10^6 cm⁻³; on the right, HO₂ is in units of pptv.
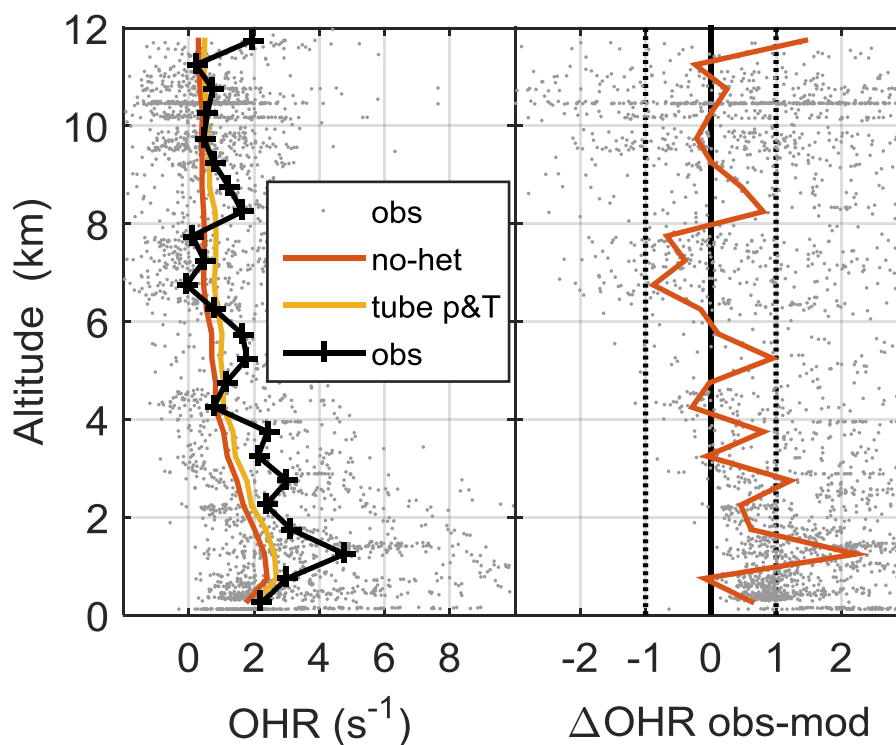
Figure 5. Median observed and model-calculated OH reactivity (left) and the difference between observed and modeled OH reactivity (right). The model-calculated OH reactivity was determined for ambient conditions (no-het) and for the OHR flow tube pressure and temperature (tube p&T). See text for explanation. Dotted vertical black lines on right are approximate indicators of measurement-model agreement.
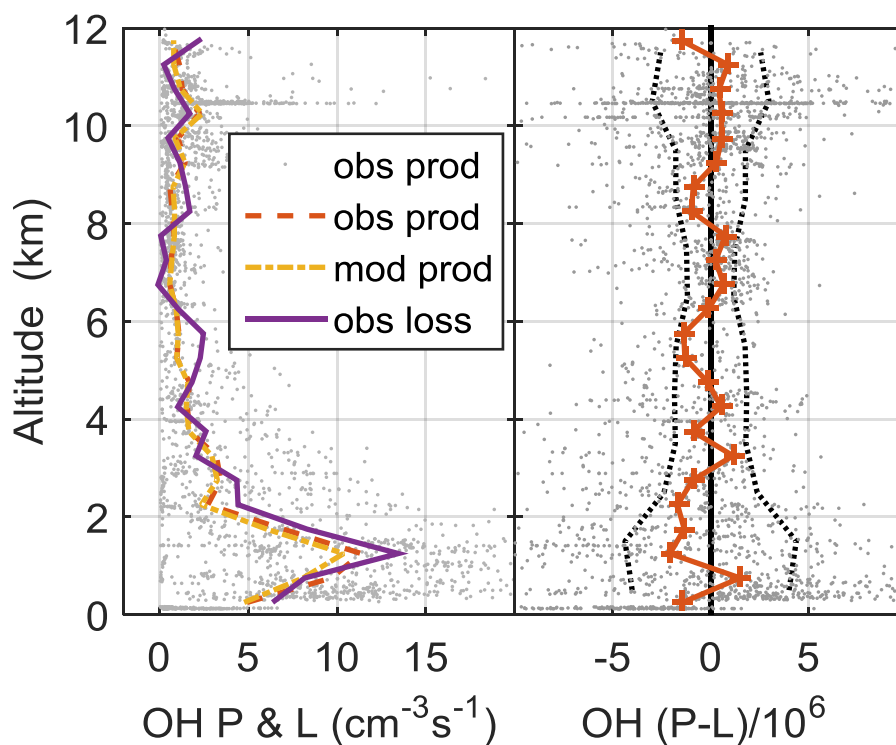
Figure 6. OH production and loss (left) and difference between measured OH production and measured OH loss, cm^{-3}s^{-1} divided by 10^6 (right). Dots are individual one-minute calculations of OH production using observed atmospheric constituents and photolysis frequencies. Dotted vertical black lines on right are indicators of OH production and loss agreement at the 1σ confidence and were determined by a propagation of error analysis.
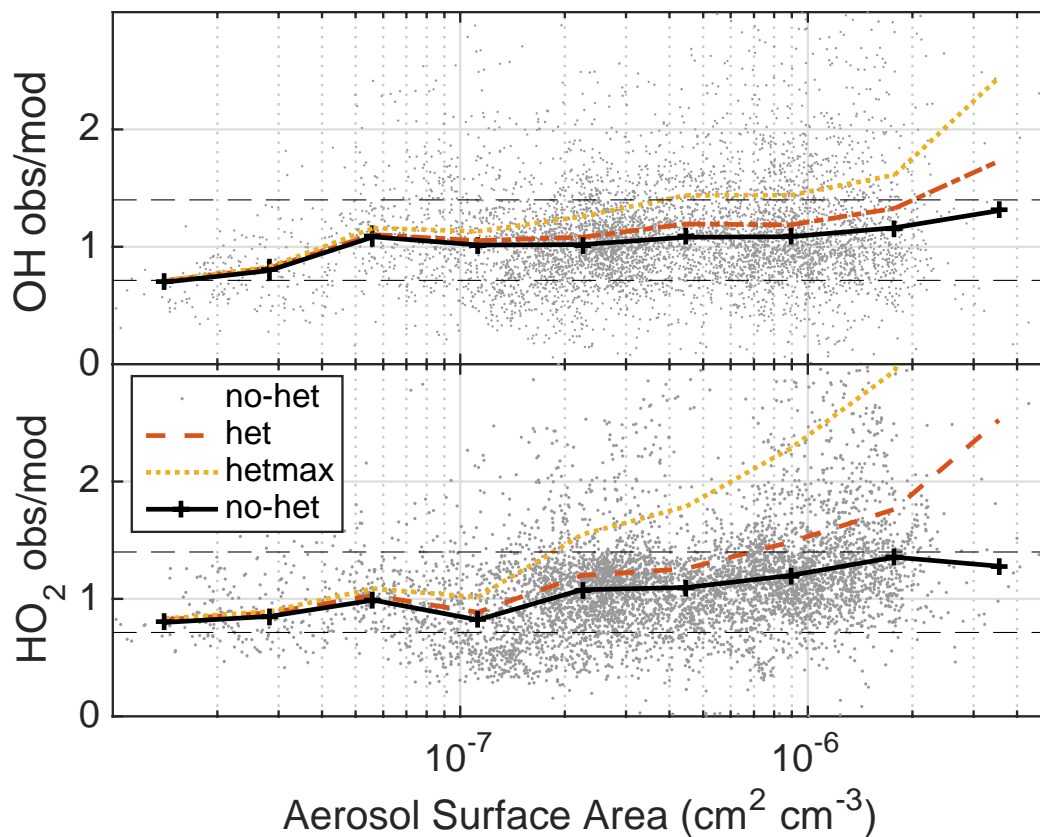
Figure 7. Median observed-to-modeled OH (top) and HO₂ (bottom) versus aerosol surface area concentration. Dotted horizontal black lines are indicators of OH production and loss agreement.
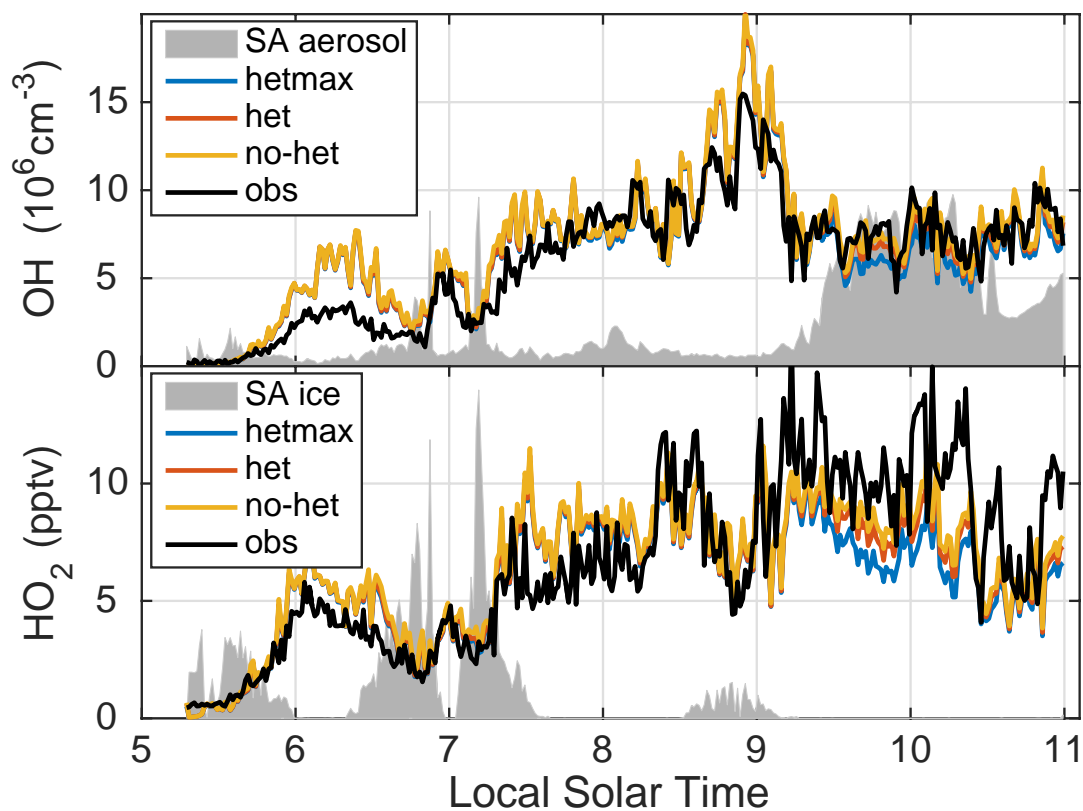
Figure 8. Evolution of OH (top) and HO$_2$ (bottom) downwind of a MCS. The het and hetmax models are essentially identical to the no-het model for this flight except in heavy aerosol from 9 am to 11 am. The gray shading is scaled aerosol surface area (top panel) and is scaled ice surface area (bottom panel).
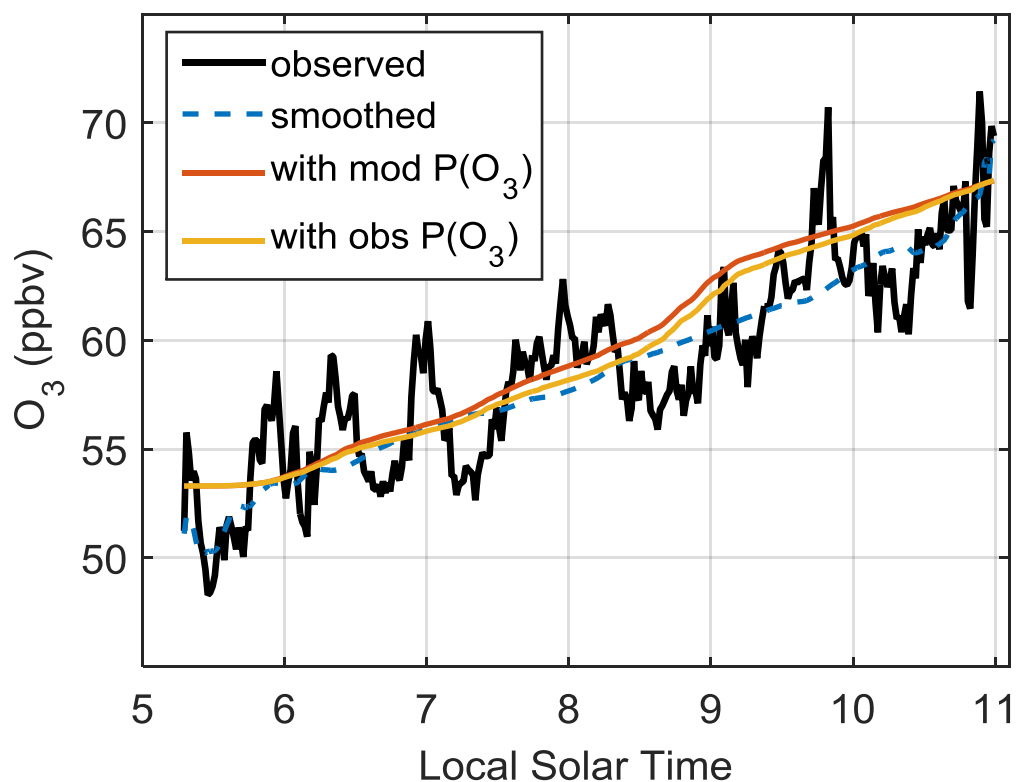
Figure 9. O₃ trend in MCS outflow. Observed O₃ - one-minute data (black line) and smoothed data (dashed blue line, 180-min filter) - show variability along the legs set perpendicular to the air flow and also show the O₃ trend with time. The calculated O₃ uses the accumulated calculated O₃ production rates for observed (yellow) and modeled HO₂ (red) and adds those values to an initial value of 53.4 ppbv to show the calculated O₃ trend.

Table 1. Scatter plot statistics for OH and HO$_2$

case	molecule	units	slope	intercept	R^2	ratio
no-het	OH	10^6 cm^{-3}	1.04	0.02	0.84	1.08
	HO$_2$	pptv	1.07	0.12	0.75	1.14
het	OH	10^6 cm^{-3}	1.12	0.03	0.86	1.16
	HO$_2$	pptv	1.22	0.27	0.69	1.33
hetmax	OH	10^6 cm^{-3}	1.30	0.04	0.84	1.36
	HO$_2$	pptv	1.66	0.42	0.55	1.87