Ozone Production and it's Sensitivity to NO_x and VOCs

Only an accurate chemical transport model working off of an accurate emission inventory can provide a full answer to the "what-if" question of what happens when emissions are changed. A complimentary approach which is independent of an emission inventory is to use observations to constrain a box model and calculate the rate of O_3 production, $P(O_3)$, and it's sensitivity to NO_x and VOCs. Through the model derived variable Ln/Q (fraction of radicals removed by reactions with NO_x/ total primary radical production), one can determine where the atmosphere is in the continuum between NO_x limited and VOC limited conditions. We present calculated $P(O_3)$ and sensitivities based on G-1 observations taken over the Mexico City plateau. The highest $P(O_3)$'s occur under VOC limited conditions suggesting that peak O_3 itself is VOC limited. Even though VOC/NO_x ratios are higher than observed in U.S. cities (which by itself tilts the atmosphere towards being NO_x limited), VOC limited conditions occur because of extremely high NO_x concentrations. Most of the time to time and point to point variability in $P(O_3)$ under these VOC limited conditions is due to variations in radical production rate. Under VOC limited conditions NO_z rather than peroxides is an end product of photochemistry. Out of 50 O_3 plumes observed from the G-1, only 2 show a correlated H_2O_2 peak, which is consistent with VOC limited conditions.

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