O_3 Formation in Central Tennessee:

Rates, Efficiencies, Precursor Sources, and Sensitivity to Emissions Reductions

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INTRODUCTION

Nashville is a moderate sized city with a population of 0.5 million people in the downtown and surrounding metropolitan area. It is the only major metropolitan area in central TN and for this reason air quality is not significantly influenced by transport of fresh emissions from other urban areas. However, similar to many other US cities of its size, Nashville is itself a significant source of oxides of nitrogen (NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs) from automotive and industrial sources. The area around Nashville is also the location of several large fossil fuel power plants that emit significant quantities of NO_x.

In combination with the meteorology prevailing during the summer season these emissions cause the formation of a relatively high background concentrations of O_3 (50 - 80 ppbv) and related photochemical product species such as aldehydes, peroxides and fine aerosol that is present throughout the region at all hours of the day. These high background O_3 concentrations in combination with high water vapor concentrations and high solar intensity prevailing during the summer, produce an environment in which fresh emissions of hydrocarbons, and NO_x react rapidly to produce more ozone.

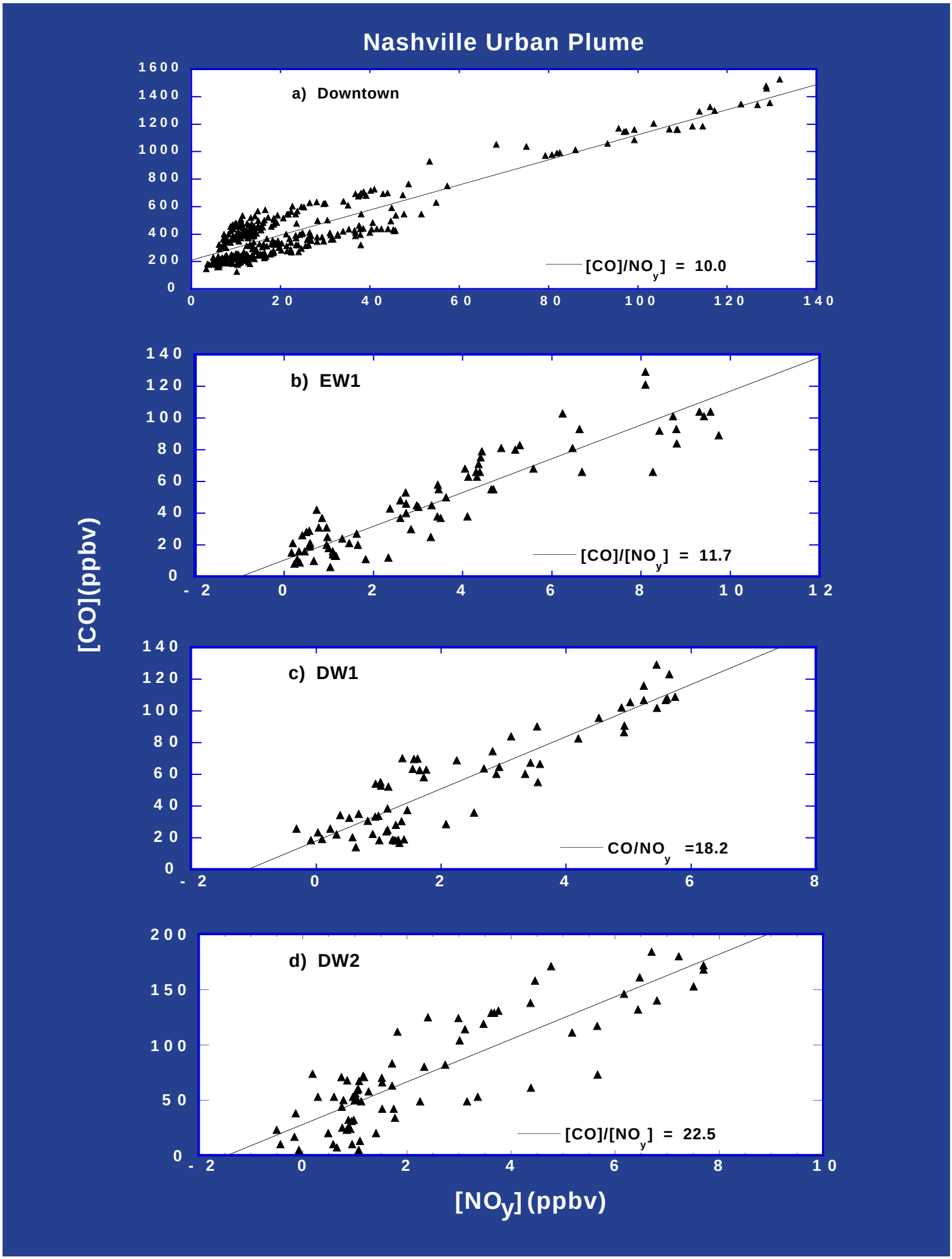
This poster focuses on estimating the NO_y lifetime in the Nashville urban plume; determining the OPEx after correcting for losses of NO_y (i.e. dry deposition of HNO_3), and; the relative importance of anthropogenic and natural hydrocarbons for O_3 production in the Nashville area.

NO_y Lifetimes and O_3 Production Efficiencies in Urban Plumes: Analysis of Field Data

Ozone Production Efficiencies

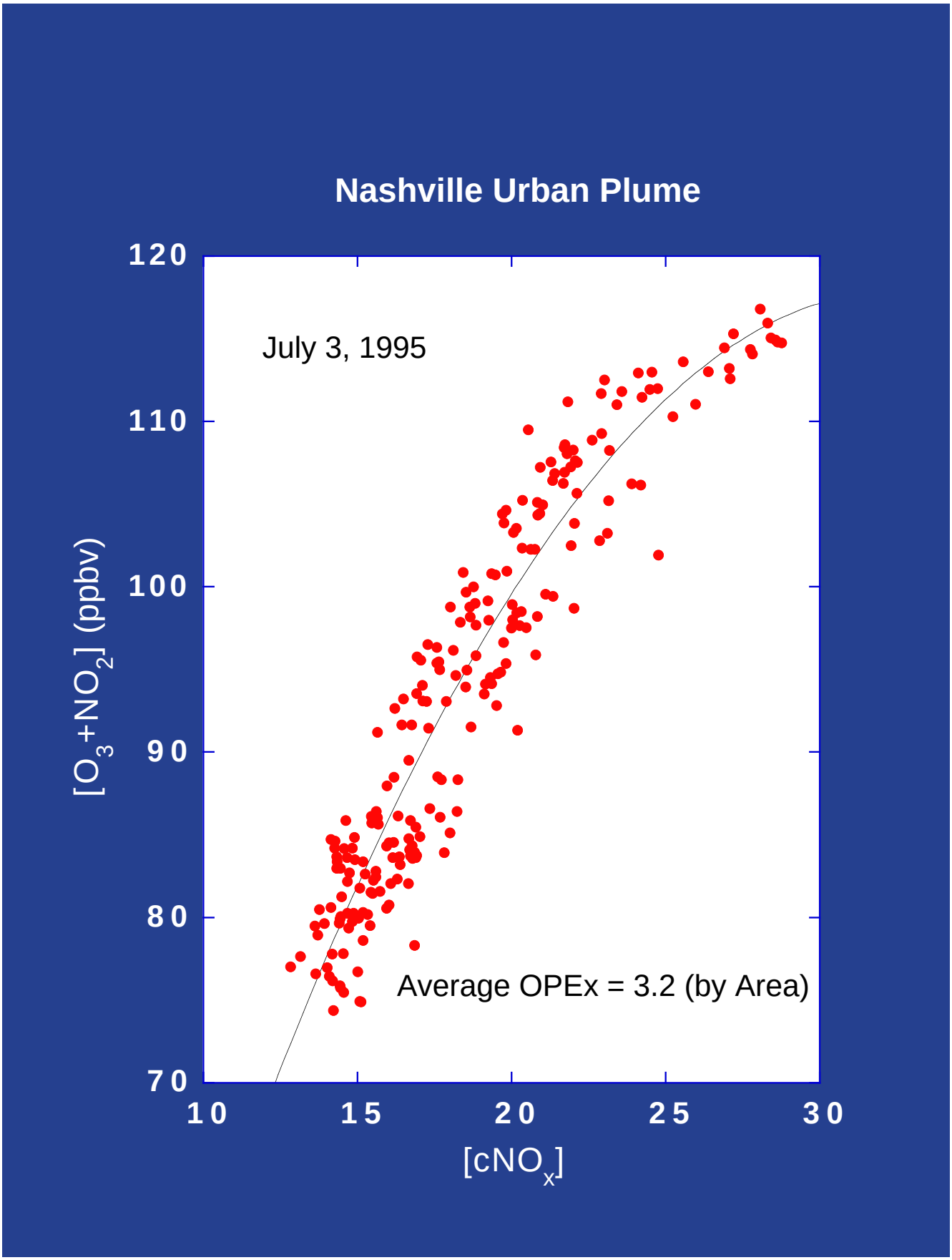
Ozone production efficiency with respect to NO_x (OPEx) is a measure of how many O_3 molecules are produced by NO_x before it is lost from the catalytic O_3 production cycle. OPEx is estimated from the relationship between O_3 and NO_z (where NO_z is defined as the concentration of NO_x oxidation products). This procedure implicitly assumes that NO_y is a conserved quantity and that the difference measurement of NO_z (NO_y - NO_x) is an adequate surrogate for the quantity of NO_x that was consumed. Although it has been recognized that the OPEx derived in this manner may be over-estimated and should be used only as an upper limit, the deposition of HNO_3 has for the most part been neglected.

To determine O_3 production efficiencies it is necessary to estimate the amount of NO_y that is lost from the system from the time of emission to the point at which the measurements are made. For the Nashville urban plume CO is used as the inert tracer. The following figure shows plots of NO_y vs CO for four intercepts of the Nashville urban plume at successively longer times downwind from Nashville. The plots indicate, as expected, an increasing slope with distance downwind of Nashville consistent with larger fractional losses of NO_y with time. The slope of these plots, in conjunction with the observed NO_y/CO ratio in downtown Nashville, is then used to estimate the amount of NO_x that is consumed, [cNO_x], from the point of emission to the point of interception of the plume.


Nashville Urban Plume
a) Downtown
[CO]/NOy] = 10.0
b) EW1
[CO]/[NOy] = 11.7
c) DW1
CO/NOy =18.2
d) DW2
[CO]/[NOy] = 22.5
[CO](ppbv)
[NOy] (ppbv)

Ozone Production Efficiencies, cont'd

The following Figure shows a plot of the concentration of odd O (defined as O3 + NO_2) versus [cNO_x] for a pass through the urban plume. Note that this plot is curved indicating that the O3 production efficiency varies from approximately 4.5 at the plume edges to about 2.6 at the plume center. This production efficiency is consistent with our understanding of ozone formation chemistry.


Nashville Urban Plume
July 3, 1995
Average OPEx = 3.2 (by Area)
120
110
100
90
80
70
10
15
20
25
30
[O3+NO2] (ppbv)
[cNOx]

NO_y Lifetimes

The slopes of the NO_y/CO plots can also be used to calculate the initial concentration of NO_y, $[NO_y]_o$. The ratios of observed $[NO_y]$ to calculated $[NO_y]_o$ are shown as a function of processing time in the following Figure. As shown, the data combine to yield a simple decay curve for NO_y. The shape of this curve may be explained as follows: The NO_y loss rate is determined by two processes- conversion of NO_x to NO_z, and dry deposition of HNO_3. This type of consecutive kinetics has the same qualitative time dependence depicted by the dotted line in the figure which is a qualitative fit to the data. During the initial stages of plume aging, $[NO_y]/[NO_y]_o$ remains relatively constant because most of the NO_y is present as NO_x. When a larger fraction of NO_x has been converted to HNO_3, the NO_y loss rate increases. These data are consistent with a 1/e lifetime for NO_y of ~ 6 hr. The corresponding lifetime of NO_x is about 2.1 hr.

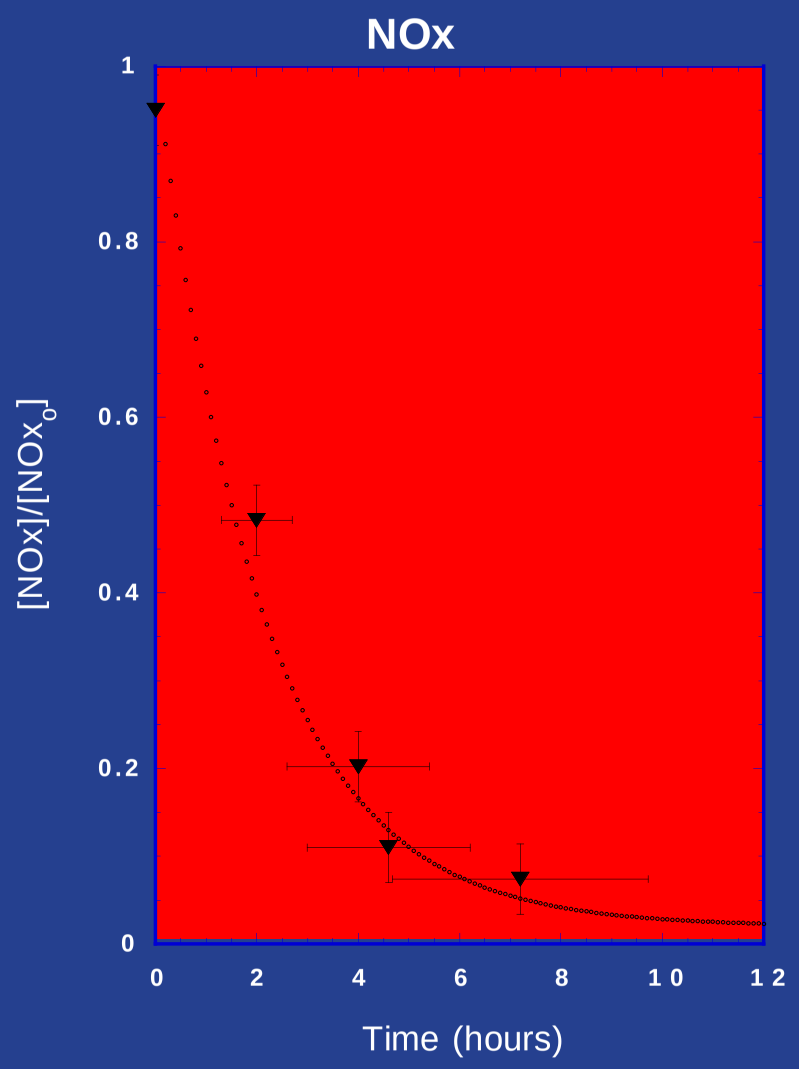
OH Concentrations

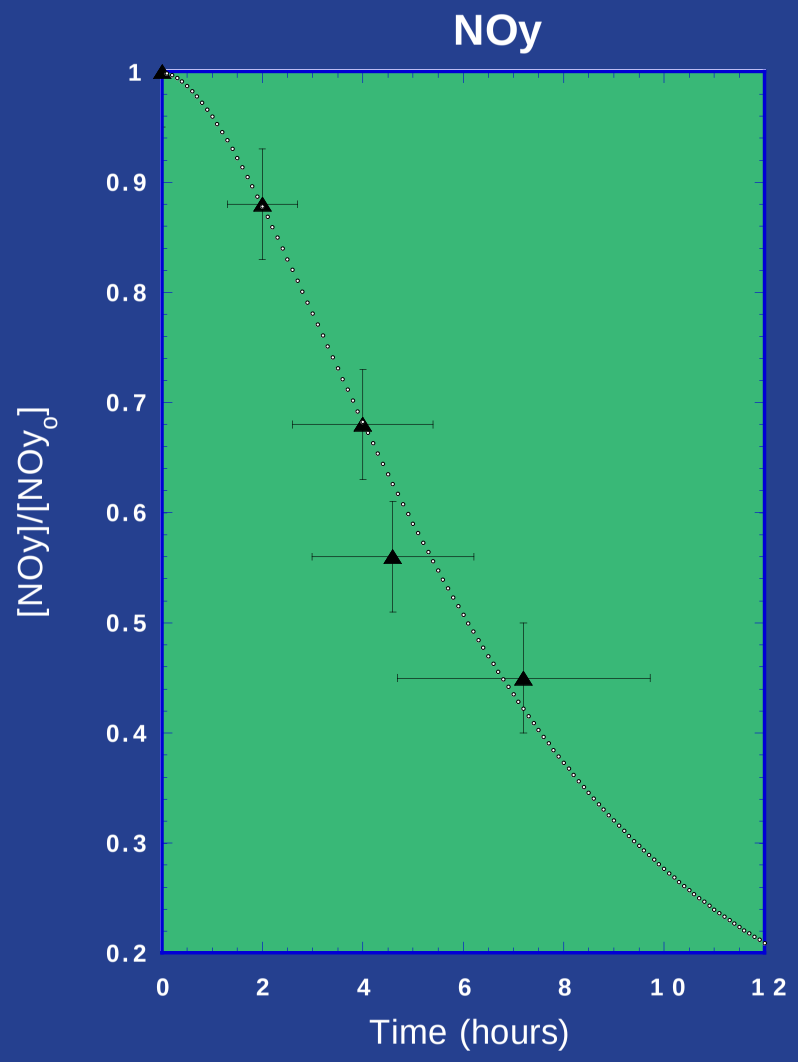
The dominant process for NO_x removal is the reaction:

$$OH + NO_2 \text{ ---> } HNO_3.$$

Since the rate constant for this reaction is known (1.1×10^{-11} cm^3 $molecule^{-1}s^{-1}$), we can use our calculated removal rate of NO_x to determine the average OH concentration. For a NO_x lifetime of 2.1 hr, we estimate an OH concentration of $1.2 +/- 0.4 \times 10^7$ molecules cm^{-3}.

Nashville Urban Plume



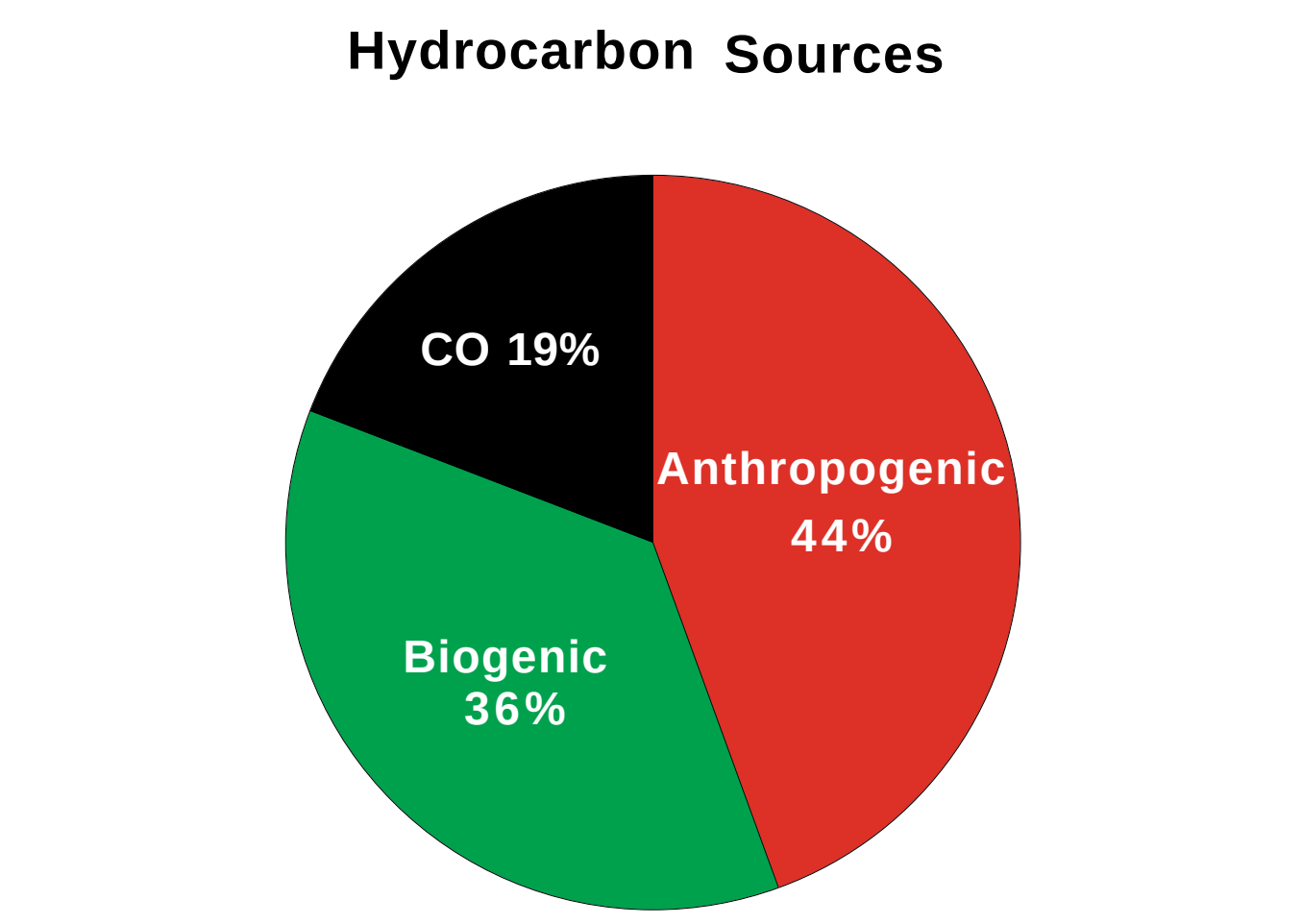


Source Apportionment of Biogenic and Anthropogenic Hydrocarbons Contributing to O_3 Production in the Nashville area.

Formation of tropospheric O_3 requires hydrocarbons as well as NO_x. An important issue is what fraction of the hydrocarbon reactivity comes from anthropogenic sources and is thus amenable to control, and what fraction comes from biogenic emissions. This issue is especially important in the southeastern US because of the presence of extensive tracts of forest which emit highly reactive hydrocarbons such as isoprene and pinenes.

The relative contribution of biogenic vs. anthropogenic hydrocarbons to O_3 production was assessed after establishing that the data could be separated according to the availability of isoprene. Two distinct regimes of low and high isoprene concentrations were identified. The urban plume data was determined to be in the low isoprene regime. Power plant plumes could be found in either regime for subsequent O_3 production. The approximate source apportionment for the urban plume, shown below, was then made on the basis of concentration (as obtained from in-flight grab samples), reactivity with OH, and the number of carbons contributing to O_3 production.

Hydrocarbons and Ozone Production
The Nashville Urban Plume



Biogenic hydrocarbons responsible for about 45% of the background O_3

Effect of VOC or NO_x Emissions Reductions

The Figure below shows the modeled effect of emissions reductions on the ozone concentrations in the Nashville urban plume. The clear bars represent the measured O_3 concentration; the blue bars, the O_3 concentration following a 35% reduction in the anthropogenic component of the hydrocarbons; the green bars, the O_3 concentration follwing a 35% reduction in total hydrocarbons, and; the red bars representing a 35% reduction in the NO_x concentration. From this Figure we may conclude that:

1. A 35% reduction in NO_x emissions has a small effect on O_3 levels.

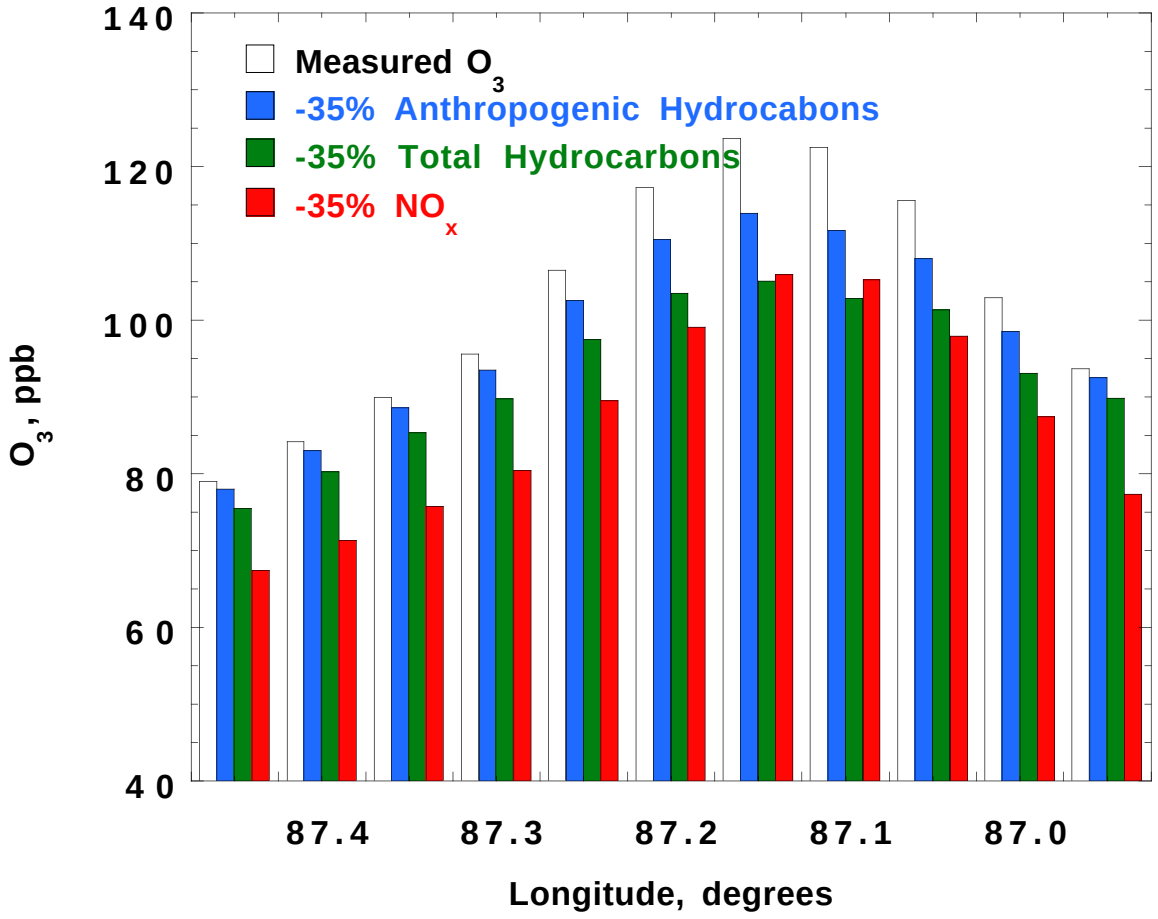
2. A 35% reduction in HC emissions (including cutting down trees) has an even smaller effect.

3. A 35% reduction in anthropogenic HC emissions has a very small effect.

Conclusion: Emission reduction strategies are not easy.

NEED TO DRASTICALLY REDUCE NO_X EMISSIONS

Effect of Emissions Reductions on Nashville O_3 Concentrations



Calculations by S. Sillman, U. Mich.

Acknowledgments

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