

1 **HO_x Observation and Model Comparison during INTEX-A 2004**

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1 **Abstract.** OH and HO₂ were measured with the Airborne Tropospheric Hydrogen Oxides
2 Sensor (ATHOS) as part of a large measurement suite from the NASA DC-8 aircraft during the
3 Intercontinental Chemical Transport Experiment – A (INTEX-A). This mission, which was
4 conducted mainly over North America and the western Atlantic Ocean in summer 2004, was an
5 excellent test of atmospheric oxidation chemistry. Throughout the troposphere, observed OH was
6 generally 0.60 of the modeled OH; below 8 km, observed HO₂ was generally 0.78 of modeled
7 HO₂. If the over-prediction of tropospheric OH is not due to an instrument calibration error, then
8 it implies less global tropospheric oxidation capacity and longer lifetimes for gases like methane
9 and methyl chloroform than currently thought. This discrepancy falls well outside uncertainties
10 in both the OH measurement and rate coefficients for known reactions and points to a large
11 unknown OH loss. If the modeled OH is forced to agree with observed values by introducing of
12 an undefined OH loss that removes HO_x (HO_x=OH+HO₂), the observed and modeled HO₂ and
13 HO₂/OH ratios are largely reconciled within the measurement uncertainty. HO₂ behavior above 8
14 km was markedly different. The observed-to-modeled HO₂ ratio increased from ~1 at 8 km to
15 more ~2.5 at 11 km with the observed-to-modeled ratio correlating with NO. The observed-to-
16 modeled HO₂ and NO were both considerably greater than observations from previous
17 campaigns. In addition, the observed-to-modeled HO₂/OH, which is sensitive to cycling
18 reactions between OH and HO₂, increased from ~1.2 at 8 km to almost 4 above 11 km. In
19 contrast to the lower atmosphere, these discrepancies above 8 km suggest a large unknown HO_x
20 source and additional reactants that cycle HO_x from OH to HO₂. In the continental planetary
21 boundary layer, the OH observed-to-modeled ratio increased from 0.6 when isoprene was less
22 than 0.1 ppbv to over 3 when isoprene was greater than 2 ppbv, suggesting that forests
23 throughout the United States are emitting unknown HO_x sources. Progress in resolving these

- 1 discrepancies requires further examination of possible unknown OH sinks and HO_x sources and a
- 2 focused research activity devoted to ascertaining the accuracy of the OH and HO₂ measurements.

1 **Index terms:**

2 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry;

3 0368 Atmospheric Composition and Structure: constituent transport and chemistry;

4 0322 Atmospheric Composition and Structure: Constituent sources and sinks;

5 0345 Atmospheric Composition and Structure: Pollution—urban and regional;

6 **Keywords:**

7 hydroxyl radical, hydroperoxyl radical, model comparison, INTEX-A, tropospheric chemistry

1 **1. Introduction**

2 Oxidation chemistry cleanses the atmosphere of chemical emissions from Earth's surface,
3 establishes the global ozone balance, and influences climate change. It is dominated by the
4 hydroxyl radical, OH, but also involves the hydroperoxyl radical, HO₂. OH and HO₂, together
5 called HO_x, are highly reactive atmospheric constituents that have a large impact on the
6 atmospheric chemistry by influencing the removal of gases emitted into the atmosphere and the
7 production of ozone and ultrafine aerosol particles.

8 The basics of HO_x photochemistry have frequently been described [see for example
9 *Jaeglé et al.*, 2000]. The abundance of OH and HO₂ is primarily influenced by the HO_x
10 production rate, the amount of NO_x (NO_x = NO + NO₂), and to some extent the types of
11 hydrocarbons [*Jaeglé et al.*, 2000; *McKeen et al.*, 1997; *Singh et al.*, 1995; 2003]. In polar
12 regions during springtime, halogen chemistry can influence HO_x and the HO₂/OH ratio in both
13 the marine boundary layer [*Sommariva et al.*, 2005] and the stratosphere [*Hanisco et al.*, 2002].

14 HO_x has a number of sources: photolysis of O₃ followed by a reaction of O(¹D) with H₂O,
15 photolysis of formaldehyde (HCHO), hydrogen peroxide (H₂O₂), and methylhydroperoxide
16 (CH₃OOH), as well as reactions between O₃ and alkenes. Its destruction is thought to be
17 controlled by the relatively few reactions: HO₂+HO₂, HO₂+OH, HO₂+RO₂, and OH+NO₂. Under
18 high NO_x conditions, HO_x has a heightened sensitivity to HO_x sources [*Olson et al.*, 2006]. Thus,
19 uncertainties in observations and reaction kinetics of HO_x precursors have a much more
20 pronounced impact on modeled HO_x at high NO_x conditions compared to lower NO_x conditions.

21 The NO_x abundance determines which reactions are the primary HO_x loss. At low NO_x,
22 HO₂ >> OH and the HO₂+HO₂ and HO₂+RO₂ reactions are the primary HO_x loss. As NO_x
23 increases, HO₂+NO→OH+NO₂ increases OH so that the HO₂+OH reaction becomes more

1 important. At high NO_x , $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$ cycles even more HO_x to OH and the reaction
 2 $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$ becomes the primary loss. As a result, for fixed HO_x production
 3 ($P(\text{HO}_x)$), OH first increases until NO_x reaches a few ppbv and then decreases as a function of
 4 NO_x , while HO_2 remains roughly unchanged until NO_x reaches values for which $\text{OH} + \text{NO}_2 + \text{M}$
 5 $\rightarrow \text{HNO}_3 + \text{M}$ is the dominant loss and then decreases even faster than OH as NO_x continues to
 6 increase. As $P(\text{HO}_x)$ increases, the peak OH is higher and shifted to greater NO_x values
 7 [McKeen *et al.*, 1997].

8 Reactions of OH with CO and volatile organic compounds (VOCs) lead to the formation
 9 of HO_2 and peroxy radicals (RO_2). This conversion of OH is rapid. The inverse of the OH
 10 lifetime, the reaction frequency, which is usually called the OH reactivity, is typically 1 s^{-1} in
 11 clean environments and $5\text{-}100 \text{ s}^{-1}$ in polluted urban environments. At the same time, HO_2 reacts
 12 with NO, producing O_3 , or with O_3 , destroying O_3 , and in the process recreates OH. This cycle
 13 between OH and HO_2 is at times faster than the production and loss of HO_x . The reaction of RO_2
 14 and NO leads to the formation of HO_2 and NO_2 . The exact photochemistry that occurs depends
 15 mainly on the HO_x production ($P(\text{HO}_x)$), NO_x , the OH reactivity, and the yield of HO_2 and RO_2
 16 from hydrocarbon oxidation [Kleinman *et al.*, 2002]. Understanding HO_x sources, sinks, and
 17 cycling is essential to develop predictive capability of pollution's influence on the atmosphere's
 18 oxidation capacity.

19 The ratio of HO_2/OH is an important indicator of the HO_x cycling between OH and HO_2 .

20 A steady-state expression for HO_2/OH comes from assuming that OH is in steady-state:

$$21 \quad \frac{[\text{HO}_2]}{[\text{OH}]} = \frac{k_{\text{OH}}}{(k_{\text{NO}+\text{HO}_2}[\text{NO}] + k_{\text{O}_3+\text{HO}_2}[\text{O}_3]) + P(\text{OH})_{\text{primary}}/[\text{HO}_2]} \quad (1)$$

22

1 where $P(\text{OH})_{\text{primary}}$ is the OH production rate from either photolysis of long-lived atmospheric
2 constituents or from reactions of O_3 with alkenes; $(k_{\text{NO}+\text{HO}_2}[\text{NO}] + k_{\text{O}_3+\text{HO}_2}[\text{O}_3])$ represents the
3 cycling reaction frequency of HO_x from HO_2 to OH; and k_{OH} is the OH reactivity with all
4 reactants, whether they be HO_x cycling or HO_x terminating reactions. We use the definition for
5 primary OH sources to be those that are independent of local HO_x [Jaeglé *et al.*, 2001]. Typically
6 the photolysis of O_3 followed by $\text{O}(^1\text{D})+\text{H}_2\text{O}$ is the most important OH primary source, although
7 the photolysis of H_2O_2 and CH_3OOH can also be important.

8 For many atmospheric environments, the primary production, $P(\text{OH})_{\text{primary}}$, and the
9 terminating OH reaction rates are much smaller than the rate of reactions that cycle HO_x between
10 OH and HO_2 and can be ignored. However, for the free troposphere between 2 km and 8 km in
11 INTEX-A, the fraction of OH production by $P(\text{OH})_{\text{primary}}$ is as often larger than OH production
12 by HO_x cycling, ranging from 0.1 to 0.9, and cannot be ignored.

13 Because HO_x photochemistry is sufficiently fast, comparisons with box models test the
14 understanding of HO_x photochemistry. While scatter plots of measurements and model
15 calculations are useful, examining the ratio of observed-to-modeled OH and HO_2 as a function of
16 important variables provides even more information. The analyses of airborne tropospheric HO_x
17 measurements from several different studies have been published [e.g., Wennberg *et al.*, 1998;
18 Crawford *et al.*, 1999; Brune *et al.*, 1998; 1999; Tan *et al.*, 2001a; Olson *et al.*, 2004; 2006].
19 When all of the studies are taken together, we can reach the conclusion that HO_x photochemistry
20 is generally understood to within about a factor of two, but that important larger differences
21 remain for some environments and conditions.

22 Considering the role of OH and HO_2 in the production of secondary pollutants and the
23 role of OH in the atmosphere's oxidation capacity, a factor of two is far from good enough.

1 Emerging from HO_x studies are a set of conclusions: (1) HO₂, and thus ozone production, is
2 greater than expected at larger NO values for many tower-based studies and some aircraft studies,
3 even though this discrepancy has been almost eliminated for two previous aircraft studies by
4 reanalyses that more fully account for HO_x precursors and have updated reaction rate coefficients
5 and products [Olson *et al.*, 2006]; (2) HO₂ and OH are larger than expected at high solar zenith
6 angles, as in the Subsonic Assessment: Ozone and Nitrogen Oxide Experiment (SONEX)
7 [Faloona *et al.*, 2000]; (3) the evidence for heterogeneous influence on HO_x is still inconclusive
8 although some studies have provided evidence for significant removal in clouds [Olson *et al.*,
9 2006]; (4) even with highly constraining measurement suites, OH and HO₂ can be either
10 significantly larger or smaller than expected in different environments and on different missions;
11 whether this variation in agreement is due to unmeasured atmospheric constituents, instrumental
12 drifts and changes, or differences in models, or a combination of all three, is not known; (5)
13 agreement between instruments has been inconsistent from comparison to comparison [Eisele *et*
14 *al.*, 2001; 2003; Ren *et al.*, 2003].

15 The Intercontinental Chemical Transport Experiment – A (INTEX-A) was an integrated
16 field experiment performed over North America in summer of 2004. It sought to understand the
17 transport and transformation of gases and aerosols on transcontinental/intercontinental scales and
18 their impact on air quality and climate. A particular focus in this study was to quantify and
19 characterize the inflow and outflow of pollution over North America. The main constituents of
20 interest are ozone and precursors, aerosols and precursors, and long-lived greenhouse gases.
21 Details about the overview and accomplishments of INTEX-A are described by Singh *et al.*
22 [2006]. A broad suite of trace gases including OH and HO₂ radicals and their precursors,
23 aerosols, and meteorological parameters were sampled *in situ* from NASA's DC-8.

1 The DC-8 encountered a variety of air masses. These include air masses that were
2 influenced by anthropogenic pollution, biomass burning, convection, the stratosphere, and
3 mixtures of these different types. These plumes are often distinguishable by their characteristic
4 composition. Anthropogenic pollution contains high CO, anthropogenic hydrocarbons, and often
5 water vapor. Biomass burning plumes can be distinguished from anthropogenic pollution by high
6 HCN and acetonitrile. Convection plumes can be distinguished by high NO_x/NO_y ratios, water
7 vapor, ultrafine particles, and ozone. Stratosphere-influenced air can be defined as air having O₃
8 greater than ~100 ppbv, CO less than ~100 ppbv, water vapor less than 200 ppmv, and low
9 hydrocarbon levels. The different composition of these air masses provides an excellent
10 opportunity to examine HO_x photochemistry for a range of conditions.

11 This paper presents HO_x observation results and a steady state modeling analysis of fast
12 photochemistry using measurements made during the INTEX-A campaign. The HO_x results from
13 INTEX-A are compared to those from previous campaigns and to results for other related
14 measurements from INTEX-A. These analyses provide evidence for the accuracy of the HO_x
15 measurements and for the characteristics of atmospheric processes or constituents that are not
16 incorporated in current models.

17

18 **2. Experiment and Model Description**

19 **2.1 OH and HO₂ Measurements**

20 The OH and HO₂ radicals were measured with the Penn State ATHOS (Aircraft
21 Tropospheric Hydrogen Oxides Sensor). ATHOS detects OH and HO₂ with laser-induced
22 fluorescence (LIF). The technique uses a pump-down technique often called the fluorescent
23 assay by gas expansion (FAGE) originally developed by *Hard et al.* [1984]. A detailed

1 description of the ATHOS instrument can be found elsewhere [*Faloona et al.*, 2004]; here an
2 abbreviated description of ATHOS is given.

3 The air sample is drawn into a low-pressure chamber through a pinhole inlet (1.5 mm)
4 with a vacuum pump. The pressure of the detection chamber varied from 12 to 3 hPa from 0 to
5 12 km altitude. As the air passes through a laser beam, OH is excited by a spectrally narrowed
6 laser with a pulse repetition rate of 3 kHz at one of several ro-vibronic transition lines near 308
7 nm ($A^2\Sigma-X^2\Pi$, $v'=0 \leftarrow v''=0$). Collisional quenching of the excited state is slow enough at the
8 chamber pressure that the weak OH fluorescence extends beyond the prompt scattering
9 (Rayleigh and wall scattering) and is detected with a time-gated microchannel plate (MCP)
10 detector. HO₂ is measured by reaction with NO followed by the LIF detection of OH. The OH
11 and HO₂ detection axes are in series: OH is detected in the first axis and HO₂ in a second axis as
12 reagent NO (>99%, Matheson, Twinsburg, OH, purified through Ascarite) is added to the flow
13 between the two axes. The OH fluorescence signal is detected 60 ns after the laser pulse has
14 cleared in the detection cells and is recorded every 0.2 seconds. The laser wavelength is tuned on
15 and off resonance with an OH transition every 10 seconds, resulting in a measurement time
16 resolution of 20 seconds. The OH fluorescence signal is the difference between on-resonance and
17 off-resonance signals.

18 The instrument was calibrated both in the laboratory and during the field campaign.
19 Monitoring laser power, Rayleigh scattering, and laser linewidth maintained this calibration in
20 flight [*Faloona et al.*, 2004]. For the calibration, water vapor photolysis by 185 nm light
21 produced OH and HO₂. Absolute OH and HO₂ mixing ratios were calculated by knowing the 185
22 nm flux, which is determined with a Cs-I phototube referenced to a NIST-calibrated
23 photomultiplier tube from the University of Colorado, the H₂O absorption cross section, the H₂O

1 mixing ratio, and the exposure time of the H₂O to the 185 nm light. The absolute uncertainty is
2 estimated to be a factor of 1.32 for both OH and HO₂, with a 2σ confidence level. The 2σ
3 precisions during this campaign were about 0.01 pptv for OH and 0.1 pptv for HO₂, with 1
4 minute integration time. Further details about the calibration process may be found elsewhere
5 [*Faloona et al.*, 2004].

6

7 **2.2 Other Measurements on the DC-8**

8 The payload of the DC-8 and the measured chemical species and parameters are briefly
9 described in *Singh et al.* [2006]. A large suite of atmospheric constituents were measured in
10 INTEX-A, including CO, O₃, H₂O, reactive nitrogen (NO, NO₂, HNO₃, HO₂NO₂, PAN), more
11 than 50 VOCs and OVOCs, and important HO_x precursors such as peroxides (H₂O₂ and
12 CH₃OOH) and aldehydes (HCHO and acetaldehyde). Spectral radiometers allowed direct
13 measurement of actinic flux used to derive key photolysis frequencies.

14 During INTEX-A, NO was measured by a commercial NO-NO_x analyzer (Model TEI
15 42C) based on the chemiluminescence technique because of problems with the primary NO
16 instrument. The commercial NO-NO_x analyzer was operated in NO only mode. A separate *in situ*
17 NO calibration system aboard the DC-8 was used for frequent NO span and background checks.
18 The detection limit of this instrument was about 50 pptv with 1 minute integration time. Due to
19 this relatively high detection limit, measurements of NO₂ were used to constrain the model rather
20 than using measurements of NO. Predictions of NO proved to be generally in good agreement
21 with measurements. A linear regression of the NO obtained from measurements and the model is
22 the equation: $\text{NO}_{\text{modeled}} = 0.92 \times \text{NO}_{\text{measured}} - 16 \text{ pptv}$, with $R^2 = 0.76$. This gives confidence that
23 NO from the model can be used at low NO, where the NO measurement is noisy and may have a

1 small offset, and at high NO, where NO obtained from measurements and from the model are in
2 excellent agreement.

3

4 **2.3 Model Description**

5 A zero-dimensional, time-dependent photochemical box model developed at NASA
6 Langley Research Center was used to calculate OH, HO₂ and other reactive intermediates. The
7 model has been described in detail in several previous studies [e.g., *Crawford et al.*, 1999; *Olson*
8 *et al.*, 2004]. The modeling approach is based on the assumption of a diurnal steady state, which
9 means that the model is integrated in time until the diurnal variation for all calculated species no
10 longer changes from day-to-day. For input, model calculations use observations from the 1-min
11 merged data set available on the INTEX-A public data archive ([ftp://ftp-](ftp://ftp-air.larc.nasa.gov/pub/INTEXA/)
12 [air.larc.nasa.gov/pub/INTEXA/](ftp://ftp-air.larc.nasa.gov/pub/INTEXA/)). The minimum set of input constraints includes observations of
13 O₃, CO, NO₂, NMHC, acetone, methanol, temperature, H₂O (dew/frost point), pressure, and
14 photolysis frequencies. For this analysis, analyzed data were limited to solar zenith angles (SZA)
15 between 0° and 85°.

16 In addition to the required constraints described above, the model has the option to
17 include additional constraints when measurements are available for hydrogen peroxide (H₂O₂),
18 methyl hydrogen peroxide (CH₃OOH), nitric acid (HNO₃), and peroxy acetyl nitrate (PAN). If
19 unavailable, these atmospheric constituents are calculated by the model based on diurnal steady
20 state. While each of the H₂O₂, CH₃OOH, HNO₃, or PAN measurements are missing for 20%-
21 35% of the measurement times, the full suite is missing less than 2% of the measurement times.
22 Model calculations taking advantage of these additional constraints are referred to as
23 “constrained.” For the purpose of model-to-measurement comparisons, an unconstrained version

1 was also run for which none of the additional constraints were exercised; i.e., the peroxides,
2 PAN, and HNO₃ were always predicted.

3 Neither the unconstrained model nor the constrained model was constrained to the
4 measured HCHO, just as was done for previous campaigns. Rather, HCHO is used as an
5 additional species for which comparisons between the observations and model may provide
6 insight into current knowledge of photochemical cycling. Evidence suggests that the differences
7 in the observed and modeled HCHO do not influence the comparisons between observed and
8 modeled OH, HO₂, and HO₂/OH [Olson *et al.*, 2004]. The HO_x results described in this
9 manuscript do not correlate with the deviations between the observed and modeled HCHO.

10 In order to maximize the number of points available for modeling, nonmethane
11 hydrocarbons were interpolated between consecutive grab samples, which were collected
12 throughout each flight at a frequency of every 4-5 minutes during horizontal flight legs and every
13 1-2 minutes during ascents and descents. Similarly, acetone and methanol were interpolated
14 between adjacent measurements to fill data gaps.

15 As in previous studies, photolysis frequencies were based on spectroradiometer
16 measurements [Shetter and Muller, 1999]. The diurnal profile for each photolysis frequency is
17 based on clear-sky model calculations using a DISORT eight-stream implementation of the
18 NCAR Tropospheric Ultraviolet Visible (TUV) radiative transfer code [Madronich and Flocke,
19 1998]. The clear-sky diurnal variation from TUV is then normalized to measured photolysis
20 frequencies at the time of observation. Unmeasured photolysis frequencies were first calculated
21 for clear sky conditions and then corrected for ambient cloud conditions based on the ratio of
22 measured-to-calculated photolysis frequency of NO₂.

1 The uncertainties in the modeled OH and HO₂ are based on the combined uncertainties of
2 the kinetic rate coefficients, the measured chemical concentrations, and the measured and
3 calculated photolysis frequencies. The uncertainties in the model due to kinetic rate constant
4 uncertainties were estimated with a Monte Carlo approach [*Thompson and Stewart, 1991;*
5 *Carslaw et al., 1999*]. The 2σ uncertainty was estimated to be ±59% for OH and ±53% for HO₂
6 in the upper troposphere, and ±28% for OH and ±24% for HO₂ in the boundary layer.

8 **3. Observations, Model Results, and Comparisons**

9 **3.1 HO_x Observations and Comparison with the Model Calculations**

10 Altitude profiles of observed OH and HO₂ spanned from a few hundred meters above the
11 surface to almost 12 km (Figure 1). Median OH was relatively constant at 0.2 pptv from altitudes
12 near the surface to 6 km, but then increased with altitude above 6 km, achieving a maximum of
13 about 0.5 pptv at 12 km. HO₂ decreased as the altitude increased, with a maximum median of
14 ~20 pptv near the surface and a minimum median of ~5 pptv at the highest altitude. The greatest
15 HO₂, almost 60 pptv, was observed just above the surface over the central United States. The
16 median HO₂/OH ratio dropped from 120 near the surface to 12 above 10 km, driven by both the
17 decrease in HO₂ and the increase in OH with altitude. At low altitudes, the spread in HO₂/OH is
18 quite large – from 20 to 300 – indicating a wide range of air composition there.

19 Overall comparisons of observed and modeled OH and HO₂ show that on average
20 observed OH and HO₂ are less than modeled OH and HO₂, but at lower HO_x mixing ratios,
21 observed OH and HO₂ generally exceeded the modeled OH and HO₂ (Figure 2). For the smallest
22 HO_x values, the observed HO_x exceeds the modeled HO_x by more than the combined 1-σ
23 uncertainties of the model and observations. However, for larger HO_x values, the modeled HO_x

1 exceeds the observed HO_x by more than the combined $1\text{-}\sigma$ uncertainties. Because the lower HO_x
2 mixing ratios were mostly observed at high altitudes, these plots suggest that the behavior of
3 HO_x should be investigated as a function of altitude.

4 Detailed statistics characterize the behavior of the observed-to-modeled ratios as a
5 function of altitude for OH, HO_2 , and HO_2/OH (Table 1). The “% within $\pm 32\%$ ” is the
6 percentage of model values that are the same as the measured values to within the measurement
7 2σ uncertainty, the “% mod>obs x 1.32” is the percentage of model values greater than 1.32
8 times the observed values, and the “% mod<obs/1.32” is the percentage of model values less than
9 the observed values divided by 1.32. Although the model also has uncertainty, using the 2σ
10 measurement uncertainty provides a good indication of the differences between the observed and
11 modeled values and where they are occurring.

12 OH is generally over-predicted by the model at all altitudes, with roughly two-thirds of
13 the modeled values exceeding observations by more than the 2σ measurement uncertainty ($\pm 32\%$)
14 (Table 1, Figure 3). The large over-prediction of OH is not specific to this model, but is seen
15 with other models as well [*Hudman et al.*, 2006]. For a smaller number of observations, OH is
16 under-predicted in continental boundary layer and in a few plumes at higher altitudes. The under-
17 prediction in the boundary layer correlates strongly with isoprene and will be discussed in detail
18 later.

19 HO_2 is generally over-predicted below 8 km but is generally under-predicted above 8 km
20 (Table 1, Figure 4). The over-prediction is not as great as for OH and the percentage of modeled
21 values exceeding 1.32 x observed values is less. Large under-predictions of HO_2 in the upper
22 free troposphere above 8 km are highly correlated with NO and will be discussed in detail later.

1 The HO₂/OH ratio is generally under-predicted throughout the troposphere (Table 1,
2 Figure 5). Below 8 km, the median observed-to-modeled ratio is less than 1.2, close to but
3 slightly exceeding the 2σ uncertainty of the relative measurements of HO₂ and OH, which is
4 ~15%. Median values of the HO₂/OH observed-to-modeled ratio is biased slightly high since OH
5 over-predictions are more severe than those for HO₂. Above 8 km, the large differences in the
6 observed-to-modeled HO₂/OH are driven more by the differences in observed-to-modeled HO₂
7 than they are in the differences between the observed-to-modeled OH.

8

9 **3.2 Comparisons of Observed and Modeled HO_x with Previous Studies**

10 ATHOS has measured OH and HO₂ during several recent field studies. The three most
11 recent are the Pacific Exploratory Mission Tropics – B (PEM-TB) [Raper *et al.*, 2001], TRACE-
12 P [Jacob *et al.*, 2003], and INTEX-A [Singh *et al.*, 2006]. PEM-TB was conducted in the tropical
13 Pacific, usually in relatively clean air. In contrast, TRACE-P was conducted off the coast of Asia
14 in air that was often quite polluted. Both occurred in spring and provide an interesting contrast to
15 INTEX-A, which was conducted either over the continental US or over the Atlantic Ocean
16 downwind of it in summer. Comparisons of these three studies are particularly compelling
17 because ATHOS was used to measure OH and HO₂ in all three and OH, HO₂, and HCHO for
18 several previous missions including PEM-TB and TRACE-P were recently recalculated using the
19 same photochemistry and constraints as were used for INTEX-A [Olson *et al.*, 2006].

20 The behavior of atmospheric constituents that interact with OH and HO₂ is quite different
21 for the three studies (Figure 6). Carbon monoxide (CO) is similar for TRACE-P and INTEX-A,
22 except at lower altitudes where Asian pollution observed during TRACE-P contained much more
23 CO than North American pollution observed during INTEX-A did. CO in both northern

1 hemisphere studies are roughly twice that observed in PEM-TB. Ozone (O_3) is similar for
2 INTEX-A and TRACE-P up to ~ 8 km, where O_3 in INTEX-A continues to increase. O_3 in PEM-
3 TB is less than half these other two studies. The greatest differences were with NO_x . Observed
4 NO_x was more than four to five times larger during INTEX-A than during TRACE-P and more
5 than an order of magnitude larger than during PEM-TB. These differences are most pronounced
6 above 8 km, where NO_x during INTEX-A was sometimes more than 1.5 ppbv.

7 The conditions among the three studies are so different. It is therefore instructive to
8 compare not only the absolute values of OH, HO_2 , and the HO_2/OH ratio, but also the ratios of
9 the measured-to-modeled OH, HO_2 , and HO_2/OH ratio for the three studies. These are plotted as
10 a function of the controlling environmental factors such as altitude (Figures 3, 4, and 5) and NO
11 (Figure 7).

12

13 **3.2.1 Comparison as a Function of Altitude**

14 The median observed-to-modeled OH ratio in INTEX-A is similar to that observed in
15 TRACE-P. On the other hand, the median observed-to-modeled OH ratio in INTEX-A is quite
16 different from that in PEM-Tropics B, where it was ~ 0.6 only below 1 km; above that, the
17 median observed-to-modeled OH ratio increases monotonically to 1.3 at 12 km.

18 The observed-to-modeled HO_2 ratio has quite different behavior as a function of altitude
19 in INTEX-A compared to that in either TRACE-P or PEM-TB. For altitudes below 8 km, the
20 observed-to-modeled HO_2 ratio is similar for INTEX-A and TRACE-P, both being less than 1,
21 whereas the observed-to-modeled HO_2 ratio was close to 1 for PEM-TB. In all three studies, the
22 ratio changed little over this altitude range. The large increase in the observed-to-modeled HO_2
23 ratio above 8 km is quite different from either TRACE-P or PEM-TB. This difference is

1 consistent with the substantially greater NO_x observed above 8 km during INTEX-A than during
2 the other two studies.

3 Enhanced NO_x was also observed during SUCCESS (Subsonic aircraft; Contrails and
4 Clouds Effect Special Study), both in and out of aircraft exhaust plumes. The ability to
5 conclusively analyze the observations made in the exhaust plumes was limited by sampling with
6 insufficient resolution to appropriately model nonlinear HO_x - NO_x interactions [Olson *et al.*,
7 2006]. For the SUCCESS observations not impacted directly by aircraft exhaust, a tendency for
8 significant deviation between modeled and observed HO_2 remains [Brune *et al.*, 1998]. However,
9 the lack of measurements of several potentially important HO_x precursors limits what can be said
10 with confidence about the under-predicted HO_2 that was observed during SUCCESS.

11 Similar behavior was observed during TRACE-P, where a subset of the TRACE-P
12 observations in stratospherically influenced air above 9 km near 35°N had an observed-to-
13 modeled HO_2 ratio of 1.6 [Olson *et al.*, 2004]. However, unlike TRACE-P, where the observed-
14 to-modeled ratio was significantly greater than 1 only in stratospherically influenced air, 92% of
15 the INTEX-A observations with an observed-to-modeled HO_2 ratio significantly greater than 1
16 were in tropospheric air that was not obviously influenced by the stratosphere. Thus this INTEX-
17 A result appears to be unprecedented.

18 The behavior of the observed-to-modeled HO_2/OH ratio is different in all three studies.
19 For PEM-TB, the observed-to-modeled ratio near 1 at lower altitudes, but above 6 km begins to
20 decrease, reaching 0.6 near 12 km. For TRACE-P, the opposite occurs; the ratio is slightly below
21 1 at low altitudes, but then increases to about 1.4 above 7 km. The INTEX-A observed-to-
22 modeled HO_2/OH ratios greater than 2 at altitudes above 8 km were not observed in the other

1 studies. The large increase in the observed-to-modeled HO₂/OH ratio at altitudes above 8 km is
2 driven more by the under-predicted HO₂ rather than the over-predicted OH.

3

4 **3.2.2 Comparison as a Function of NO**

5 Both OH and HO₂ qualitatively show the expected behavior as a function of NO for
6 INTEX-A (Figure 7), although important quantitative differences occur. For OH, the observed-
7 to-modeled ratios for PEM-TB, TRACE-P, and INTEX-A are fairly constant with increasing NO,
8 even though they are less than 1 for TRACE-P and INTEX-A. In the cleanest conditions, the
9 ratios are close to 1 for both PEM-TB and TRACE-P. The two ratios then diverge until NO ~100
10 pptv, where they once again converge. Interestingly, for PEM-TB, the observed-to-modeled OH
11 ratio of ~0.6 that occurs for NO > 100 pptv came from only a few hours of observations on one
12 flight when the DC-8 was downwind of recent convection over the Pacific Ocean. These few
13 measurements provide additional evidence that the chemistry associated with convection may be
14 responsible for over-predicted OH in the free troposphere.

15 The observed-to-modeled HO₂ ratio increases from values below and near 1 to values
16 more than 1 when NO is more than a few hundred pptv in all three studies, although the amount
17 of change is different for the three studies. It is worth noting that the highest NO values were
18 observed in the upper troposphere during INTEX-A, while the highest NO values were observed
19 in boundary layer during TRACE-P.

20

21 **3.3 HO_x Budget Calculations**

22 Examining the HO_x production and loss provides information about the balance between
23 HO_x sources and sinks. The HO_x production consists of the production from the following

1 processes: O₃ photolysis followed by the O(¹D)+H₂O reaction, HCHO photolysis (the radical-
 2 produced pathway only), H₂O₂ photolysis, and the ozonolysis of alkenes. HO_x loss includes the
 3 OH reaction with NO₂ and the reactions among OH, HO₂ and RO₂. For this discussion, RO₂ was
 4 calculated by the box model.

5 The main P(HO_x) was the reaction O¹D+H₂O below 7 km and the photolysis of HCHO
 6 above 7 km (Figure 8(a)). Photolysis of H₂O₂ did not contribute much to P(HO_x). For the HO_x
 7 loss, HO₂-RO₂ self-reactions were the main processes below 8 km and the OH+NO_x reactions
 8 became the main loss processes above 8 km (Figure 8(b)).

9

10 **3.4 Diurnal Average of Calculated Ozone Production**

11 The net ozone production in the troposphere is given to a close approximation by

$$\begin{aligned}
 12 \quad P(\text{O}_3)_{\text{net}} = P(\text{O}_3) - L(\text{O}_3) = & k_{\text{NO}+\text{HO}_2} [\text{NO}][\text{HO}_2] + \sum_i k_{\text{NO}+\text{RO}_{2i}} [\text{NO}][\text{RO}_{2i}] \\
 13 \quad & - k_{\text{OH}+\text{NO}_2+\text{M}} [\text{M}][\text{NO}_2][\text{OH}] - k_{\text{O}^1\text{D}+\text{H}_2\text{O}} [\text{O}^1\text{D}][\text{H}_2\text{O}] \quad (2) \\
 14 \quad & - k_{\text{HO}_2+\text{O}_3} [\text{O}_3][\text{HO}_2] - k_{\text{OH}+\text{O}_3} [\text{O}_3][\text{OH}]
 \end{aligned}$$

15

16 where $k_{\text{NO}+\text{HO}_2}$, $k_{\text{NO}+\text{RO}_{2i}}$, $k_{\text{OH}+\text{NO}_2+\text{M}}$, $k_{\text{O}^1\text{D}+\text{H}_2\text{O}}$, $k_{\text{HO}_2+\text{O}_3}$, and $k_{\text{OH}+\text{O}_3}$ are reaction rate coefficients.

17 The diurnally averaged values of the ozone production and loss terms come from the time-
 18 dependent model simulations. In order to determine the O₃ budget based on observed values of
 19 HO_x, the model was run with the computed diurnal profiles of OH and HO₂ scaled throughout
 20 the diurnal cycle to match the observed concentrations at the appropriate time of day. The
 21 resulting calculated O₃ production was mainly from the HO₂ + NO reaction, especially at
 22 altitudes greater than 5 km (Figure 9 (a)). At altitudes around 10 km, the O₃ production from
 23 RO₂+NO accounted for less than 10% of the total. For the O₃ loss rate, O₃ photolysis followed

1 by the $O(^1D) + H_2O$ reaction was the main O_3 loss process below 5 km, while O_3 reactions with
2 OH and HO_2 became the main O_3 loss above 6 km because of low H_2O mixing ratios at these
3 altitudes (Figure 9(b)).

4 Net calculated ozone production with a median value of 1.3 ppbv d^{-1} was found for the
5 lowest altitude, while a median loss of 1.3 ppbv d^{-1} was found for the lower troposphere (1-5 km).
6 For observations above 9 km, a median net O_3 production rate of 7.0 ppbv d^{-1} was calculated
7 (Figure 9(c)). For the upper altitudes, the O_3 production drops to 4.5 ppbv d^{-1} when model
8 predictions of HO_x are used rather than observed values. This significant difference underscores
9 the importance of understanding the upper tropospheric HO_x discrepancies in the INTEX-A data.
10 The important role of lightning NO_x is also emphasized by the large rates of net production in
11 INTEX-A compared to previous campaigns. Ozone production in the upper troposphere during
12 TRACE-P was less than 1.5 ppbv d^{-1} [Davis *et al.*, 2003] and was $\sim 0.5 \text{ ppbv d}^{-1}$ during PEM-
13 Tropics B [Olson *et al.*, 2001].

14

15 **4. Discussion**

16 Disagreements between observed and modeled HO_x can be caused by instrument error,
17 missing or incorrect chemistry in the model, instrument errors for measurements that are crucial
18 for modeling HO_x , or unmeasured atmospheric constituents that strongly influence HO_x . This
19 situation is complicated by the possibility of changing instrument calibrations and operation and
20 model revisions. As a result, comparisons of measured and modeled HO_x should be examined
21 continually for evidence of discrepancies with either the measurements or the models and for
22 clues to the causes of those discrepancies.

1 Three significant differences between observed and modeled HO_x become apparent in the
2 INTEX-A data: over-predicted OH throughout the troposphere, with over-predicted HO₂ below 8
3 km; under-predicted HO₂ above 8 km; and under-predicted OH in the continental planetary
4 boundary layer.

6 **4.1 Over-predicted OH throughout the troposphere**

7 OH was generally over-predicted through the troposphere; HO₂ was generally over-
8 predicted below 8 km. If the observed-to-modeled OH ratios, which were ~0.6 for TRACE-P and
9 INTEX-A and ~1.0 for PEM-TB, are representative and the OH observations are correct, then
10 they suggest that unknown chemistry is suppressing OH throughout the free troposphere in
11 northern midlatitudes. An implication of this over-prediction is that current modeled atmospheric
12 oxidation rates would be too high and the lifetimes of long-lived atmospheric gases like methane
13 and methyl chloroform would be greater than currently thought. Even if OH is suppressed in
14 only the northern midlatitudes, the lifetimes of medium-to-short-lived atmospheric constituents
15 associated with midlatitude emissions would be significantly lengthened, thus allowing transport
16 to have a greater role in determining their distributions.

17 A concern is that the less-than-expected observed OH and HO₂ comes from an error in
18 the instrument calibration. However, the OH and HO₂ generated by our calibration system is the
19 same to within 10% as the OH and HO₂ generated by the independent calibration systems of two
20 other research groups [*Ren et al.*, 2003; G. Huey, private communication, 2006]. ATHOS has no
21 absolute in-flight calibration, but several monitors and periodic in-flight diagnostics ensure that
22 the calibration is known in flight. It is possible that the angle of air entering the sampling inlet
23 during flight is not being well simulated during the calibration. However, all laboratory and in-

1 flight diagnostics indicate that the calibration is not sensitive to the angle or velocity of the
2 sampled airflow over the range encountered in flight [*Faloona et al.*, 2004]. We have found no
3 evidence that the observed-to-modeled HO_x differences come from an error in the instrument
4 calibration.

5 That median observed HO₂ was only 0.78 of modeled HO₂ and median observed OH was
6 only 0.60 of modeled OH has two implications. First, total hydrogen oxides, HO_x (HO_x = HO₂ +
7 OH) are either being reduced by an unknown HO_x loss or have a production rate, P(HO_x), that is
8 smaller than calculated. Second, the observed-to-modeled HO₂/OH ratio of ~1.2 indicates that
9 the balance between OH and HO₂ is also being affected.

10 The observed and modeled HO_x can be brought into agreement by P(HO_x) that is smaller
11 than calculated if the dominant HO_x source, O₃ photolysis followed by O(¹D)+H₂O (Figure 8), is
12 less than calculated by about a factor of two. Such a large difference is not consistent with
13 uncertainties in the measurements of photolysis frequencies, O₃, and H₂O and with many other
14 studies in which O₃ photolysis followed by O(¹D)+H₂O is the primary OH source and good
15 agreement is obtained between observed and modeled OH. Thus, greater-than-expected HO_x loss
16 is the most likely cause.

17 Consider three possibilities for additional HO_x loss: the rate coefficient for
18 HO₂+HO₂→H₂O₂+O₂ is larger than the accepted value; HO₂+RO₂ reactions are faster or RO₂ is
19 greater than calculated; or the amount, number, or reaction rate coefficients for atmospheric
20 constituents that react with OH to terminate HO_x (and not merely cycle to HO₂) are greater than
21 currently known.

22 A test for errors in the rate coefficient is possible for HO₂+HO₂→H₂O₂+O₂ because of
23 two independent hydrogen peroxide measurements that were on the DC-8. The reaction

1 HO₂+HO₂→H₂O₂+O₂ is the only known gas-phase atmospheric H₂O₂ source. The predominant
2 H₂O₂ losses are by reaction with OH and by photolysis. The steady-state equation shows the
3 dependence of steady-state H₂O₂ on HO₂:

$$4 \quad [H_2O_2]_{ss} = \frac{k_{HO_2+HO_2} [HO_2]^2}{J_{H_2O_2} + k_{H_2O_2+OH} [OH]} \quad (3)$$

6
7 where J_{H₂O₂} is the photolysis frequency for H₂O₂. H₂O₂ may very well not be at steady state
8 because the H₂O₂ photochemical lifetime is approximately 20 sunlit hours, steady state is
9 achieved in about 5 days, H₂O₂ can be injected into the middle and upper troposphere by
10 convection, and H₂O₂ is readily taken up by cloud drops and may react with other dissolved
11 gases in the cloud drops. Even for the unconstrained diurnal steady state model, which is based
12 on HO_x and peroxide concentrations achieving the same values over a 24-hour period, H₂O₂ may
13 not achieve steady-state.

14 Despite this caveat, the unconstrained model matches the observed H₂O₂ from 1 to 8 km
15 (Figure 10). Confidence in the H₂O₂ measurements is high because the two H₂O₂ measurements
16 agree, on average, to within 10% from 100 pptv to 5000 pptv. In addition, the instantaneous
17 steady-state calculation (see Equation (3)) using the observed HO₂ and OH is a factor of 1.7
18 lower but has the same behavior with altitude as the observed H₂O₂. This difference is just at the
19 limit of the 2σ absolute uncertainty of the HO₂ and OH measurements propagated through the
20 steady-state equation (Equation 3). The agreement between the observed and modeled H₂O₂ to
21 well within measurement uncertainties for much of the troposphere is strong evidence that an
22 error in the rate coefficient for HO₂+HO₂→H₂O₂+O₂ is not the cause of the over-predicted HO_x.

1 The second possibility – under-predicted RO₂ or errors in the RO₂ rate coefficients – is
2 more difficult to test because RO₂ was not measured on the DC-8 in INTEX-A. In order to
3 account for the HO₂ observed-to-modeled ratio, $k_{\text{HO}_2+\text{CH}_3\text{O}_2}[\text{CH}_3\text{O}_2]$ would need to be more than
4 4 times larger than calculated by the model and other $k_{\text{HO}_2+\text{RO}_2}[\text{RO}_2]$ would need to be
5 approximately 30 times larger. This large increase in CH₃O₂ or RO₂ or their reaction rate
6 coefficients with HO₂ is inconsistent with the hydrocarbon measurements. Some additional
7 evidence is provided by the reasonable agreement between modeled and observed HCHO, which
8 is the dominant intermediate resulting from the oxidation of most hydrocarbons and an indication
9 of the integrated impact of hydrocarbon oxidation [A. Fried, manuscript in preparation]. Thus,
10 this possibility seems as unlikely as the first one.

11 The third possibility – OH reactions accounting for extra HO_x loss – requires the
12 candidate reaction to be a termination reaction for HO_x (i.e., no subsequent HO₂ or peroxy
13 radical formation). To find the needed additional OH reactivity, OH reactivity was added to the
14 model until the modeled OH agreed with the observed OH for each 1-minute data point. The
15 additional OH reactivity required to bring observed and modeled OH into agreement decreases
16 from almost 1 s⁻¹ near the surface to 0.2 s⁻¹ at 6 km and then decreases further to less than 0.1 s⁻¹
17 above 10 km (Figure 11). It is about 0.7 of the calculated OH reactivity from other known losses
18 below 6 km and 0.2 above 6 km, both rather large increases in total OH reactivity.

19 This additional reactivity has an impact on the agreement between observed and modeled
20 HO₂ and thus between the observed and modeled HO₂/OH ratio (Table 2).

21 The agreement between the observed and modeled HO₂ is dramatically improved in both
22 the middle and lower and troposphere when compared to the agreement without the added OH
23 reactivity as in Table 1. Since OH is forced to agree with observations in these calculations, these

1 statistics also apply to the HO₂/OH ratio. For the upper troposphere above 8 km, agreement
2 actually worsens, but this is expected since HO₂ was already under-predicted at these altitudes.
3 Thus an additional OH termination reaction could account for the over-prediction of HO₂ and
4 HO₂/OH in the lower and middle troposphere as well as that of OH throughout the troposphere.

5 What could be the identity of the atmospheric constituent that has under-predicted OH
6 reactivity? Although we do not know its identity, we can identify some of its characteristics.
7 First it is widely distributed throughout the troposphere. Second, its mixing ratio or reaction rate
8 coefficient, which may be temperature dependent, must decrease with height. Third, it appears in
9 both clear and cloud regions and does not correlate with particle surface area density or volume
10 density. Fourth, if its reaction rate coefficient is $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, then its mixing
11 ration will be about 20 ppbv near Earth's surface and 2 ppbv above 10 km. Finally, if the
12 difference between the observed-to-modeled HO_x in the northern midlatitudes and in the tropics
13 is not an instrument artifact, then it does not occur in the tropics. We are searching for an
14 atmospheric constituent that has these characteristics.

15

16 **4.2 Under-predicted HO₂ above 8 km Altitude**

17 Convection had a large impact on the atmospheric composition in this altitude range
18 during INTEX-A [Bertram *et. al.*, 2006), most notably with enhancements in lightning NO_x
19 (Figure 6), but also for peroxides (Figure 10), and sometimes other constituents. Above 8 km,
20 more than 2/3 of the observations of HO₂ and HO₂/OH were greater than expected, while only a
21 small number of OH observations were. As noted above, attempts to reconcile OH at this altitude
22 only worsen comparisons between model and observed HO₂ and HO₂/OH above 8 km.

1 Could this under-predicted HO₂ be an instrument artifact? An offset to the HO₂ signal
2 would make HO₂ appear larger than it is. However, the observed-to-modeled HO₂ ratio is
3 uncorrelated with observed HO₂, which varied from 2 pptv to 20 pptv above 8 km. In addition,
4 no single offset HO₂ value can be found to improve the agreement between the observed and
5 modeled HO₂. These results rule out a constant offset in the HO₂ signal. The only gas that is
6 known to photolyze in the ATHOS laser beam to produce HO₂, but no OH, is formaldehyde, but
7 the HCHO measured in INTEX-A is orders of magnitude too small to produce the observed
8 signals.

9 It is interesting that the steady-state H₂O₂ based on the observed HO₂ has the same
10 variation with altitude as the observed H₂O₂, even though the observed H₂O₂ is 1.7 times larger
11 than the steady state value (Figure 10). At altitudes above 8 km, the observed H₂O₂ becomes
12 more than five times larger than the H₂O₂ calculated with the unconstrained model, unlike below
13 between 1 and 8 km where observed and modeled H₂O₂ agree.

14 The large underestimation of H₂O₂ by the box model above 8 km relates to the possible
15 influence of convective transport. As already noted, convective influence was widespread during
16 INTEX-A. While the lightning NO_x associated with convection would be expected to inhibit the
17 formation of H₂O₂, convective transport could sustain a small background for H₂O₂ in the upper
18 troposphere. Indeed, median H₂O₂ above 8 km is more than an order of magnitude less than
19 median values in the lowest km (177 pptv vs. 2109 pptv) allowing for the possibility that
20 convective transport could explain upper tropospheric H₂O₂ even after significant scavenging.

21 This convective transport is corroborated by global CTM calculations for the INTEX-A
22 period from the GEOS-Chem model [*Hudman et al.*, 2006]. Box model calculations based on
23 GEOS-Chem chemical conditions were able to reproduce the OH and HO₂ distributions of

1 GEOS-Chem, but H_2O_2 is severely under-predicted similar to the INTEX-A observations. This
2 similarity between GEOS-Chem and box model results suggests that the under-prediction of
3 H_2O_2 is not due to chemistry, but rather a physical process (e.g., convective transport) not
4 represented in the box model.

5 The large observed-to-modeled HO_2 ratio above 8 km is not consistent with observed
6 pernitric acid (HO_2NO_2). If HO_2NO_2 were in steady-state with HO_2 and NO_2 , the calculated
7 steady-state value of HO_2 would need to be lower than even the modeled HO_2 . This difference is
8 consistent with the possibility of the earlier mentioned termination reaction for OH that actually
9 improves the model-to-observed comparison for HO_2NO_2 [Kim *et al.*, 2006].

10 If the observed HO_2 is not an instrument artifact, then the under-predicted HO_2 indicates
11 an additional unknown HO_x source or a reduced HO_x sink; the under-predicted HO_2/OH
12 indicates either slower HO_x cycling from HO_2 to OH or faster HO_x cycling from OH to HO_2 .

13 Consider first the under-prediction of HO_2 . Either an additional unknown HO_x source or a
14 reduced HO_x sink must be capable of improving the observed-to-modeled HO_2 agreement above
15 8 km without making the agreement worse at lower altitudes. Thus, the cause of HO_2 under-
16 prediction must be insignificant from 2 to 8 km and must have increasing importance from 8 to
17 11 km.

18 If less-than-expected HO_x loss is the cause, then the reduced HO_x would need to be an
19 error in the known termination reactions of OH with NO_2 , NO, HNO_3 , and HO_2NO_2 because
20 they dominate above 8 km and are insignificant below 8 km (Figure 8). However, for terminal
21 HO_x loss by reaction with NO_x to be the cause of the HO_2 under-prediction, the HO_x loss rate by
22 these reactions would have to be 5 to 8 times less than expected. This difference is well outside

1 uncertainties for the measured reactants and reaction rate coefficients. Thus, a reduced HO_x sink
2 is unlikely to be the cause of the HO₂ under-prediction.

3 If under-predicted HO_x production is the cause, then the HO_x source could be either an
4 error in the known HO_x sources or additional unknown HO_x sources. The known, equally
5 dominant HO_x sources in the altitude region are O₃ photolysis followed by O(¹D)+H₂O and
6 HCHO photolysis. In order to bring modeled and observed HO₂ into agreement, an additional
7 HO_x source of 1x10⁶ molecules cm⁻³ s⁻¹ is needed above 10 km. This amount is 2-3 times larger
8 than the known HO_x sources (Figure 8). Below 10 km, this source would need to decrease to less
9 than ~10⁵ molecules cm⁻³ s⁻¹ at 6 km and below. It is worth noting that this increase with altitude
10 of the needed additional HO_x source is similar to the observed increase in NO_x with increasing
11 altitude (Figure 6).

12 Can the HO₂ under-prediction come from errors in a known source? The O₃ photolysis
13 and HCHO photolysis are about equal HO_x sources above 8 km. The HO_x production rate from
14 either one of them would need to be increased by a factor of 4 to 6 above 10 km. O₃ photolysis
15 could not be low by that much at 10 km and still be consistent with the HO_x observed-to-
16 modeled ratios below 10 km, where O₃ photolysis is the dominant HO_x source. This
17 inconsistency rules out an error in O₃ photolysis as the cause of the HO₂ under-prediction. An
18 error in the HCHO photolysis would have to be in the photolysis frequency because modeled and
19 observed HCHO are in good agreement in the upper troposphere [A. Fried, manuscript in
20 preparation]. It is quite unlikely that the HCHO photolysis frequency could be in error by a
21 factor of 4 to 6. Thus errors in the known HO_x sources are not likely to be the cause of the HO₂
22 under-prediction.

1 Thus, unknown HO_x sources are the most likely cause of the HO₂ under-prediction. One
2 characteristic of the unknown source is that it correlates with NO. For the observed-to-modeled
3 HO₂ ratio above 8 km, the HO₂ observed-to-modeled ratio = 0.002 x NO (in pptv) + 0.70 with R²
4 = 0.52. In previous studies, it was assumed that the chemistry and HO_x sinks were understood
5 and that the under-predicted HO₂ was due to missing HO_x sources that were emitted along with
6 the NO [see for example *Folkins et al.*, 1997; *Wennberg et al.*, 1998; *Jaeglé et al.*, 2000]. While
7 we have been able to quantify the additional HO_x production that would be needed, to identify its
8 altitude dependence, and to show a correlation with NO, we have not been able to identify this
9 additional unknown HO_x source.

10 A second issue is the under-predicted HO₂/OH ratio. This ratio indicates that reactions
11 and reactants that cycle HO_x between OH and HO₂ are not being properly represented in the
12 model. The HO₂/OH under-prediction can be explained by either slower reactions of HO₂ with
13 NO or faster OH reactions that cycle OH to HO₂. At these altitudes, the reaction frequency of
14 HO₂+NO→OH+NO₂ is an order of magnitude faster than primary OH production (Equation 1).
15 The reaction frequency for HO₂+NO would need to be less than ½ its calculated value; this
16 difference is unlikely and inconsistent many other studies. It is possible that other reactants with
17 HO₂, such as BrO, are present, but their reactions with HO₂ would make HO₂/OH smaller, not
18 larger. Thus, the under-predicted HO₂/OH ratio indicates the presence of unknown reactants or
19 reactions with OH that cycle HO_x from OH to HO₂.

20 In this case, the needed increase in the OH reactivity is proportional to the observed-to-
21 modeled HO₂/OH ratio. As a result, the needed additional OH reactivity is ~0.15 s⁻¹ at 8 km,
22 about ½ of the calculated OH reactivity, and ~0.5 s⁻¹ above 10 km, almost twice the calculated
23 OH reactivity. Interestingly, the needed OH reactivity is roughly proportional to the increase in

1 NO_x in that altitude range, suggesting that the convective processes that enhanced NO_x also
2 yielded additional, unknown OH reactants.

3 Evidence suggests that the cause of the under-predicted HO_x is unrelated to the cause of
4 the under-predicted HO₂/OH ratio. This evidence comes from the differences observed in
5 tropospheric air and stratosphere-influenced air. In the stratosphere-influenced air, the observed-
6 to-modeled OH and HO₂ increase from ~1 at 7 km to ~2 at 10 km before decreasing again to 1
7 above 11 km (Figure 12). The median observed-to-modeled HO₂/OH ratio, on the other hand,
8 remains very close to 1.0 for the entire altitude range of 7-12 km. This behavior is quite different
9 from that of the tropospheric air at the same altitudes, as shown in Figure 5 and from the
10 TRACE-P observation in stratosphere-influenced air, in which the mean HO₂/OH observed-to-
11 modeled ratio was 1.25 [Olson *et al.*, 2006].

12 For INTEX-A stratosphere-influenced air, the greatest observed-to-modeled OH and HO₂
13 ratios occur in dry air that contains over 300 ppbv of ozone. In contrast, the observed-to-modeled
14 ratios for OH, HO₂, and HO₂/OH are all close to 1 for the stratosphere-influenced air observed at
15 11.5 km. This air was encountered on a flight early over the Pacific Ocean during INTEX-A and
16 may not have been affected by convection recently.

17 In the presence of greater NO, the differences in OH and HO₂ between the model
18 constrained to observed HNO₃, H₂O₂, CH₃OOH, and HO₂NO₂ and the model unconstrained by
19 these observations grows (Figure 13). This behavior indicates that the modeled OH and HO₂ are
20 quite sensitive to the model constraints, especially above 8 km altitude where the NO was
21 increasing. In this altitude region, the cycling of HO₂ due to NO dominates the primary
22 production of HO_x and makes HO_x more sensitive to small differences in the constraints placed
23 on the model photochemistry.

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4.3 Under-predicted OH in the Continental Planetary Boundary Layer

During INTEX-A, the observed-to-modeled OH ratio is frequently much greater than one below 2 km altitude above ground level, in the planetary boundary layer. The location of these large ratios coincides with forested regions where isoprene is abundant, primarily from the Gulf Coast states up through Appalachia and the Midwest. The observed-to-modeled OH ratio is a strong function of isoprene (Figure 14). It increases slowly from 0.6 to 1 as isoprene increases from less than 10 pptv to 500 pptv, but for isoprene levels exceeding 500 pptv, the observed-to-modeled OH ratio rapidly increased to ~3 as isoprene increases.

This observation from INTEX-A is consistent with tower-based observations made with a different configuration of the same instrument. In the summers of 1998 and 2000, OH and isoprene measurements were made on a tower at the PROPHET site in a Michigan forest [Tan et al., 2001b]. The median daytime ($SZA < 60^\circ$) observed-to-modeled OH ratio depends on isoprene in a way that is consistent with and overlaps the INTEX-A measurements, as seen by the triangles in Figure 14.

The reasons for the higher-than-expected OH at high isoprene levels are not clear, but most likely are due to a missing OH source in the model. For PROPHET, the agreement between observed and modeled OH is improved by introducing additional terpenes that react with O_3 to form OH [Tan et al., 2001b]. In addition, the difference between the observed and calculated OH reactivity is consistent with the emission of unmeasured terpenes that have ratios of O_3 reactions with terpenes that form OH to the OH reactions with terpenes that are similar to that of terpinolene, a sesquiterpene [DiCarlo et al., 2004]. That the under-predicted OH was observed over several forested areas during INTEX-A provides strong evidence that this effect is not

1 specific only to the PROPHET site in northern lower Michigan, but is, in fact, a more
2 widespread property of the atmospheric chemistry over forests.

3

4 **5. Summary and Conclusions**

5 Measurements of OH and HO₂ were compared to the model calculations in the INTEX-A
6 summer 2004 campaign. This study provides an excellent opportunity to test oxidation chemistry
7 in pollution plumes throughout the troposphere and the following conclusions can be drawn from
8 this study.

9 First, for most of the troposphere, observed OH and HO₂ were less than expected from
10 model calculations. On average observed OH was 0.6 of modeled OH and observed HO₂ was
11 0.78 of modeled HO₂. This observed-to-modeled comparison is similar to that for TRACE-P,
12 another mid-latitude study, but is different from that for PEM-TB, a tropical study, for which
13 observed and modeled HO₂ generally agreed to within a factor of 1.3. In contrast, above 8 km
14 during INTEX-A, the observed-to-modeled HO₂ ratio increased from about 1 at 8 km to about 3
15 at 11 km.

16 Second, HO_x budget analysis shows that the main HO_x sources are O₃ photolysis
17 followed by the O(¹D)+H₂O reaction below 7 km and the photolysis of HCHO above 7 km. The
18 main HO_x sinks are the HO₂-RO₂ self-reactions below 8 km and OH+NO_x reactions above 8 km.

19 Third, O₃ budget analysis shows that the diurnally averaged calculated net O₃ loss rate
20 was 1.3 ppbv d⁻¹ at altitudes between 1 and 5 km. Above 9 km, the diurnally averaged calculated
21 net O₃ production rate was 4.5 ppbv d⁻¹ using modeled HO₂ and 7.0 ppbv d⁻¹ using observed HO₂.
22 This difference between the calculated net O₃ production from the modeled HO₂ and the
23 observed HO₂ is significant and a concern.

1 Fourth, the under-predicted OH and HO₂ for the two studies in northern midlatitudes -
2 TRACE-P and INTEX-A – and the agreement between observed and modeled OH and HO₂ for a
3 study in the tropics - PEM-TB - suggests the presence of unknown atmospheric constituents or
4 unknown reactions with OH that are suppressing the observed OH throughout much of the
5 troposphere at northern midlatitudes. An unknown reaction or reactant with OH that terminates
6 HO_x and has an OH reactivity comparable to the known OH reactions would improve the
7 agreement between observed and modeled OH and HO₂. If this discrepancy is due to emission
8 sources and not to measurement calibrations and changes in measurements calibrations from
9 study to study, then the lifetime of gases that are destroyed by OH, the atmosphere's oxidation
10 capacity, and the evolution of the atmosphere's oxidation capacity will all need to be re-
11 examined.

12 Fifth, the under-predicted HO₂ at altitudes above 8 km suggests the presence of an
13 unknown HO_x source or an error in the model's chemistry involving some of the other
14 atmospheric constituents. The consistency in the increase of the observed-to-modeled HO₂ ratio
15 altitude and the increase in NO with altitude suggests that an unknown HO_x source comes from
16 the convective processes that cause the enhanced NO. Evidence from the constrained and
17 unconstrained model runs indicates that OH and HO₂ are particularly sensitive to the NO.

18 Sixth, the observed-to-modeled OH ratio in the planetary boundary layer in forested
19 regions is a strong function of isoprene. It increases slowly from 0.6 to 1 as isoprene increases
20 from less than 10 pptv to 500 pptv, but for isoprene levels exceeding 500 pptv, the observed-to-
21 modeled OH ratio rapidly increased to ~3. This isoprene dependence of observed-to-modeled
22 OH ratio is consistent with the PROPHET measurements, indicating that this under-predicted
23 OH, if not due to instrument artifacts, occurs in widespread forested regions.

1 It seems more likely to us that, if the over-predicted OH throughout much of the
2 troposphere and under-predicted HO₂ above 8 km are not measurement artifacts, then their
3 causes are due to unknown atmospheric constituents that are acting as HO_x sources or OH sinks
4 or to unknown reactions and not to large errors in the measurements of either atmospheric
5 constituents or the photochemical rate coefficients. These three major differences between
6 observed and modeled HO_x appear to have different causes.

7 Because the over-predicted OH throughout the troposphere, under-predicted HO₂ above 8
8 km, and under-predicted OH above forests have strong implications for understanding global-
9 scale tropospheric oxidation chemistry, finding the causes for these differences should be a high
10 priority. Progress in resolving these discrepancies requires further examination of possible
11 unknown OH sinks and HO_x sources and a focused research activity devoted to ascertaining the
12 accuracy of the OH and HO₂ measurements.

13

14 **Acknowledgment**

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16 would like to thank the DC-8 crew and support staff during the INTEX-A preparation and
17 deployment periods for making this work possible.

18

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20

1 **Figure captions:**

2 **Figure 1.** Observed OH and HO₂ mixing ratios and HO₂/OH ratio as a function of altitude during
3 INTEX-A. Small dots are the 1-minute averaged data; the linked circles denote median
4 values in 0.5 km altitude bins.

5 **Figure 2.** Comparison of observed and modeled OH (a) and HO₂ (b) for INTEX-A. The straight
6 solid lines indicate the 1:1 lines, the dashed lines indicate the 1- σ uncertainty in the model
7 ($\pm 30\%$ for OH and $\pm 27\%$ for HO₂), the solid line with circles are the median values for the
8 observations, and the dash-dot lines are the 1- σ uncertainty for the observations ($\pm 16\%$).

9 **Figure 3.** Comparison of the vertical profiles of (left) measured (circles) and modeled (stars) OH
10 for INTEX-A and (right) measured-to-modeled OH ratios in INTEX-A (circles), TRACE-P
11 (stars) and PEM Tropics B (triangles). Individual INTEX-A 1-minute measurements are
12 shown (gray dots).

13 **Figure 4.** Comparison of the vertical profiles of (left) measured (circles) and modeled (stars)
14 HO₂ for INTEX-A and (right) measured-to-modeled HO₂ ratios in INTEX-A (circles),
15 TRACE-P (stars) and PEM Tropics B (triangles). Individual INTEX-A 1-minute
16 measurements are shown (gray dots).

17 **Figure 5.** Comparison of the vertical profiles of (left) measured (circles) and modeled (stars)
18 HO₂/OH for INTEX-A and (right) measured-to-modeled HO₂/OH in INTEX-A (circles),
19 TRACE-P (stars) and PEM Tropics B (triangles). Individual INTEX-A 1-minute
20 measurements are shown (gray dots).

21 **Figure 6.** Comparisons of the altitude profiles for atmospheric constituents for PEM Tropics B
22 (triangles), TRACE-P (stars), and INTEX-A (circles) for (left) CO, (middle) NO_x, and (right)
23 O₃. Individual 1-minute measurements for INTEX-A are shown as gray points.

1 **Figure 7.** Comparison of NO dependence for (a) OH and (b) HO₂ of (up) measured (circles) and
2 modeled (stars) values and (down) measured-to-modeled ratios in INTEX-A (circles),
3 TRACE-P (stars) and PEM Tropics B (triangles). Individual INTEX-A 1-minute
4 measurements are shown (gray dots). Concentrations of NO calculated in the model are used
5 in this figure.

6 **Figure 8.** Vertical median profiles of (a) HO_x production: total (thick line), from O(¹D)+H₂O
7 (circles), from HCHO photolysis (stars), and from H₂O₂ photolysis (triangles); and (b) HO_x
8 loss rates: total (thick line), due to HO₂+HO₂/RO₂ (circles), due to OH+HO₂ (stars), and due
9 to OH+NO_x (triangles) during INTEX-A. Small gray dots show the 1-minute data for (a) total
10 HO_x production rate and (b) total HO_x loss rate. All the production and loss rates were
11 calculated from the measurements, except for RO₂+HO₂ where RO₂ levels were calculated in
12 the model.

13 **Figure 9.** Vertical median profiles of (a) instantaneous O₃ production rate: total (circles), from
14 HO₂+NO (stars), and from RO₂+NO (triangles) where RO₂ levels were calculated in the
15 model; (b) O₃ loss rate: total (circles), due to O(¹D)+H₂O (stars), due to O₃+OH (triangles),
16 and due to O₃+HO₂ (solid line); and (c) net O₃ production rate during INTEX-A. Small gray
17 dots show the 1-minute data for (a) total O₃ production rate, (b) total O₃ loss rate, and (c) net
18 O₃ production.

19 **Figure 10.** Variation of median H₂O₂ with altitude for the unconstrained instantaneous model
20 (dotted line), the steady-state calculation using observed OH and HO₂ (solid line), and the
21 measurements of the University of Rhode Island (circles) and California Institute of
22 Technology (stars). Steady-state H₂O₂ calculated from observed HO₂ are shown for each
23 minute (gray dots).

1 **Figure 11.** Altitude variation of the calculated OH reactivity (grey dots), altitude-averaged
2 calculated OH reactivity (stars), and the additional OH reactivity needed in the model to
3 bring the measured and modeled HO₂ into agreement (circles).

4 **Figure 12.** Observed-to-modeled OH, HO₂, and HO₂/OH ratios in stratosphere-influenced air.
5 Shown are 1-km median values (circles and lines) and individual 1-minute values (gray dots).

6 **Figure 13.** Ratio of constrained-to-unconstrained models for OH (a) and HO₂ (b) as a function of
7 NO. Individual 1-minute comparisons are presented (gray dots) as well as median values
8 (circles and lines).

9 **Figure 14.** The observed-to-modeled OH ratio as a function of isoprene. Individual 1-minute
10 measurements (gray points) and median values for isoprene intervals (circles) are shown for
11 data taken at less than 1 km altitude and solar zenith angle less than 60°. Median observed-to-
12 modeled OH ratios from the PROPHET tower in a Michigan forest in summer 2000 are also
13 shown (triangles).

14

1

Table 1. Statistics for HO_x observed-to-modeled ratios

OH obs/mod	Overall	0-2 km	2-8 km	8-12 km
median (mean)	0.60 (0.79)	0.66 (1.04)	0.57 (.66)	0.60 (0.76)
% within $\pm 32\%$	18%	18%	17%	19%
% mod < obs/1.32	10%	22%	3%	9%
% mod > obs x 1.32	72%	59%	79%	72%
HO ₂ obs/mod	Overall	0-2 km	2-8 km	8-12 km
median (mean)	0.78 (1.75)	0.83 (0.96)	0.69 (1.28)	1.25 (3.35)
% within $\pm 32\%$	38%	54%	31%	36%
% mod < obs/1.32	16%	11%	<1%	47%
% mod > obs x 1.32	46%	36%	69%	17%
HO ₂ /OH obs/mod	Overall	0-2 km	2-8 km	8-12 km
median (mean)	1.28 (1.64)	1.17 (1.17)	1.17 (1.22)	2.20 (2.88)
% within $\pm 32\%$	42%	45%	57%	13%
% mod < obs/1.32	47%	34%	33%	83%
% mod > obs x 1.32	11%	21%	10%	4%

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Table 2. Statistics for HO₂ observed-to-modeled ratio with added OH reactivity

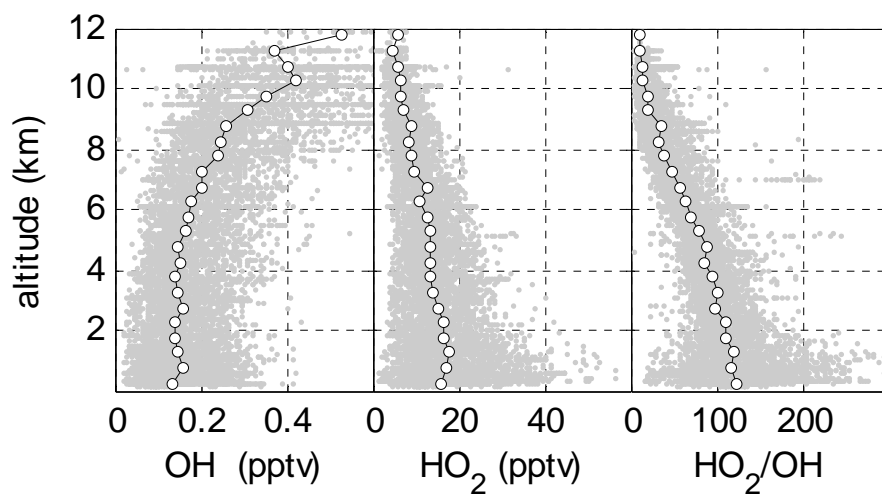
HO ₂ obs/mod	Overall	0-2 km	2-8 km	8-12 km
median (mean)	1.13 (1.58)	1.08 (1.17)	1.01 (1.10)	2.31 (2.88)
% within $\pm 32\%$	55%	67%	72%	13%
% mod < obs/1.32	35%	21%	15%	84%
% mod > obs x 1.32	10%	12%	13%	4%

5

1 **Figure 1.** Observed OH and HO₂ mixing ratios and HO₂/OH ratio as a function of altitude during
2 INTEX-A. Small dots are the 1-minute averaged data; the linked circles denote median values in
3 0.5 km altitude bins.

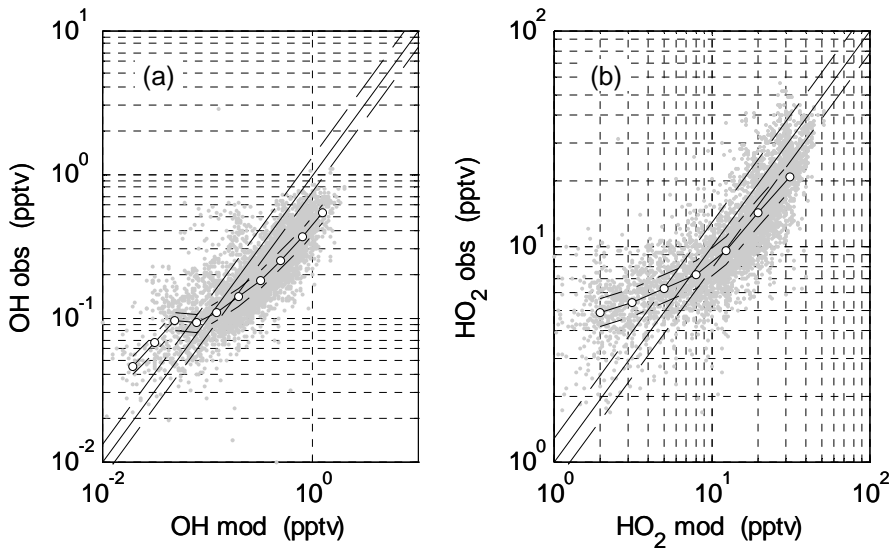
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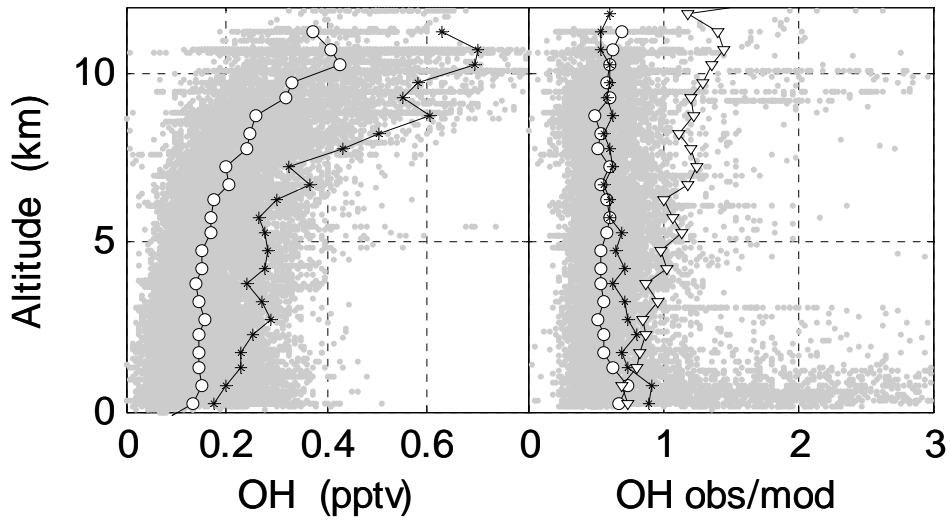


1 **Figure 2.** Comparison of observed and modeled OH (a) and HO₂ (b) for INTEX-A. The straight
2 solid lines indicate the 1:1 lines, the dashed lines indicate the 1- σ uncertainty in the model
3 ($\pm 30\%$ for OH and $\pm 27\%$ for HO₂), the solid line with circles are the median values for the
4 observations, and the dash-dot lines are the 1- σ uncertainty for the observations ($\pm 16\%$).

5

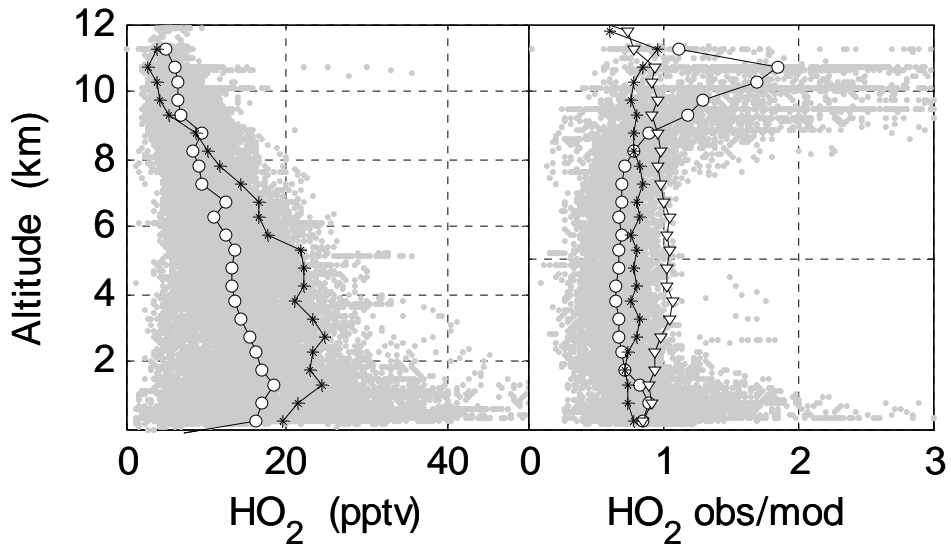


1 **Figure 3.** Comparison of the vertical profiles of (left) measured (circles) and modeled (stars) OH
2 for INTEX-A and (right) measured-to-modeled OH ratios in INTEX-A (circles), TRACE-P
3 (stars) and PEM Tropics B (triangles). Individual INTEX-A 1-minute measurements are
4 shown (gray dots).



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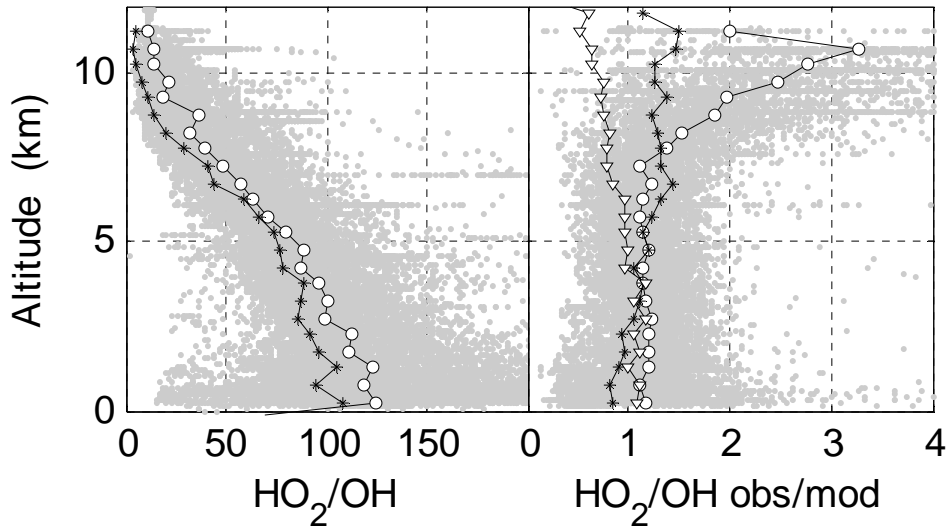
1 **Figure 4.** Comparison of the vertical profiles of (left) measured (circles) and modeled (stars)
2 HO₂ for INTEX-A and (right) measured-to-modeled HO₂ ratios in INTEX-A (circles),
3 TRACE-P (stars) and PEM Tropics B (triangles). Individual INTEX-A 1-minute
4 measurements are shown (gray dots).



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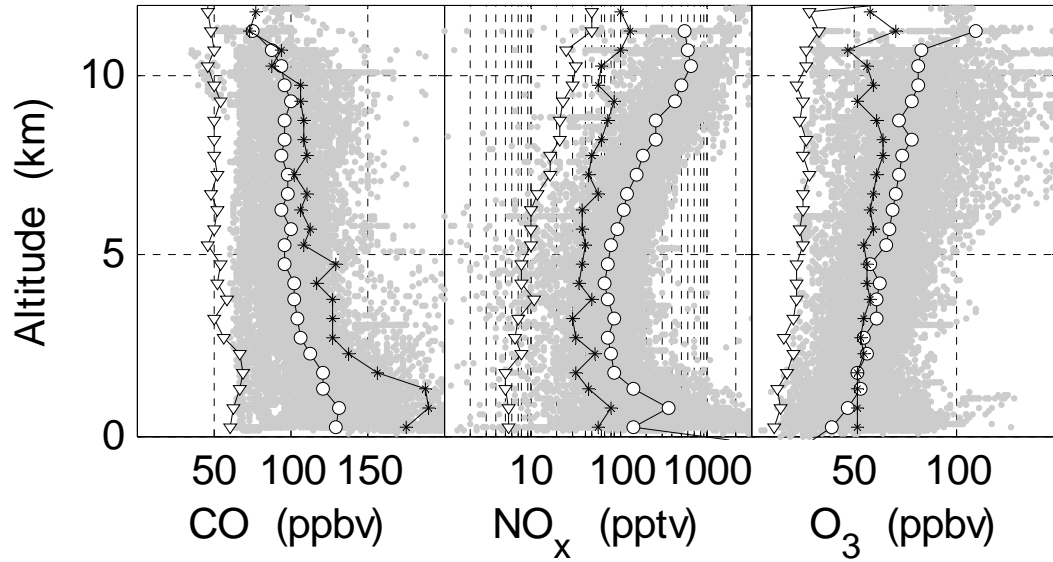
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1 **Figure 5.** Comparison of the vertical profiles of (left) measured (circles) and modeled (stars)
2 HO_2/OH for INTEX-A and (right) measured-to-modeled HO_2/OH in INTEX-A (circles),
3 TRACE-P (stars) and PEM Tropics B (triangles). Individual INTEX-A 1-minute
4 measurements are shown (gray dots).



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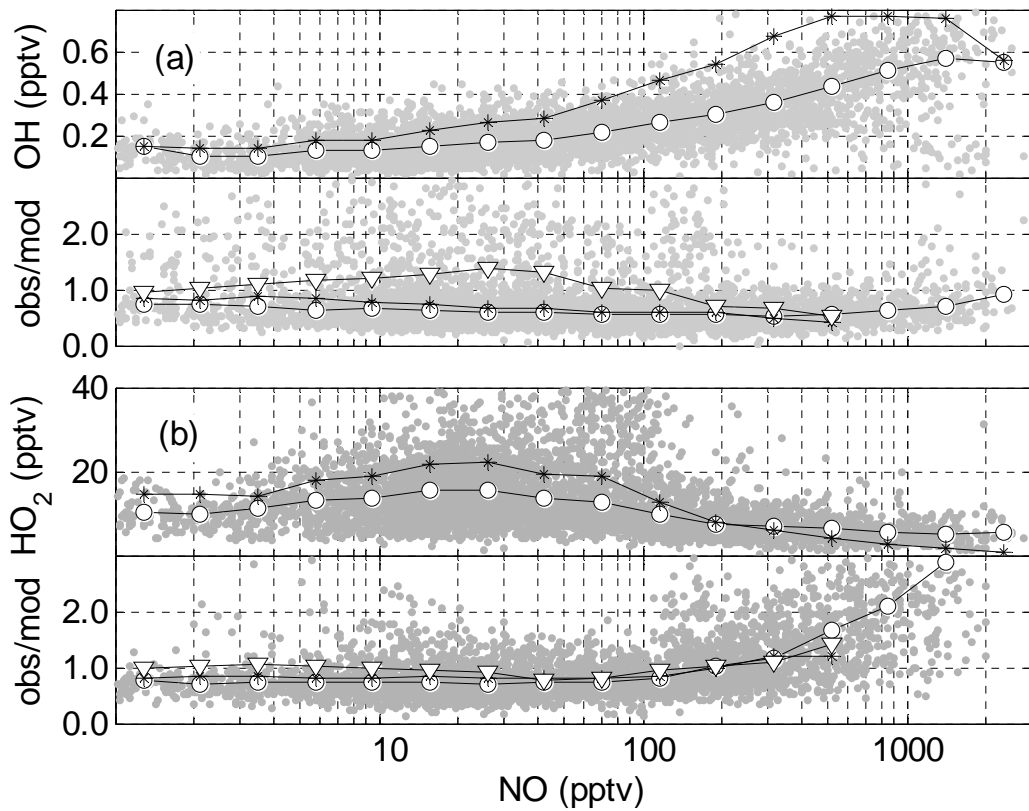
1 **Figure 6.** Comparisons of the altitude profiles for atmospheric constituents for PEM Tropics B
2 (triangles), TRACE-P (stars), and INTEX-A (circles) for (left) CO, (middle) NO_x, and (right)
3 O₃. Individual 1-minute measurements for INTEX-A are shown as gray points.



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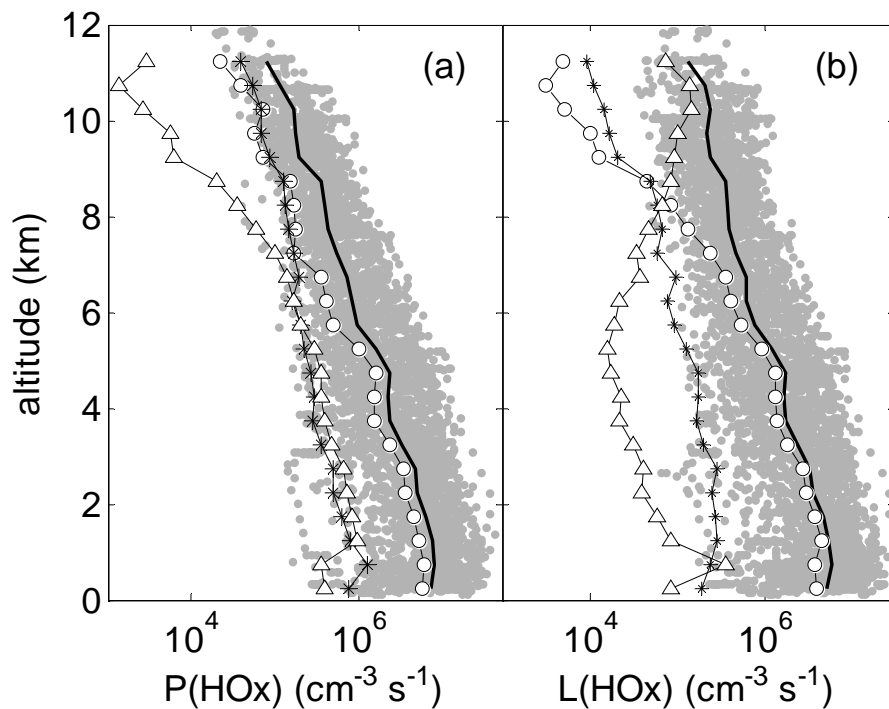
2 **Figure 7.** Comparison of NO dependence for (a) OH and (b) HO₂ of (up) measured (circles) and
3 modeled (stars) values and (down) measured-to-modeled ratios in INTEX-A (circles),
4 TRACE-P (stars) and PEM Tropics B (triangles). Individual INTEX-A 1-minute
5 measurements are shown (gray dots). Concentrations of NO calculated in the model are used
6 in this figure.



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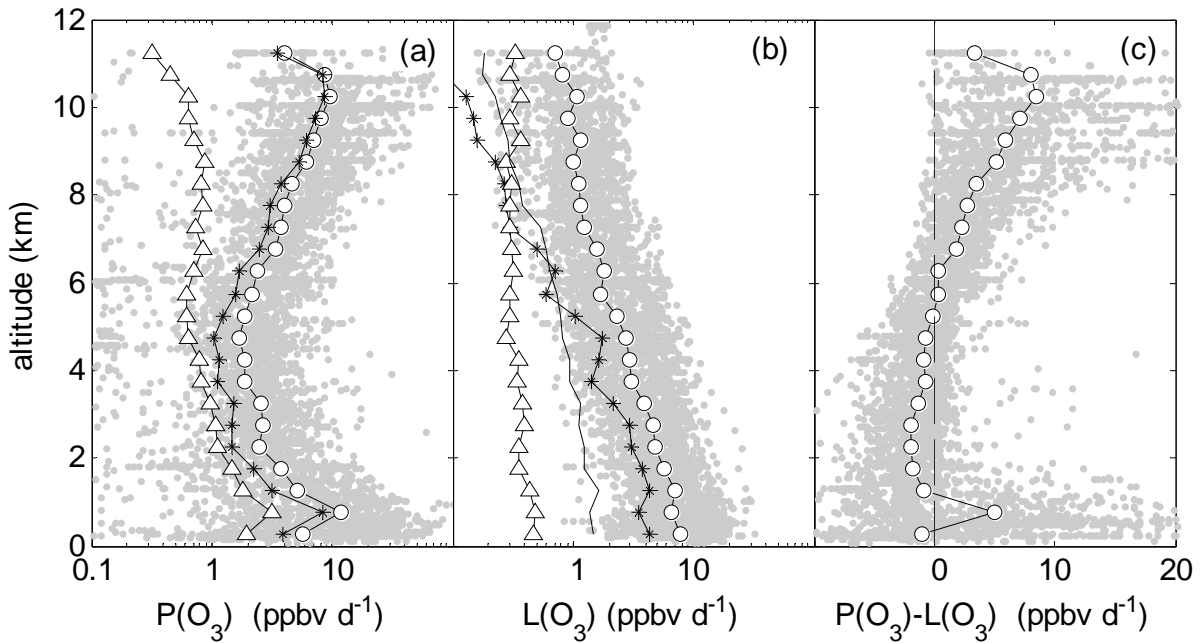
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1 **Figure 8.** Vertical median profiles of (a) HO_x production: total (thick line), from $\text{O}(^1\text{D})+\text{H}_2\text{O}$
2 (circles), from HCHO photolysis (stars), and from H_2O_2 photolysis (triangles); and (b) HO_x
3 loss rates: total (thick line), due to $\text{HO}_2+\text{HO}_2/\text{RO}_2$ (circles), due to $\text{OH}+\text{HO}_2$ (stars), and due
4 to $\text{OH}+\text{NO}_x$ (triangles) during INTEX-A. Small gray dots show the 1-minute data for (a) total
5 HO_x production rate and (b) total HO_x loss rate. All the production and loss rates were
6 calculated from the measurements, except for RO_2+HO_2 where RO_2 levels were calculated in
7 the model.
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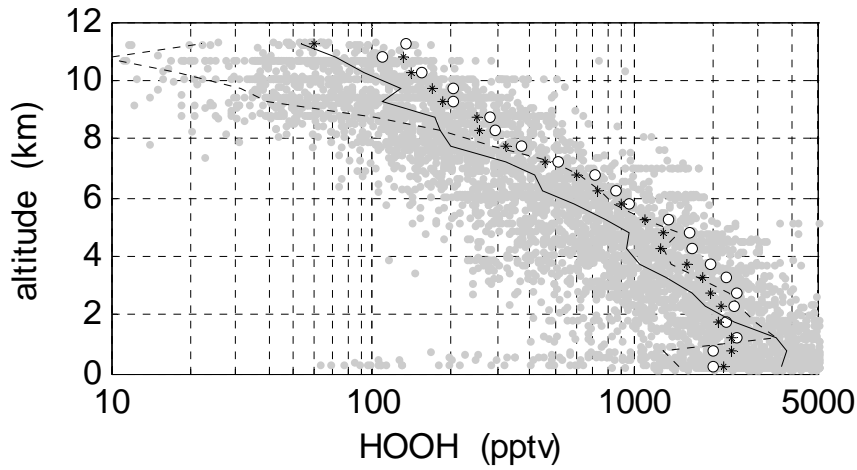
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1 **Figure 9.** Vertical median profiles of (a) O₃ production rate: total (circles), from HO₂+NO (stars),
 2 and from RO₂+NO (triangles) where RO₂ levels were calculated in the model; (b) O₃ loss
 3 rate: total (circles), due to O(¹D)+H₂O (stars), due to O₃+OH (triangles), and due to O₃+HO₂
 4 (solid line); and (c) net O₃ production rate during INTEX-A. Small gray dots show the 1-
 5 minute data for (a) total O₃ production rate, (b) total O₃ loss rate, and (c) net O₃ production.
 6



1 **Figure 10.** Variation of median H_2O_2 with altitude for the unconstrained instantaneous model
2 (dotted line), the steady-state calculation using observed OH and HO_2 (solid line), and the
3 measurements of the University of Rhode Island (circles) and California Institute of
4 Technology (stars). Steady-state H_2O_2 calculated from observed OH and HO_2 are shown for
5 each minute (gray dots).

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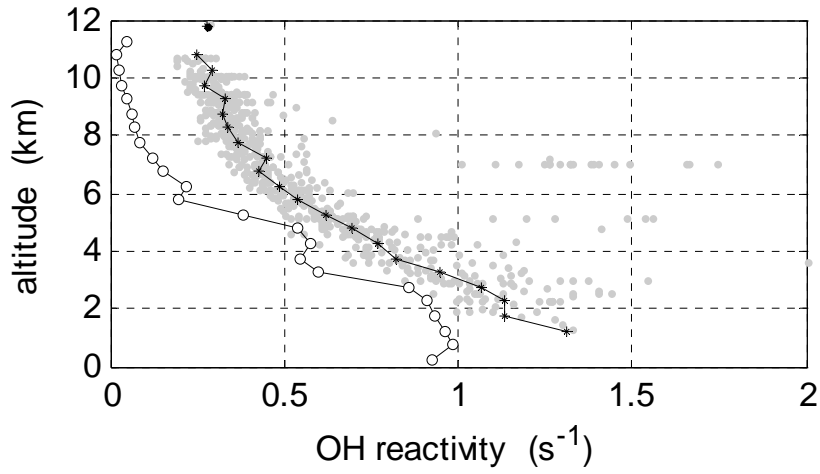


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1 **Figure 11.** Altitude variation of the calculated OH reactivity (grey dots), altitude-averaged
2 calculated OH reactivity (stars), and the additional OH reactivity needed in the model to
3 bring the measured and modeled HO₂ into agreement (circles).

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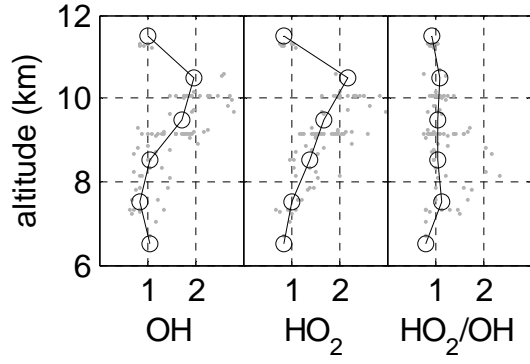
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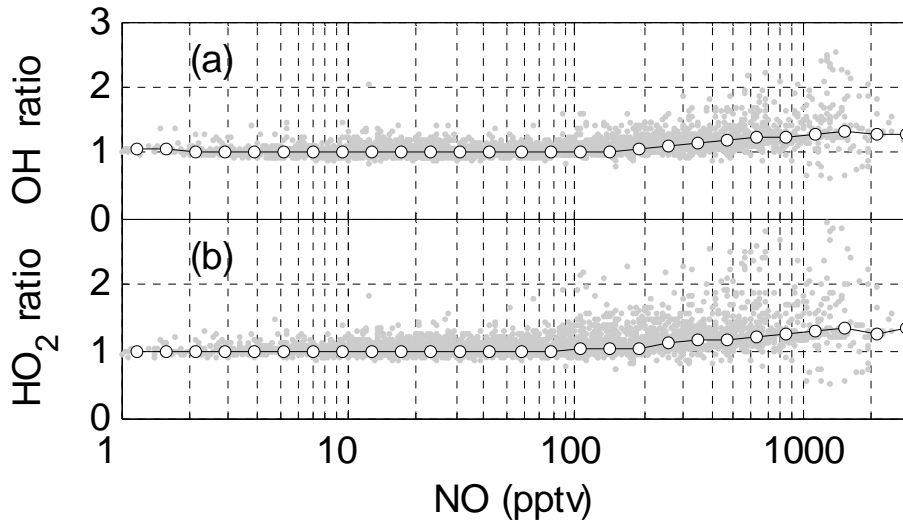
- 1 **Figure 12.** Observed-to-modeled OH, HO₂, and HO₂/OH ratios in stratosphere-influenced air.
2 Shown are 1-km median values (circles and lines) and individual 1-minute values (gray dots).



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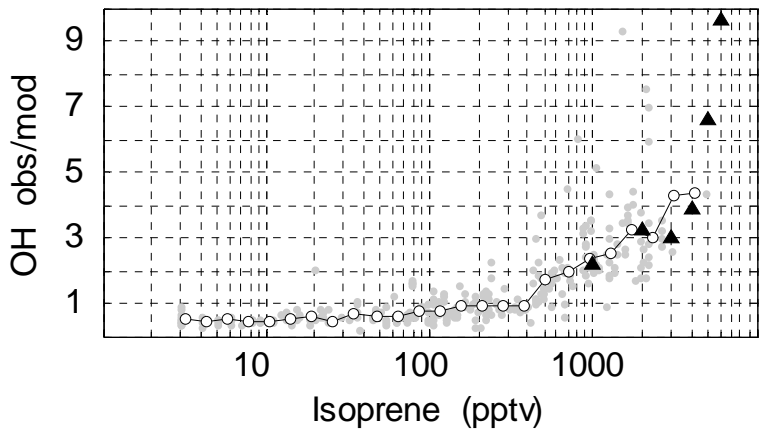
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Figure 13. Ratio of constrained-to-unconstrained models for OH (a) and HO₂ (b) as a function of NO. Individual 1-minute comparisons are presented (gray dots) as well as median values (circles and lines).



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Figure 14. The observed-to-modeled OH ratio as a function of isoprene. Individual 1-minute measurements (gray points) and median values for isoprene intervals (circles) are shown for data taken at less than 1 km altitude and solar zenith angle less than 60° . Median observed-to-modeled OH ratios from the PROPHET tower in a Michigan forest in summer 2000 are also shown (triangles).



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