

Appendix E

Overview: VOC / NO_x Ratios and Ozone Production

Appendix E provides a brief overview of how the relative presence of ambient VOC concentrations to NO_x levels can influence the potential to produce tropospheric ozone. This appendix is designed to provide some basic ozone science background to Section 4.5 (“Morning (6-9A CST) VOC / NO_x ratios in Milwaukee, 1994-2007”).

The relation between O₃, NO_x and VOC is driven by complex nonlinear photochemistry. As noted in Section 4.1 of the Attainment Demonstration - the availability of VOCs and NO_x in the morning along with their differing rates of reaction with the [•]OH radical can greatly influence how much ozone is formed for a given site-day (Seinfeld and Pandis, 1998).

The O₃-NO_x-VOC connection can be illustrated by isopleth plots (Figure E-1) generated from applying a basic ozone model called the Empirical Kinetic Modeling Approach (EKMA) to VOC and NO_x concentrations (Finlayson-Pitts and Pitts, 1993). This graph shows peak ozone as a function of the ratio of VOC to NO_x concentrations. It identifies two regimes with different O₃-NO_x-VOC sensitivities (referred to as “limited” in the graph).

The straight line in the center of Figure E-1 represents a constant VOC/NO_x ratio = 8/1. This line bisects the ozone isopleths where they transition from the fairly vertical lines (i.e., left side of the graph) where ozone changes are fairly sensitive to changes in VOCs [VOC-sensitive (limited)] to the mostly horizontal isopleths on the graph’s right, where ozone changes are quite responsive to NO_x fluctuations [NO_x-sensitive (limited)].

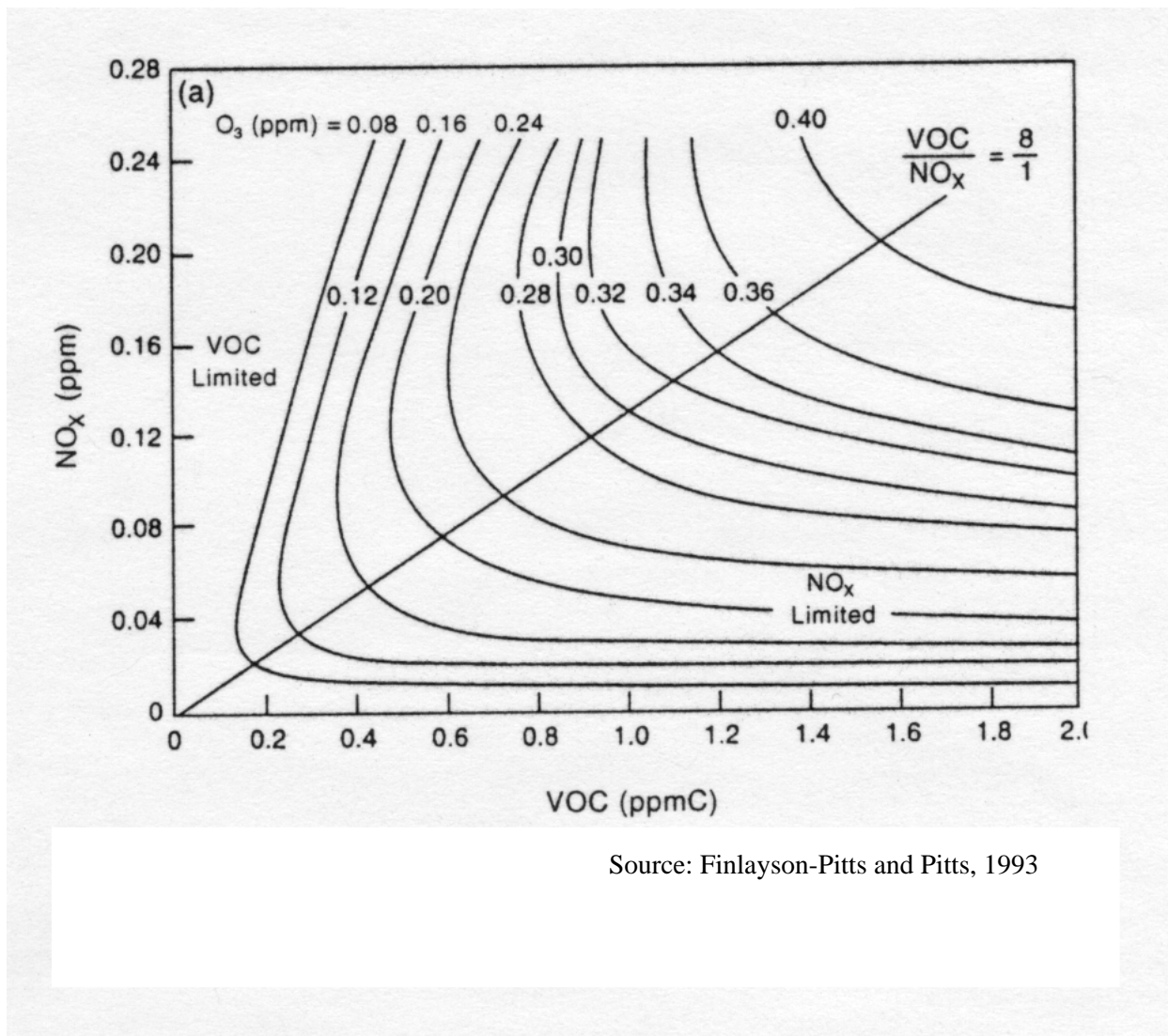
The VOC/NO_x ratio = 8/1 is considered an approximate reference point for determining the break in sensitivity of the air mass to precursor levels and the relative benefits of NO_x vs. VOC controls (NESCAUM, 1995). Graphically represented in Figure 20, the simplified goal of an efficient ozone control program is to reduce one type precursor emissions so as to move perpendicular towards lower ozone isopleths lines (i.e., de-optimizing the VOC/NO_x ratio that favors high ozone production). Where a region’s base VOC / NO_x ratio is established can greatly influence the direction in developing appropriate control strategies.

The NO_x-sensitive regime is typical of less urbanized, more rural air masses where biogenic VOCs make a much bigger contribution to VOCs levels and there are usually negligible, if any major NO_x sources (i.e., burning fossil fuels in factories, power plants and large numbers of motor vehicles). In a NO_x-sensitive air mass, it is most effective to de-optimize the VOC/NO_x ratio for maximum ozone production by reducing NO_x (i.e., moving downward to lower ozone isopleths on the right side of Figure E-1).

A VOC-sensitive air mass (left portion of Figure E-1) typically represents an urban area with low VOC/NO_x ratios - where NO_x emissions have much greater influence and there are relatively little biogenic VOCs to offset the NO_x. In this air mass ozone concentrations are most efficiently lowered (i.e., de-optimizing the VOC / NO_x ratio for maximum ozone production) by reducing VOCs (i.e., moving from right to left to smaller ozone isopleths on the left half of Figure E-1).

Figure E-1

A typical EKMA 2-dimensional depiction of ozone isopleths generated from initial mixtures of VOCs and NO_x in air



References

Finlayson-Pitts B.J. and N. Pitts, 1993: VOCs, NO_x and ozone production. **J. Air Waste Mgmt Assoc.**, **43**:1093-1101.

NESCAUM (Northeast States for Coordinated Air Use Management), 1995: **Preview of 1994 Ozone Precursor Concentrations in the Northeastern U.S.** Ambient Monitoring and Assessment Committee. Available at <http://capita.wustl.edu/nescaum/Reports/PAMS94/>

Seinfeld, J.H. and S.N.. Pandis, 1998: **Atmospheric Chemistry and Physics: From Air Pollution to Climate Change.** John Wiley and Sons, Inc. 923 pp.