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

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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.

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