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Nitrogen oxide chemistry in an urban plume: investigation of the chemistry of peroxy and multifunctional organic nitrates with a Lagrangian model

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Abstract

Air quality in the outflow from urban centers affects millions of people, as well as, natural and managed ecosystems downwind. In locations where there are large sources of biogenic VOCs downwind of urban centers, the outflow is characterized by a high VOC reactivity due to biogenic emissions and low NO_x. However most field and chamber studies have focused on limiting cases of high NO_x or of near zero NO_x. Recent measurements of a wide suite of VOCs, O₃ and meteorological parameters at several locations within the Sacramento urban plume have provided a detailed benchmark for testing our understanding of chemistry in a plume transitioning from high NO_x to low NO_x and high VOC reactivity. As an additional simplification, the strong mountain valley circulation in the region makes this urban plume a physical realization of a nearly idealized Lagrangian plume. Here, we describe a model of this plume. We use a Lagrangian model representing chemistry based on the Master Chemical Mechanism (MCM) v3.1 along with mixing and deposition. We discuss the effects of entrainment

- ¹⁵ of background air, the branching ratio for the production of isoprene nitrates and the effects of soil NO_x emissions on the composition of the evolving plume. The model predicts that after 2–3 h of chemical processing only 45% of the peroxynitrates (Σ PNs) are PAN and that most (69%) RONO₂ are secondary alkyl nitrate products of the reaction of OH with RONO₂. We find the model is more consistent with the observations
- ²⁰ if: a) the yield of Σ PNs from large and multi-functional aldehydes is close to zero; and b) the reaction between OH and RONO₂ produces multifunctional nitrates as opposed to either HNO₃ or NO₂ as is typical in most currently adopted reaction mechanisms. Model results also show that adding NO_x emissions throughout the transect increases the available NO_x in the downwind regions, but modeled ozone concentrations were
- $_{\rm 25}$ little affected by the increased NO_x.

Interactive Discussion

1 Introduction

Ozone is produced by a series of catalytic reactions involving the oxidation of organic molecules in the presence of NO_x ($NO_x \equiv NO + NO_2$) and sunlight (Haagen-Smit, 1952). While the basic chemistry of the catalytic cycles is well known, demonstrating that we

⁵ have an accurate and complete understanding of the chemistry, especially the role of various chain termination steps, remains elusive and challenging because direct simultaneous measurements of key radical species and the molecules that are formed during chain termination reactions are not routine and in some cases not yet possible. An additional limitation is that the most extensive tests of our understanding of ozone
 ¹⁰ production chemistry using ambient measurements have focused on limiting cases of high NO_x or of near zero NO_x.

Here we take advantage of measurements of a wide suite of VOCs, O_3 and meteorological parameters at several locations within the Sacramento urban plume that provide a detailed benchmark for testing our understanding of chemistry in a plume

- transitioning from high NO_x to low NO_x under conditions of near constant and high VOC reactivity. As an additional simplification, the strong mountain valley circulation in the region makes this urban plume a physical realization of a nearly idealized Lagrangian plume. We evaluate a Lagrangian model representing chemistry based on the Master Chemical Mechanism (MCM) v3.1 along with mixing and deposition in this
- ²⁰ plume. The model is compared to observations of NO_x and its oxidation products, including total peroxynitrates (Σ PNs), total alkyl nitrates (Σ ANs) and HNO₃. We begin (Sect. 2) with a brief review of our understanding of the transport and chemistry of the Sacramento plume, followed by a description of the model (Sect. 3). The model and observations are compared in Sect. 4, along with descriptions of the constraints on
- some of the more uncertain parameters in the model. In Sect. 5 we consider the sensitivity of the model to soil NO_x emissions and provide estimates for *N* deposition along the model transect. We conclude with suggested improvements to the representation of NO_x oxidation chemistry in the current generation of photochemical mechanisms.

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2 The Sacramento urban plume

The western slope of the Sierra Nevada experiences extremely regular wind patterns, especially during the summer. Figure 1 shows the study region and provides an overview of the flow patterns that affect it. Daytime heating causes upslope flow that

- ⁵ draws air from California's Central Valley eastward into the higher elevations of the Sierra Nevada Mountains. In the evening, cooling in the valley causes a flow reversal and the air drains from higher elevations back toward the valley floor. As a result, daytime chemistry is approximately described as a flow reactor with dilution as evidenced in the diurnal patterns observed in many primary and secondary chemicals observed in the region (van Ooy and Carroll, 1995; Baker et al., 1999; Lamanna and Goldstein,
- 1999; Dillon et al., 2002; Schade et al., 2002; Day et al., 2003; Cleary et al., 2005, 2007; Murphy et al., 2006a, b, 2007; Day et al., 2008, 2009).

The chemical composition of the Sacramento urban plume is especially well characterized as a result of these observations which include regional ozone studies, many

- ¹⁵ summers and several complete annual cycles of measurements at a Ponderosa Pine plantation near the University of California-Blodgett Forest Research Station (UC-BFRS), short-term studies at Granite Bay (GB), and Big Hill, and observations from aircraft. These observations have been used to describe the behavior of anthropogenic and biogenic species including VOC, nitrogen oxides and O₃ and they have been used
- to gain insight of the photochemistry in the plume in the Sacramento area and in the downwind Mountain Counties (Baker et al., 1999; Lamanna and Goldstein, 1999; Schade and Goldstein, 2001; Dreyfus et al., 2002; Kurpius et al., 2002a; Schade et al., 2002; Day et al., 2003; Cleary et al., 2005, 2007; Murphy et al., 2006a, b, 2007; Day et al., 2008, 2009).
- The most complete overview of factors affecting the photochemistry in the region is presented by Murphy et al. (2006b) who analyzed observations of day-of-week patterns and diurnal profiles of odd oxygen ($O_x \equiv O_3 + NO_2$), ozone and its precursors. They report that the sites in the Sacramento Valley Air Quality District (Sacramento itself and

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its closest suburbs; see Fig. 1) are more likely to exceed the national 8-h ozone standard (75 ppb) on the weekend, while sites in the Mountain Counties (regions downwind of the city) are more likely to exceed the national ozone standard on the weekdays. Murphy et al., (2006b, 2007) separate the effects of a) titration by NO, b) odd-oxygen production and c) carryover of O_x and O_x precursors from the previous day. They show that the transition between NO_x -limited and NO_x -saturated photochemical regimes occurs near or just downwind of the suburban boundary of the Sacramento metropolitan area and that carryover from the previous day plays an important role in O_x concentrations in the region. These are results with important policy implications as they suggest

that further NO_x reductions in the region will be immediately effective at reducing ozone in the suburbs and provide a quantitative estimate for how much additional NO_x reduction is required (50%) to reduce ozone in the center of the city. Murphy et al. (2006b) also use isoprene observations as a diagnostic of OH concentrations that supports the conclusions of their analysis. They show that lower NO_x on the weekend translates
 to lower OH concentrations in the rural areas and to higher OH near the urban core confirming that NO_x has a direct effect on oxidation rates (and ozone production rates)

3 A Lagrangian – MCM model of the Sacramento plume

in the plume.

We build on a previous analysis by Dillon et al. (2002) who developed a Lagrangian model incorporating oxidation and mixing and then used observations of VOCs for which the only source was assumed to be the Sacramento region to constrain the model. In that research, a nonlinear least square optimization of the decrease in VOC from the initial urban value to that observed at UC-BFRS resulted in determination of the average OH concentration and the average dilution rate during the transit. At the peak impact of the Sacramento plume at UC-BFRS, the derived parameters were a dilution rate of 0.23±0.07 h⁻¹ and an OH concentration of 11±5×10⁶ molecules cm⁻³. We have investigated the performance of this model in more detail, finding that



these two parameters are not as cleanly separated by the original VOC data set as initially believed and that they are anti-correlated, thus a low value for the OH concentration requires high mixing rate and vice versa. Schade et al. (2002) derived a similar OH of $9-13 \times 10^6$ molecules cm⁻³, based on the observed diurnal cycle of MTBE and its ratio to 2-methyl-butane. Dreyfus et al. (2002) derived a value of 9 $(\pm 4) \times 10^6$ molecules cm⁻³ based on the observed daytime methylvinyl ketone to methacrolein (MVK/MACR) ratio. These two studies do not explicitly treat dilution, thus making the implicit assumption that dilution affects the pairs of species (MTBE and 2-methyl-butane or MVK and MACR) equally. Nevertheless, they do arrive at essentially the same value for OH as Dillon et al. (2002). The average OH experienced 10 during the plume transport, is of course not the OH at any one location. We know that the decreases in NO_{v} that occur during transport result first in an OH increase and then an OH decrease (Murphy et al., 2006b). This fact makes it desirable to develop a model capable of describing the changing OH field throughout the plume evolution instead of an effective concentration. We do that by incorporating a full photochemi-15 cal model into the Lagrangian framework outlined by Dillon et al. (2002). This model represents mixing, photochemistry, and dry deposition as occurring in a box that is

transported from Granite Bay, at the edge of the urban center, to UC-BFRS at a rate set by the local winds. Among the advantages of this model are the ability to easily
tune the model parameters or to fit them in a non-linear least squares sense, and the ability to use a model with as complete a representation of the chemistry as desired.

The model is formulated as follows. The change in concentration of a compound X with time is described by Eq. (1):

$$d[X]/dt = P_{x} - L_{x} + E_{x} - D_{x} - M_{x}$$
(1)

where *P* is photochemical production, *L* is photochemical loss, *E* represents emissions, *D* is deposition, and *M* represents mixing and entrainment of background air. The model uses Eq. (1) to compute the time-dependent chemical evolution of "*n*" molecules $X_1 - X_n$ in the air parcel.

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The chemical mechanism representing both the production (P_x) and loss (L_x) terms of Eq. (1) (see Appendix 1 for the detailed reaction set) includes 370 reactions, 170 specific chemicals and 7 lumped species representing the oxidation of VOCs by OH and O₃ in the presence of NO_x as described by the Master Chemical Mechanism

- ⁵ v3.1 (MCM) (Bloss et al., 2005a, b). Photolysis rate coefficients are taken from the TUV model (Madronich, 1987; Madronich and Flocke, 1998), with an ozone column of 300 DU and an aerosol vertical optical depth of 0.235, and from MCM (Bloss et al., 2005a, b) and vary according to solar zenith angle. Exception to strict adherence to MCM protocols are as follows.
- 1) Oxidation by the nitrate radical is not included because its concentration is assumed to be small during the daytime (12:00–17:00 LT) due to its short photolytic life-time (τ =5 s at noon).

2) Rate constants are taken from Sander et al. (2006) when available; otherwise rate constants are taken from MCM (Bloss et al., 2005a, b) (e.g. $IsopO_2 + RO_2$).

3) Isoprene and MBO are treated according to the MCM through the third generation oxidation products. After this point the products are lumped into a generic aldehyde species.

4) Monoterpene oxidation, represented by the oxidation of α -pinene, is treated according to Atkinson and Arey (2003).

- ²⁰ 5) The oxidation mechanism for isoprene nitrates allows the products of this reaction to be either a more highly functionalized alkyl nitrate (hydroxy alkyl nitrate) or NO_2 (Farmer and Cohen, 2008; Paulot et al., 2009; Perring et al., 2009). The MCM treats these reactions as producing NO_2 with 100% efficiency. In our reference model, isoprene nitrates (INs) are oxidized at the double bond instead of the nitrate group, to give
- ²⁵ a lumped class of more functionalized hydroxy alkyl nitrates at unit yield. Upon further oxidation (with τ_{OH} ~50 h), this secondary class of isoprene nitrates releases NO₂. Oxidation of all non-isoprene ANs are treated as prescribed by MCM.

6) Alkoxy radicals are assumed to react instantly with O_2 .

The resulting mechanism includes numerous individual aldehydes, ketones, organic

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acids, alcohols and peroxides. It includes 12 specific and 1 lumped alkyl or multifunctional nitrate and 9 specific and 1 lumped peroxy acyl nitrate. It includes a lumped aldehyde and a lumped organic peroxide.

- HO_x species are calculated at each time step assuming they are in photostationary state with the NO_x , VOC and sunlight. Important sources of HO_x in the model include the reaction of O^1D with water, photolysis of CH_2O to produce HO_2 , photolysis of methylglyoxal and reactions of O_3 with VOCs to produce OH, HO_2 and RO_2 species. There are a total of 14 specific RO_2 and 10 specific $RCOO_2$ and lumped values representing other RO_2 and other $RCOO_2$ radicals.
- ¹⁰ Modeled emissions of biogenic VOCs including isoprene, MBO and terpenes vary with temperature, PAR and land cover based on Steiner et al. (2006). Terpenes are assumed to be emitted in the form of α -pinene. Anthropogenic emissions are assumed to be zero. Biogenic NO_x emissions are estimated from measured fluxes of soil NO_x in the oak forests of the Sierra Nevada foothills (Herman et al., 2003). A consistent ¹⁵ emission flux of 10 ppt m s⁻¹ (5.7 ng (N) m⁻² s⁻¹) is applied to the entire transect.
 - Peroxy acyl nitrates, alkyl and multifunctional nitrates and HNO_3 are assumed to have deposition velocities (V_{dep}) of 1.1 cm/s, 2.7 cm/s and 3.4 cm/s, respectively (Farmer and Cohen, 2008). Deposition of O_3 is included with a V_{dep} of 0.8 cm/s (Kurpius et al., 2002b). Deposition of other species is neglected.
- ²⁰ We use the boundary layer averaged temperature which we estimate based on observed surface temperatures at Granite Bay and at UC-BFRS and the environmental lapse rate (6.5°C/km); the temperature is varied during the plume transit. The boundary layer height is assumed to be 800 m above the surface at all points along the transect.
- ²⁵ Calculations of the chemical evolution of the plume depends on accurate estimation of mixing/dilution rates as this is the single most important factor affecting concentrations. Mixing is assumed to be of the form:

 $d[X]/dt = -k_d([X] - [X]_{bg})$

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(2)

where k_d represents the dilution rate and the quantity $[X]_{bg}$ refers to the concentration of the species X in the background air that the plume is mixing with. In this formulation, we believe the calculation is most representative of the center line of the plume and that the single mixing parameter is likely more representative of vertical than horizontal 5 mixing.

At characteristic wind speeds, air masses passing over Granite Bay at 12:00 LT represent the initial conditions for air masses that reach the UC-BFRS at 17:00 LT. We chose this temporal window both to coincide with peak ozone concentrations and other urban influences at UC-BFRS at the end of the day, and to minimize uncertainty in the initial conditions associated with a dynamically growing planetary boundary layer. Planetary boundary layer growth is a strong and obvious feature in the measurements between 06:00 LT and 10:00 LT.

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The model is initialized with the noontime (11:00 LT to 13:00 LT median) observations of NO₂, total peroxynitrates (Σ PNs), total alkyl and multifunctional nitrates

- (ΣANs), HNO₃, a wide suite of anthropogenic and biogenic VOCs and O₃ obtained at Granite Bay, CA (38° N 44.23′, 121° W 12.01′, 277 m a.s.l. during the period of 19 July– 15 September 2001. This site is located 30 km north-east of Sacramento, CA, at the eastern edge of the suburban sprawl. These measurements and methods are described in detail by Cleary et al. (2005) and Millet et al. (2005). In this paper, we use
- ²⁰ data from Tuesdays through Fridays because differences in weekend emission patterns result in differences in chemistry (Murphy et al., 2006b; Murphy et al., 2007). Initial CO concentrations are based on measurements by the California Air Resources Board (CARB, 2009) at the North Highlands site located between one and two hours upwind of Granite Bay (~16 km) and methane is set at 1.85 ppm. A 3-h spin-up period
- initialized with 09:00 LT observations is used to set the concentration of species not measured and to obtain a speciated composition of ΣPNs and ΣANs. During the spinup period, emissions of all measured species are tuned so that final values at noon match the observations. Table 1 shows a list of the input parameters. Following this initialization, the plume is then propagated forward in time and space to represent the

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evolution of the Sacramento plume in the region downwind of anthropogenic influence. We determine the constant k_d by updating the analysis of Dillon et al. (2002) and using VOCs with lifetimes with respect to 3×10^6 molecules cm⁻³ of OH ranging from 1 to 6.5 d. Using a single value for OH, we find an average [OH]=8±3×10⁶ molecules cm⁻³ and k_d =0.24±0.06 h⁻¹. These are similar to those obtained by Dillon et al. (2002) (OH=11±5×10⁶ molecules cm⁻³; k_d =0.23±0.07 h⁻¹). In the current analysis, the two parameters are only weakly anti-correlated. The largest uncertainty in determining these parameters is knowledge of the background concentration. We use estimates of free tropospheric (above the planetary boundary layer) values based on measurements made directly along this transect on the return flight from the NASA TC4 experiment in 2007.

As noted above, an advantage of the model structure we have developed is that we are not forced to use a single value of OH. If we allow OH to vary during transport in response to changes in VOC reactivity, NO_x, peroxy radical concentrations, and other relevant production and loss terms, the optimization leads to k_d =0.31 (±0.026) h⁻¹ and an average OH of 5.0×10⁶ molecules cm⁻³. This value for k_d is used in the analysis described below. Additional details of the determination of OH and k_d are described in Appendices B and C.

4 Analysis of nitrogen oxide partitioning

²⁰ In this section we provide an analysis of the model output with respect to nitrogen oxide partitioning using observations of NO_x, Σ PNs, Σ ANs, and HNO₃ at UC-BFRS. We discuss the sensitivity of the model results to various physical parameters such as k_d , soil NO_x emissions, and deposition rates. Further, we explore the impact of some of the more uncertain parameters in the chemical mechanisms for acyl peroxy ²⁵ nitrates and hydroxy alkyl nitrates. Finally, we summarize our recommendations for a revised chemical mechanism that is consistent with recent research on isoprene



nitrates (Paulot et al., 2009; Perring et al., 2009) and PAN (LaFranchi et al., 2009; Wolfe et al., 2009).

4.1 Total nitrogen oxides

Comparison of the *Reference* model to observed nitrogen oxide concentrations at UC-5 BFRS is summarized in column 1 of Table 2 and shown graphically in Fig. 2. Figure 3 is a plot of the individual components of NO_{ν} over time as the plume travels from Granite Bay to UC-BFRS. ΣNO_v is initialized at the observed value of 13.18 ppb and is observed at to be 3.38 ppb at UC-BFRS. The predicted mixing ratio is 2.95 ppb, 15% lower than observed. Most of this decrease (77%) in ΣNO_v over the transect is calculated to be due to entrainment with the remaining 23% due to deposition. Perfect agreement between the model and observations could be achieved by increasing the initial NO_v from 13.18 ppb to 16 ppb, increasing the background NO_v by a factor of 1.75 from 0.825 ppb to 1.4 ppb, decreasing the mixing rate by 13% (0.31 h^{-1} to 0.27 h^{-1}), or decreasing the ratio of the deposition velocities (Vdep) to the planetary boundary layer (PBL) height by 45%. The changes needed in initial ΣNO_v and in ΣNO_v background 15 are both larger than what the observations suggest is a possible range. The change in the ratio of V_{dep} to PBL height is also unreasonably large. A 13% decrease in the dilution rate is just outside the range of uncertainty of the parameter $(0.31(\pm 0.026) h^{-1})$ estimated from a fit to the 10 VOCs described above and in Appendix B. This indicates that some combination of errors is the cause of the difference between the model and observations.

4.2 NO_x

The initial ΣNO_y at Granite Bay is 60% NO_x . As the plume evolves, NO_x is diluted by entrainment of cleaner air, is oxidized, and is produced by decomposition of PNs and oxidation of ΣANs and HNO_3 . Mixing of background air accounts for 50% of the reduction in NO_x observed in the model and 26% is due to oxidation of NO_2 to HNO_3 .

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The remaining decrease in NO_x is the loss by oxidation to Σ ANs (6%) and Σ PNs (18%), less the amount recycled from these compounds back to NO_x. The model predicts that NO_x at UC-BFRS is 734 ppt; this is an underestimate of 18%, about the same as the 15% underestimation of total NO_y. The model predicts that 25% of Σ NO_y at UC-⁵ BFRS is in the form of NO_x, in good agreement with observations (26%), indicating that the model does a reasonable job of reproducing the partitioning between NO_x and NO_z (NO_z= Σ PNs + Σ ANs + HNO₃).

4.3 ΣPNs

Peroxy acyl nitrates are formed through the reaction of peroxy acyl radicals with NO₂. Σ PNs are a unique in the class of nitrogen oxides because they thermally dissociate to release NO_x. Therefore, at the moderately high temperatures characteristic of the summer months in the region studied, Σ PNs are a source of NO_x. The observations of peroxy acyl nitrates at Granite Bay and UC-BFRS account for the sum of all the species of the form RO₂NO₂, as discussed by Cleary et al. (2007) and Day et al. (2002).

- Figure 4a shows ΣPNs and its components along the transect in the *Reference* model. We calculate concentrations of 9 speciated peroxy acyl nitrates including PAN and MPAN as well as a lumped peroxy acyl nitrate. After the initial 3-h spin up time, we calculate the initial ΣPNs to be 54% PAN, 11% MPAN, and 10% other speciated PNs with the remaining 25% a lumped PN. Cleary et al. (2007) estimate the partitioning
- ²⁰ of Σ PNs at Granite Bay based on measurements and estimates of aldehydes in the region. They calculate the Σ PNs to be a mixture of 70% PAN, 10% PPN, 3% MPAN with the remaining 17% other C₄-C₉PNs. The differences point to a variety of possible errors in VOC oxidation chemistry of MCM and the resulting aldehyde estimates at Granite Bay.
- The components of ΣPNs calculated at UC-BFRS are 45% PAN, 39% lumped PNs, 7% MPAN, 6% 2-hydroxy-2-methyl peroxypropionyl nitrate (C4PAN5) which is a peroxy acyl nitrate species formed via the oxidation of MBO and 3% distributed among the 6 remaining speciated peroxy acyl nitrates. Glycoaldehyde, an oxidation product of both





MBO and isoprene, is a major source of non-speciated PNs in the model. Another significant source of these lumped PNs is the unspeciated class of aldehydes, which are the sum of all untracked of anthropogenic VOCs, including many 1st generation oxidation products of AVOCs. These predictions of speciation are inconsistent with recent observations at UC-BFRS (LaFranchi et al., 2009; Wolfe et al., 2009) and with analysis of several previous data sets where Σ PNs and individual PNs were measured (Wooldridge et al., 2009). In each of these studies, PAN is typically 80–90% of Σ PNs, with the remaining 10–20% being comprised of MPAN and PPN. PPN is not tracked in the model due to a lack of observations of propanal; we expect that inclusion of PPN would add 5–10% to the Σ PNs budget in this model (LaFranchi et al., 2009). Using an estimated propanal concentration along the transect, we find that when PPN is 10% of

ΣPNs, the ΣPNs/NO_x ratio increases by 10%. The modeled ΣPNs/NO_x ratio is 1.052, close to the observed value of 1.09. The ΣPNs/NO_y ratio is 0.26, slightly lower than the observed value of 0.28. There are

- ¹⁵ significant discrepancies, however, between the Σ PNs composition in the model and that observed at UC-BFRS. Specifically, PAN is too small relative to Σ PNs, and the lumped PNs are too large. Since the Σ PNs/NO_x ratio is in relative agreement with observations, despite these discrepancies, it is likely that there are two or more canceling errors in the model resulting in: a) an underestimate of the peroxy acetyl (PA) radical
- ²⁰ abundance, leading to an underestimate of PAN, and b) a compensating overestimate of the stability of the unspeciated class of PNs or the abundance of its precursors, leading to unrealistically high concentrations of these species as a fraction of Σ PNs.

An underestimate of PA radical sources is common in many previous studies where isoprene chemistry is important (Roberts et al., 2001; Roberts et al., 2006; Cleary

et al., 2007). However, recent observations of PAN at UC-BFRS have shown that the total PA radical source can be quantified by including production from acetaldehyde, methylvinyl ketone (MVK), methyl glyoxal, methacrolein, and biacetyl (LaFranchi et al., 2009). The only molecule that is not tracked in the model is biacetyl, which photolyzes to give 2 PA radicals and was found to be responsible for 15–25% of the total PA





radical source at UC-BFRS (LaFranchi et al., 2009). An additional source of error, however, is that MVK (Dreyfus et al., 2002) and acetaldehyde (Schade and Goldstein, 2001) at UC-BFRS are underestimated in the model by 10% and 100%, respectively. Artificially adding sources of acetaldehyde, biacetyl, and MVK along the transect to ⁵ match observations of these oVOCs at UC-BFRS increases the PA radical production rate by nearly a factor of 2.

An overestimate of the abundance of lumped PNs in the model is not surprising, given that a wide variety of oVOCs of varying chain-length and functionality are treated identically in their ability to form PNs. It is likely that many of these aldehydes do not form PNs in the atmosphere. For example, Magneron et al. (2005) found no evidence for PN formation in an experimental study of the oxidation of glycoaldehyde, an important component of lumped PNs in the MCM chemistry. Additionally, Carrasco, et al. (2006) studied the fate of 2-hydroxy-2-methylpropanal (C4PAN5, in Fig. 3) using the EUPHORE outdoor simulation chamber and observed a 100% apparent yield for acetone production following reaction with OH, whether NO_x was present or not,

¹⁵ for acetone production following reaction with OH, whether NO_x was present or r apparently indicating the corresponding PN is not formed.

To incorporate the above discussion into the model, a model scenario (PNs₁ in Table 2) was run in which the production of unspeciated PNs is set to zero and the PA production rate is doubled (by artificially increasing acetaldehyde and biacetyl sources).

- Figure 4b shows the PNs composition along the transect in this model scenario. Relative to the *Reference* case, there is a significant increase in the fraction of Σ PNs that are PAN and a net decrease in the Σ PNs/NO_x ratio. The model output in this case underestimates the observed Σ PNs/NO_x ratio by 22%, indicating that a further increase in the PA radical source at some point along the transect is required. Not account-
- $_{25}$ ing for PPN production in this model scenario could account for 25–50% of the 22% underestimate in the $\Sigma PNs/NO_x$ ratio.



Interactive Discussion



4.4 **ΣANs**

Observations of total alkyl and multifunctional nitrates at Granite Bay and UC-BFRS have been described by Cleary et al. (2005) and Day et al. (2003). The ΣANs composition predicted at UC-BFRS in the *Reference* model is 68% a lumped hydroxy alkyl nitrate that is the product of the reaction of isoprene-derived RONO₂ (INs) with OH, 11% isoprene nitrates, 17% alkyl nitrates produced from MBO oxidation, 3% primary Σnon-speciated ANs and 1% the sum of the 4 other speciated alkyl nitrates (MVKANO₃, C₅₈NO₃, CH3NO₃, and AromaticNO₃) that are tracked in the model. Figure 5 shows the time evolution of these fractions of ΣANs in the reference model along with the ΣANs observed at UC-BFRS. Isoprene nitrates and their oxidation products comprise a large fraction of ΣANs in the model. This detailed calculation supports previous assertions and calculations that ΣANs are a complex mixture (Day et al., 2003) and that they are a major NO_y reservoir. Further, the calculation indicates that the primary ANs are a small fraction of the total, even in regions with a very strong influence from biogenics.

¹⁵ The parameters used in predicting ANs are among the more uncertain ones in the model. Alkyl nitrates are produced via the reaction of RO₂ with NO

$$RO_2 + NO \xrightarrow{(1-\alpha)} RO + NO_2$$
 (R1a)

 $RO_2 + NO \xrightarrow{\alpha} AN$

where α , known as the branching ratio, is the fraction of the time an AN is produced instead of an NO₂ molecule. For many molecules the branching ratio is not well known. Oxidation products of ANs are even less well understood. Reactions of ANs can lead to a multifunctional compound that retains the $-ONO_2$ functional group (R2a) or release NO₂ (R2b).

 $\mathsf{AN} + \mathsf{OH} \to \mathsf{ANOH}$

²⁵ AN + OH \rightarrow oVOC + NO₂

(R1b)

(R2a)

(R2b)

Laboratory measurements of α for isoprene span a range from 4.4% to 15% (Tuazon and Atkinson, 1990; Chen et al., 1998; Chuong and Stevens, 2002; Sprengnether et al., 2002) with more recent values between 8% and 12% (Patchen et al., 2007; Paulot et al., 2009). In MCM, as well as in our reference model, the average branching ratio represented by the 4 isoprene nitrates isomers is 10.8%.

5

The effects of Reaction (R2) and the role of isoprene nitrates have been the subject of several recent manuscripts (Horowitz et al., 2007; Farmer and Cohen, 2008; Ito et al., 2009; Perring et al., 2009). Analyses of field data have resulted in estimates for combined parameters reflecting α for isoprene and the relative yield of ANOH in Reaction (R2) (via R2a). These variables affect the NO_x budget and production of ozone

- ¹⁰ action (R2) (via R2a). These variables affect the NO_x budget and production of ozone on regional and global scales (Ito et al., 2009). Horowitz et al. (2007) recommended α =4% as a best fit to ΣAN data with 60% of ΣANs reacting via path 2a and 40% via 2b. Perring et al. (2009) compared field observations of the ΣANs and CH₂O correlation and found a set of α 's, lifetimes to OH, and ANOH yields (R2a) (4.4%, 16 h, and 97%; 8%, 2.5 h, and 79%; and 12%, 95 min, and 67%) that were each consistent with
- observations. Previous analysis by Farmer and Cohen (2008) at UC-BFRS suggested that 70–94% of the products of R2 are ANOH.

The slope of O_3 vs. ANs has been previously used to derive the effective branching ratio for the reaction of RO_2 with NO to produce ΣANs (Day et al., 2003; Rosen et al., 2004) and ΣANS (Day et al., 2005) and ΣANS (Day et al., 2004) and ΣANS (Day et al., 2005) and ΣANS (Day et al., 2005)

- ²⁰ 2004; Cleary et al., 2005). This assumes that the production rates ($P(O_3)$ and $P(\Sigma ANs)$) are the only relevant processes that affect their respective concentrations. Using this method, Day et al. (2003) calculated an effective branching ratio of 2.5% at UC-BFRS and Cleary et al. (2005) calculated an effective branching ratio of 4.2% at Granite Bay. If we repeat these analyses for UC-BFRS, generating a range of model predictions by
- ²⁵ varying the temperature and initial NO_x (details of these different model scenarios will be presented in a future manuscript), the slope of modeled O₃ to modeled Σ ANs is 83 and the calculated effective yield is 2.4%, approximately equal to the 2.5% inferred from observations by Day et al. (2003).

Despite the good agreement in the estimated effective yield, there are other pro-

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cesses besides $P(O_3)$ and $P(\Sigma ANs)$ that affect the slope of this line which should be considered. In particular, the lifetime of ΣANs , a rather uncertain quantity due to uncertainties in the branching for Reaction (R4), will have a large effect on the O_3 vs. ΣANs slope. The ratio of ΣANs to NO_x is, perhaps, a better indicator of whether the balance ⁵ between ΣANs production and loss is modeled properly, since NO_x is both a precursor to and a potential reaction product of ΣANs .

The ratio of Σ ANs to NO_x (0.52) is underestimated in the *Reference* model by 13%. The underestimate of the Σ ANs/NO_x ratio indicates that the model does not accurately simulate the competition between Σ ANs production and its conversion back to NO_x in the atmosphere, resulting in too little Σ ANs production, too much NO_x recycling, or some combination of both. It should be noted that the Σ ANs/NO_x ratio in the

10

model is relatively insensitive to changes made to the Σ PNs chemistry (as discussed in Sect. 4.3).

It is important, therefore, to probe the effects of changes to the ΣANs production rate and the branching of Reaction (R2) independently in order to better evaluate the performance of the model and its sensitivities to each of these unknown parameters. Since isoprene is a significant portion of the VOC reactivity is the model, we can constrain the model with the findings of some recent studies on isoprene nitrate production and loss rates, thus testing our assumptions about the remaining fraction of ΣANs. In the

²⁰ following discussion, we study the effects of varying α and the yield for Reaction (R2a) within the constraints laid out by Paulot et al. (2009) and Perring et al. (2009) and assess how these changes to the MCM chemistry scheme affect the $\Sigma ANs/NO_x$ ratio in the model and how they compare to observations at UC-BFRS.

First the MCM α values were scaled to 4.4% or 12% for isoprene nitrate production, while keeping the split between Reaction (R2a) and (R2b) as in the *Reference* case. The effect of changing α for isoprene results in a Σ ANs concentration at UC-BFRS of 324 ppt in the 4.4% case (ANs_1 in Table 2) and 394 ppt in the 12% case (ANs_2), an overall change in Σ ANs of 20% between the two extremes. The change in the Σ ANs/NO_x in these two scenarios is also significant, varying from 0.43, when α is

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4.4%, to 0.54, when α is 12%. The observed value is 0.59, suggesting an error in the model associated with the branching ratios of other alkyl nitrates or with the fate of the Σ ANs class.

Second, we examine the impact of introducing an NO₂ recycling scheme to the 5 model for isoprene nitrate oxidation that is consistent with Perring et al. (2009) and Paulot et al. (2009). In this scheme, the nitrate-peroxy radicals ($IsopNO_3O_2$), resulting from addition of OH to the isoprene nitrate double bond (R3), are tracked explicitly, in the same manner that other RO₂ species are treated in the MCM. Paulot et al. (2009) found that when IsopNO₃O₂ reacts with NO, 50% of the reactions lead to nitrate group retention (R4a) with the remaining 50% leading to recycling of NO₂ (R4b). Reaction 10 of IsopNO₃O₂ with HO₂ and RO₂ (R4c) has yet to be studied experimentally; we assume here that this reaction always leads to retention of the nitrate group. The reaction series of (R3) and (R4) is analogous to (R2), as written above, however, it allows for a variable NO₂ yield, depending on the [NO]/[HO₂+RO₂] ratio, which determines the branching between Reaction (R4a, b) and (R4c). When this chemistry is incorporated 15 into the model, the NO₂ yield ranges from 41-50% and is 46% on average across the transect.

 $IN + OH \rightarrow IsopNO_3O_2$ (R3)

 $IsopNO_3O_2 + NO \rightarrow ANOH + NO_2$ (yield = 50%)

IsopNO₃O₂ + NO
$$\rightarrow$$
 oVOC + 2 NO₂ (yield = 50%)

 $IsopNO_3O_2 + HO_2, RO_2 \rightarrow ANOH$

25

Paulot et al. (2009) also tracked a number of the second generation nitrate-containing products of Reaction (R4a). Since we do not treat the individual second generation nitrates explicitly, we vary the lifetime for this unspeciated pool of compounds so that the effective IN (both primary and secondary) lifetime equals 2.5 h, when α =8%, and 95 min, when α =12%. This allows for a direct comparison with two sets of NO₂ yields



(R4a)

(R4b)

(R4c)



and branching ratios identified by Perring et al. (2009) that are consistent with observations of Σ ANs and CH₂O in the boundary layer over the Southeast US. The lifetime of the primary INs to Reactions (R3)+(R4b) is constrained by the MCM rate constants, limiting the range of potential effective lifetimes for isoprene nitrates to less than 5 h in the model. The results from four different model scenarios using different combinations of α_{isop} and IN lifetime (tuned by varying the rate of Reaction (R2) for the secondary

INs) are shown in Table 2 (ANs_3-ANs_6).

5

Introducing this NO₂ recycling mechanism to the model has a dramatic effect on the $\Sigma ANs/NO_x$ ratio, resulting in a 104% underestimation in the first case (ANs_3: $\alpha = 8\%$, $\tau = 2.5$ h) and a 123% underestimation in the second case (ANs_4: $\alpha = 12\%$,

- ¹⁰ α =8%, τ = 2.5 h) and a 123% underestimation in the second case (ANs_4: α =12%, τ =100 min). The model can be improved by progressively lowering α , while simultaneously increasing in the secondary ANs lifetime. However, even at the deposition-limited lifetime for the secondary isoprene nitrates (8 h) the Σ ANs/NO_x ratio is underestimated by 50% (ANs_5: using the corresponding α =6%, with an effective τ =4.9 h). The highest possible IN yield and lifetime (ANs_6: α =12%, τ =4.5 h) still underestimates the
- Σ ANs/NO_x ratio by 36%. In all of these cases, the NO₂ recycling mechanism leads to an underestimation of the amount of Σ ANs produced at a given NO_x abundance. The Σ ANs/NO_x ratio was found to be sensitive to the soil NO_x source strength, increasing with decreasing emissions; setting the NO_x emissions to zero improves the model predictions by about 10–15%.

If the N-containing product of Reaction (R2b) were HNO₃ instead of NO₂, the ΣANs/NO_x ratio would improve; this would, however, be inconsistent with the HNO₃/NO_x ratio, as it is already overestimated (see Sect. 4.5). Assuming this chemistry is correct, we find that we can close the gap between the model and the observations, while including the Paulot isoprene nitrate mechanism, if nearly 100% of the non-isoprene alkyl nitrates retain their nitrate functionality upon oxidation by OH. As these nitrates are mostly MBO-derived, one interpretation of these results is that a significant fraction of MBO-derived nitrates reacts primarily via (R2a). Additionally, while terpene-derived nitrates are calculated to be a minor fraction of ΣANs, there is substan-

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tial uncertainty in their secondary chemistry and they may in fact be a larger fraction of Σ ANs in the region. Other possibilities of paired errors, of course, exist. A better understanding of the production and fate of nitrates from MBO and terpene oxidation is required to adequately constrain Σ ANs chemistry in the region.

5 4.5 HNO₃

10

Nitric acid accounts for 25% of the initial ΣNO_y concentration and 32% of the ΣNO_y observed at UC-BFRS. Its mixing ratios along the transect are controlled by production due to reaction of OH with NO₂, entrainment of air with a lower concentration (62%), and loss to deposition (37%). Loss of HNO₃ to oxidation by OH accounts for less than 1% of the loss of HNO₃. The *Reference* model HNO₃ is within a few percent of the observations, however, the HNO₃/NO_x ratio is overestimated by 14%.

 HNO_3 concentration at UC-BFRS is sensitive to the assumptions made with respect to the ΣPNs and ΣANs chemistry, as discussed above. In a revised model (*Rev.* in Table 2), which incorporates changes to the ΣPNs chemistry and allows for NO_2 re-

- ¹⁵ cycling by isoprene nitrates as discussed above, the concentration of HNO₃ increases relative to the reference model due higher sustained NO_x as a result of increased recycling from Σ ANs and a lower concentration of Σ PNs precursors. The HNO₃/NO_x ratio is overestimated by 12% in the revised model, slightly lower than that in the *Reference* model.
- ²⁰ Tuning of the average Σ ANs branching ratio, the yield of Reaction (R2), and the acyl peroxy radical production rate in the model can simultaneously minimize the error in the HNO₃/NO_x, Σ ANs/NO_x, and Σ PNs/NO_x ratios to under 10% for each. It is suspected, therefore, that uncertainties in the chemistry of Σ PNs and Σ ANs are linked to the discrepancy between the modeled and observed HNO₃/NO_x ratio.

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5 Atmosphere-biosphere exchange of nitrogen

5.1 Soil NO_x emissions

Herman et al. (2003) made measurements of soil NO_x emissions in the oak forests of the Sierra Nevada foothills to the west of UC-BFRS. They observed fluxes in the range of 5.8 to 15 ppt m s⁻¹ (3.3 to 8.6 ng (N) m⁻² s⁻¹) in the summer which is a total source of 0.131 to 0.338 ppb if the emissions are assumed to be constant between Granite Bay and UC-BFRS. A soil NO_x source in the middle of this range (10 ppt m s⁻¹) was chosen.

In order to understand the effects of soil NO_x emissions, we ran a zero soil emissions scenario for the *Reference* model (E_NO_0 , in Table 2). In this case, the absence of a soil NO_x source leads to a worsening of the agreement of the NO_x/NO_y ratio from a 2% underestimate to a 10% underestimate. Total NO_y at UC-BFRS decreases in the model by about 100 ppt or 4% in the absence of soil NO_x emissions. An important result is that modeled ozone concentrations are little affected by this change. A soil NO_x source of 45 ppt m s⁻¹ (25.8 ng (N) m⁻² s⁻¹), 3 times larger than prior observations, is required to match observations of total NO_y; however, an accompanying increase in HO_x radical concentrations would be required to keep the NO_x/NO_z ratio in agreement.

We conclude that a soil NO_x source in the range of observations by Herman et al. (2003) is consistent with the observed NO_x/NO_y ratio, but has little effect on the total NO_y abundance or on ozone production. It should be noted that these conclusions are sensitive to the imposed NO_x background in the model of 100 ppt and they suggest that the background is sustained by soil NO_x emissions.

5.2 Nitrogen deposition

The model allows us to estimate the extent of N deposition, facilitated by the conversion of NO_x to NO_z , that occurs in the downwind regions of the Sacramento urban area. While speciation within the NO_7 class is important due to differences in deposition

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rates for ΣPNs vs. ΣANs vs. HNO_3 , and while there are known errors in the model with respect to ΣANs and ΣPNs chemistry, nevertheless, first-order approximations can be made about the magnitude of N deposition along the model transect because of the agreement between observed and modeled NO_x/NO_z ratios, particularly in the *Reference* model.

We use the *V*_{dep} calculated by Farmer and Cohen (Farmer and Cohen, 2008) to represent deposition of ΣPNs, ΣANs and HNO₃. The deposition falls off as the plume is advected from Granite Bay. In the *Reference* model, the N-deposition ranges from 82 ng (N) m⁻² s⁻¹ at Granite Bay to 26 ng (N) m⁻² s⁻¹ at UC-BFRS. Of the total N deposited, 79% is due to HNO₃ deposition, 11% to ΣANs deposition and 10% to the deposition of ΣPNs. The average deposition throughout the transect is 55 ng (N) m⁻² s⁻¹ which is approximately 17 kg (N) ha⁻¹ yr⁻¹. Bytnerowizc and Fenn (1996) report values that range from 0.5 to 35 kg (N) ha⁻¹ yr⁻¹ for California based on measurements of NO₃⁻¹ and NH₄⁺ rinsed off of foliage. Tarnay et al. (2001) estimate the flux of nitrogen to the Lake Tahoe Basin to be 1.7 to 2.9 kg N ha⁻¹ yr⁻¹ based on measurements of HNO₃ and NH₃. These values are lower than those obtained in this study because of the lower concentration of nitrogen species further away from the source region (Sacramento).

The nitrogen deposition rate calculated here is much larger than the rate of N emission from soils estimated in the model $(2 \text{ ng}(\text{N}) \text{ m}^{-2} \text{ s}^{-1} \text{ or } 0.6 \text{ kg}(\text{N}) \text{ ha}^{-1} \text{ yr}^{-1})$, suggesting a net accumulation of nitrogen in the region's ecosystem of 16 kg (N) ha⁻¹ yr⁻¹.

6 Conclusions

A Lagrangian box model representing mixing, photochemistry and dry deposition was used to describe the evolution of the plume originating in the Sacramento Area as it is advected into the western Sierra. The model was used to consider effects of a variety of poorly understood processes that affect the chemical evolution of organic nitrogen within the plume. Comparisons of the model with observations of NO_{y,i} at UC-BFRS show that the model captures many of the observed features of the plume chemistry 9, 27099–27165, 2009

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of NO_y. This is the first such model that provides a detailed representation of the partitioning of NO_y in an urban plume backed by observations of NO_x, Σ ANs, Σ PNs, and HNO₃.

We find that significant deviations from observations of speciated PNs at UC-BFRS
 (LaFranchi et al., 2009; Wolfe et al., 2009) and elsewhere (Roberts et al., 2007; Wooldridge et al., 2009) occur in the model when lumped aldehydes are given the opportunity to form PNs indiscriminately and with the same efficiency as PAN. A PAN/ΣPNs ratio of 80%, in good agreement with observations, can be attained if this lumped PN species is not allowed to form and is accompanied by an increase in the concentration of PAN precursors.

We also find that there is significant uncertainty surrounding the production and fate of Σ ANs. Incorporating recent findings about isoprene nitrate chemistry into the model leads to large errors in Σ ANs abundance. Given these new constraints on isoprene nitrates, the results indicate that the reaction of other ANs with OH must produce more oxidized Σ ANs, as opposed to HNO₃ or NO₂ as is present in other models. It is recommended that future laboratory and modeling experiments focus on understanding the formation yield and NO_x recycling rate for MBO- and terpene-derived nitrates.

Finally, model results show that adding biogenic NO_x emissions throughout the transect increases the available NO_x at UC-BFRS, but modeled ozone concentrations were

²⁰ little affected by the increased biogenic NO_x . Nitrogen deposition is estimated to be 17 kg (N) ha⁻¹ yr⁻¹, on average, along the model transect leading to a net nitrogen accumulation in the biosphere of 16 kg (N) ha⁻¹ yr⁻¹ through exchange with the atmosphere.

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Appendix A

Chemical mechanism

Definitions used in the following mechanism:

RO₂=non-speciated organic peroxy radical

RCOO₂=non-speciated peroxy acyl radical

¹⁰ $\Sigma RO_2 = \Sigma RO_2 + \Sigma RCOO_2$ (both speciated and non-speciated)

Aldehyde=non-speciated aldehyde

RONO₂≡non-speciated alkyl nitrate

15

5

IN-OH≡second generation isoprene nitrate (hydroxy alkyl nitrate)

 $\gamma \equiv NO_2$ yield for IN-OH+OH reactions (0% or 50%)

20 RCOO₂NO₂=non-speciated peroxy acyl nitrate

ROOH≡non-speciated organic peroxide

	Benzene + OH \rightarrow 0.648 HO ₂ + 0.352 AromaticO ₂ + 0.118 Aldehyde	(A1)
25	Ethylbenzene + OH \rightarrow 0.28 HO ₂ + 0.72 AromaticO ₂ + 0.1 Aldehyde	(A2)
	Toluene + OH \rightarrow 0.28 HO ₂ + 0.72 AromaticO ₂ + 0.1 Aldehyde	(A3)

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	<i>m</i> -xylene + OH \rightarrow 0.46 HO ₂ + 0.54 AromaticO ₂ + 0.29 Aldehyde	(A4
	o-xylene + OH → 0.40 HO ₂ + 0.6 AromaticO ₂ + 0.24 Aldehyde	(A5
	p -xylene + OH \rightarrow 0.275 HO ₂ + 0.725 AromaticO ₂ + 0.115 Aldehyde	(A6
	$CH_2O + OH \rightarrow HO_2 + CO$	(A7
5	α -pinene + OH \rightarrow 0.44 HO ₂ + 0.1 acetone + 0.44 pinonaldehyde	(A8
	$HCOCO_2H + OH \rightarrow HO_2 + CO$	(A9
	Isopaoh + OH \rightarrow HO ₂ + 0.5 HC ₄ CCHO + 0.5 HC ₄ ACHO	(A10
	Isopboh + OH → 0.75 HO ₂ + IsopbO ₂ + 0.25 CH ₃ O ₂ + 0.75 CH ₂ O + 0.75 MVK +0.25 MVKOH	(A11
10	Isopdoh + $OH \rightarrow HO_2 + HCOC5$	(A12
	Glyoxal + OH \rightarrow 0.6 HO ₂ + 0.4 HCOCO ₃ + 1.2 CO	(A13
	Acetol + $OH \rightarrow HO_2 + Mgly$	(A14
	$HOCH_2CO_2H + OH \rightarrow HO_2 + CH_2O$	(A15
	$MACROH + OH \rightarrow HO_2 + CH_2O + ACETOL$	(A16
15	$MACROOH + OH \rightarrow MACRO_2$	(A17
	$HOCH_2CHO + OH \rightarrow 0.2 HO_2 + 0.8 RCOO_2 + 0.2 glyoxal$	(A18
	$ACO_2H + OH \rightarrow HO_2 + CO + CH_2O$	(A19
	$HO12CO_3C4 + OH \rightarrow HO_2 + BIACETOH$ 27123	(A20





	$HC_4ACO_2H + OH \rightarrow HO_2 + CO + ACE$	ETOL	(A21)	1000
	$MBOACO + OH \rightarrow HO_2 + MBOCOCO$)	(A22)	
	$MBOBCO + OH \rightarrow C_4OH_2CO_3$		(A23)	9, 27099–27165, 2009
	$MBOAOH + OH \rightarrow HO_2 + MBOACO$		(A24)	Nitrogen oxide
5	ipropol + OH \rightarrow 0.861 HO ₂		(A25)	urban plume
	$IPRHOCO_2H + OH \rightarrow HO_2 + acetone$		(A26)	I. M. Pérez et al.
	Methanol + OH \rightarrow HO ₂ + CH ₂ O		(A27)	
	n-butane + OH \rightarrow RO ₂		(A28)	Title Page
	hexane + OH \rightarrow RO ₂		(A29)	Abstract Introduction
10	i-butane + OH \rightarrow RO ₂		(A30)	Conclusions References
	i-pentane + OH \rightarrow RO ₂		(A31)	Tables Figures
	n-pentane + OH \rightarrow RO ₂		(A32)	I ∢ ►I
	methylpentanes + $OH \rightarrow RO_2$		(A33)	▲ ▶
	heptane + OH \rightarrow RO ₂		(A34)	Back Close
15	2,2-dimethylpropane + $OH \rightarrow RO_2$		(A35)	Full Screen / Esc
	$C_2CI_4 + OH \rightarrow RO_2$		(A36)	Printer-friendly Version
	$CH_2CI_2 + OH \rightarrow RO_2$		(A37)	Interactive Discussion
	$CH_3CI + OH \rightarrow RO_2$		(A38)	

	Cyclopentane + $OH \rightarrow RO_2$	(A39)		
	$MTBE + OH \rightarrow RO_2$	(A40)	AC	PD
	1-butene + OH \rightarrow RO ₂	(A41)	9, 27099–2	7165, 2009
	propyne + $OH \rightarrow RO_2$	(A42)	Nitroge	n oxide
5	ethane + $OH \rightarrow RO_2$	(A43)	urban	plume
	ethanol + OH \rightarrow RO ₂ + 0.95 HO ₂ + 0.887 acetaldehyde	(A44)	I. M. Pér	rez et al.
	1,3-butadiene + OH \rightarrow RO ₂	(A45)		
	C2-pentene + OH \rightarrow RO ₂	(A46)	Title	Page
	cyclopentene + $OH \rightarrow RO_2$	(A47)	Abstract	Introduction
10	MEK + OH \rightarrow RO ₂ + 0.2772 acetaldehyde	(A48)	Conclusions	References
	2-methylpropene + $OH \rightarrow RO_2$	(A49)	Tables	Figures
	1-pentene + $OH \rightarrow RO_2$	(A50)	I	۰
	Propane + $OH \rightarrow RO_2$	(A51)	•	E State
	propene + $OH \rightarrow RO_2$	(A52)	Back	Close
15	t2-butene + OH \rightarrow RO ₂	(A53)	Full Scre	en / Esc
	t2-pentene + OH \rightarrow RO ₂	(A54)	Printer-frien	dly Version
	3-methyl-1-butene + $OH \rightarrow RO_2$	(A55)	Interactive	Discussion
	2-methyl-1-butene + OH \rightarrow RO ₂	(A56)	<u></u>	O

	α -pinene + OH \rightarrow 0.82 RO ₂ + 0.21 CH ₂ O	(A57)	1000
	pinonaldehyde + OH \rightarrow 0.228 RO ₂ + 0.772 RCOO ₂	(A58)	ACPD
	acetone + $OH \rightarrow RO_2$	(A59)	9, 27099–27165, 2009
	$HCOC5 + OH \rightarrow RO_2$	(A60)	Nitrogen oxide
5	MVKOH + OH \rightarrow RO ₂	(A61)	urban plume
	isopropol + OH \rightarrow 0.139 RO ₂ + 0.861 acetone	(A62)	I. M. Pérez et al.
	pentanal + OH \rightarrow 0.19 RO ₂ + 0.81 RCOO ₂	(A63)	
	isoprene + OH \rightarrow 0.164 IsopaO ₂ + 0.491 IsopbO ₂ + 0.086 IsopcO ₂ +0.259 IsopdO ₂	(A64)	Title Page Abstract Introduction
10	MVK + OH \rightarrow 0.3 HMVKAO ₂ + 0.7 HMVKBO ₂	(A65)	Conclusions References
	MACR + OH \rightarrow 0.43 MACRO ₂ + 0.57 MACRO3	(A66)	Tables Figures
	$HC_4CCHO + OH \rightarrow 0.52 C57O_2 + 0.48 HC_4CCO_3$	(A67)	I∢ ►I
	$HC_4ACHO + OH \rightarrow 0.52 C58O_2 + 0.48 HC_4ACO_3$	(A68)	
	$CH_4 + OH \rightarrow CH_3O_2$	(A69)	Back Close
15	$CH_3CO_2H + OH \rightarrow CH_3O_2$	(A70)	Full Screen / Esc
	$CH_3COOH + OH \rightarrow CH_3O_2$	(A71)	Printer-friendly Version
	$MBO + OH \rightarrow 0.67 MBOAO_2 + 0.33 MBOBO_2$	(A72)	Interactive Discussion
	$MBOAOOH + OH \rightarrow MBOAO_2 + MBOACO$ 27126	(A73)	

	$MBOBOOH + OH \rightarrow MBOBO_2 + MBOBCO$	(A74)	
	Hexanal + OH \rightarrow RCOO ₂	(A75)	
	$HC_4CCO_3H + OH \rightarrow RCOO_2$	(A76)	9, 27099–27165, 2009
	$HOCH_2COCHO + OH \rightarrow RCOO_2$	(A77)	Nitrogen oxide
5	$HC_4ACO_3H + OH \rightarrow RCOO_2$	(A78)	urban plume
	Aldehyde + $OH \rightarrow RCOO_2$	(A79)	I. M. Pérez et al.
	$HCOCO_3H + OH \rightarrow HCOCO_3$	(A80)	
	$MACO_3H + OH \rightarrow MACRO3$	(A81)	Title Page
	mgly + OH \rightarrow CH ₃ CO ₃ + CO	(A82)	Abstract Introduction
10	$HC_4CCO_2H + OH \rightarrow CH_3CO_3 + HOCH_2CHO$	(A83)	Conclusions References
	$CO_23C3CHO + OH \rightarrow CH_3CO_3 + 2 CO$	(A84)	Tables Figures
	$CH_3COCO_2H + OH \rightarrow CH_3CO_3$	(A85)	14 > 1
	$MACO_{2}H + OH \rightarrow CH_{3}CO_{3} + CH_{2}O$	(A86)	• •
	Acetaldehyde + $OH \rightarrow CH_3CO_3$	(A87)	Back Close
15	$ACO_3H + OH \rightarrow ACO_3$	(A88)	Full Screen / Esc
	Vglyox + OH \rightarrow ACO ₃ + CO	(A89)	Printer-friendly Version
	$CO_2H_3CHO + OH \rightarrow CO_2H_3CO_3$	(A90)	Interactive Discussion
	$C_4OH_2CO_3H + OH \rightarrow C_4OH_2CO_3$ 27127	(A91)	CCC D

	Ibutaloh + OH \rightarrow IPRHOCO ₃	(A92)	
	$IPRHOCO_3H + OH \rightarrow IPRHOCO_3$	(A93)	
	$MBOBCOCO + OH \rightarrow IPRHOCO_3 + CO$	(A94)	9, 27099–27165, 2009
	$IsopaNO_3 + OH \rightarrow IsopaNO_3O_2$	(A95)	Nitrogen oxide
5	$IsopbNO_3 + OH \rightarrow IsopbNO_3O_2$	(A96)	urban plume
	$IsopcNO_3 + OH \rightarrow IsopcNO_3O_2$	(A97)	I. M. Pérez et al.
	$IsopdNO_3 + OH \rightarrow IsopcNO_3O_2$	(A98)	
	$C58NO_3 + OH \rightarrow NO_2 + Aldehyde$	(A99)	Title Page
	$HMVKANO_3 + OH \rightarrow NO_2 + Aldehyde$	(A100)	Abstract Introduction
10	AromaticNO ₃ + OH \rightarrow NO ₂ + Aldehyde	(A101)	Conclusions References
	$MBOANO_3 + OH \rightarrow NO_2 + Aldehyde$	(A102)	Tables Figures
	$MBOBNO_3 + OH \rightarrow NO_2 + Aldehyde$	(A103)	∢ ▶
	$IN-OH+OH \rightarrow NO_2 + Aldehyde$	(A104)	✓ ►
	$RONO_2 + OH \rightarrow NO_2 + Aldehyde$	(A105)	Back Close
15	$CH_3NO_3 + OH \rightarrow NO_2 + CH_2O$	(A106)	Full Screen / Esc
	$PAN + OH \rightarrow NO_2 + CO + CH_2O$	(A107)	Printer-friendly Version
	C4PAN5 + OH \rightarrow NO ₂ + CO + acetone	(A108)	Interactive Discussion
	C4OH2CPAN + OH \rightarrow NO ₂ + CO + Ibutaloh 27128	(A109)	CC I

	$RCOO_2NO_2 + OH \rightarrow NO_2 + Aldehyde$		(A110)	
	$ACRPAN + OH \rightarrow NO_2 + CO + HOCH$	I ₂ CHO	(A111)	
	$MPAN + OH \rightarrow NO_2 + CO + ACETOL$		(A112)	9, 27099–27165, 2009
	$GLYPAN + OH \rightarrow NO_2 + CO$		(A113)	Nitrogen oxide
5	$C5PAN19 + OH \rightarrow NO_2 + CO + HO12$	2CO ₃ C4	(A114)	urban plume
	C4PAN6 + OH \rightarrow NO ₂ + CO + Mgly		(A115)	I. M. Pérez et al.
	$C5PAN17 + OH \rightarrow NO_2 + CO + MACF$	ROH	(A116)	
	$CO + OH \rightarrow HO_2$		(A117)	Title Page
	$ISOPAOOH + OH \rightarrow HC_4ACHO$		(A118)	Abstract Introduction
10	$ISOPBOOH + OH \rightarrow Isopbo2$		(A119)	Conclusions References
	$ISOPCOOH + OH \rightarrow HC_4CCHO$		(A120)	Tables Figures
	$ISOPDOOH + OH \to HCOC5$		(A121)	∢ ▶
	C58OH + OH \rightarrow glyoxal + ACETOL		(A122)	•
	C57OOH + OH \rightarrow C57O ₂		(A123)	Back Close
15	$BIACETOH + OH \rightarrow CO_23C3CHO$		(A124)	Full Screen / Esc
	$\text{CO}_2\text{H}_3\text{CO}_3\text{H} + \text{OH} \rightarrow \text{CO}_2\text{H}_3\text{CO}_3$		(A125)	Printer-friendly Version
	$HMVKBOOH + OH \rightarrow BIACETOH$		(A126)	Interactive Discussion
	$CH_3OOH + OH \rightarrow CH_3O_2$	07400	(A127)	

	$HMVKAOOH + OH \rightarrow CO_2H_3CHO$	(A128)		
	C58OOH + OH \rightarrow C58O ₂	(A129)	AC	
	$MVKOOH + OH \rightarrow VGLYOX$	(A130)	9, 27099–2	7165, 2009
	$MBOCOCO + OH \rightarrow CO + IPRHOCO_3$	(A131)	Nitroge	n oxide
5	$\text{HCOOH} + \text{OH} \rightarrow \text{HO}_2$	(A132)	chemist urban	ry in an plume
	$CH_3CO_3H + OH \rightarrow CH_3CO_3$	(A133)	I. M. Pér	ez et al.
	Isopao2 + $\Sigma RO_2 \rightarrow 0.8 HO_2 + 0.1$ Isopaoh + 0.8 HC ₄ CCHO + 0.1 HC ₄ ACHO	(A134)		
	Isopbo2+Σ RO ₂ \rightarrow 0.6 HO ₂ + 0.1856 CH ₃ O ₂ + 0.6 CH ₂ O + 0.6 MVK	(A135)	Title I	Page
	+0.2 MVKOH + 0.2 Isopboh		Abstract	Introduction
10	Isopco2+ Σ RO ₂ \rightarrow 0.8 HO ₂ + 0.8 CH ₂ O + 0.1 Isopaoh + 0.1 HC ₄ CCHO	(A136)	Conclusions	References
	+0.8 HC ₄ ACHO		Tables	Figures
	Isopdo2 + $\Sigma \text{ RO}_2 \rightarrow 0.8 \text{ HO}_2 + 0.8 \text{ MACR} + 0.1 \text{ HCOC}_5 + 0.1 \text{ IsopdOH}$	(A137)	14	►I
	$Isopao2 + NO \rightarrow 0.892 HO_2 + 0.892 NO_2 + 0.108 IsopaNO_3$	(A138)	•	•
	+0.892 HC ₄ CCHO		Back	Close
15	Isopbo2 + NO → 0.947 HO ₂ + 0.237 CH ₃ O ₂ + 0.947 NO ₂ + 0.710 CH ₂ O +0.710 MVK + 0.053 IsopbNO ₃ + 0.237 MVKOH	(A139)	Full Scre	en / Esc
	$Isopco2+NO \rightarrow 0.902 \ HO_2 + 0.902 \ NO_2 + 0.08 \ IsopcNO_3 + 0.902 \ HC_4 ACHO$	(A140)	Printer-frien	dly Version
	Isopdo2 + NO \rightarrow 0.893 HO ₂ + 0.893 NO ₂ + 0.893 CH ₂ O + 0.893 MACR +0.107 IsopdNO ₂	(A141)	Interactive	Discussion
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	Isopao2 + $HO_2 \rightarrow 0.706$ ISOPAOOH	(A142)	
	Isopbo2 + $HO_2 \rightarrow 0.706$ ISOPBOOH	(A143)	
	Isopco2 + $HO_2 \rightarrow 0.706$ ISOPCOOH	(A144)	9, 27099–27165, 2009
	Isopdo2 + $HO_2 \rightarrow 0.706$ ISOPDOOH	(A145)	Nitrogen oxide
5	$IsopaNO_3O_2 + HO_2 \rightarrow IN-OH$	(A146)	urban plume
	$IsopbNO_3O_2 + HO_2 \rightarrow IN-OH$	(A147)	I. M. Pérez et al.
	$IsopcNO_3O_2 + HO_2 \rightarrow IN-OH$	(A148)	
	$IsopdNO_3O_2 + HO_2 \rightarrow IN-OH$	(A149)	Title Page
	$IsopaNO_3O_2 + \Sigma RO_2 \rightarrow IN-OH$	(A150)	Abstract Introduction
10	$IsopbNO_3O_2 + \Sigma RO_2 \rightarrow IN-OH$	(A151)	Conclusions References
	$IsopcNO_3O_2 + \Sigma RO_2 \rightarrow IN-OH$	(A152)	Tables Figures
	$IsopdNO_3O_2 + \Sigma RO_2 \rightarrow IN-OH$	(A153)	∢ ▶
	IsopaNO ₃ O ₂ + NO $\rightarrow \gamma$ NO ₂ + γ Aldehyde + (1- γ) IN-OH	(A154)	•
	IsopbNO ₃ O ₂ + NO $\rightarrow \gamma$ NO ₂ + γ Aldehyde + (1- γ) IN-OH	(A155)	Back Close
15	$IsopcNO_{3}O_{2} + NO \rightarrow \gamma NO_{2} + \gamma Aldehyde + (1 - \gamma) IN-OH$	(A156)	Full Screen / Esc
	IsopdNO ₃ O ₂ + NO $\rightarrow \gamma$ NO ₂ + γ Aldehyde + (1- γ) IN-OH	(A157)	Printer-friendly Version
	$MVKO_2 + \Sigma RO_2 \rightarrow 0.6 ACO_3 + 0.6 CH_2O + 0.2 MVKOH + 0.2 VGLYOX + 0.2 MVKOOH$	(A158)	Interactive Discussion

	$MVKO_2 + NO \rightarrow ACO_3 + NO_2 + CH_2O$	(A159)	
	$MVKO_2 + HO_2 \rightarrow 0.625 MVKOOH$	(A160)	ACPD 9, 27099–27165, 2009
	HMVKAO ₂ + Σ RO ₂ → 0.6 HO ₂ + 0.6 CH ₂ O + 0.6 Mgly + 0.2 CO ₂ H ₃ CHO +0.2 HO12CO ₃ C4	(A161)	Nitrogen oxide
5	$\label{eq:hmvkaO2} \begin{split} HMVKAO_2 + NO &\rightarrow 0.983 \ HO_2 + 0.983 \ NO_2 + 0.983 \ CH_2O + 0.98 \ Mgly \\ + 0.017 \ HMVKANO_3 \end{split}$	(A162)	urban plume
	$HMVKAO_2 + HO_2 \rightarrow 0.625 HMVKAOOH$	(A163)	
	HMVKBO ₂ +Σ RO ₂ → 0.6 CH ₃ CO ₃ +0.6 HOCH ₂ CHO + BIACETOH +0.2 HO12CO ₃ C4	(A164)	Title Page Abstract Introduction
10	$HMVKBO_2 + NO \rightarrow CH_3CO_3 + NO_2 + HOCH_2CHO$	(A165)	Conclusions References
	$HMVKBO_2 + HO_2 \rightarrow 0.625 HMVKBOOH$	(A166)	Tables Figures
	$MACRO_2 + \Sigma RO_2 \rightarrow 0.7 HO_2 + 0.3 MACROH + 0.7 ACETOL$	(A167)	∢ ▶
	$MACRO_2 + NO \rightarrow HO_2 + NO_2 + ACETOL$	(A168)	•
	MACRO ₂ + HO ₂ \rightarrow 0.625 MACROOH	(A169)	Back Close
15	$C57O_2 + \Sigma \text{ RO}_2 \rightarrow 0.7 \text{ HO}_2 + 0.7 \text{ Mgly} + 0.7 \text{ HOCH}_2\text{CHO}$	(A170)	Full Screen / Esc
	$C57O_2 + NO \rightarrow HO_2 + NO_2 + Mgly + HOCH_2CHO$	(A171)	Printer-friendly Version
	$C57O_2 + HO_2 \rightarrow 0.706 C57OOH$	(A172)	Interactive Discussion
	C58O ₂ + Σ RO ₂ → 0.7 HO ₂ + 0.7 glyoxal + ACETOL + 0.3 C58OH 27132	(A173)	CC O

	C58O ₂ + NO → 0.981 HO ₂ + 0.981 NO ₂ + 0.019 C58NO ₃ + 0.981 glyoxal +0.981 ACETOL	(A174)
	$C58O_2 + HO_2 \rightarrow 0.706 C58OOH$	(A175)
	$CH_3O_2 + \Sigma RO_2 \rightarrow HO_2 + 0.665 CH_2O + 0.335$ Methanol	(A176)
5	$CH_3O_2 + NO \rightarrow 0.999 HO_2 + 0.999 NO_2 + 0.999 CH_2O + 0.001 CH_3NO_3$	(A177)
	$CH_3O_2 + HO_2 \rightarrow CH3OOH$	(A178)
	$\label{eq:mboac} \begin{split} \text{MBOAO}_2 + \Sigma \ \text{RO}_2 \rightarrow 0.6 \ \text{HO}_2 + 0.6 \ \text{acetone} + 0.6 \ \text{HOCH}_2 \text{CHO} + 0.2 \ \text{MBOAOH} \\ + 0.2 \ \text{MBOACO} \end{split}$	(A179)
10	$\label{eq:mboard} \begin{split} MBOAO_2 + NO &\rightarrow 0.936 \ HO_2 + 0.936 \ acetone + 0.936 \ HOCH_2CHO \\ + 0.064 \ MBOANO_3 \end{split}$	(A180)
	$MBOAO_2 + HO_2 \rightarrow 0.706 MBOAOOH$	(A181)
	$MBOBO_2 + \Sigma RO_2 \rightarrow 0.6 HO_2 + 0.6 CH_2O + 0.6 Ibutaloh + 0.2 MBOAOH + 0.2 MBOBCO$	(A182)
15	$\label{eq:mbob} \begin{split} MBOBO_2 + \ NO &\rightarrow 0.974 \ HO_2 + 0.974 \ CH_2O + 0.974 \ Ibutaloh \\ + 0.026 \ MBOBNO_3 \end{split}$	(A183)
	$MBOBO_2 + HO_2 \rightarrow 0.706 MBOBOOH$	(A184)
	AromaticO ₂ + Σ RO ₂ \rightarrow HO ₂	(A185)
	AromaticO ₂ + NO \rightarrow 0.9 HO ₂ + 0.9 NO ₂ + 0.1 Aldehyde	(A186)
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	AromaticO ₂ + HO ₂ \rightarrow 0.9 Aldehyde + AromaticOOH	(A187)		ACPD	
	$\text{HCOCO}_3 + \Sigma \text{ RO}_2 \rightarrow 0.7 \text{ HO}_2 + 0.7 \text{ CO} + 0.3 \text{ HCOCO}_2\text{H}$	(A188)			
	$HCOCO_3 + NO \rightarrow HO_2 + NO_2 + CO$	(A189)		9,27099–27165,20	
	$HCOCO_3 + HO_2 \rightarrow 0.29 HCOCO_2H + 0.71 HCOCO_3H$	(A190)		Nitrogen oxide	en oxide
5	$HCOCO_3 + NO_2 + M \rightarrow GLYPAN + M$	(A191)		urban	ry in an plume
	$MACO_3 + \Sigma RO_2 \rightarrow 0.7 CH_3CO_3 + 0.7 CH_2O + 0.3 MACO_2H$	(A192)		I. M. Pé	rez et al.
	$MACO_3 + NO \rightarrow CH_3CO_3 + NO_2 + 0.7 CH_2O$	(A193)	-		
	$MACO_3 + HO_2 \rightarrow 0.71 MACO_3H + 0.29 MACO_2H$	(A194)		Title	Page
	$MACO_3 + NO_2 + M \rightarrow MPAN + M$	(A195)		Abstract	Introduction
10	$CH_3CO_3 + \Sigma RO_2 \rightarrow 0.7 CH_3O_2 + 0.3 CH_3CO_2H$	(A196)		Conclusions	References
	$CH_3CO_3 + NO \rightarrow CH_3O_2 + NO_2$	(A197)		Tables	Figures
	$CH_3CO_3 + HO_2 \rightarrow 0.29 CH_3CO_2H + 0.71 CH_3CO_3H$	(A198)		14	۶I
	$CH_3CO_3 + NO_2 + M \rightarrow PAN + M$	(A199)		•	•
	$ACO_3 + \Sigma RO_2 \rightarrow 0.7 HO_2 + CO + 0.7 CH_2O + 0.3 ACO_2H$	(A200)		Back	Close
15	$ACO_3 + NO \rightarrow HO_2 + NO_2 + CO + CH_2O$	(A201)		Full Scre	een / Esc
	$ACO_3 + HO_2 \rightarrow 0.29 ACO_2H + 0.71 ACO_3H$	(A202)		Printer-frier	ndly Version
	$ACO_3 + NO_2 \rightarrow ACRPAN + M$	(A203)		Interactive	Discussion
	$\label{eq:HC4} \begin{split} HC_4CCO_3 + \Sigma \; RO_2 &\rightarrow 0.7 \; CH_3CO_3 + 0.3 \; HC_4CCO_2H + 0.7 \; HOCH_2CHO \\ 27134 \end{split}$	(A204)		œ	B Y

	$HC_4CCO_3 + NO \rightarrow CH_3CO_3 + NO_2 + HOCH_2CHO$	(A205)
	$HC_4CCO_3 + HO_2 \rightarrow 0.29 HC_4CCO_2H + 0.71 HC_4CCO_3H$	(A206)
	$HC_4CCO_3 + NO_2 + M \rightarrow C5PAN19 + M$	(A207)
	$\text{HC}_4\text{ACO}_3 + \Sigma \text{ RO}_2 \rightarrow 0.7 \text{ HO}_2 + 0.7 \text{ CO} + 0.7 \text{ ACETOL} + 0.3 \text{ HC}_4\text{ACO}_2\text{H}$	(A208)
5	$HC_4ACO_3 + NO \rightarrow HO_2 + NO_2 + CO + ACETOL$	(A209)
	$HC_4ACO_3 + HO_2 \rightarrow 0.29 HC_4ACO_2H + 0.71 HC_4ACO_3H$	(A210)
	$HC_4ACO_3 + NO_2 + M \rightarrow C5PAN17 + M$	(A211)
	$CO_2H_3CO_3 + \Sigma RO_2 \rightarrow HO_2 + Mgly$	(A212)
	$CO_2H_3CO_3 + NO \rightarrow HO_2 + NO_2$	(A213)
10	$CO_2H_3CO_3 + HO_2 \rightarrow CO_2H_3CO_3H$	(A214)
	$CO_2H_3CO_3 + NO_2 + M \rightarrow C4PAN6 + M$	(A215)
	$C_4OH_2CO_3 + \Sigma RO_2 \rightarrow HO_2 + Ibutaloh$	(A216)
	$C_4OH_2CO_3 + NO \rightarrow HO_2 + NO_2 + Ibutaloh$	(A217)
	$C_4OH_2CO_3 + HO_2 \rightarrow C_4OH_2CO_3H$	(A218)
15	$C_4OH_2CO_3 + NO_2 + M \rightarrow C4OH2CPAN + NO_2 + M$	(A219)
	$IPRHOCO_3 + \Sigma RO_2 \rightarrow 0.7 HO_2 + 0.7 \text{ acetone} + 0.3 IPRHOCO_2 H$	(A220)
	$IPRHOCO_3 + NO \rightarrow HO_2 + NO_2 + acetone$	(A221)
	$\begin{array}{r} IPRHOCO_3 + \ HO_2 \rightarrow 0.29 \ IPRHOCO_2H + 0.71 \ IPRHOCO_3H \\ 27135 \end{array}$	(A222)





	$IPRHOCO_3 + NO_2 + M \rightarrow C4PAN5 + NO_2 + M$	(A223)	
	Isoprene + $O_3 \rightarrow 0.2625 HO_2 + 0.27 OH + 0.044 MVKOO + 0.054 MVKO_2$ +0.066 MACROO + 0.051 CH ₃ O ₂ + 0.11 CH ₂ OO + 0.1575 CH ₃ CO ₃	(A224)	9, 27099–27165, 2009
_	$+0.522 \text{ CO} + 0.7085 \text{ CH}_2\text{O} + 0.3 \text{ MACR} + 0.2 \text{ MVK} + 0.1275 \text{ propene}$	(1005)	Nitrogen oxide chemistry in an
5	$+0.28 \text{ CH}_3\text{CO}_3 + 0.56 \text{ CO} + 0.75 \text{ CH}_2\text{O} + 0.1 \text{ acetaldehyde} + 0.5 \text{ Mgly}$	(A223)	urban plume
	$\begin{aligned} MACR + \ O_3 &\to 0.41 \ HO_2 + 0.82 \ OH + 0.09 \ MGLYOO + 0.09 \ CH_2OO \\ &+ 0.41 \ CH_3CO_3 + 0.82 \ CO + 0.5 \ CH_2O + 0.5 \ Mgly \end{aligned}$	(A226)	Title Page
10	$\label{eq:HC4} \begin{split} HC_4CCHO + O_3 &\rightarrow 0.445 \; HO_2 + 0.89 \; OH + 0.055 \; GAOO + 0.055 \; MGLYOO \\ &+ 0.445 \; CH_3CO_3 + 0.89 \; CO + 0.445 \; CH_2O + 0.5 \; Mgly \\ &+ 0.5 \; HOCH_2CHO \end{split}$	(A227)	Abstract Introduction Conclusions References
	HC ₄ ACHO + O ₃ → 0.89 HO ₂ + 0.89 OH + 0.055 GLYOO + 0.055 ACLOO +0.89 CO + 0.5 glyoxal + 0.5 ACETOL	(A228)	Tables Figures
15	$\begin{split} MVKOH + & O_3 \rightarrow 0.18 \; HO_2 + 0.46 \; OH + 0.12 \; HMGLOO + 0.12 \; CH_2OO \\ & + 0.28 \; RCOO_2 + 0.57 \; CO + 0.5 \; CH_2O + 0.1 \; HOCH_2CHO \\ & + 0.5 \; HOCH_2COCHO \end{split}$	(A229)	Image: Addition of the sector of the sec
	$\begin{split} MBO + \mathrm{O}_3 &\rightarrow 0.48 \ \mathrm{HO}_2 + 0.36 \ \mathrm{OH} + 0.072 \ \mathrm{MBOOO} + 0.168 \ \mathrm{CH}_2 \mathrm{OO} \\ &+ 0.64 \ \mathrm{CO} + 0.3 \ \mathrm{CH}_2 \mathrm{O} + 0.168 \ \mathrm{acetone} + 0.7 \ \mathrm{Ibutaloh} + 0.06 \ \mathrm{ipropol} \end{split}$	(A230)	Printer-friendly Version
	α -pinene + O ₃ \rightarrow 0.81 OH + 0.185 CH ₂ O + 0.6 acetone + 0.26 pinonaldehyde	(A231)	

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	Propene + $O_3 \rightarrow 0.28 \text{ HO}_2 + 0.36 \text{ OH} + 0.28 \text{ CH}_3\text{O}_2$ +0.12 CH ₂ OO + 0.12 CH ₃ CHOO + 0.56 CO + 0.5 CH ₂ O +0.5 acetaldehyde	(A232)	ACPD 9, 27099–27165, 2009
5	1-butene + $O_3 \rightarrow 0.28 HO_2 + 0.78 RO_2 + 0.36 OH + 0.12 CH_2OO + 0.56 CO$ +0.5 CH ₂ O + 0.1 ethane + 0.12 Aldehyde	(A233)	Nitrogen oxide chemistry in an
	t2-butene + $O_3 \rightarrow 0.125 HO_2 + 0.57 OH + 0.695 CH_3O_2 + 0.18 CH_3CHOO$ +0.57 CO + acetaldehyde	(A234)	I. M. Pérez et al.
	2-methylpropene + $O_3 \rightarrow 0.41 HO_2 + 1.41RO_2 + 0.82 OH + 0.09 CH_2OO$ +0.41 CO + 0.5 CH ₂ O + 0.59 acetone	(A235)	Title Page Abstract Introduction
10	1-pentene + $O_3 \rightarrow 0.28 \text{ RO}_2$ + 0.18 OH + 0.12 CH ₂ OO + 0.18 CO + 0.5 CH ₂ O +0.1 propane + 0.62 Aldehyde	(A236)	Conclusions References Tables Figures
	t2-pentene + O ₃ → 0.125 HO ₂ + 0.3475 RO ₂ + 0.57 OH + 0.3475 CH ₃ O ₂ +0.09 CH ₃ CHOO + 0.57 CO + 0.5 acetaldehyde +0.0625 ethane + 0.59 Aldehyde	(A237)	4 F 4 F
15	c2-pentene + O ₃ → 0.125 HO ₂ + 0.3475 RO ₂ + 0.57 OH + 0.3475 CH ₃ O ₂ +0.09 CH ₃ CHOO + 0.57 CO + 0.5 acetaldehyde +0.0625 ethane + 0.59 Aldehyde	(A238)	Back Close Full Screen / Esc Printer-friendly Version
	2-methyl-1-butene + $O_3 \rightarrow 0.41 \text{ HO}_2 + 0.41 \text{ RO}_2 + 0.82 \text{ OH} + 0.09 \text{ CH}_2\text{OO}$ +0.41 CO + 0.5 CH ₂ O + 0.59 MEK	(A239)	Interactive Discussion
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	3-methyl-1-butene + $O_3 \rightarrow 0.28 \text{ RO}_2 + 0.18 \text{ OH} + 0.18 \text{ CO} + 0.5 \text{ CH}_2\text{O}$ +0.1 propane + 0.62 Aldehyde	(A240)	ACI 9, 27099–27	PD 7165, 2009
	1,3-butadiene + $O_3 \rightarrow 0.42 \text{ HO}_2 + 0.08 \text{ OH} + 0.12 \text{ CH}_2\text{OO} + 0.67 \text{ CO}$ +0.5 CH ₂ O + 0.175 ethane + 0.62 Aldehyde	(A241)	Nitroger	n oxide
5	Cyclopentene + $O_3 \rightarrow RO_2$	(A242)	chemistr urban r	ry in an olume
	m -xylene + $O_3 \rightarrow RO_2$	(A243)	I. M. Pére	ez et al.
	o -xylene + $O_3 \rightarrow RO_2$	(A244)		
	p -xylene + $O_3 \rightarrow RO_2$	(A245)	Title P	age
	$O_3 + h\nu \rightarrow O^1D + O_2$	(A246)	Abstract	Introduction
10	$NO_2 + h\nu + O_2 \rightarrow NO + O_3$	(A247)	Conclusions	References
	$CH_3OOH + h\nu \rightarrow OH + HO_2 + CH_2O$	(A248)	Tables	Figures
	$CH_3OOH + h\nu \rightarrow HO_2 + CH_2O$	(A249)	14	۶I
	$ACO_3H + h\nu \rightarrow OH + HO_2 + CO + CH_2O$	(A250)	•	F
	C57OOH + $h\nu \rightarrow$ OH + HO ₂ + Mgly + HOCH ₂ CHO	(A251)	Back	Close
15	C58OOH + $h\nu \rightarrow OH + HO_2 + glyoxal + ACETOL$	(A252)	Full Scree	en / Esc
	$CH_3COCO_2H + h\nu \rightarrow HO_2 + CH_3CO_3$	(A253)	Printer-frience	dly Version
	$CH_3NO_3 + h\nu \rightarrow HO_2 + NO_2 + CH_2O$	(A254)	Interactive D	Discussion
	$CH_3CO_3H + h\nu \rightarrow OH + CH_3O_2$ 27138	(A255)		Ð BY

	$CO_2H_3CO_3H + h\nu \rightarrow OH + HO_2 + glyoxal$	(A256)			
	$CO_2H_3CO_3H + h\nu \rightarrow HO_2 + CH_3CO_3 + HCOCO_3H$	(A257)		ACPD 9, 27099–27165,	PD
	$CO_23C3CHO + h\nu \rightarrow HO_2 + CH_3CO_3 + 2CO$	(A258)	_		7 105, 2008
	$CO_23C3CHO + h\nu \rightarrow HCOCO_3 + CH_3CO_3$	(A259)		Nitroge	n oxide
5	$CO_2H_3CHO + h\nu \rightarrow 2 HO_2 + CO + HOCH_2CHO$	(A260)		urban	plume
	$HC_4ACO_3H + h\nu \rightarrow OH + HO_2 + CO + ACETOL$	(A261)		I. M. Pé	rez et al.
	$HC_4ACHO + h\nu \rightarrow 2 HO_2 + 2 CO + ACETOL$	(A262)			
	$HC_4ACHO + h\nu \rightarrow HO_2 + HC_4ACO_3$	(A263)		Title	Page
	$HC_4CCO_3H + h\nu \rightarrow OH + HOCH_2CHO$	(A264)		Abstract	Introduction
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	ISOPBOOH + h ν → OH + 0.75 HO ₂ + 0.25 CH ₃ O ₂ + 0.75 CH ₂ O + 0.75 MVK +0.25 MVKOH	(A273)
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Appendix B

Dilution and OH

The mixing term in Eq. (1) plays an important role in the processing of the Sacramento plume as it flows further downwind. This term is determined empirically with respect to hydrocarbon species measured both at Granite Bay and UC-BFRS.

Dillon et al. (2002) estimated the dilution rate for the Sacramento urban plume to be 0.23 (±0.09) h⁻¹ based on a nonlinear least square optimization of the decay in the concentrations of VOCs. We find that this calculation leads to a dilution that is strongly anti-correlated with the effective OH. Dillon et al. (2002) also calculate the dilution ⁵ into the Sierra Nevada using the HYSPLIT model obtaining a rate of dilution of 0.3 to 0.5 h⁻¹. Zaveri et al. (2003) estimated the rate of dilution in Nashville, Tennessee to be 0.11 h⁻¹ based on the rate at which the urban plume broadened downwind of the downtown area during the 1999 SOS campaign. Stickler et al. (2007) calculate rates of entrainment of free troposphere air into the planetary boundary layer of 0.01 to 0.15 h⁻¹. Kramp and Volz-Thomas (1997) calculate values in the range of 0.20 to 0.43 h⁻¹ in the region of Freiburg, Germany. There is broad consistency in these values.

Equation (1), which describes the change in concentration of a compound X with time, can be simplified to:

¹⁵
$$d[X]/dt = -k_d([X] - [X]_{bg}) - k_{OH+X}[X][OH]$$

for hydrocarbons that have negligible photochemical production, emission and deposition throughout the transect. The term $k_d([X]-[X]_{bg})$ in Eq. (B1) represents the entrainment of background air with concentration $[X]_{bg}$ at a rate of k_d . The term $k_{OH-X}[X][OH]$ represents the photochemical loss of X as it reacts with OH with rate k_{OH+X} . Concentrations of X as a function of time are obtained by integrating (B1) numerically. Follow-

- trations of X as a function of time are obtained by integrating (B1) numerically. Following Dillon et al. (Dillon et al., 2002), we determine k_d and OH by nonlinear least squares fit of Eq. (B1) using various hydrocarbons observations at Granite Bay and UC-BFRS. We use 9 hydrocarbons with lifetimes ranging from 1 to 6.5 d at an OH concentration of 3×10⁶ molecules cm⁻³. Table B1 shows the concentration of these species at Granite Bay, at UC-BFRS. The concentrations of hydrocarbons of anthropogenic origin
- Granite Bay, at UC-BFRS. The concentrations of hydrocarbons of anthropogenic origin observed at UC-BFRS during weekdays spans from 20% to almost 90% of what is observed at Granite Bay 5 h earlier, with the highest conserved fraction observed for benzene which has the longest photochemical lifetime.



(B1)



We define two different background scenarios, the GLOBAL_{bg} and LOCAL_{bg}. The GLOBAL_{bg} is an estimate of free troposphere air in the region based on observations made during the summer of 2007 in the region from an airplane platform during the TC4 campaign and is representative of a low global background. The LOCAL_{bg} takes advantage of measurements made at Big Hill that are characteristic of the free troposphere air (Murphy et al., 2006a) and is representative of a high local background. A more detailed description of the background definitions is presented in Appendix C. We obtain a k_d of 0.24 ± 0.06 h⁻¹ and an average OH of $8\mp3\times10^6$ molecules cm⁻³ for the GLOBAL_{bg} case and a k_d of 0.4 ± 0.1 h⁻¹ and an average OH of 5 $\pm4\times10^6$ molecules cm⁻³ for the LOCAL_{bg} scenario. Dillon et al. (2002) obtain a k_d of 0.23 ± 0.09 h⁻¹ and an OH of $1.1\pm0.5\times10^7$ molecules cm⁻³. The differences are due to both the variation in the VOC used and to the background values.

If instead of a fixed OH we allow OH to vary along the transect based on the fully couple model, the optimization leads to a value of k_d of $0.43 h^{-1}$ for LOCAL_{bg} and of $0.31 h^{-1}$ for GLOBAL_{bg} and an average OH of 4.6×10^6 molecules cm⁻³ and 5.0×10^6 molecules cm⁻³ for the LOCAL_{bg} and the GLOBAL_{bg}, respectively. The spread in these values gives a sense of how the choice of background concentrations affects the dilution and OH derived. The decrease in concentration of VOCs due to entrainment of background air ranges from 60% to 85% in the different scenarios.

20 Appendix C

Definition of background air

As described by Murphy et al. (2006a), on an average summer day, an airmass moves roughly 100 km from east to west during the daytime and then backtracks approximately 50 km to the west during the night when the flow is reversed. This pattern results in air sloshing back and forth along the western slopes of the Sierra and con-

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tributes to an increase in the regional background of species of anthropogenic origin as the week progresses. Because of this behavior, the regional background of species with anthropogenic influence is hard to define. The vertical and horizontal distribution of species in the area, depicted for ozone by Carroll and Dixon (2002), adds to the difficulty in defining the regional background. They find significant variation in ozone at a horizontal scale of a few kilometers and vertical layering above the mixed layer.

As described before, the 0-D representation of the plume is most characteristic of the center line of the plume where vertical mixing dominates. Vertical mixing is characterized by entrainment of free troposphere air from aloft. We describe two possible

- scenarios for estimating free troposphere concentrations of species that are influenced by anthropogenic emissions. For one estimate of free troposphere air in the region, we use observations made during the summer of 2007 in the region from an airplane platform during the TC4 campaign (TC4 Data Archive, 2009). This definition of a background airmass is representative of a low global background and is used in the *Ref-*
- *erence* scenario. The second method takes advantage of measurements made at Big Hill that are characteristic of the free troposphere air. This second definition of a background airmass results in higher values. The VOC GLOBAL_{bg} is approximately 40% of the VOC LOCAL_{bg}. The nitrogen oxides LOCAL_{bg} is similar to the GLOBAL_{bg}. The GLOBAL_{bg} concentration of species not measured during TC4 is estimated to be 40% of their LOCAL_{bg} value.

Definition of the high local background is based on observations of NO₂, ΣPNs, ΣANs and HNO₃ as well as meteorological parameters and O₃ that were made during the summer of 2003 at Big Hill (38.84°N, 120.41°W, 1860 m) approximately 20 km southeast of UC-BFRS. These measurements, which are described in detail by Murphy et al. (2006a), show influence by the free troposphere during some nights. Regional background concentrations for NO₂, HNO₃, ΣPNs, ΣANs and O₃ are estimated based

on plots of the species vs. $[H_2O]$ for nights that show influence by free troposphere air. Background concentrations for anthropogenic VOCs are determined based on the linear regression of their plots vs. $\Sigma NO_{y,i}$ ($\Sigma NO_{y,i} = NO_2 + \Sigma PNs + \Sigma ANs + HNO_3$) at



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UC-BFRS for nighttime data, if observations are available, or at Granite Bay. This background will be referred to $LOCAL_{bq}$.

Table B1 (in Appendix B) presents the observations at Granite Bay (GB) and UC-BFRS and compares the model outputs of hydrocarbons that are used to fit the rate of entrainment with UC-BFRS observations for both $LOCAL_{bg}$ and $GLOBAL_{bg}$. As mentioned before, the rate of entrainment calculated for the $LOCAL_{bg}$ scenario is $0.43 h^{-1}$ while the rate of entrainment for the $GLOBAL_{bg}$ scenario is $0.31 h^{-1}$. The background concentrations for these species for both background scenarios are also included in the table. As mentioned before, the $LOCAL_{bg}$ concentrations for VOCs are higher than the GLOBAL_{bg} concentrations. As k_d is calculated based on background concentrations,

- the outputs are comparable for most anthropogenic VOCs for both background definitions. Most are within 20% of the observed value except for isopentane and toluene in the $GLOBAL_{bg}$ scenario, both of which are within 25% of the observations. An exception is benzene for which the calculated outputs are significantly different in both
- ¹⁵ cases. Although we cannot explain this difference, one possible explanation is that the regional background of benzene has decreased between 2001, the year the data was collected at GB and UC-BFRS, and 2007, the year during which the TC4 data was obtained. Harley et al. (2006) show that the benzene concentration has steadily decreased between 2001 and 2004 in the San Francisco Bay area indicating that it is not unlikely that the same has occurred in the Sacramento area and downwind.

Neither of the two estimates presented above are adequate to describe the characteristic mixing ratios in the free troposphere of species that are direct biogenic emissions or products of the oxidation of these emitted species. Species that are influenced by biogenic emissions or by oxidation of biogenic VOCs can have background ²⁵ concentrations that are hard to define because they can reach higher concentrations at night, the period during which the LOCAL_{bg} is defined. These species included isoprene, MBO, α -pinene, which are directly emitted by vegetation, and MVK, MACR and acetaldehyde which are produced in the oxidation process of isoprene. Additionally, acetaldehyde, acetone, ethanol and methanol are all oxygenated VOCs that have

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been shown to have upward fluxes at UC-BFRS (Schade and Goldstein, 2001) and thus also have hard to define backgrounds. Background concentrations of species affected by biogenic emissions are based on the lowest observed values at UC-BFRS when observations are available. Background concentrations for species that are not

- ⁵ routinely monitored like many of the larger organic peroxides and acids formed from isoprene oxidation are assumed to be zero. Background concentrations of glycoaldehyde, hydroxyacetone, glyoxal and methylglyoxal are assumed to be 50% of the means value observed by Spaulding et al. (2003) at UC-BFRS. Background concentrations of hydrogen peroxide, methyl hydroperoxide, and formaldehyde are taken from observa-
- ¹⁰ tions over North America between 1 and 6 km during INTEX-A (Snow et al., 2007). The background concentrations for these species are the same for both the LOCAL_{bg} and the GLOBAL_{bg} scenarios and setting them to zero does not lead to significant differences in the model results.

The different background concentrations were used to test the sensitivity of the model to background concentrations and rates of entrainment as described in the previous section. The GLOBAL_{bg} scenario was used as the *Reference* case scenario for testing the sensitivity of other parameters in the model.

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Species	Initial value					
Acetaldehyde	1.18					
Acetone	2.9					
terpenes	0.013+0.009+0.0008 ^a					
Benzene	0.097					
Butane	0.28					
1.3-butadiene	0.0048					
1-butene	0.011					
2-butene	0.0027					
CoCla	0.044					
C2-pentene	0.0021					
CH_CL	0.06					
CH_CL	0.61					
CHCI	0.0144					
CO	200*					
Cyclopentane	0.028					
2.2-dimethpropane	0.0054					
Ethylbenzene	0.043					
Ethanol	1.36					
Heptane	0.059					
Hexane	0.075					
Hexanal	0.121					
Isobutane	0.17					
Isopentane	0.5					
Isoprene	0.85					
MACR	0.32					
MBO	-					
Methyl ethyl ketone	0.24					
Methanol	6					
2-methylpropene	0.027					
Methylpentanes	0.23					
MTBE	1.3					
MVK	0.5					
<i>m</i> -xylene	0.077					
o-xylene	0.052					
p-xylene	0.056					
Pentane	0.181					
Pentanal	0.083					
1-pentene	0.0163					
Propane	0.7					
Propene	0.082					
Propyne	0.013					
t-2-butene	0.0027					
t-2-pentene	0.0046					
3-methyl-1-butene	0.0149					
Toluene	0.29					
2-methyl-1-butene	0.0083					
0 ₃	53					
NO ₂	5.7					
NO	1.99					
2PNs	1.08					
2ANs	1.1					
HNO ₃	3.3					

^a α-pinene+limonene+3-carene

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Table 2. Summary of model results for various scenarios.

	Ref.	% Diff ^d	E_NO_0	% Diff	ANs_1	% Diff	ANs_2	% Diff	ANs_3	% Diff	ANs_4	% Diff	ANs_5	% Diff	ANs_6	% Diff	PNs_1 ^e	% Diff	Rev. ^f	% Diff	Obs.
NO emissions ^a	10		0		10		10		10		10		10		10		10		10		-
α_{isop}	10.8		10.8		12		4.4		8		12		6		12		10.8		12		-
IN Lifetime ^b	9.3		9.3		9.4		8.6		2.5		1.7		4.9		4.6		9.1		4.5		-
NOx	734	-17.6	657	-31.4	732	-17.9	748	-15.4	830	-4.0	867	0.5	775	-11.4	782	-10.4	736	-17.3	785	-9.9	863
NO	85	2.4	76	-9.2	85	2.4	86	3.5	96	13.5	100	17.0	89	6.7	91	8.8	84	1.2	90	7.8	83
NO ₂	649	-20.2	581	-34.3	647	-20.6	662	-17.8	734	-6.3	767	-1.7	686	-13.7	691	-12.9	652	-19.6	695	-12.2	780
PNs	772	-21.8	754	-24.7	765	-22.9	809	-16.2	825	-13.9	815	-15.3	814	-15.5	783	-20.1	646	-45.5	658	-42.9	940
ANs	383	-33.2	380	-34.2	394	-29.4	324	-57.4	240	-112.5	229	-122.7	303	-68.3	341	-49.6	385	-32.5	341	-49.6	510
HNO ₃	1056	-1.3	1041	-2.8	1053	-1.6	1073	0.3	1102	2.9	1109	3.5	1081	1.0	1070	0.0	1097	2.5	1110	3.6	1070
NOv	2945	-14.9	2832	-19.5	2944	-14.9	2953	-14.6	2996	-12.9	3012	-12.3	2973	-13.8	2976	-13.7	2864	-18.1	2895	-16.9	3383
O ₃ (ppbv)	72.6	-0.6	72.4	-0.8	72.5	-0.7	73	0.0	73.3	0.4	73.2	0.3	73.0	0.0	72.7	-0.4	73.2	0.3	73.3	0.4	73
NO _x /NO _y	0.249	-2.4	0.232	-9.9	0.249	-2.4	0.253	-0.8	0.277	7.9	0.288	11.5	0.3	2.3	0.3	2.7	0.257	0.8	0.271	5.9	0.255
NO _x /NO _z	0.332	-3.0	0.302	-13.2	0.331	-3.3	0.339	-0.9	0.383	10.7	0.405	15.6	0.4	3.1	0.4	3.9	0.356	3.9	0.372	8.1	0.342
PNs/NO _x	1.052	-3.6	1.148	5.1	1.045	-4.2	1.082	-0.7	0.994	-9.6	0.940	-15.9	1.050	-3.7	1.001	-8.8	0.878	-24.1	0.838	-29.9	1.089
ANs/NO _x	0.522	-13.3	0.578	-2.2	0.538	-9.8	0.433	-36.4	0.289	-104.4	0.264	-123.7	0.391	-51.2	0.436	-35.5	0.523	-13.0	0.434	-36.0	0.591
HNO ₃ /NO _x	1.439	13.8	1.584	21.7	1.439	13.8	1.434	13.6	1.328	6.6	1.279	3.1	1.395	11.1	1.368	9.4	1.490	16.8	1.414	12.3	1.240

^a soil NO emission flux (ppt $m s^{-1}$)

^b effective isoprene nitrate lifetime (hours) to Reaction (R4b) ^c all concentrations are pptv unless otherwise noted

^d % difference between model and observations, calculated as 100%×(Model-Observed)/(Model) ^e modified PNs scenario described in Sect. 4.3

f revised model featuring changes to PNs and ANs chemistry

Table 3. Table B1. Hydrocarbons observations (ppb) used to fit the rate of entrainment of background air, background air concentrations (ppb), the lifetime to OH assuming a 12 h average OH of 3×10^6 molecules cm⁻³ (days) and outputs (ppb) for the different background definitions. All concentrations are in ppb.

Species	τ _{OH} (davs)	Obs. at GB	Obs. at UC-BFBS		LOCAL	7	GLOBAL _{bg}				
	(44)			Bg	Model	% dif. ^a	Bg	Model	% dif.		
benzene	6.53	0.097	0.085	0.075	0.083	-2	0.020	0.39	78		
n-butane	3.04	0.28	0.083	0.073	0.093	11	0.035	0.085	2		
ethyl benzene	1.03	0.043	0.010	0.010	0.010	0	0.005	0.010	0		
hexane	1.48	0.075	0.015	0.010	0.016	6	0.004	0.015	0		
i-butane	3.32	0.17	0.060	0.045	0.060	0	0.025	0.060	0		
i-pentane	1.98	0.50	0.12	0.080	0.11	-9	0.020	0.15	20		
methyl pentanes	1.48	0.23	0.050	0.030	0.050	0	0.012	0.050	0		
n-pentane	2.35	0.18	0.050	0.037	0.050	0	0.020	0.050	0		
Toluene	1.25	0.29	0.065	0.050	0.062	5	0.050	0.080	19		

^a % dif.=100×($\frac{Model-Observation}{Model}$)

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Fig. 1. Map of study region, with prevailing day time wind pattern shown.



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Fig. 2. Comparison of modeled and observed NO_v partitioning at UC-BFRS.

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Fig. 3. Time evolution of NO_v species. UC-BFRS observations indicated by black circle.









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Fig. 4. Time evolution of ΣPNs and their major individual PNs. Other speciated PNs include the sum of ACRPAN, C5PAN17, C5PAN19, C4OH2CPAN, C4PAN6 and GLYPAN (as referred to by MCM). UC-BFRS observations indicated by black circle. **(a)** *Reference* model **(b)** modified PNs chemistry model scenario.



Fig. 4. Continued.

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Fig. 5. Time evolution of Σ ANs and of the major classes of ANs. Other speciated ANs included the sum of C58NO₃, CH3NO₃, HMVKANO₃ (as referred to by MCM) and aromaticNO₃, which includes alkyl nitrates derived from toluene, ethyl benzene, *m*-xylene, *o*-xylene and *p*-xylene. UC-BFRS observations indicated by black circle.