

Reactive nitrogen in Mexico City and its relation to ozone-precursor sensitivity: results from photochemical models

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Received: 25 September 2008 – Published in Atmos. Chem. Phys. Discuss.: 9 December 2008

Revised: 15 May 2009 – Accepted: 21 May 2009 – Published: 2 June 2009

Abstract. We use results of a 3-D photochemistry/transport model for ozone formation in Mexico City during events in 1997 to investigate ambient concentrations of reactive nitrogen in relation to ozone-precursor sensitivity. Previous results from other locations suggest that ratios such as O_3/NO_y and H_2O_2/HNO_3 might provide measurement-based indicators for NO_x -sensitive or VOC-sensitive conditions. Mexico City presents a different environment due to its high concentrations of VOC and high level of pollutants in general. The model predicts a correlation between PAN and O_3 with relatively high PAN/ O_3 (0.07), which is still lower than measured values. The model PAN is comparable with results from a model for Paris but much higher than were found in Nashville in both models and measurements. The difference is due in part to the lower temperature in Mexico City relative to Nashville. Model HNO_3 in Mexico City is unusually low for an urban area and PAN/ HNO_3 is very high, probably due to the high ratio of reactivity-weighted VOC to NO_x . The model predicts that VOC-sensitive chemistry in Mexico is associated with high NO_x , NO_y and NO_x/NO_y and with low O_3/NO_y and H_2O_2/HNO_3 , suggesting that these indicators work well for Mexico City. The relation between ozone-precursor sensitivity and either O_3/NO_z or O_3/HNO_3 is more ambiguous. VOC-sensitive conditions are associated with higher O_3/HNO_3 than would be found in NO_x -sensitive conditions, but model O_3/HNO_3 associated with both NO_x -sensitive and VOC-sensitive chemistry is higher in Mexico than in other cities. The model predicts a mixed pattern of ozone-precursor sensitivity in Mexico City, with VOC-sensitive conditions in the morning and NO_x -sensitive in the afternoon, in contrast to results from other models for more recent events that predicted strongly VOC-sensitive conditions throughout the day. The difference in predicted ozone-

precursor sensitivity is most likely due to different emission rates and to changes in emissions over time. The model with mixed sensitivity predicts much lower ambient NO_x and NO_x/NO_y than the strongly VOC-sensitive model.

1 Introduction

The relation between ozone and its two main precursors, volatile organic compounds (VOC) and nitrogen oxides (NO_x), remains a major source of uncertainty in polluted regions. It is generally known that for some conditions the rate of ozone production increases with increasing NO_x , while for other conditions ozone production decreases with increasing NO_x and increases with VOC. However it is difficult to determine which conditions are prevalent for individual urban areas. As a result it is often difficult to develop effective control strategies for reducing ambient ozone.

Ozone-precursor sensitivity is usually determined based on results of 3-dimensional chemistry/transport models, but the model predictions are subject to considerable uncertainty. Predicted O_3 - NO_x -VOC sensitivity is sensitive in particular to emission rates for NO_x and VOC, the assumed reactivity of VOC emissions and the photochemical representation. It is especially difficult to derive methods for evaluating the accuracy of model sensitivity predictions. Models are routinely evaluated in comparison with ambient O_3 , but it is frequently possible to generate similar O_3 in model scenarios with opposite results for O_3 -precursor sensitivity (e.g. Pierce et al., 1998).

In recent years efforts have been made to derive information about ozone-precursor sensitivity directly from ambient measurements. These “observation-based methods” provide a way to corroborate or refute the predictions for O_3 -precursor sensitivity from models and also provide ways to evaluate model performance that are linked to the accuracy of the model sensitivity predictions. These methods include



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evaluations based on ambient NO_x and VOC (e.g. Kleinman et al., 2005), methods based on the difference between week-day and weekend O_3 (Stephens et al., 2008) and methods based on reactive nitrogen and peroxides (Sillman, 1995; Sillman and He, 2002). Methods based on direct measurement of HO_2 radicals are also in preparation based on work described in Thornton et al. (2002) and Shirley et al. (2006).

Here, we focus on the predicted behavior of reactive nitrogen and peroxides in the Mexico City region. Previous results have shown that species ratios and correlations between O_3 , reactive nitrogen and peroxides show distinctly different patterns for NO_x -saturated (VOC-sensitive) conditions as opposed to NO_x -sensitive conditions, and that the patterns appear to be similar for many urban areas in the US and in Europe. When predicted species ratios and correlations are different for NO_x -sensitive and VOC-sensitive conditions, then comparisons with measured values can provide an indirect evaluation of the accuracy of model ozone-precursor sensitivity. By contrast, when predicted species correlations show similar patterns for both NO_x -sensitive and VOC-sensitive environments, then model agreement with measured values may not provide a basis for evaluating the accuracy of model sensitivity predictions.

Air pollution in Mexico has been the subject of intense study in recent years (e.g. Molina et al., 2007). Conditions in Mexico City differ from other urbanized regions in many ways, including emission rates, VOC speciation, ambient temperatures and photolysis rates (due to altitude). As a result the cycling of reactive nitrogen and its relation to odd hydrogen radicals can be very different from other locations. We will evaluate the predicted correlations among secondary species in Mexico City from a 3-D photochemical model in contrast to results obtained from models and measurements in other cities, and determine whether these correlations are good predictors of O_3 - NO_x -VOC sensitivity. Results will be used to identify measurements that might resolve the uncertain relation between ozone and precursors in Mexico City.

2 Background

Correlations between secondary reaction products in photochemically active regions reflect several different processes: background concentrations for each species, relative rates of photochemical production within the region, photochemical lifetimes and other removal processes. In regions where photochemical production dominates, correlations between species may provide an evaluation of model photochemistry.

For gas-phase species related to O_3 , three different processes dominate. Peroxides are produced by the reactions



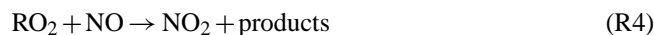
where RO_2 and ROOH represent hydrocarbon chains ending in $-\text{O}_2$ and $-\text{OOH}$ respectively (for example, CH_3O_2 and CH_3OOH). Nitric acid is produced by



O_3 is produced by a reaction sequence initiated by reactions with the form



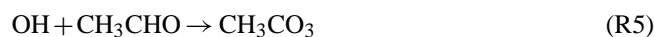
followed by



NO_2 then photolyzes to produce O_3 . Other species, including PAN and other organic nitrates, are produced by similar reaction sequences.

The contrast between NO_x -sensitive and VOC-sensitive photochemistry is closely related to the relative rates of formation of peroxides (R1a and b) and nitric acid (R2), both of which are sinks for odd hydrogen radicals and thus indirectly affect the rate of ozone formation (Sillman, 1995; Kleinman et al., 1997; Kleinman, 2005; Thornton et al., 2002). Consequently, a high value for the ratio $\text{H}_2\text{O}_2/\text{HNO}_3$ is associated with NO_x -sensitive photochemistry and a low value is associated with VOC-sensitive photochemistry. Rates of formation of ozone (R3 and R4) and nitric acid (R2) also reflect differences in photochemistry, and the correlation between these species may also reflect differences in O_3 - NO_x -VOC sensitivity, although less directly than $\text{H}_2\text{O}_2/\text{HNO}_3$.

The relation between O_3 and PAN is fundamentally different from the relation between O_3 and HNO_3 . PAN is produced by the reaction



followed by



The PAN precursor acetaldehyde (CH_3CHO) is produced from the oxidation of primary VOC in the presence of NO_x and is also emitted directly. Similar reaction sequences occur for other PAN precursors (such as methylglyoxal). This sequence is analogous to Reactions (R3) and (R4), leading to ozone formation. Consequently, ambient O_3 is expected to correlate with PAN but the correlation is not related to O_3 - NO_x -VOC sensitivity (Sillman et al., 2002). In addition, at warm temperatures PAN and CH_3CO_3 approach a steady state value with PAN proportional to O_3 (Sillman et al., 1990). For NO_x mixing ratios of 1 ppb or higher the dominant removal sequence for PAN is



followed by



The steady state concentration of PAN resulting from (R5), (R6), (R7) and (R8) is

$$[\text{PAN}] = \frac{k_5 k_6}{k_7 k_8} \left(\frac{\text{NO}_2}{\text{NO}} \right) [\text{OH}][\text{CH}_3\text{CHO}] \quad (1)$$

where k_n represents the rate for reaction n . The ratio NO_2/NO forms a steady state with O_3 and is proportional to O_3 (e.g. Cantrell et al., 1992). PAN is therefore expected to increase with O_3 , and the ratio PAN/O_3 should increase in proportion to local photochemical productivity.

3 Model description and application

Here we analyze the model simulations of the Mexico City Metropolitan Area by West et al. (2004). West et al. (2004) used the CIT model of atmospheric chemistry and transport, with the SAPRC-99 chemical mechanism (Carter, 2000), and using meteorological inputs from previous modeling using the Regional Atmospheric Modeling System (RAMS, Fast and Zhong, 1998). The model was applied to six two-day periods during the IMADA measurement campaign in March of 1997, where the model was allowed to initialize during the first day of each pair, and results were analyzed on the second day. The model horizontal domain was 85.5×90 km with 4.5 km resolution. The model had 15 vertical layers extending to 4.6 km above the surface.

Model predictions of VOCs, CO, and NO_x were compared with surface measurements of these species, and on the basis of this comparison, emissions of VOCs were increased by a factor of three relative to the official Mexico City inventory, and of CO by a factor of two. The model predicted NO_x concentrations well, particularly with little bias during the daytime. The increases in VOC and CO emissions were supported by other results using VOC/NO_x and CO/NO_x ratios over many years (Arriaga-Colina et al., 2004). With these corrections, the model reproduced both the spatial pattern and timing of ozone concentrations well overall, and particularly on 2, 4, and 14 March.

On 4 March 1997, winds were from the north and sustained during the day. Peak concentrations of ozone over the city occurred early in the day (12–13 h), while the overall predicted peak concentration occurred south of the city at 14–15 h. These results agree with ozone measurements that show that the peak occurred early in the city center, and later south of the city. We also show results for 2 March, a day characterized by light and variable winds and somewhat higher ozone. Afternoon winds from the south blew the peak ozone back over the city, such that the peak concentrations occurred over the city at 13–15 h (in contrast with 4 March). Model results also agreed with measured peak O_3 both in terms of geographical distribution and the absolute peak (235 ppb measured, 199 ppb modeled). Lastly, 14 March was characterized by lower afternoon temperatures (22–24°C in contrast to 27°C), south winds and peak O_3 to

the north of the city. The model underestimated peak O_3 on this day (164 ppb at 14–15 h modeled, 201 ppb at 15–16 h measured), but the model average O_3 over all measurement sites during the afternoon agreed with the measured average to within a few ppb.

West et al. (2004) reported extensive comparisons between model results and measured O_3 , VOC and NO_y during the event. They found generally good agreement for these species following their adjustment in emission rates. West et al. (2004) also compared model results with previous measurements of PAN (Gaffney et al., 1999) and total nitric acid (gas phase HNO_3 plus particulate nitrate, Chow et al., 2002). They found that model PAN was lower than the average measurements by a factor of two, while total nitric acid was only slightly underestimated (26%).

Because of the small size of the model domain, the results may be especially sensitive to boundary conditions. The results also will not include the effect of ozone production and precursor emissions at the regional scale and upwind from Mexico City. West et al. (2004) reported that boundary conditions had relatively little impact on model VOC in the Mexico City urban center. However, results for locations outside the urban center and downwind plume may be sensitive to boundary conditions.

4 Results

4.1 Comparison between Mexico City, Paris and Nashville

Figure 1 shows model correlations for O_3 versus NO_x reaction products (NO_y - NO_x , or NO_z) for the ensemble of model locations in Mexico City at 13–14 h and 15–16 h on 4 March. The correlation shows surface values of O_3 versus NO_z for the entire model domain, which includes both Mexico City and the surrounding rural area. The figure also shows equivalent correlations from model-based studies in two different locations: Nashville (Sillman et al., 1998) and Paris (Sillman et al., 2003). The previous studies also included comparisons with measured O_3 versus NO_z for the model events and generally good agreement. Results are also shown for HNO_3 , PAN and other organic nitrates. The Nashville model results for PAN are also consistent with the measured correlations between O_3 and PAN in the region reported by Roberts et al. (1998). Measured HNO_3 was not available for comparison in the previous studies.

Results show that the model correlation for O_3 versus summed NO_z in Mexico is similar to correlations in Nashville and in Paris. There is also little change in the correlation between 13–14 h and 15–16 h. Because this correlation is associated with the ozone production efficiency per NO_x (e.g. Trainer et al., 1993), this result suggests that the ozone production efficiency in Mexico City is similar to other locations. However, the results are very different for

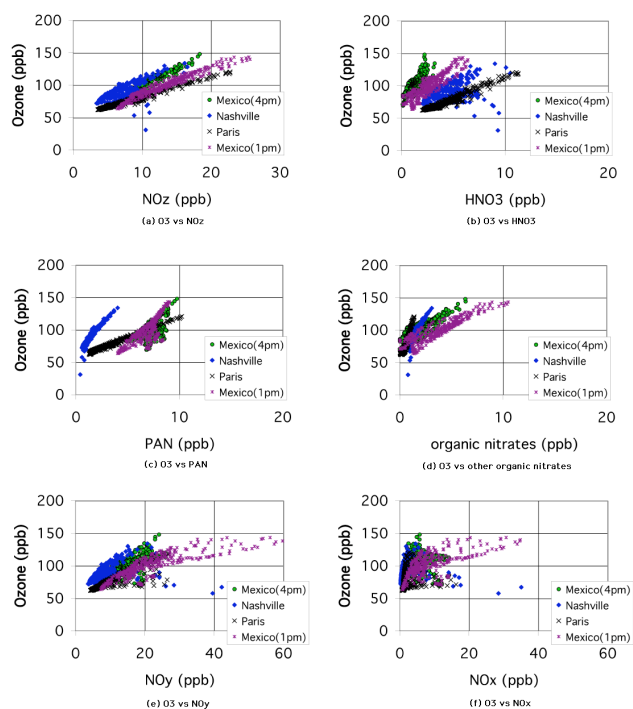


Fig. 1. Model O₃ vs. reactive nitrogen in ppb at four locations: Mexico City on 4 March 1997 at 12–13 h LT (purple asterisks), and 15–16 h (green circles), Nashville (blue diamonds) and Paris (X's). Results are shown for (a) summed NO_x reaction products (NO_z), (b) HNO₃, (c) PAN (d) other organic nitrates, (e) summed total reactive nitrogen (NO_y), and (f) NO_x.

correlations involving specific reaction products. Results for O₃ versus HNO₃ show a positive correlation between the two species at each location but with different O₃/HNO₃ ratios. The O₃/HNO₃ ratio is lowest for Paris, somewhat higher for Nashville, and much higher in the model for Mexico. The O₃/HNO₃ ratio for Mexico also changes between 13–14 h and 15–16 h at the locations with highest O₃, increasing from 20 at 13–14 h to 50 at 15–16 h. By contrast the model O₃/HNO₃ associated with peak O₃ is 10 for Paris and 14 for Nashville. HNO₃ represents approximately 50% of total NO_z in Paris and in Nashville but just 20% in Mexico City.

Significant differences among the three locations also appear for PAN. Absolute modeled concentrations of PAN are comparable in Mexico and Paris, and are significantly higher than in Nashville. The model PAN is approximately 50% lower than the average from an ensemble of measurements at one station in Mexico City (Gaffney et al., 1999). High concentrations of PAN were also reported in model results by Lei et al. (2007). The O₃/PAN ratio is much higher for Nashville than for the other cities. O₃/PAN ratios are similar for Paris and Mexico, although the slope between O₃ and PAN is lower for Paris. Results for Mexico are similar at 13–14 h and 15–16 h on 4 March, although on 2 March the O₃-PAN correlation for Mexico showed greater scatter. The

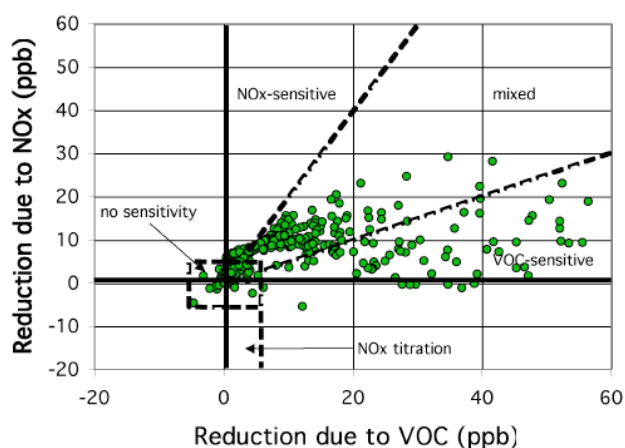
measurements from Gaffney et al. (1999) showed a loose correlation between PAN and O₃ with an average PAN/O₃ ratio equal to .12 for O₃ above 100 ppb. The model PAN/O₃ is significantly lower (.07) but the measured PAN, O₃, and PAN/O₃ still fall within the range of measured values. Results for other organic nitrates showed much higher concentrations in relation to O₃ for Mexico than for either Nashville or Paris.

The correlation between O₃ and NO_y is weaker than the correlation between O₃ and NO_x reaction products. The model correlation for Mexico at 15–16 h is comparable to the model results for Nashville and Paris. All three cases show O₃ generally increasing with NO_y and a similar range of values, and all three cases include some locations with much lower O₃/NO_y, probably reflecting fresh NO_x emissions. The correlation for Mexico at 13–14 h differs in that it includes a number of locations with high O₃ and much higher NO_x. At the other sites and at Mexico at 16 h the highest O₃ is associated with 20–25 ppb NO_y, but in Mexico at 14 h the highest O₃ is associated with NO_y between 25 and 50 ppb. The O₃/NO_y ratio associated with high O₃ is also much lower. The high NO_y in Mexico at 14 h is due to larger NO_x and lower rates of photochemical processing (related to NO_x/NO_y). O₃ generally increases with NO_y for NO_y below 25 ppb but not for higher NO_y.

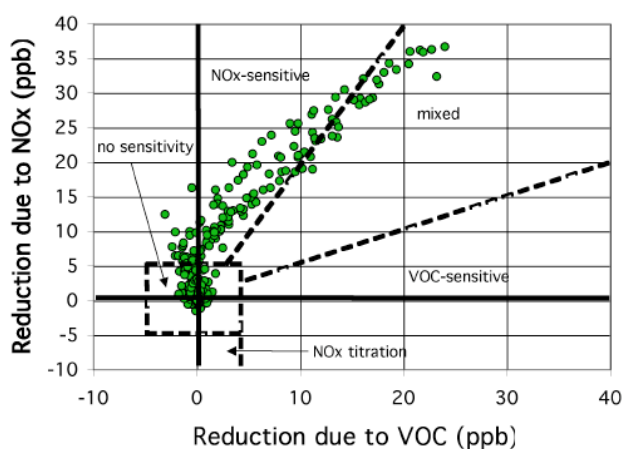
There is little correlation between O₃ and NO_x at any of the sites, and the highest O₃ is often associated with relatively low NO_x. In Paris and Nashville the highest O₃ is found in downwind locations following removal of NO_x. Mexico at 16 h shows this pattern, and peak O₃ in Mexico is associated with 6 ppb NO_x. Mexico at 14 h shows a different pattern. At that time O₃ is predicted to increase with NO_x and NO_x associated with peak O₃ ranges from 6 to 20 ppb.

4.2 Ambient species and ozone-precursor sensitivity

Model predictions for O₃-precursor sensitivity are derived by repeating the original model scenario (a) with a 50% reduction in emission of anthropogenic hydrocarbons and (b) with a 50% reduction in anthropogenic NO_x. The resulting change in O₃ at each model location relative to the initial scenario is shown in Fig. 2 for 2 March, 12–13 h and 15–16 h. As shown in the figure, the response to reduced VOC and NO_x varies greatly with the time of day and model location. At some locations O₃ decreases in response to a reduction in NO_x but changes little in response to VOC, while at other locations O₃ decreases in response to a reduction in VOC but changes little in response to NO_x. Many model locations show a mixed response with reduced O₃ in response to reductions in either VOC or NO_x. The main feature of the model sensitivity predictions is a shift from predominantly VOC-sensitive conditions at 12–13 h to NO_x-sensitive conditions at 15–16 h. A similar shift was predicted for 4 March and 14 March. For 13–14 h and 14–15 h the model predicted a mixed response with a roughly equal reduction in O₃



(a) March 2, 1997, 12-13 h



(b) March 2, 1997, 15-16 h

Fig. 2. Predicted reduction in surface O_3 in each model horizontal grid resulting from (i) a 50% reduction in anthropogenic VOC and (ii) a 50% reduction in NO_x , shown for 2 March at (a) 12–13 h and (b) 15–16 h. The dashed lines identify the five categories for predicted O_3 - NO_x -VOC sensitivity used in subsequent figures: NO_x -sensitive, mixed, VOC-sensitive, locations dominated by NO_x titration, and locations with little sensitivity to VOC and NO_x (usually found near the upwind boundary).

resulting from reductions in either VOC or NO_x . These sensitivity predictions differ from the model results reported by Lei et al. (2007), which found predominantly VOC-sensitive chemistry during a different event, as discussed later.

Although the predicted response to precursor reductions was generally similar for all three days there was an important difference in geographical distribution. On 4 March the highest O_3 was found in the plume south of Mexico City. Peak O_3 within the city itself occurred at 12–13 h and was associated with strongly VOC-sensitive conditions in the model. By contrast, on 2 March the ozone plume remained in the city through 15–16 h so that peak ozone within the city

occurred later (13–15 h) and showed sensitivity to both VOC and NO_x . The size of the predicted reduction in O_3 generally increases with O_3 . However, the reductions due to reduced VOC at 12–13 h tend to be larger than the reductions due to reduced NO_x at 15–16 h. The latter feature is especially noteworthy on 4 March. Much of the model domain (including urban Mexico City) has moderately high O_3 (100–120 ppb) at 15–16 h. Ozone at this hour shows greater sensitivity to NO_x than to VOC, but even a 50% reduction in NO_x is predicted to yield only a small (5%–10%) reduction in O_3 over most of the model domain. The largest reduction due to reduced NO_x (associated with the highest O_3 at 15–16 h) was 18%. By contrast, a 50% reduction in VOC is predicted to yield a 20%–30% reduction in O_3 (including peak O_3) at 12–13 h, although reduced VOC had little effect on O_3 at 15–16 h.

As will be discussed below, O_3 -precursor sensitivity predictions are very uncertain and there is contradictory evidence from other models in the case of Mexico. Here we intend to use the sensitivity results to identify specific species concentrations that are associated with NO_x -sensitive or VOC-sensitive photochemistry. This approach has been used extensively before (e.g. Sillman and He, 2002) to provide a basis for evaluating the accuracy of model predictions through a measurement-based program.

In order to evaluate the relation between predicted O_3 -precursor sensitivity and ambient species concentrations we will use the following definitions, which are also illustrated in Fig. 2. A location is defined as NO_x -sensitive at a given time if O_3 at that hour decreases by at least 5 ppb in response to reduced NO_x and if the decrease in response to reduced NO_x is at least twice as large as the decrease in response to reduced VOC. A location is defined as VOC-sensitive if O_3 decreases by at least 5 ppb in response to reduced VOC and if the decrease in response to reduced VOC is at least twice as large as the decrease in response to reduced NO_x (or if O_3 increases in response to reduced NO_x). A location is defined as having mixed sensitivity if O_3 decreases by at least 5 ppb in response to either reduced VOC or reduced NO_x and if the decrease in response to reduced VOC and reduced NO_x differ by less than a factor of two. Lastly, a location is defined as dominated by NO_x titration if O_3 increases by 5 ppb or more in response to reduced NO_x and does not decrease by 5 ppb or more in response to reduced VOC. The latter condition usually occurs in plumes from large power plants with very high NO_x , low VOC and little photochemical activity other than the removal of O_3 through reaction with directly emitted NO. In this study no locations met the definition for NO_x titration during the time periods shown. Locations that do not show a 5 ppb change in response to either reduced NO_x or reduced VOC are omitted from the subsequent analysis. Species concentrations at these omitted locations generally represented the model boundary conditions (sometimes combined with direct emissions) with little photochemical processing. Similar definitions were used by Sillman and He (2002).

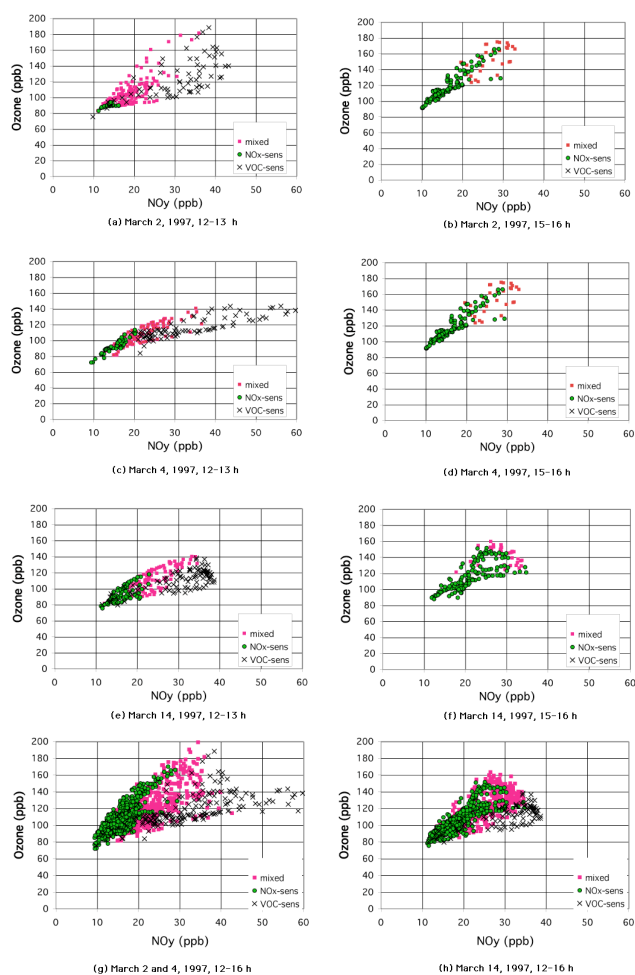


Fig. 3. O_3 vs. NO_y (ppb) sorted by precursor sensitivity. Locations are identified as primarily sensitive to NO_x (green circles), primarily sensitive to VOC (Xs), and with mixed sensitivity (pink squares). Results are for (a) 2 March, 12–13 h; (b) 2 March, 15–16 h; (c) 4 March, 12–13 h; (d) 4 March, 15–16 h; (e) 14 March, 12–13 h; (f) 14 March, 15–16 h; (g) composite of 4 hourly intervals from 12 h to 16 h on 2 and 4 March; and (h) composite of 4 hourly intervals from 12 h to 16 h on 14 March, all in 1997.

These sensitivity categories are used to characterize the predicted change in ozone in response to reduced NO_x or VOC at specific hours and will be used in combination with predicted ambient concentrations at the same hour. The sensitivity categories for a given location at one hour do not necessarily apply to other times; some locations change from VOC-sensitive to NO_x -sensitive at different hours (Fig. 2).

Figure 3 shows model O_3 versus NO_y for Mexico City for 2, 4 and 14 March with locations identified based on model precursor sensitivity. Results are shown for surface values over the full model domain (including Mexico City and the surrounding rural area), excluding locations that showed little sensitivity response to either NO_x or VOC. The sensitivity categorizations illustrate the shift from pri-

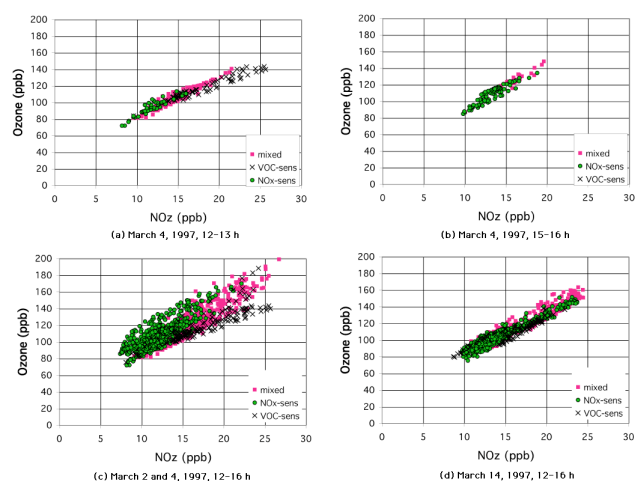


Fig. 4. O_3 vs. NO_z (ppb) sorted by precursor sensitivity. Locations are identified as primarily sensitive to NO_x (green circles), primarily sensitive to VOC (Xs), and with mixed sensitivity (pink squares). Results are for (a) 4 March, 12–13 h; (b) 4 March, 15–16 h; (c) composite of 4 hourly intervals from 12 h to 16 h on 2 and 4 March; and (d) composite of 4 hourly intervals from 12 h to 16 h on 14 March, all in 1997.

marily VOC-sensitive conditions at 12–13 h on both days to primarily NO_x -sensitive conditions at 15–16 h. The figure also shows a change in the values of ambient O_3 versus NO_y that apparently corresponds with the change in predicted sensitivity. VOC-sensitive conditions generally correspond with model NO_y greater than 30 ppb and O_3/NO_y ratios lower than 4.5. NO_x -sensitive conditions are associated with NO_y below 25 ppb and O_3/NO_y ratios higher than 4.5 (and usually higher than 6). Similarly, the model shows a shift in ambient NO_y and O_3/NO_y between 12–13 h and 15–16 h that matches the predicted shift from VOC-sensitive to NO_x -sensitive conditions. The difference in ambient mixing ratios associated with NO_x -sensitive and VOC-sensitive conditions is also illustrated by composite plots (Fig. 3g and h), which show O_3 versus NO_y for all four hour intervals from 12 to 16 h on the same plot. The composite plots show a clear separation between the values for predicted O_3 and NO_y associated with NO_x -sensitive and VOC-sensitive conditions on 2 March and 4 March. The separation between NO_x -sensitive and VOC-sensitive values is somewhat less on 14 March. There are also a few instances of VOC-sensitive conditions coincident with O_3 and NO_y that would suggest NO_x -sensitive conditions, and vice versa. These are most obvious in Fig. 3e. The link between O_3/NO_y and predicted ozone-precursor sensitivity is consistent with results from models in other locations described by Sillman and He (2002) and Sillman (1995).

Figure 4 shows model O_3 versus NO_z associated with precursor sensitivity. In this and subsequent plots we show results at 12–13 h and 15–16 h only for 4 March, along with

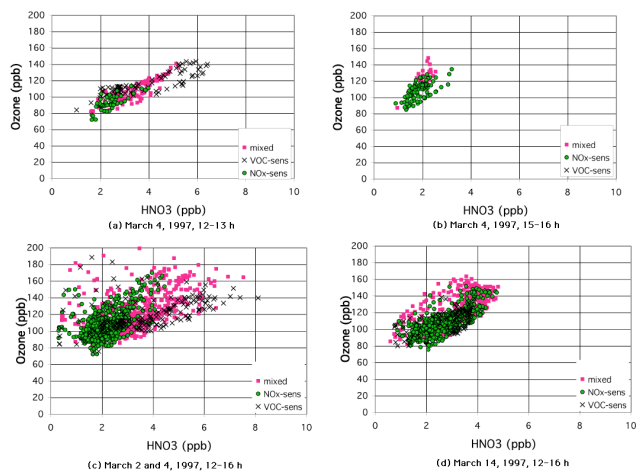


Fig. 5. O_3 vs. HNO_3 (ppb) sorted by precursor sensitivity, as in Fig. 4.

composite plots for 12–16 h for all three days. Here the difference between NO_x -sensitive and VOC-sensitive locations is relatively small. On 2 March and 4 March the NO_x -sensitive locations (visible primarily at 15–16 h) have NO_z below 17 ppb while the VOC-sensitive locations (at 12–13 h), with few exceptions, have NO_z between 15 and 25 ppb. The correlation between O_3 and NO_z among NO_x -sensitive locations, if extended to higher NO_z , would show higher O_3 relative to NO_z in comparison with the VOC-sensitive locations. The VOC-sensitive locations mostly have O_3/NO_z ratios below 7, while the NO_x -sensitive locations had higher ratios. This difference between NO_x -sensitive and VOC-sensitive conditions is consistent with results from locations described by Sillman and He (2002) and Sillman et al. (2003). However on 14 March the O_3 - NO_z correlation is nearly identical for both NO_x -sensitive and VOC-sensitive conditions, and corresponds with the correlation associated solely with VOC-sensitive conditions on the other days.

Even on 2 March and 4 March the difference in O_3/NO_z between NO_x -sensitive and VOC-sensitive locations in the model for Mexico is smaller than in models for other locations. There is also significant overlap between O_3 - NO_z correlations associated between NO_x -sensitive and VOC-sensitive conditions, so that it may not be possible to clearly distinguish between NO_x -sensitive and VOC-sensitive correlation patterns. The difference between NO_x -sensitive and VOC-sensitive conditions corresponds to a difference in NO_z of less than 30%. This is comparable to the 20% uncertainty in model ambient concentrations attributed to uncertainties in chemical reaction rates (Gao et al., 1996). The O_3 - NO_z slope shown in Fig. 4 (for 4 March) was significantly lower at 12–13 h and higher at 15–16 h (4 vs. 6), but the difference in slope was not consistent among the three model days. The slope for 2 March was similar at 12–13 h and 15–16 h (6).

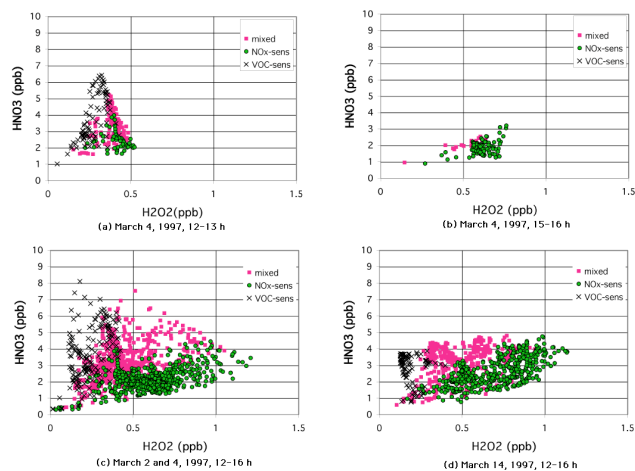


Fig. 6. H_2O_2 vs. HNO_3 (ppb) sorted by precursor sensitivity, as in Fig. 4.

Results for O_3 versus HNO_3 (Fig. 5) also show a difference between NO_x -sensitive and VOC-sensitive locations on 2 March and 4 March, and a corresponding shift in values between 12–13 h and 15–16 h. The VOC-sensitive locations mostly have HNO_3 (interpreted to represent the sum of gas-phase HNO_3 and particulate NO_3) greater than 3.5 ppb and O_3/HNO_3 below 30. The NO_x -sensitive locations have HNO_3 below 3.2 ppb and O_3/HNO_3 above 40. However, these results differ from results in other locations. Sillman (1995) and Sillman and He (2002) found that VOC-sensitive conditions usually corresponded to O_3/HNO_3 below 15 and that NO_x -sensitive conditions usually corresponded to O_3/HNO_3 between 20 and 30 (assuming O_3 above 100 ppb). Much of the O_3 and HNO_3 associated with NO_x -sensitive conditions in Sillman and He (2002) would be associated with VOC-sensitive conditions in the model for Mexico City shown here. There is also much greater overlap between the values associated with VOC-sensitive conditions and with NO_x -sensitive conditions in the model for Mexico City. Some VOC-sensitive locations have low HNO_3 and high O_3/HNO_3 , equivalent to the NO_x -sensitive locations. On 14 March there is again no difference between the values of O_3 and HNO_3 associated with NO_x -sensitive and VOC-sensitive conditions, in contrast with results on 2 March and 4 March and in contrast with previous results from other cities.

O_3 versus PAN (not shown) shows no discernible difference between NO_x -sensitive and VOC-sensitive locations. This result was also reported by Sillman et al. (2003) for Paris.

Results for H_2O_2 versus HNO_3 (Fig. 6) show a large difference between NO_x -sensitive and VOC-sensitive locations and an equivalent shift in values between 12–13 h (VOC-sensitive) and 15–16 h (NO_x -sensitive). VOC-sensitive locations mostly have low H_2O_2 (<0.5 ppb) and low

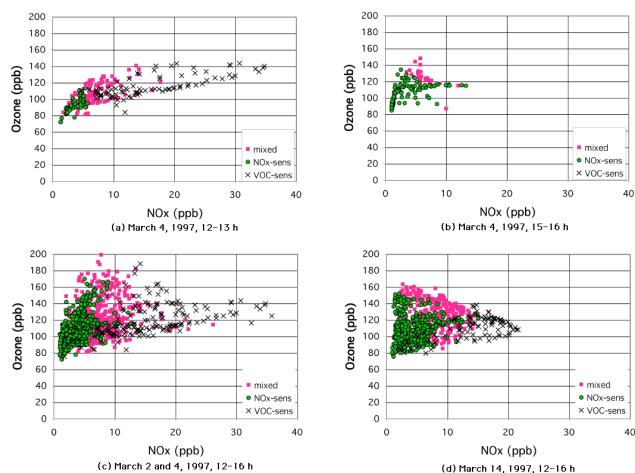


Fig. 7. O₃ vs. NO_x (ppb) sorted by precursor sensitivity, as in Fig. 4.

H₂O₂/HNO₃ ratios (<0.1). NO_x-sensitive locations have higher H₂O₂ (0.2–1 ppb) and H₂O₂/HNO₃ (>0.2). This difference between NO_x-sensitive and VOC-sensitive locations is similar on all three model days, including 14 March. As in previous studies (Sillman and He, 2002), there is little correlation between H₂O₂ and HNO₃ except possibly in subregions with either uniformly NO_x-sensitive or uniformly VOC-sensitive conditions. However there is a large difference in H₂O₂/HNO₃ values associated with NO_x-sensitive and VOC-sensitive chemistry.

Model H₂O₂ and HNO₃ are both much lower than the model values in Sillman and He (2002) but the H₂O₂/HNO₃ ratios associated with NO_x-sensitive and VOC-sensitive conditions are similar to the values reported by Sillman and He. The low H₂O₂ may be due in part to the model boundary conditions (with zero H₂O₂), although we do not anticipate elevated H₂O₂ upwind from Mexico City. It is noteworthy that the model predicts NO_x-sensitive conditions even for low H₂O₂. Low ambient H₂O₂ is often interpreted as evidence for VOC-sensitive conditions (e.g. Nunnermacker et al., 2008). Here, relatively low H₂O₂ can coincide with NO_x-sensitive conditions because HNO₃ is also very low.

Lastly, results for O₃ versus NO_x (Fig. 7) show a significant difference between NO_x-sensitive and VOC-sensitive locations on all three days. VOC-sensitive locations were associated with NO_x above 10 ppb, while NO_x-sensitive locations were associated with lower values. O₃ versus NO_x was proposed by McKeen et al. (1991) as a way to distinguish between NO_x-sensitive and VOC-sensitive locations. It was omitted by Sillman and He (2002) because they found many exceptional situations in which high NO_x corresponded with NO_x-sensitive conditions and lower NO_x with VOC-sensitive conditions. We did not find similar exceptions in Mexico City.

Ozone-precursor sensitivity in the model for Mexico City is also strongly correlated with the NO_x/NO_y ratio (Fig. 8)

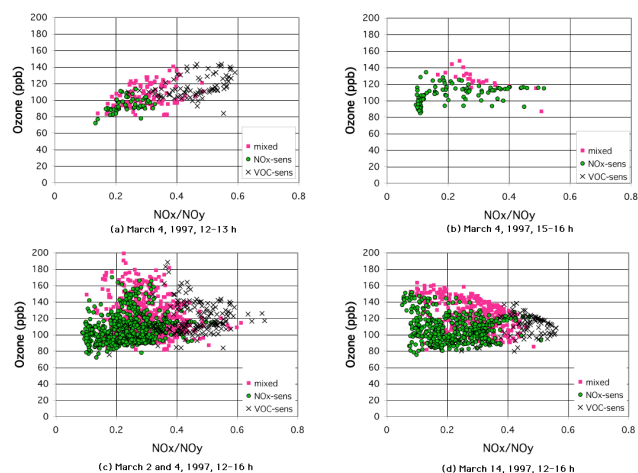


Fig. 8. O₃ vs. NO_x/NO_y (ppb) sorted by precursor sensitivity, as in Fig. 4.

that is widely used to represent photochemical aging (e.g. Olzszyna et al., 1994). VOC-sensitive locations have NO_x/NO_y greater than 0.4, while NO_x-sensitive locations have lower NO_x/NO_y. This result also may not be applicable to other locations, but it may be useful in evaluating model ozone-precursor predictions for Mexico.

5 Discussion

The model results for Mexico show two distinct features in comparison with other regions: a relatively high amount of organic nitrates (especially PAN) and low HNO₃; and differences in the correlation between ozone-precursor sensitivity and model values for secondary species. The model predicts that VOC-sensitive chemistry is associated with high NO_y and with low O₃/NO_y and H₂O₂/HNO₃, in agreement with previous results. In contrast with some previous results, however, ozone-precursor sensitivity was also strongly correlated with the ratios O₃/NO_x and NO_x/NO_y and was weakly correlated with O₃/NO_z and O₃/HNO₃. The results also have some implications for O₃-NO_x-VOC sensitivity in Mexico, especially when considered in comparison with results from other investigations.

5.1 PAN and HNO₃

The predicted ratio of PAN to O₃ is comparable to the predicted ratio in Paris and is higher than the ratio in Nashville by a factor of two. This result can be analyzed in relation to the PAN steady state Eq. (1). Two factors might contribute to a higher PAN/O₃ ratio: a larger rate of production due to Reaction (R5) (OH+CH₃CHO) and equivalent reactions for other PAN sources; or a slower rate of decomposition for PAN (R6) due to lower temperatures.

The rate of Reaction (R5) is broadly representative of all VOC+OH reactions and is likely to vary in proportion to the rate of production of O₃. A significant increase in the PAN/O₃ ratio would be possible if the rate of production of O₃ during the events in Mexico and in Paris was larger than the rate of production in Nashville, despite similar O₃ concentrations. This would occur if the Nashville model represented downwind conditions with transported O₃. The Nashville event was associated with a multi-day regional pollution episode with up to 85 ppb O₃ in rural upwind locations, so it is expected that rates of ozone production would be lower in Nashville than in Mexico for a given O₃ concentration.

Another possibility is that the speciated VOC in Mexico and in Paris contained a higher proportion of specific precursors of PAN than the VOC in Nashville. This is a likely possibility for Mexico because subsequent measurements showed large decreases in both PAN and the PAN/O₃ ratio, as a result of large reductions in emission of light olefins (Marley et al., 2007).

While these are possibilities, the differences in PAN and PAN/O₃ can also be explained by the influence of temperature on the PAN decomposition rate. Maximum surface temperature during the model events was much warmer in Nashville (307 K) than in Paris (300) or in Mexico (300). Based on current rate estimates (Sander et al., 2003) the PAN decomposition rate in Nashville should be higher than the rate in Paris or in Mexico by a factor of three. These large rate differences may be partially compensated by differences in the height of the convective mixed layer. The estimated mixed layer height was higher in Nashville (2600 m) than in Paris (2000 m) but comparable to the mixing heights for Mexico (2700–3200 m on 2 and 4 March, 1900–2600 on 14 March, from West et al., 2004). The PAN lifetime (40 min at 298 K, 10 min at 307 K) is somewhat shorter than the time scale for mixing in an active convective boundary layer, so that the effective removal rate for PAN is also influenced by the temperature throughout the mixed layer. If the PAN decomposition rate is based on the estimated average temperature within the convective mixed layer, the rate is still faster in Nashville than in Paris by approximately a factor of two. Due to the deeper convective mixed layer in Mexico, the effective PAN decomposition rate in Mexico should be slower than in Paris, and should be slower than in Nashville by at least a factor of three. Therefore, the difference in the PAN decomposition rate is sufficient to explain the difference in PAN/O₃ by itself.

The PAN/HNO₃ ratio also shows large differences between Mexico and the other locations. The PAN/HNO₃ increases from 0.4 (Nashville) to 1 (Paris) to 3 or higher in Mexico. This difference in PAN/HNO₃ between Nashville and Paris is comparable to the difference in PAN/O₃ between the two locations, and can also be explained by the difference in the PAN decomposition rate associated with temperature. However, the difference between Mexico and

the other cities is much larger for PAN/HNO₃ than for PAN/O₃, and cannot be explained solely in terms of temperature. The formation of PAN and HNO₃ is driven by Reactions (R5) (OH+CH₃CHO) and (R2) (OH+NO₂) respectively. The higher PAN/HNO₃ in Mexico suggests a higher ratio of CH₃CHO (or of other organic precursors of PAN) to NO₂ or, more generally, a higher ratio of reactivity-weighted VOC to NO_x. The high VOC/NO_x ratio in Mexico was included in the model emissions, and recent measurements have found that the ratio of reactivity-weighted VOC to NO_x in Mexico is higher than in New York City by a factor of ten (Shirley et al., 2006).

The high PAN/HNO₃ ratio also has implications for the behavior of odd hydrogen radicals (OH and HO₂) in Mexico City. Normally the formation of peroxides and HNO₃ represent the main radical sinks. Here, the net formation of PAN and other organic nitrates is much larger than the formation rates for both peroxides and HNO₃. This may pose a problem for the constrained steady state (CSS) evaluations of measured OH and HO₂ (e.g. Shirley et al., 2006; Volkamer et al., 2007). The CSS calculations determine the expected OH and HO₂ based on measured concentrations of long-lived species (NO, NO₂, O₃, speciated VOC). It is difficult to include net formation of PAN in this representation because the measurements may not include the direct precursors of PAN (acetaldehyde and methyl glyoxal). Shirley et al. (2006) found good agreement between calculated and measured OH and HO₂ despite their apparent omission of PAN as a radical sink, but the role of PAN may represent a significant uncertainty.

5.2 Indicators for NO_x-VOC sensitivity

Results from the Mexico City simulations show significant differences from previous results (Sillman, 1995; Sillman and He, 2002) in the use of ratios such as O₃/NO_z, O₃/HNO₃ and H₂O₂/HNO₃ as measurement-based “indicators” of O₃-NO_x-VOC sensitivity. The differences are especially important because these types of ratios and correlations provide useful evidence on NO_x-VOC sensitivity only if they behave consistently in models for a wide range of conditions. If a particular ratio appears to be correlated with NO_x-VOC sensitivity only for certain model conditions, then it is unclear whether the correlation reflects the underlying photochemical process or whether it is accidental.

Here we have found that H₂O₂/HNO₃ in the model for Mexico correlates with model NO_x-VOC sensitivity consistently with results from other cities. The H₂O₂/HNO₃ ratio is also related more closely to NO_x-VOC chemistry than the other ratios. O₃/NO_y also correlates with model NO_x-VOC sensitivity in the same way as in the previous studies, but the behavior of individual NO_y species is somewhat different. The ratio O₃/NO_x is strongly correlated with NO_x-VOC sensitivity in Mexico and this accounts for most of the correlation between O₃/NO_y and NO_x-VOC sensitivity. In the

previous results from Sillman and He (2002) high O_3/NO_x tended to correlate with NO_x -sensitive conditions, but there were significant exceptions in which high O_3/NO_x coincided with VOC-sensitive chemistry.

The major difference from previous results involves O_3/NO_z and O_3/HNO_3 . Both of these ratios show a small difference between NO_x -sensitive and VOC-sensitive conditions on two of the three model days, and no difference on the third day (14 March). The poor results for these ratios may be due in part to the much higher net production of PAN and other organic nitrates in Mexico as opposed to other locations. The ratio O_3/PAN is usually not correlated at all with NO_x -VOC-sensitivity (Sillman et al., 2003), so that if NO_z consists mainly of organic nitrates the correlation between O_3/NO_z and NO_x -VOC-sensitivity should be weaker. In this context it is noteworthy that the 14 March event had somewhat lower afternoon temperatures than the other days ($24^\circ C$ vs. $27^\circ C$), which leads to higher concentrations of PAN.

In addition to showing a weaker correlation with NO_x -VOC-sensitivity, the ratio O_3/HNO_3 also showed a shift towards higher values for both NO_x -sensitive and VOC-sensitive conditions in the model for Mexico relative to models for other locations. Elsewhere it was found that NO_x -sensitive chemistry was associated with O_3/HNO_3 greater than 15, but in the model for Mexico VOC-sensitive chemistry is associated with O_3/HNO_3 as high as 30. This shift may also be due to the high rate of formation of organic nitrates and the high PAN/HNO₃.

The rationale for O_3/HNO_3 as a NO_x -VOC sensitivity indicator is based on the radical chemistry summarized in Sect. 2. NO_x -sensitive chemistry occurs when the formation rate of peroxides (R1a and R1b) is high relative to the formation rate of nitric acid (R2) and VOC-sensitive chemistry occurs when the formation rate of HNO₃ is larger by more than a factor of 2. The larger formation rate of HNO₃ as a fraction of the total radical source leads to lower O_3/HNO_3 and O_3/NO_z in VOC-sensitive locations. In Mexico, however, the radical sink is dominated by formation of PAN and other organic nitrates. Formation of HNO₃ is smaller as a fraction of the total radical sink even when it is large relative to formation of peroxides. Consequently the O_3/HNO_3 associated with NO_x -sensitive and VOC-sensitive conditions in Mexico are both larger than the values associated with NO_x -sensitive and VOC-sensitive conditions in other locations.

Sillman (1995) noted that the accumulated sink for odd hydrogen radicals may be represented by the sum $2H_2O_2+NO_z$ and that the ratio $O_3/(2H_2O_2+NO_z)$ remains invariant in polluted regions for both NO_x -sensitive and VOC-sensitive conditions. Since NO_x -sensitive chemistry occurs when formation of peroxides is high relative to formation of HNO₃, NO_x -sensitive chemistry should in theory be associated with high values of the ratio $O_3/(HNO_3+NO_z)$. NO_x -sensitive and VOC-sensitive regions coincide with high (>6) and low (<5) values for $O_3/(HNO_3+NO_z)$ in both the model for Mexico and the models for Nashville, Paris and elsewhere reported

by Sillman and He (2002). Since Mexico has much lower HNO₃/NO_z than other locations, the corresponding values for O_3/HNO_3 associated with both NO_x -sensitive and VOC-sensitive locations are higher than elsewhere.

Though not shown here, the high PAN/HNO₃ may also affect the L_n/Q approach developed by Kleinman et al. (1997, 2005) to evaluate how instantaneous production of O_3 varies with NO_x and VOC. The L_n/Q is based on the rate of removal of NO_x (L_n), and the relative rate of production of odd hydrogen radicals (Q), assuming that formation of HNO₃ is the dominant radical sink. An L_n/Q greater than 0.5 identifies a situation in which formation of HNO₃ is greater than formation of peroxides and indicates local VOC-sensitive chemistry. A modification may be necessary for cases in which formation of organic nitrates represents the dominant radical sink.

A change in rate of PAN formation should not affect the relative sensitivity of O_3 to NO_x and VOC directly because PAN formation represents a sink for both NO_x and radicals. However, a change in PAN formation can affect the interpretation of measurements that are associated with NO_x -sensitive and VOC-sensitive conditions, including O_3/NO_z , NO_x/NO_y and L_n/Q .

5.3 Implications for ozone-precursor sensitivity

Model-based predictions for the response of O_3 to reduced NO_x and VOC in urban areas are always subject to significant uncertainty. The uncertainties are especially important in this case because emission of VOC have been increased by a factor of three relative to the original inventory. The increased emission rates have been justified based on ambient measurements (Arriaga-Colina et al., 2004; West et al., 2004) but the process implies significant uncertainty, both for VOC by itself and for VOC relative to NO_x . Model predictions for O_3 - NO_x -VOC sensitivity are sensitive to emission rates for total VOC and also to VOC speciation. There are also uncertainties related to various model dynamical and photochemical properties (e.g. Thornton et al., 2002). O_3 -precursor sensitivity also can vary from day to day, and the three events described here may not be representative.

Results from this model suggest mixed sensitivity to NO_x and VOC, rather than a purely NO_x -sensitive or VOC-sensitive environment. Results also suggest a shift from a primarily VOC-sensitive environment before 14 h to a more NO_x -sensitive environment after 16 h. The instantaneous production rates for O_3 in the model (as opposed to the O_3 concentrations) shift from being primarily VOC-sensitive in the morning to primarily NO_x -sensitive after noon. This prediction might be tested though evaluation of instantaneous production rates based on measured NO and HO₂ (as in Shirley et al., 2006). A shift from VOC-sensitive conditions during the morning hours to NO_x -sensitive conditions during the afternoon has been found previously in many locations (e.g. Milford et al., 1994, Kleinman et al., 2005) and may be

due to photochemical aging or to increased vertical dilution. Lei et al. (2008) also reported a shift towards NO_x -sensitive conditions associated with photochemical aging in the plume downwind from Mexico City.

The sensitivity results described here contrast sharply with the findings of Lei et al. (2007, 2008). Lei et al. (2007) applied a photochemical model to a different episode (13–16 April 2003) and concluded that O_3 remains predominantly sensitive to VOC throughout the day. The sensitivity predictions from Lei et al. (2007) are also consistent with results from Stephens et al. (2008) based on the contrast between weekday and weekend O_3 .

The most likely reason for the difference in sensitivity predictions between West et al. (2004) and Lei et al. (2007) is the decrease in VOC emission rates and VOC/ NO_x emission ratios between 1997 and 2003. Results from Zavala et al. (2009) suggest that CO and VOC emissions from mobile sources decreased by approximately 40% over this time period while NO_x emissions remained unchanged. Marley et al. (2007) also reported evidence of a significant decrease in emissions of light olefins based on changes in ambient PAN concentrations. Other possible reasons for the difference include different estimations of VOC emissions and different meteorological conditions during the simulated events. It has also been suggested that vertical mixing is too rapid in the CIT model used here (Velasco et al., 2007), which can also lead to a more NO_x -sensitive simulation, but West et al. (2004) report good agreement with NO_y measurements, suggesting that errors in vertical mixing may not be large.

West et al. (2004) and Lei et al. (2007) both increased VOC emissions with respect to their base inventories, but Lei et al. increased emissions by 65% whereas West et al. increased emissions by 200%. The resulting VOC emissions were 1425 kton per year in West et al. and 900 kton per year in Lei et al. The lower VOC emissions in Lei et al. result in a more VOC-sensitive model. The adjustment by Lei et al. also varied for individual VOCs, including a factor-of-9 increase for HCHO and no increase for alkenes. The resulting VOC speciation differed from West et al. West et al. and Lei et al. both evaluated their model results using measured O_3 , VOC and NO_y and both interpreted the available NO_x measurements as representing NO_y . The smaller emissions adjustment used by Lei et al. were also supported by measurement-based analyses, although with some uncertainty (Velasco et al., 2005, 2007). It is also possible that the different emissions adjustments used by West et al. and Lei et al. reflect reductions in ambient VOC between 1997 and 2003. Accuracy of the emission inventory (including both total VOC, VOC/ NO_x ratios and VOC speciation) has historically had a large impact on model predictions for ozone-precursor sensitivity (e.g. Pierce et al., 1998).

The difference between the models is also closely associated with differences in ambient NO_x and NO_y in the models. The results here show that VOC-sensitive conditions in the model by West et al. are associated with model ambient NO_x

above 10 ppb and NO_y above 30 ppb, while NO_x -sensitive conditions are associated with lower NO_x and NO_y . Median NO_x during the afternoon is below 10 ppb. By contrast, in the model by Lei et al., NO_x varies from 10 to 80 ppb between 12 h and 17 h and is rarely below 10 ppb. The high NO_x values in the model by Lei et al. correspond with VOC-sensitive conditions in the model by West et al., and the NO_x -sensitive conditions in the model by West et al. correspond to lower ambient NO_x than is found in the model by Lei et al. NO_x/NO_y ratios were also much higher in Lei et al. (2007). The VOC-sensitive response in Lei et al. was associated with NO_z/NO_y equal to 0.7 or lower (equivalent to NO_x/NO_y equal to 0.3 or higher), and the region with low NO_x/NO_y coincides with high O_3 . In the model by West et al. high O_3 coincided with NO_x/NO_y from 0.2 to 0.6 and the lower values ($\text{NO}_x/\text{NO}_y < 0.4$) had NO_x -sensitive chemistry. In addition to having lower NO_x/NO_y , the model by West et al. predicted NO_x -sensitive chemistry for somewhat higher NO_x/NO_y than was reported by Lei et al. (2007, 2008).

This difference in ambient NO_x could be caused by differences in meteorology or by differences in NO_x emission rates. The episode investigated by Lei et al. (15 April 2003) had unusually stagnant conditions, which leads to higher NO_x and NO_y and also makes VOC-sensitive chemistry more likely (Milford et al., 1994). The difference in NO_x could also be caused by differences in VOC emission rates and speciation, since formation of organic nitrates appears to be the dominant removal process for NO_x .

The difference between the sensitivity predictions from the models by West et al. and Lei et al. might be resolved by careful measurement of NO_x and NO_y . In this context it is noteworthy that Shirley et al. (2006) measured NO_x at a site in Mexico City during 2003 and found median afternoon values equal to 20 ppb, though with a wide range of variation.

6 Conclusions

We have investigated correlations between ozone and reactive nitrogen in a model of a 1997 event in Mexico City, in contrast with similar results from other cities. These correlations are often linked with model predictions of the response of ozone to reductions in precursor emissions.

Results showed that the model ratio of PAN to O_3 is higher than in many other locations, but comparable to model results for Paris. The high PAN relative to O_3 is attributed to the relatively low temperature in comparison to other locations during events with elevated O_3 , which increases the photochemical lifetime of PAN. The model ratio of PAN to HNO_3 is unusually high and cannot be explained by temperature. We expect that it reflects the high ratio of VOC to NO_x in Mexico City and the high reactivity of VOCs. Measurements show PAN significantly higher than the model values and HNO_3 comparable to model values.

The model predicts that ozone in Mexico City shows mixed sensitivity to NO_x and VOC, in contrast to model studies of more recent (2003) events (Lei et al., 2007) and measurement-based studies (Stephens et al., 2008) that predicted strongly VOC-sensitive chemistry in Mexico. The difference in predicted O_3 - NO_x -VOC sensitivity is most likely due to changes in emissions between 1997 and 2003 or to uncertainties in emission rates in general. The difference in sensitivity predictions is associated with differences in predicted ambient NO_x during the afternoon, which were frequently below 10 ppb in the model used here and 10–90 ppb in the more VOC-sensitive model from Lei et al., 2007. The lower ambient NO_x may be caused by higher VOC emissions and more rapid conversion from NO_x to organic nitrates.

Results were also used to explore the relation between ozone-precursor sensitivity and model ambient values of species that might provide a measurement-based test for the accuracy of the sensitivity predictions. NO_x -sensitive conditions were found to be associated with high values of $\text{H}_2\text{O}_2/\text{HNO}_3$ and O_3/NO_y , as has been found for other locations. NO_x -sensitive conditions were also associated with high O_3/HNO_3 , but the O_3/HNO_3 ratio was much higher than in other locations regardless of model NO_x -VOC sensitivity. O_3/HNO_3 behaves differently in Mexico City than elsewhere because removal of odd hydrogen radicals is dominated by the formation of PAN and other organic nitrates rather than by the formation of HNO_3 and peroxides. This supports the use of some of the measurement-based indicators of ozone sensitivity developed elsewhere ($\text{H}_2\text{O}_2/\text{HNO}_3$ and O_3/NO_y) by showing that they also apply in a different chemical and meteorological context. However it suggests that caution should be used in interpreting the ratios O_3/HNO_3 and O_3/NO_z as indicators of ozone sensitivity.

These results suggest that long-term measurements of NO_x and NO_y might be especially useful in characterizing the ozone-precursor relation in Mexico City.

Acknowledgements. Support for this work was provided by the National Science Foundation grant #0454838. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

Edited by: L. Molina

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