A reevaluation of airborne HOₓ observations from NASA field campaigns

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Submitted to:

Journal of Geophysical Research – Atmospheres

August 23, 2005
ABSTRACT

In-situ observations of tropospheric HOx (OH and HO2) obtained during four NASA airborne campaigns (SUCCESS, SONEX, PEM-Tropics B and TRACE-P) are reevaluated using the NASA Langley time-dependent photochemical box model. Special attention is given to previously diagnosed discrepancies between observed and predicted HO2 which increase with higher NOx levels and at high solar zenith angles. This analysis shows that much of the model discrepancy at high NOx during SUCCESS can be attributed to modeling observations at time-scales too long to capture the nonlinearity of HOx chemistry under highly variable conditions for NOx. Discrepancies at high NOx during SONEX can be moderated to a large extent by complete use of all available precursor observations. Differences in kinetic rate coefficients and photolysis frequencies available for previous studies versus current recommendations also explain some of the disparity. Each of these causes is shown to exert greater influence with increasing NOx due to both the chemical nonlinearity between HOx and NOx and the increased sensitivity of HOx to changes in sources at high NOx. In contrast, discrepancies at high solar zenith angles will persist until an adequate nighttime source of HOx can be identified. It is important to note that this analysis falls short of fully eliminating the issue of discrepancies between observed and predicted HOx for high NOx environments. These discrepancies are not resolved with the above causes in other data sets from ground-based field studies. Nevertheless, these results highlight important considerations in the application of box models to observationally based predictions of HOx radicals.
1.0 INTRODUCTION

Since Levy [1971] first proposed that the hydroxyl radical (OH) could be photochemically produced within the troposphere, the cycling of odd hydrogen, or HO\textsubscript{x} (OH + HO\textsubscript{2}), has been a topic of intense study. Oxidation by OH is the major loss for most trace gases (e.g., carbon monoxide, methane, and non-methane hydrocarbons), and the oxidation of NO by HO\textsubscript{2} is responsible for photochemical production of ozone. The tropospheric distribution of HO\textsubscript{x} is highly variable in time and space owing to short photochemical lifetimes of a few seconds or less for OH and a few minutes for HO\textsubscript{2}. To enable the study of the natural response of HO\textsubscript{x} to changes in atmospheric conditions, simultaneous measurements of HO\textsubscript{x} and species that influence its formation, loss, and cycling are necessary at high temporal and spatial resolution.

The first viable techniques for measuring tropospheric HO\textsubscript{x} appeared in the early 1990’s [Heard and Pilling, 2003 and references therein]. While such measurements are still far from routine, their deployment has become a valuable part of airborne and ground-based studies focused on understanding tropospheric photochemistry. NASA’s airborne field campaigns have deployed HO\textsubscript{x} instruments on several aircraft (i.e., ER-2, DC-8, and P-3B). Here we focus on observations from NASA’s DC-8 aircraft which has flown the Penn State Airborne Tropospheric Hydrogen Oxide Sensor (ATHOS) in four successive field campaigns (SUCCESS, SONEX, PEM-Tropics B and TRACE-P). These data are highlighted due to the extensive suite of supporting measurements in the
DC8 payload and also because of outstanding issues that have resulted from previous analysis.

Analysis of HO\textsubscript{x} from these campaigns have highlighted discrepancies between observed and predicted HO\textsubscript{2}, casting doubt on our theoretical understanding of middle and upper tropospheric HO\textsubscript{x}. These include discrepancies at high NO\textsubscript{x} [Brune et al., 1999; Faloona et al., 2000; Olson et al., 2004] and at high solar zenith angles (SZA) [Brune et al., 1999; Jaegle et al., 2000]. Evidence for possible uptake of HO\textsubscript{2} on aerosols or liquid cloud water particles has also been discussed [Brune et al., 1999; Jaegle et al., 2000; Olson et al., 2004]. While previous studies from the various investigators have used similar models and approaches, there are differences in model implementation and the use of available observations to constrain model calculations. Additionally, there has been sufficient evolution of recommendations for kinetic rate coefficients and photolysis frequencies to warrant a reexamination of the data. A reevaluation of these data is presented here, with particular emphasis on these discrepancies.

2.0 DESCRIPTION OF DATA AND MODELING APPROACH

2.1 NASA DC-8 Observations.

Table 1 lists general information concerning the four NASA DC8 aircraft campaigns addressed here, including locations and deployment dates. For each campaign, HO\textsubscript{x} measurements were obtained from ATHOS which is an in-situ
laser induced fluorescence OH detection system based on fluorescence assay by gas expansion. The absolute accuracy of ATHOS measurements is listed as +/- 40% in earlier studies [Mather et al., 1997], and Faloona et al. [2004] refines this value to +/- 32%. Examples of the lower limits of detection estimated for one-minute integration times and environmental conditions typical of the TRACE-P field campaign (northwest Pacific springtime) are less than approximately 0.003 pptv (OH) and 0.03 pptv (HO₂) in the upper troposphere, and 0.01 pptv (OH) and 0.1 pptv (HO₂) in the lower troposphere [Faloona et al., 2004]. For an in-depth review of characteristics and calibration for ATHOS, see Faloona et al. [2004].

Information on other photochemical measurements for each of the campaigns can be found in Table 1 and in the included references. The typical suite of observations includes meteorological and navigational measurements, radiance and particle measurements, and measurements of basic gas phase species such as O₃, CO, CH₄, NOₓ (NO and NO₂). Additional measurements may include hydrogen and methylhydrogen peroxides (H₂O₂ and CH₃OOH), nitric acid (HNO₃), peroxyacetyl nitrate (PAN), a wide array of non-methane hydrocarbons (NMHCs), aldehydes, acetone, and other oxygenated hydrocarbons such as methanol (CH₃OH). Time-merged data sets are routinely produced for the campaigns whereby the raw data measurements, obtained with a variety of time integrations, are averaged to a common time scale (typically one minute) for purposes of modeling. The base reanalysis presented here uses the publicly available one-minute data merge for each campaign.
2.2 Modeling.

The modeling approach is based on the assumption of a diurnal steady state, which is typical of most previous analyses of data sets of this type [e.g., Davis et al., 1996; Jacob et al., 1996; Crawford et al., 1997, 1999; Jaegle et al., 1998; 2000; Olson et al., 2001; 2004; Frost et al., 2002]. At a minimum, the model calculation for each individual data point is constrained by coincident observations of O$_3$, CO, NO, CH$_4$, NMHCs, acetone, temperature, dew point, and pressure. With the exception of NO, constraining parameters are held constant throughout the simulated model diurnal cycle. NO varies diurnally; however, total short-lived nitrogen (NO+NO$_2$+NO$_3$+2N$_2$O$_5$+HONO+HNO$_4$) is held constant with partitioning accomplished by the model. The amount of short-lived nitrogen is determined such that NO matches the observed value at the time of measurement. Other model-calculated species are integrated in time until a reproducible diurnal cycle is achieved, and the predictions at the exact time of day that the observed input data was obtained is used as the instantaneous model predictions for that data point. Several optional constraints may be implemented if desired and if measurements are available, including H$_2$O$_2$ and CH$_3$OOH, HNO$_3$, PAN, methanol, ethanol (C$_2$H$_5$OH), and acetic and formic acids (HCOOH and CH$_3$COOH). Otherwise these species are predicted by the model.
To maximize the number of points available for modeling, missing data for NMHCs, acetone, and CH$_3$OH are filled where possible. During SUCCESS, no measurements of these species were available, so concentrations are assumed to equal linear functions of CO derived from data during PEM-West B [McKeen et al., 1997]. A few missing upper tropospheric acetone and CH$_3$OH measurements during TRACE-P are similarly filled using correlations to CO derived from data during that campaign. Otherwise, missing NMHCs, acetone, and methanol during SONEX and TRACE-P are linearly interpolated from adjacent data points within +/- 15 minutes and +/- 500 m altitude. For this analysis, analyzed data are limited to solar zenith angles (SZA) less than 80°.

As in previous studies, photolysis frequencies are based on spectroradiometer measurements [Shetter and Müller, 1999]. Diurnal variation of these measured photolysis frequencies are based on clear-sky model calculations using a DISORT four-stream implementation of the NCAR Tropospheric Ultraviolet Visible (TUV) radiative transfer code [Madronich and Flocke, 1998]. The clear sky diurnal variation from TUV is normalized such that it matches the measured photolysis frequency at the time of observation. Unmeasured photolysis frequencies are normalized by the ratio of observed to clear-sky photolysis of NO$_2$. Dry and wet deposition for soluble species is implemented as in Logan et al. [1981]. Aerosol and cloud uptake for HO$_2$ is not directly computed in the model such that potential impacts may be inferred by
evaluating correlations between model-to-measurement agreement and aerosol surface area.

Current reactions and rates for basic HO\textsubscript{x}-NO\textsubscript{x}-CH\textsubscript{4}-CO chemistry in the NASA Langley time-dependent photochemical box model are generally those recommended by Sander et al. [2003]. In addition to these, the model uses the rate for O\textsuperscript{1}D quenching by N\textsubscript{2} given by Ravishankara et al. [2002], temperature dependent quantum yields for acetone photolysis from Blitz et al. [2004], and the parameterization for near-IR photolysis of HNO\textsubscript{4} as described in Roehl et al., [2002]. NMHC chemistry is built from that in Lurmann et al. [1986], with appropriate rate updates from IUPAC recommendations (Atkinson et al, [2003]) when recommendations from Sander et al. [2003] are not available. For sensitivity studies, an earlier version of the model is run to reflect reactions, rates, and photolytic information available circa 1997 [DeMore et al., 1997; Lurmann et al., 1986; Atkinson et al., 1992].

3.0 Review of previous findings

A prominent and often cited uncertainty in HO\textsubscript{x} theory diagnosed from early analyses of these airborne data sets arises from the tendency for models to underpredict HO\textsubscript{2} under high NO\textsubscript{x} conditions. Figure 1 shows the HO\textsubscript{2} observed-to-calculated ratio (obs/calc) as a function of NO from SUCCESS and SONEX data originally presented in Faloona et al. [2000], but reproduced here with the Langley model (circa 1997 version). During SONEX, model predictions exceed
observations by up to a factor of 5 for NO\textsubscript{x} greater than several hundred pptv [Brune et al., 1999; Jaegle et al., 1999; Faloona et al., 2000]. A similar but more dramatic correlation is evident from the SUCCESS data, with HO\textsubscript{2} underpredicted by factors of up to several hundred for NO\textsubscript{x} at ppbv levels [Brune et al., 1998; Tan et al., 1998; Faloona et al., 2000]. Subsequent analyses have revealed similar behavior in other data sets, particularly ground-based studies, including conditions in an urban setting (NY city) [Ren et al., 2003], in the Nashville urban plume [Thornton et al., 2002; Martinez et al., 2003], and in more remote settings [Kanaya et al., 2001; 2002]. Olson et al. [2004] also found during TRACE-P that for the upper 5% of NO observations (i.e., greater than 135 pptv), upper tropospheric data exhibited a tendency for relatively higher obs/calc ratios of HO\textsubscript{2} while lower tropospheric data showed no such tendency. The possibility of instrument artifacts contributing to these discrepancies has been investigated and is described as unlikely [Faloona et al., 2000; Ren et al., 2004]. Potential explanations suggested in the literature include missing or incomplete theory for HO\textsubscript{x}-NO\textsubscript{x} chemistry [Brune et al., 1999; Faloona et al., 2000], and the presence of unmeasured HO\textsubscript{x} precursors transported to higher altitudes by convection in conjunction with high concentrations of NO\textsubscript{x} from convection or lightning [Brune et al., 1999; Jaegle et al., 2001].

Another discrepancy revealed from earlier analyses of airborne data sets relates to the uptake of HO\textsubscript{2} onto liquid cloud particles or onto ice in cirrus clouds [Faloona et al., 1998; Jaegle et al., 2000]. Jaegle et al. [2000] reported model
HO$_2$ overestimates of factors of 1.5 to 2 times within upper tropospheric cirrus clouds during SONEX, though large overpredictions also extended to areas well outside the cirrus. Laboratory studies measuring the uptake of OH and HO$_2$ onto ice are sparse, though at least one study reports the measurement of reactive uptake coefficients [Cooper and Abbatt, 1996]. Alternately, Olson et al. [2004] found that evidence of significant in-cloud HO$_2$ loss during TRACE-P was primarily limited to the lower and middle altitudes. While the median HO$_2$ overprediction within clouds at middle and lower altitudes (< 6 km) was 31% larger than that for clear air points, the difference was only 9% at altitudes above 6 km.

Discrepancies in HO$_2$ predictions have also been identified at high solar zenith angles, with model underpredictions of up to a factor of 5 during SONEX at both sunrise and sunset [Brune et al., 1999; Jaegle et al., 2000]. Jaegle et al. [2000] determined that while photolysis of HONO produced at night by heterogeneous conversion of NO$_2$ could account for an additional source of HO$_2$ some time after sunrise, it could not explain the non-zero HO$_2$ observations prior to, at, and just after sunrise. Other proposed missing sources of HO$_2$ at high solar zenith angles include photolysis of peroxides and CH$_2$O at sunrise, near-IR photolysis of HNO$_4$, and uncertainties in HNO$_4$ formation and loss kinetics [Brune et al. 1999; Jaegle et al., 2000].

In this reanalysis, additional explanations for the HO$_2$ discrepancies are proposed, such as unsuitable modeling approaches. These include using model
input values for NO that are averaged over highly inhomogeneous conditions; i.e., an average that incorporates a large range of NO concentrations is inadequate to predict an associated average of $\text{HO}_2$ because of the non-linear relationship between $\text{HO}_x$ and $\text{NO}_x$. The incomplete use of available precursor measurements is investigated and is shown to have a larger influence on $\text{HO}_x$ predictions for high $\text{NO}_x$ relative to lower $\text{NO}_x$ levels. The impact of updated photochemical kinetics is also examined.

4.0. Results

4.1. $\text{NO}_x$ inhomogeneity during SUCCESS.

SUCCESS (SUbsonic aircraft: Contrail and Cloud Effects Special Study) flights were focused on observing atmospheric conditions within and around aircraft contrails. This resulted in observations with high temporal and spatial variability, especially for periods when the DC8 sampled fresh contrails in the wake of NASA’s 757 and T-39 aircraft. The modeled and archived data used in Faloona et al. [2000] are based on one-minute average conditions. While this is typical in the analysis of airborne field data, one minute along a flight path for typical DC8 speeds is equivalent to a flight distance of approximately 12 km, over which significant inhomogeneity in observed NO can occur. This is illustrated by examples of one-minute periods from the SUCCESS flight on May 5, 1996 which show one-second measurements of NO spanning several orders of magnitude.
(see Figures 2a, 2c, and 2e). The associated one-minute average of NO is indicated by the dashed lines.

Figures 2b, 2d, and 2f demonstrate the impact of modeling data obtained during a given one-minute period using one-second sample resolution (equivalent to ~0.2 km sample length) versus a single calculation based on averaged conditions (~12 km sample length). When conditions are modeled using data obtained at the one-second scale and then averaged, HO$_2$ (solid line) can exceed the value predicted from using averaged conditions by more than an order of magnitude (dashed lines). Arrows in Figures 2b, 2d and 2f indicate observed HO$_2$ over each one minute period.

Figure 3 shows results when SUCCESS data containing high one-minute averages of NO are modeled using the higher resolution (one-second) data (black symbols). These predictions of HO$_2$ using data obtained at the one-second scale have been averaged back into equivalent one-minute periods for comparison with the original calculations and the observations. Other than a subset of the points at highest NO$_x$ (~$10^4$ pptv), the tendency for increasing underprediction of HO$_2$ with increasing NO$_x$ is largely eliminated (original results are shown by gray symbols). The subset of points that remain with significant model underpredictions of HO$_2$ have been identified as residing in fresh plumes less than a few hundred seconds in age, shown by black open squares in Figure 3.
The discrepancies for data within fresh plumes are likely due to additional inhomogeneity at scales not resolvable even by data obtained at the one-second scale, and to the invalidity of photochemical equilibrium assumptions around fresh plume edges where the exchange reactions between OH and HO\textsubscript{2} are not necessarily fast relative to turbulent dynamics [Lewellen and Lewellen, 2001]. Lewellen and Lewellen [2001] show results from a high-resolution, large-eddy numerical simulation with simplified NO\textsubscript{x} and HO\textsubscript{x} chemistry which suggests that order-of-magnitude fluctuations of NO occur at spatial scales on the order of a few meters within fresh aircraft plumes up to ten minutes of age or more. Given the typical DC8 speed of ~200 m per second, the resulting in a one-second sampling length encompasses a highly variable mix of polluted and background air along a fresh wake. In addition, the HO\textsubscript{x} measurement was made from the underside of the DC-8, while the NO\textsubscript{x} measurement was made from the side, a distance of a few meters. This spatial separation is comparable to the scale of NO\textsubscript{x} inhomogeneity and further complicates the validity of photochemical equilibrium conditions.

The SUCCESS data provide an excellent example of how high spatial variability in NO can greatly complicate or even prevent a reasonable model evaluation of HO\textsubscript{x} observations. Given the sub-second variability below the resolution of the SUCCESS observations, further analysis of this data to quantify the impact of inhomogeneous conditions is impractical.
4.2 Cloud Inhomogeneity during TRACE-P.

Airborne sampling in cloudy regions presents another source of inhomogeneity that can impact the evaluation of HO\textsubscript{x} photochemistry. This is clearly demonstrated by data from TRACE-P. Figure 4 shows the HO\textsubscript{2} obs/calc ratio calculated from the one-minute merge for TRACE-P as a function of altitude. As reported by Olson et al. [2004], large overpredictions for HO\textsubscript{2} were predominantly explained by data associated with cloud penetrations (open black symbols in Figure 4). Data points were identified as “within cloud” based on observations of 10-20 micron particles from the Forward Scattering Spectrometer Probe (FSSP) onboard the DC8. These determinations were further corroborated through visual inspection of in-flight videotapes. Median values for obs/calc HO\textsubscript{2} show a clear distinction between those data identified as in-cloud (0.65) versus those in clear air (0.83). The difference in median ratios is presumed to be due to uptake of HO\textsubscript{2} in cloud droplets, a process not represented in the model calculations. Despite the difference in median values, ratios for data identified as in-cloud exhibit a wide range of values and significantly overlap with clear air data.

Some insight into the variability of obs/calc HO\textsubscript{2} for in-cloud data can be gained by looking at sub-minute variability in cloud conditions based on one second FSSP data. The original determination of in-cloud data did not differentiate between brief and prolonged cloud penetrations. Figure 5 shows the one-minute HO\textsubscript{2} obs/calc ratio for in-cloud points as a function of duration of the
actual cloud encounter. Clearly, many of the points identified as in-cloud from the one-minute averaged FSSP data include samples of limited (few seconds) cloud exposure, and these points show little to no evidence of HO$_2$ uptake from the obs/calc ratio. However, even for more substantial cloud encounters, the duration of the cloud penetration alone is insufficient to explain the large deviations in HO$_2$. Cloud liquid water volume also appears to play an important part, as the greatest discrepancies are for combined prolonged encounters and large cloud liquid water volumes. Conversely, some prolonged cloud encounters (50-60 sec) with lesser cloud liquid water volumes suggest no significant uptake of HO$_2$.

These results offer additional insight into the behavior of obs/calc HO$_2$ during cloud encounters; however, they also demonstrate the difficulty in evaluating cloud impacts on HO$_x$ from an airborne platform. Without focused sampling within clouds at lower flight speeds, airborne data is unlikely to provide more than a qualitative sense for the impact of heterogeneous uptake on HO$_2$.

4.3. HO$_x$ sensitivity to model inputs and kinetics during SONEX

Similar to SUCCESS, SONEX data have been shown to increasingly underpredict HO$_2$ with increasing NO$_x$ [e.g., Brune et al., 1999; Faloona et al., 2000; Jaegle et al., 2000]. Unlike SUCCESS, NO$_x$ inhomogeneity does not explain this tendency and can be demonstrated to impact only a few data points. However, a detailed reanalysis of the SONEX data exhibits a much weaker tendency versus NO$_x$ than does previously reported results [e.g., Faloona et al.,]
2000] (see Figure 6). To understand this difference, a series of model sensitivity calculations was conducted. The sensitivity calculations account for several key differences between these current model calculations and those presented by Faloona et al. The differences include taking advantage of the full suite of available non-methane hydrocarbons and oxygenated hydrocarbons (e.g., CH$_3$OH) measurements, constraining model calculations with observed peroxide observations, and implementing updates to photolysis rates and kinetic rate coefficients based on current recommendations.

As noted earlier, a set of base calculations intended to reproduce the results of Faloona et al. were conducted using an earlier version of the Langley box model dating back to 1997. This incarnation of the model is based on gas kinetic and photolysis recommendations consistent with the state of knowledge at the time of the archived model results used by Faloona et al. (circa 1998). The base calculations were also conducted with the limited set of nonmethane hydrocarbons used by Faloona et al.: ethane, propane, C$_4$ alkanes, and acetone. Finally, observations of additional photochemical species such as H$_2$O$_2$, CH$_3$OOH, methanol, PAN, and HNO$_3$, were not used to constrain the base calculations according to the method of Faloona et al. Table 2 offers a comparison of the base calculations with the archived results used by Faloona et al. based on median values of predicted HO$_2$ and the obs/calc ratio for three ranges of NO (less than 100 pptv, 100 to 200 pptv, and greater than 200 pptv).
These statistics show the base calculations to be in general agreement with the originally archived results.

Building upon the base calculations, the next set of calculations took full advantage of the nonmethane hydrocarbon observations available from the SONEX data. These included C_5 and higher alkanes, C_2H_4, higher alkenes, aromatics. Results given in Table 2 show that relative to the base run, the median value of predicted HO_2 increased the most (17%) for NO greater than 200 pptv. The impact on median values from expanded hydrocarbons for data with NO less than 200 pptv was minor (~2%).

The statistical impact on HO_2 due to broadening the mix of hydrocarbons is striking given the small total number of points that are significantly affected. Less than 4% of the data points showed an increase in HO_2 greater than 10%; however the preponderance of points affected most severely is weighted to high NO_x conditions. Although SONEX flights were predominantly over the remote northern Atlantic, it was not unusual to measure a broad mix of hydrocarbons. For example, 64% of reported measurements for C_2H_4 were at observable levels (i.e., greater than the 2 pptv limit of detection), with a median value of 12 pptv, and toluene was detected at observable levels 17% of the time with a median concentration of 7 pptv. When alkenes and aromatics are present at enhanced concentrations coincident with high NO_x, the impact on HO_x can be significant. As an example, predicted HO_2 from a portion of a SONEX flight in the middle troposphere (4.5 km) rose by a factor of two from 1.8 pptv to 3.6 pptv when the
mix of hydrocarbons was expanded to include measurements of $C_2H_4$ (86 ppt), propene (22 pptv), and toluene (65 pptv).

In subsequent calculations, constraint of peroxides ($H_2O_2$ and $CH_3OOH$), $CH_3OH$, PAN and $HNO_3$ based on their observations was added. This led to further increases in calculated $HO_2$ of 18% for NO greater than 200 pptv, 11% for NO between 100 and 200 pptv, and 6% for NO less than 100 pptv (Table 2), with the vast majority of the increase due to constraint of peroxides. The constraint of peroxides to observations resulted in a nearly universal increase in predicted upper tropospheric $HO_x$ because measured values of $H_2O_2$ above 8 km during SONEX were 30% larger than model-predicted values, and measurements of $CH_3OOH$ were more than a factor of 2.5 larger than calculations. $H_2O_2$ observations above the 15 pptv limit of detection were available for 86% of the SONEX data points used in this analysis, and $CH_3OOH$ observations above LOD were available 40% of the time, so the results in Figure 2 reflect a mixture of constrained and predicted peroxide information. It is important to note that while constraining peroxides to observed values offers a more realistic assessment of $HO_2$, it does not necessarily provide insight. Rather, it demonstrates that peroxides are not well represented by the model. This may be due to kinetic uncertainties or physical processes not represented in the model (e.g., convection or heterogeneous production from $HO_2$ [Jaegle et al., 2000]).

The final set of calculations builds upon the previous sets by incorporating updated gas kinetic and photolysis data. These updates include those in Sander
et al. [2003], temperature dependent acetone quantum yields recommended by Blitz et al. [2004], parameterization for near-IR HNO$_4$ photolysis as suggested in Roehl et al. [2002], and the updated rate for quenching of O($^1$D) by N$_2$

[Ravishankara et al., 2002]. Results from this simulation (Table 2) reflect a median increase of HO$_2$ of an additional 17% and 9% for NO greater than 200 pptv and NO between 100 to 200 pptv, respectively, while the median increase was limited to less than 5% for NO below 100 pptv.

These increases in calculated HO$_2$ are primarily linked to three of the kinetics updates. The current recommended rate for the termolecular reaction OH+NO$_2$+M (nitric acid formation) from Sander et al. [2003] is about 33% slower at upper tropospheric conditions (temperature ~225K) than that used in the base calculations [DeMore et al., 1997], resulting in a decreased sink for HO$_x$ at high NO$_x$ conditions. Increases in HO$_2$ due to this reaction update in the SONEX data are as much as 20 to 50% for NO$_x$ > 500 pptv. Predictions of HO$_2$ also increase due to the inclusion of near-IR photolysis for HNO$_4$, particularly at high solar zenith angles and at high NO$_x$. The median increase in HO$_2$ due to this reaction is 10% for solar zenith angles between 70 and 80, but ranges as high as 50%. Alternately, the slower photolysis of acetone based on the temperature-dependent quantum yields from Blitz et al. [2004] moderates the increases in HO$_2$ driven by the initial two kinetics changes.

The disproportionate response of HO$_2$ to additional precursor information and changes in kinetics at high NOx is clearly evident. The overall increase in
HO$_2$ relative to the beginning base run is 61% for NO greater than 200 pptv, 24% for the medium-range NO, and 14% for NO less than 100 pptv.

4.4 The Importance of Solar Zenith Angle during SONEX.

While much of the tendency for HO$_2$ underprediction at high NO$_x$ during SONEX is removed by the sensitivity calculations outlined above, it may be argued that some residual tendency for increased model underprediction of HO$_2$ at high NO$_x$ remains (Figure 6). Upon further examination, however, it appears that the remaining tendency is more closely related to solar zenith angle (Figure 7). Examination of Figure 7 shows that a trend in the ratio, particularly at sunrise, exists for all NO$_x$ concentrations, with highest obs/calc ratios (underpredictions) at the highest SZAs. Conversely, even high concentrations of NO$_x$ at low SZA show relatively lower values of obs/calc ratio (model overpredictions).

Discrepancies in agreement at high solar zenith angle are related to the observation of small, but significant, amounts of HO$_x$ at night by the ATHOS instrument. For example, the median measurement of HO$_2$ between solar zenith angles of 90° and 105° during SONEX was 0.62 pptv with values ranging from 0 to 1.3 pptv. During TRACE-P, median measured HO$_2$ for solar zenith angles between 90° and 130° was 1.4 pptv. Sources of nighttime HO$_x$ involving ozonolysis of alkenes are included in the model, but are inadequate to explain these observations. At low solar zenith angles, both SONEX and TRACE-P data generally overpredict HO$_2$. This creates a trend in agreement with solar zenith angle for both sunrise and sunset as the model begins the day with too little HO$_x$,
peaks at midday with too much HO\textsubscript{x}, and decays to negligible levels compared to observations as the sun sets.

5.0. Discussion

The results presented above highlight the challenge involved in the application of detailed photochemical models to study HO\textsubscript{x} in high NO\textsubscript{x} environments. Analysis of measurements at high resolution is necessary to ensure that averaging over large fluctuations in NO does not lead to erroneous results. Other environments where highly variable conditions occur (e.g., clouds) must also be given special attention. A more subtle problem relates to the heightened sensitivity of HO\textsubscript{x} chemistry under high NO\textsubscript{x} conditions evident in the reanalysis of SONEX data. When NO\textsubscript{x} is present at sufficient levels, the production and loss pathways of HO\textsubscript{x} shift such that its concentrations become much more sensitive to sources. Thus, changes in precursor inputs to the model and/or uncertainties in their observations and reaction rates have a more pronounced impact on HO\textsubscript{x} predictions compared to conditions with lower NO\textsubscript{x} levels. A theoretical discussion of this impact relative to analysis of HO\textsubscript{x} data is also discussed in Folkins and Chatfield [2000].

Figure 8 outlines a simplified scheme for HO\textsubscript{x} production and loss. This mechanism is by no means intended to be complete. HO\textsubscript{x} losses through OH+HO\textsubscript{2} and HO\textsubscript{2}+NO\textsubscript{2} are omitted and the detailed intermediate steps of NMHC oxidation are not shown. Nevertheless, the scheme is sufficient to demonstrate
the important shifts that occur in HO\textsubscript{x} chemistry between high NO\textsubscript{x} and low NO\textsubscript{x} conditions. In the absence of NO\textsubscript{x}, HO\textsubscript{x} production is primarily driven by ozone photolysis followed by the reaction of O('D)+H\textsubscript{2}O. OH oxidation of CO, CH\textsubscript{4}, and various NMHCs lead to the production of HO\textsubscript{2} and organic peroxy radicals, and HO\textsubscript{x} loss is driven predominantly by the HO\textsubscript{2} self reaction and reaction with other peroxy radicals. The dependence of HO\textsubscript{x} loss on the HO\textsubscript{x} abundance leads to a system that is highly buffered since a change in source strength is mitigated by an opposite response in loss rate.

As NO\textsubscript{x} increases, it influences HO\textsubscript{x} chemistry in three important ways: 1) NO\textsubscript{x} amplifies the production of HO\textsubscript{x} from the oxidation of NMHCs, 2) NO\textsubscript{x} pushes the partitioning of HO\textsubscript{x} towards OH, and 3) NO\textsubscript{x} becomes the dominant loss for HO\textsubscript{x} via OH+NO\textsubscript{2}. The dominance of this loss removes the buffering of HO\textsubscript{x} concentrations as HO\textsubscript{x} self reactions become less important. This NO\textsubscript{x} sensitivity is all the more important for the dry upper troposphere where the source of HO\textsubscript{x} from ozone photolysis followed by O('D)+H\textsubscript{2}O becomes less important relative to sources such as photolysis of acetone, photolysis of convectively transported peroxides, and oxidation of hydrocarbons. This suggests that interpretation of HO\textsubscript{x} measurements in a high NO\textsubscript{x}, non-urban environment cannot be achieved without adequate precursor measurements (e.g., peroxides, acetone, methanol, and NMHCs). It also suggests that sources of uncertainty, either in measurements or chemical mechanisms, will have a greater impact on results for a high NO\textsubscript{x} environment.
Data from PEM-Tropics B were also reevaluated in this study. Because this mission took place over the remote equatorial Pacific during the northern hemisphere spring, NO$_x$ levels encountered were much lower than during the other three campaigns. Median NO$_x$ during PEM-Tropics B at altitudes above 8 km was 28 pptv, compared to 82 pptv during SUCCESS, 95 pptv during SONEX, and 75 pptv during TRACE-P. In addition, high solar zenith angles were encountered much less often than during the other campaigns. As a result, any trend in the discrepancy between observed and measured HO$_x$ as a function of NO$_x$ or solar zenith angle could not be discerned.

Throughout this analysis, the focus has been on trends in the agreement between model-calculated and observed HO$_x$, and we have refrained from addressing the question of absolute agreement. The issue of absolute agreement is complicated by several factors. First, the quality of precursor observations has changed over time. For instance, SUCCESS data lack any observations for NMHCs, methanol, peroxides, or acetone. Solar zenith angle trends during SONEX render agreement based on bulk statistics somewhat ambiguous (e.g., results in Table 1). It is difficult to determine which data is most appropriate for comparison when calculations range from over to under-prediction based on time of day. Furthermore, characterization of the performance of the ATHOS instrument has evolved over time and important corrections for wall losses at low temperatures and pressures determined during PEM-Tropics B (on the order of 25%) have not been retroactively applied to the SONEX data. Note that after the
corrections to the PEM-Tropics B data, the absolute agreement was generally very good, with model predictions within better than 20% of observations throughout the troposphere. Finally, the uncertainty in both model calculations of \( \text{HO}_x \) and \( \text{HO}_x \) observations themselves is +/- 30 - 40%, which leaves much of the data within reach of what could be considered good agreement.

6.0 Summary

This study presents a reanalysis of data from four NASA field campaigns (SUCCESS, SONEX, PEM-Tropics B and TRACE-P) with an emphasis on explaining previously diagnosed trends in the agreement between calculated \( \text{HO}_x \) and its observations. Early analysis of these campaigns found large discrepancies in \( \text{HO}_x \) associated with high \( \text{NO}_x \) and at high solar zenith angles. Additional discrepancies were found in relation to cloudy conditions.

High spatial variability of NO at resolutions much smaller than those implied by one-minute along a DC8 flight path (~12 km) was encountered by the aircraft during SUCCESS. The tendency for \( \text{HO}_2 \) underprediction of several orders of magnitude at ppbv levels of \( \text{NO}_x \) is determined to be due to this inhomogeneity. As a result of the nonlinear chemistry between \( \text{NO}_x \) and \( \text{HO}_x \), averaging NO over these variable conditions results in predictions of \( \text{HO}_2 \) that are erroneously low. Another impact of inhomogeneity in field data is evident in interpretation of \( \text{HO}_2 \) within cloudy regions during TRACE-P. Data obtained at a time scale of one-second (~0.2 km) suggests that the diagnosed impact of \( \text{HO}_2 \)
uptake in cloud droplets is dependent upon both the duration of the cloud encounter within the averaging sample (one-minute for TRACE-P) and on the cloud liquid water content.

A heightened sensitivity of HO\textsubscript{x} chemistry under high NO\textsubscript{x} conditions appears to be largely responsible for the previously diagnosed tendency for HO\textsubscript{2} underprediction at high NO\textsubscript{x} during the SONEX campaign. Model-predictions of HO\textsubscript{2} increase disproportionately more for high NO\textsubscript{x} conditions relative to those with lower NO\textsubscript{x} when additional observational constraints are included in the analysis (including peroxides, methanol, and expanding NMHCs to include the full suite of measured species). The heightened response of HO\textsubscript{x} under high NO\textsubscript{x} is also evident when model photochemical kinetics were updated. When all available constraints are included in the model and current kinetics are used, predictions of HO\textsubscript{2} increase by a total of 61% for high NO (> 200 pptv), by 24% for NO between 100 and 200 pptv, and by 11% for low NO (< 100 pptv) relative to the original results. These results highlight the critical importance of precursor measurements (e.g., peroxides, acetone, and NMHCs) for interpretation of HO\textsubscript{x} measurements in a high NO\textsubscript{x} environment.

Although much of the discrepancy for HO\textsubscript{2} in the SONEX data has been explained here, a residual trend in HO\textsubscript{2} agreement remains associated with the solar zenith angle. This trend is driven by the presence of non-trivial observations of HO\textsubscript{x} at nighttime that current model theory is incapable of explaining. Additionally, it is important to point out that although most of the trend in
agreement related to high NO$_x$ concentrations can be explained for the SONEX and the SUCCESS data sets, other data sets remain with similar trends with NO$_x$, and these discrepancies have not yet been resolved.
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