

A reevaluation of airborne HO_x observations from
NASA field campaigns

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ABSTRACT

In-situ observations of tropospheric HO_x (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 NO_x levels and at high solar zenith angles. This analysis shows that much of the model discrepancy at high NO_x during SUCCESS can be attributed to modeling observations at time-scales too long to capture the nonlinearity of HO_x chemistry under highly variable conditions for NO_x. Discrepancies at high NO_x 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 NO_x due to both the chemical nonlinearity between HO_x and NO_x and the increased sensitivity of HO_x to changes in sources at high NO_x. In contrast, discrepancies at high solar zenith angles will persist until an adequate nighttime source of HO_x can be identified. It is important to note that this analysis falls short of fully eliminating the issue of discrepancies between observed and predicted HO_x for high NO_x 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 HO_x 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_x (OH + HO₂), 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 HO₂ is responsible for photochemical production of ozone. The tropospheric distribution of HO_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 HO₂. To enable the study of the natural response of HO_x to changes in atmospheric conditions, simultaneous measurements of HO_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_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_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_x from these campaigns have highlighted discrepancies between observed and predicted HO_2 , casting doubt on our theoretical understanding of middle and upper tropospheric HO_x . These include discrepancies at high NO_x [Brune *et al.*, 1999; Falloona *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_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_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, NO_x (NO and NO₂). Additional measurements may include hydrogen and methylhydrogen peroxides (H₂O₂ and CH₃OOH), nitric acid (HNO₃), peroxyacetylnitrate (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 O₃, CO, NO, CH₄, 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+NO₂+NO₃+2N₂O₅+HONO+HNO₄) 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 H₂O₂ and CH₃OOH, HNO₃, PAN, methanol, ethanol (C₂H₅OH), and acetic and formic acids (HCOOH and CH₃COOH). Otherwise these species are predicted by the model.

To maximize the number of points available for modeling, missing data for NMHCs, acetone, and CH_3OH 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_3OH 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 Møller, 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_x - NO_x - CH_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 O¹D quenching by N_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_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_x theory diagnosed from early analyses of these airborne data sets arises from the tendency for models to underpredict HO_2 under high NO_x conditions. Figure 1 shows the HO_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_x greater than several hundred pptv [Brune *et al.*, 1999; Jaegle *et al.*, 1999; Faloon *et al.*, 2000]. A similar but more dramatic correlation is evident from the SUCCESS data, with HO_2 underpredicted by factors of up to several hundred for NO_x at ppbv levels [Brune *et al.*, 1998; Tan *et al.*, 1998; Faloon *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_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 [Faloon *et al.*, 2000; Ren *et al.*, 2004]. Potential explanations suggested in the literature include missing or incomplete theory for HO_x - NO_x chemistry [Brune *et al.*, 1999; Faloon *et al.*, 2000], and the presence of unmeasured HO_x precursors transported to higher altitudes by convection in conjunction with high concentrations of NO_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_2 onto liquid cloud particles or onto ice in cirrus clouds [Faloon *et al.*, 1998; Jaegle *et al.*, 2000]. Jaegle *et al.* [2000] reported model

HO₂ 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 HO₂ 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 HO₂ loss during TRACE-P was primarily limited to the lower and middle altitudes. While the median HO₂ 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 HO₂ 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 NO₂ could account for an additional source of HO₂ some time after sunrise, it could not explain the non-zero HO₂ observations prior to, at, and just after sunrise. Other proposed missing sources of HO₂ at high solar zenith angles include photolysis of peroxides and CH₂O at sunrise, near-IR photolysis of HNO₄, and uncertainties in HNO₄ formation and loss kinetics [Brune *et al.* 1999; Jaegle *et al.*, 2000].

In this reanalysis, additional explanations for the HO_x 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 HO₂ because of the non-linear relationship between HO_x and NO_x. The incomplete use of available precursor measurements is investigated and is shown to have a larger influence on HO_x predictions for high NO_x relative to lower NO_x levels. The impact of updated photochemical kinetics is also examined.

4.0. Results

4.1. 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, HO₂ (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 HO₂ 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 HO₂ 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 ($\sim 10^4$ pptv), the tendency for increasing underprediction of HO₂ 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 HO₂ 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 HO₂ 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_x and HO_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_x measurement was made from the underside of the DC-8, while the NO_x measurement was made from the side, a distance of a few meters. This spatial separation is comparable to the scale of NO_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_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_x photochemistry. This is clearly demonstrated by data from TRACE-P. Figure 4 shows the HO₂ 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 HO₂ 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 HO₂ 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 HO₂ 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 HO₂ 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 HO₂ 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 HO₂ 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 HO₂. 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 HO₂.

These results offer additional insight into the behavior of obs/calc HO₂ 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 HO₂.

4.3. HO_x sensitivity to model inputs and kinetics during SONEX

Similar to SUCCESS, SONEX data have been shown to increasingly underpredict HO₂ 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_3OH) 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_2O_2 , CH_3OOH , 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 HNO₄ photolysis as suggested in *Roehl et al.* [2002], and the updated rate for quenching of O(¹D) by N₂ [*Ravishankara et al.*, 2002]. Results from this simulation (Table 2) reflect a median increase of HO₂ 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 HO₂ are primarily linked to three of the kinetics updates. The current recommended rate for the termolecular reaction OH+NO₂+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 HO₂ due to this reaction update in the SONEX data are as much as 20 to 50% for NO_x > 500 pptv. Predictions of HO₂ also increase due to the inclusion of near-IR photolysis for HNO₄, particularly at high solar zenith angles and at high NO_x. The median increase in HO₂ 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 HO₂ driven by the initial two kinetics changes.

The disproportionate response of HO₂ to additional precursor information and changes in kinetics at high NO_x is clearly evident. The overall increase in

HO₂ 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 HO₂ 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 HO₂ 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 HO₂ 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 HO₂ 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 HO₂. 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_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_x in high NO_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_x chemistry under high NO_x conditions evident in the reanalysis of SONEX data. When NO_x is present at sufficient levels, the production and loss pathways of HO_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_x predictions compared to conditions with lower NO_x levels. A theoretical discussion of this impact relative to analysis of HO_x data is also discussed in *Folkins and Chatfield* [2000].

Figure 8 outlines a simplified scheme for HO_x production and loss. This mechanism is by no means intended to be complete. HO_x losses through $\text{OH}+\text{HO}_2$ and HO_2+NO_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_x chemistry between high NO_x and low NO_x conditions. In the absence of NO_x , HO_x production is primarily driven by ozone photolysis followed by the reaction of $\text{O}(^1\text{D}) + \text{H}_2\text{O}$. OH oxidation of CO, CH_4 , and various NMHCs lead to the production of HO_2 and organic peroxy radicals, and HO_x loss is driven predominantly by the HO_2 self reaction and reaction with other peroxy radicals. The dependence of HO_x loss on the HO_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_x increases, it influences HO_x chemistry in three important ways: 1) NO_x amplifies the production of HO_x from the oxidation of NMHCs, 2) NO_x pushes the partitioning of HO_x towards OH, and 3) NO_x becomes the dominant loss for HO_x via $\text{OH} + \text{NO}_2$. The dominance of this loss removes the buffering of HO_x concentrations as HO_x self reactions become less important. This NO_x sensitivity is all the more important for the dry upper troposphere where the source of HO_x from ozone photolysis followed by $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ 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_x measurements in a high NO_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_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 HO_x and HO_x observations themselves is $\pm 30 - 40\%$, 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 HO_x and its observations. Early analysis of these campaigns found large discrepancies in HO_x associated with high 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 HO_2 underprediction of several orders of magnitude at ppbv levels of NO_x is determined to be due to this inhomogeneity. As a result of the nonlinear chemistry between NO_x and HO_x , averaging NO over these variable conditions results in predictions of HO_2 that are erroneously low. Another impact of inhomogeneity in field data is evident in interpretation of 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 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_x chemistry under high NO_x conditions appears to be largely responsible for the previously diagnosed tendency for HO_2 underprediction at high NO_x during the SONEX campaign. Model-predictions of HO_2 increase disproportionately more for high NO_x conditions relative to those with lower NO_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_x under high NO_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_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_x measurements in a high NO_x environment.

Although much of the discrepancy for HO_2 in the SONEX data has been explained here, a residual trend in HO_2 agreement remains associated with the solar zenith angle. This trend is driven by the presence of non-trivial observations of HO_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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