
2.1. NATIONAL AND REGIONAL OZONE AIR QUALITY TRENDS, 1982-2001
William F. Hunt, Jr. and Fred Vukovich

How do we determine whether or not air quality is improving in the United States? How do we take millions of hourly ozone measurements and turn them into reliable environmental information (sentences that tell the truth) to help decision-makers in industry and in state, provincial, county, municipal, regional, and federal government organizations focus on air-quality management programs that are both efficient and cost-effective? Each year for the past 30 years, the US Environmental Protection Agency has evaluated the status and trends of the nation’s air quality and published an annual report to the nation (USEPA, 1982-2003). As described in Section 1.2 of this SOS-3 report, SOS scientists also augmented the mainly urban-focused EPA ozone measurements with additional regional background measurements at SON, SCION, and SENIOR network sites in the 10-state SOS region. Both EPA and SOS measurements of ozone concentrations and engineering estimates of emissions trends have been analyzed and compared. Key findings (summarized in bold type) are focused on the 20-year trend between 1982 and 2001 and the 10-year trend between 1992 and 2001.

Progress in determining the effectiveness of air pollution control programs is based on trends in both ambient air quality measurements and emission inventory data. Ozone is not emitted directly into the air. It is formed by photochemical reactions among volatile organic compounds (VOC), nitrogen oxides (NOx), and carbon monoxide (CO) in the atmosphere. VOC are emitted from biogenic and geogenic sources, motor vehicles, chemical plants, refineries, factories, consumer and commercial products, and industrial sources. Nitrogen oxides are produced during lightning strikes, in well-fertilized cropland and pastures, and by motor vehicles, power plants, and other combustion sources. Accumulation of ozone also is affected by the weather – hot summers produce more exceedances of the ozone standard. Both ozone and its chemical precursors can be transported from both local and distant upwind sources.

KEY CITATION:
2.1.1 US National Ambient Air Quality Standards

Exposures to high concentrations of ambient ozone have been linked to human health effects and damage to crops, forests, and engineering materials (USEPA, 1996). Table 2.1.1. shows the National Ambient Air Quality Standards (NAAQS) for ozone – the one-hour standard and the recently promulgated and more stringent 8-hour ozone standard. The one-hour ozone standard requires that the number of days per calendar year with daily maximum hourly concentrations exceeding 0.12 parts per million (ppm) must be less than or equal to one day. The 8-hour standard requires that the 3-year average of the annual fourth highest daily maximum 8-hour average ozone values must be less than or equal to 0.08 ppm.

Table 2.1.1. US National Ambient Air Quality Standards (NAAQS) for Ozone

<table>
<thead>
<tr>
<th>Primary Standard (Public health effects)</th>
<th>Secondary Standard (Welfare effects on crops, forests and materials)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type of Average</strong></td>
<td><strong>Allowable Standard Concentration</strong></td>
</tr>
<tr>
<td>1-hour&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.12 ppm (235 µg/m&lt;sup&gt;3&lt;/sup&gt;)</td>
</tr>
<tr>
<td>8-hour&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.08 ppm (157 µg/m&lt;sup&gt;3&lt;/sup&gt;)</td>
</tr>
</tbody>
</table>

a. Parenthetical value is an approximately equivalent concentration.
b. Not to be exceeded more than once per year on average.
c. 3-year average of annual 4<sup>th</sup> highest concentration.

The health- and welfare-related NAAQS apply in all states and must be achieved in all 50 states. Each state is required to submit a State Implementation Plan, which describes how the state will decrease air pollution in order to keep ambient ozone concentrations below the NAAQS. The USEPA has established a series of programs to help states achieve the NAAQS. These programs include:

1) new source performance standards for all major categories of polluting facilities;
2) emission limit standards for mobile and stationary sources;
3) the prevention of significant deterioration rules, the cornerstone of which is a process known as New Source Review (NSR);
4) control technique guidelines for controlling air pollutants from specific industries; and
5) other regulations in order to decrease pollutant emissions.

How well does the air pollution control program work, given all these control measures?

KEY CITATION:

2.1.2 Available Ozone Monitoring Data

Compliance with the NAAQS for ozone is assessed by direct measurements of ambient pollutant concentrations. Ozone measurements are made at several hundred monitoring sites across the United States. Most emission estimates are based on engineering calculations of the total tonnages of chemical precursors that are released into the air. Emission estimates are derived from many factors, including the amount of industrial activity, technology changes, fuel consumption, vehicle miles traveled, and other activities that affect precursor emissions. In 1994, EPA began its program of continuous emissions monitoring of sulfur dioxide and nitrogen oxides emissions from power plants in the electric utility industry. Additional emissions information can be found at http://www.epa.gov/oar/oaqps/.

Air quality monitoring in the United States is largely conducted by state and local air pollution control agencies. In 1999, there were 705 ozone trend sites meeting the 10-year trend criteria. The trend sites were selected as national trend sites if they have complete data for at least eight of the ten years either between 1982 and 1991 or 1992 and 2001. The annual data completeness criteria for ozone require that at least 50 percent of the hours must be collected during the ozone season. This trend is based upon data from 379 air monitoring sites.

Air monitoring sites are identified as National Air Monitoring Stations (NAMS), State and Local Air Monitoring Stations (SLAMS), Photochemical Assessment Monitoring Stations (PAMS) or other. NAMS were established to assess national policy decisions and trends. SLAMS are used for the same purposes, but are tailored for the State's immediate compliance monitoring needs. The principal purpose of PAMS is to improve monitoring of ozone and its major precursors – NOx and VOC – and thus to help make better national policy decisions. The PAMS objectives are to: evaluate control strategies, corroborate volatile organic compound and nitrogen oxide emission inventories, evaluate photochemical grid models, corroborate ozone attainment decisions, determine ozone concentrations, VOC, and NOx trends, characterize VOC, and help assess risks resulting from selected air toxic pollutants.
2.1.3 National Trends in Ozone Concentrations and Precursor Emissions

- During the past 20 years (1982-2001), US national average ambient one-hour ozone concentrations have decreased about 18 percent and the corresponding 8-hour average ozone concentrations have decreased about 11 percent. See Figures 2.1.1 and 2.1.2 below.

Figure 2.1.1. National trend in the second maximum daily hourly ozone concentration, 1982-2001 (Source: Air Trends. [http://www.epa.gov/airtrends/](http://www.epa.gov/airtrends/)).

Figure 2.1.2. National trend in the fourth highest daily maximum 8-hour average ozone concentration, 1982-2001 (Source: Air Trends. [http://www.epa.gov/airtrends/](http://www.epa.gov/airtrends/)).
During the past 20 years (1982-2001), estimated annual emissions of VOC in the United States as a whole decreased about 16 percent; but estimated annual emissions of NO\textsubscript{x} in the United States as whole increased by about 9 percent. See Figures 2.1.3 and 2.1.4.

**VOC Emissions, 1982–2001**

![VOC Emissions Graph]

**NO\textsubscript{x} Emissions, 1982–2001**

![NO\textsubscript{x} Emissions Graph]

Figure 2.1.3. National trend in VOC emissions, 1982-2001 (Source: Air Trends. [http://www.epa.gov/airtrends/](http://www.epa.gov/airtrends/)).

Figure 2.1.4. National trend in nitrogen oxides emissions, 1982-2001 (Source: Air Trends. [http://www.epa.gov/airtrends/](http://www.epa.gov/airtrends/)).
This significant decrease in emissions of VOC occurred simultaneously with significant increases in economic growth and human population. The gross domestic product of the US increased 161 percent, energy consumption increased 42 percent, and vehicle miles traveled increased 149 percent over the 1982-2001 time period and the U. S. population increased 39 percent.

2.1.4 Differences in National and Regional Trends in Ambient Ozone Concentrations

Figure 2.1.5. shows the 20-year trends in annual second highest daily maximum one-hour ozone concentration, both for the nation as a whole (lower left corner) and also for each of EPA’s 10 major regions across the nation (see map below). As indicated earlier, the decrease in one-hour ozone exposure for the nation as a whole was about 18%. The largest 20-year trend decreases were observed in the northeastern state and the far western states (24-32%) and the smallest decreases were observed in the southeastern states and mid-Atlantic states (7-10%).

Figure 2.1.5. Twenty-year trends in daily one-hour maximum ozone concentrations in the 10 EPA Regions, 1982-2001 (Source: Air Trends. http://www.epa.gov/airtrends/).
As shown in Table 2.1.2, however, a very different series of trends were observed during the last 10 years (1992-2001) than during the previous 10 years (1982-1991) or the whole 20-year period between 1982 and 2001. There has been a notable lack of further progress during the most recent 10-year period – only a 3 percent decrease in the 2nd highest daily maximum one-hour O₃ concentration and “no change” in the 4th highest daily maximum 8-hour average.

This lack of progress over the past ten years stimulated the USEPA to propose its 1997 “NOₓ SIP Call” which requires establishment of a “cap-and-trade program” for large sources of NOₓ emissions in 22 eastern states similar to the existing successful “SO₂ cap-and-trade program.”

Table 2.1.2. Comparison of 20-year trends (1982-2001) and the most recent 10-year trends (1992-2001) in ozone exposures in the nation as a whole and the 10 EPA Regions.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Nation as a whole</td>
<td>18% decrease</td>
<td>3% decrease</td>
<td>No Change</td>
</tr>
<tr>
<td>Region 1 New England</td>
<td>24% decrease</td>
<td>1% decrease</td>
<td>2% decrease</td>
</tr>
<tr>
<td>Region 2 NJ, NY, PR</td>
<td>17% decrease</td>
<td>5% decrease</td>
<td>7% decrease</td>
</tr>
<tr>
<td>Region 3 PA, MD, DE, &amp; VA</td>
<td>10% decrease</td>
<td>10% increase</td>
<td>11% increase</td>
</tr>
<tr>
<td>Region 4 Southeast</td>
<td>7% decrease</td>
<td>2% increase</td>
<td>4% increase</td>
</tr>
<tr>
<td>Region 5 Great Lakes</td>
<td>14% decrease</td>
<td>3% decrease</td>
<td>5% decrease</td>
</tr>
<tr>
<td>Region 6 South Central</td>
<td>16% decrease</td>
<td>5% decrease</td>
<td>1% increase</td>
</tr>
<tr>
<td>Region 7 Midwest</td>
<td>6% decrease</td>
<td>3% increase</td>
<td>1% increase</td>
</tr>
<tr>
<td>Region 8 Rocky Mountain</td>
<td>15% decrease</td>
<td>7% decrease</td>
<td>7% increase</td>
</tr>
<tr>
<td>Region 9 CA, AZ, NV</td>
<td>32% decrease</td>
<td>21% decrease</td>
<td>16% decrease</td>
</tr>
<tr>
<td>Region 10 Northwest</td>
<td>29% decrease</td>
<td>19% increase</td>
<td>25% increase</td>
</tr>
</tbody>
</table>

In fact, for both the one-hour and the 8-hour ozone measurements, ozone exposures have *increased* rather than *decreased* in seven of the ten EPA Regions. Only the far western states (Regions 9 and 10) have shown continuing *decreases* in both one-hour and 8-hour ozone exposures. The South Central Region (Region 6), which includes Texas, was mixed with a 5 percent *decrease* in the one-hour statistic and a one percent *increase* in the 8-hour statistic. The
largest *increases* in ozone exposures (11 percent) occurred in the Mid-Atlantic States (Region 3) for the 4th highest daily maximum 8-hour measurements.

It is not unexpected that the percent increase or decrease in the 2nd highest daily maximum one hour statistic for the nation as a whole or EPA region would be greater than the percent increase or decrease for 4th highest daily maximum 8-hour average. This is true because the ozone concentration for the daily maximum one-hour standard is further away from the natural background concentration than the 8-hour standard.

2.1.5 **Comparative Climatology of Ozone and Ozone Precursors Within SOS and Other Regions**

Regional and subregional variability in diurnal maximum ozone concentrations (DMOC) in both urban and non-urban locales within the SOS region and in other parts of the eastern United States were studied and compared with weather and climate factors. These investigations support the following conclusions.

• Ozone accumulation in the mid-Atlantic (EPA Region 3) and southeastern states (EPA Region 4) is largely decoupled from that in the northeastern US with higher average concentration in most southern states than in most northeastern states (EPA Regions 1, 2, and 3). These differences among regions are due in part to the higher frequency of weather-front passages in northeastern states, and the greater frequency of air-stagnation events in the southeastern states.

• On a climatological scale, interannual variations in either temperature or cloud cover explained about 80% of the variability in DMOC.

• In examining short time episodes, the most persistent relationship between surface ozone and weather parameters was between ozone concentrations and surface wind speed – with stagnation periods leading to the highest DMOC. When a 15-year time series of ozone concentrations was examined with a 15-year time series of meteorological patterns, however, the most persistent relationship was between ozone and cloud cover. When days with ozone concentrations equal to or greater than 100 ppb, were extracted from the 15-year time series and examined separately, only wind speed and cloud cover were important. Neither temperature nor dew point was important on these high ozone days.

• Regional emissions control strategies may decrease the frequency of ozone exceedance events, but episodic control strategies probably will be necessary to eliminate exceedance events completely.

• Substantial month-to-month variability in DMOC is observed within the SOS region, suggesting that different states may need to apply more stringent episodic controls in different months of the year.

• A recent experiment using an ozone-screening model to predict DMOC in Baltimore, MD over a 15-year time period indicated that applying NOx emissions control strategies alone
may increase rather than decrease the number of high ozone episodes. These results suggest that there may be danger in applying NO\textsubscript{x} emissions control strategies without looking into the overall effects of these strategies. They also suggest that basing NO\textsubscript{x} control strategies on a few episodes may be a necessary condition, but may not be a sufficient condition for decisions aimed at controlling the formation of ozone and decreasing the number of high ozone episodes. In fact, decreasing emissions of VOC may be a more effective way to control ozone formation and to decrease the number of high ozone days. These suggestions from observations in Baltimore may be applicable to other urban areas in the eastern United States.

- In Baltimore, MD, weekdays in 1994-97 had about 39% more NO\textsubscript{x}, 59% more CO, and 27% more VOC than weekend days, but about 13% more ozone on weekends. Decreases in NO\textsubscript{x} emissions less than about 39% apparently will induce an ozone disbenefit in the urban core of Baltimore, but decreases in NO\textsubscript{x} emissions sufficient to avoid exceedance events in the urban core also will significantly decrease ozone exposures in nearby suburban areas.

- Also, in Baltimore, OH reactivity with isoprene was the largest (38-40%) of the total OH reactivity with the PAMS' VOC and was the same on weekend days and on weekdays. OH reactivity with trimethylbenzene and toluene was 7% larger on weekdays than on weekends and thus responsible for an important part of the weekend/weekday difference. Carry-over of partially oxidized VOC either from upwind (e.g., Washington DC) sources or from previous-day oxidation (i.e., in stagnation conditions) may lead to enhanced ozone production in Baltimore.

KEY PUBLICATIONS:


2.1.6 Twenty-Year Trends in Two Selected Urban Areas

Ambient ozone trends are influenced by year-to-year variability in meteorological conditions, population growth, and changes in the amounts and ratios VOC to NOx. To better reflect the influence of changes in precursor emissions, Cox and Chu (1993) developed a mathematical method by which influence of the most important meteorological factors (temperature and wind speed) can be removed (filtered out) of the data. Figure 2.1.5 shows the results of such analyses for two selected urban areas of special interest to SOS scientists – Raleigh, NC and Phoenix, AZ. While the unadjusted ambient ozone monitoring data reflect the year-to-year variability in all ozone-conducive conditions, the meteorologically adjusted trends provide a better indication of the impact of changes in emissions of ozone precursors alone.

![Raleigh 8-hour Ozone Trends](image1)

![Phoenix 8-hour Ozone Trends](image2)

Figure 2.1.6. Twenty-year trends in meteorologically adjusted and non-adjusted 8-hour ozone exposures in Raleigh, NC and Phoenix, AZ. (William Cox, Personal Communication, March 2003).

2.1.7 Twenty Year Trends in Ozone Exposures in National Parks

During the past 10 years (1992-2001), 8-hour ozone concentrations in 25 of our national parks increased nearly 8 percent. EPA reports (Air Trends. [http://www.epa.gov/airtrends/](http://www.epa.gov/airtrends/)) that nine monitoring sites in eight of these parks experienced statistically significant upward trends in 8-hour ozone exposures. The eight parks include Great Smoky Mountains (NC and TN), Big Bend (TX), Cape Romain (SC), Cowpens (SC), Denali (AK), Everglades (FL), Mammoth Cave (KY), and Voyagers (MN). Most of these parks are located in the Southeastern States, which experienced a 4 percent increase in the 4th highest daily maximum 8-hour average over the 1992-2001 time period. For the remaining 17 parks, the 8-hour ozone concentrations at eight sites increased only slightly between 1992 and 2001, while seven sites showed decreasing concentrations and two were unchanged.
2.2. OZONE PRECURSOR EMISSIONS STUDIES
Carlos Cardelino and David Allen

Substantial uncertainties in emissions estimates and emissions inventories of ozone precursors contribute to shortcomings in the prediction and diagnosis of ozone concentrations by emission-based air quality models. SOS has taken several approaches to overcome weaknesses in emission estimates. One approach is to try to reconcile ambient measurements with emission estimates. Another approach is the development of day-specific inventories instead of the commonly used but imprecise typical summer day inventories. In addition to these improvements, SOS also has conducted research on ammonia emissions and on non-traditional sources of NOx; these results will be integrated into air quality models to study ozone and particulate matter. The results of these studies are summarized in this section.
2.2.1 Contribution of distant forest fires to regional oxidant concentrations

Measurements taken during aircraft flights during the SOS 1995 Nashville/Middle Tennessee Ozone Study and subsequent back-trajectory modeling results indicate an important influence from forest fires in Canada on CO and ozone concentrations in the central and eastern US. Episodes of elevated levels of CO were detected at several monitoring sites across the study region during SOS95. Model simulations of CO transport indicated the source region to be areas of large forest fires in Northwest Territory of Canada.

Use of wildfire emission rates of CO, NOx, and non-methane hydrocarbons in a three-dimensional photochemical transport model improved comparison of modeled estimates of ozone with ambient measurements from rural ozone monitors during the summer of 1995. Forest fires influenced the build-up of ozone episodes in the southeastern US by increasing the background CO concentrations in air after passages of cold fronts that normally would cleanse the atmosphere. Fires in Canada during the SOS’ Nashville ‘95 study induced an increase of 10 – 30 ppbv in ambient concentration of ozone near Nashville, TN during the period of strongest fire influence.

Key findings from this research are summarized below.

- Emissions from distant forest fires can contribute to regional concentrations of carbon monoxide and to regional concentrations of ozone concentrations.

KEY CITATIONS:
2.2.2 Biogenic Emissions in Nashville and Houston

CO and isoprene dominate OH reactivity in the non-urban boundary layer of the Nashville Study area. Isoprene plays a prominent role in photochemical ozone formation in predominantly forested areas of the southern part of the study area. The influence of CO is reasonably constant over the area but is more significant relative to isoprene in the northern areas. Methane also acts as an oxidizable ozone precursor in areas of low isoprene. Isoprene and its oxidation products, methacrolein and methylvinyl ketone, were measured at an urban forested site in Nashville during the 1999 SOS field study. Emissions inventories indicate that isoprene was predominantly from biogenic sources. Isoprene concentrations and concentrations of oxidation products can be explained with a 1-D photochemical model. Isoprene’s contribution to the instantaneous ozone production rate at this urban location was significant.

A new land-use database created for the state of Texas was used with an improved biogenic emissions model, GLOBEIS2, to produce more accurate biogenic emission inventories, both in magnitude and spatial resolution, compared to previous inventories. Observational data collected during the TexAQS 2000 study indicate that biogenic sources of VOC are located mainly north of the Houston metropolitan area, and were not the dominant contributor to urban ozone formation, although biogenic emissions may be important at some locations. The major differences in biogenic emissions between Houston and both Atlanta and Nashville may be explained in part by the greater abundance of isoprene-emitting trees (mainly oak forests) in the land cover of the suburban and rural areas surrounding Atlanta and Nashville than in similar rural areas near Houston. Summary statement for this work:

- Biogenic emissions of isoprene are more important to urban ozone production in Nashville, TN and Atlanta, GA than in Houston, TX.

KEY CITATIONS:
2.2.3 Daily Variability of Motor Vehicle Emissions

In many urban areas, motor vehicle emissions account for a significant portion of the overall emissions inventory of ozone precursors. Mobile source emissions can be characterized by analyzing traffic data measured using traffic counters. A method to study the daily variability of mobile emissions from the different types of urban and rural roads was developed by SOS. The method is based on hourly traffic volume data and emission factors. This method has been used to describe daily variability of mobile emissions in the metropolitan areas in and around Atlanta, GA and Nashville, TN. Key results of the method applied to the Atlanta metropolitan area are summarized below.

- Interstate roads, with only 2% of the total mileage, contain 30% of the total traffic volume. Local roads with 74% of the total mileage contribute only 19% of the total traffic.

- The temporal distribution of mobile emissions is strongly dependent on the region (urban or rural), the type of road (interstate, principal, secondary or local) and the day of the week (see Figure 2.2.2).

- The vehicle classification distribution by road type obtained from traffic counters is significantly different from the default distribution contained within the Mobile5a computer model. When applied to a specific-day inventory, the use of observed data, as opposed to default data, produces changes in emissions that vary by 8% (VOC), 9% (CO) and 19% (NOx).

- Compared to a typical summer day, the day-to-day range of mobile emission variability was 26 to 28% for urban areas and 19 to 13% for rural areas.

KEY CITATION:
2.2.4 Motor Vehicle Emissions in Three Urban Areas

- Observations of CO, VOC, and NOx emissions from motor vehicles – including passenger cars, light-duty trucks, and both diesel-powered and gasoline-powered heavy duty trucks – were essentially identical with similar observations in other urban areas in the southern US such as Nashville, TN and Atlanta, GA.

This finding is based primarily on measurements of CO, VOC, and NOx emissions integrated over thousands of individual vehicles of each type in the Washburn Tunnel in Houston, TX during the TexAQS 2000 Study and similar measurements during intensive field measurement campaigns in Atlanta, GA in 1992 and 1995 and Nashville, TN in 1995, and 1999.

KEY CITATIONS:


2.2.5 Use of Survey Data to Determine Ozone Sensitivity to Point Sources

Photochemical modeling studies depend on the correct location and amount of emissions from point sources. SOS researchers used survey data that include daily activity logs for the largest point sources in the Atlanta region to estimate VOC and NO\textsubscript{x} point source day-specific emissions. The emissions were based on actual operating schedules rather than the more crudely estimated “typical summer day emissions.” The major findings of this study are:

- The daily variability in point-source NO\textsubscript{x} emissions was found to be as much as 24% with respect to typical summer day emissions.
- Although the daily variability of point-source VOC emissions was as large as 28%, their contribution to total VOC emissions was not very significant.
- Numerical simulations suggest that changes in point-source NO\textsubscript{x} emissions can have either a positive or a negative effect on ambient ozone concentrations, depending on the geographical location of the NO\textsubscript{x} sources (rural vs urban areas).

Table 2.2.1. Summary of numerical simulations evaluating the impact of two power plants: Bowen and McDonough (after Chang et al., 1996).

<table>
<thead>
<tr>
<th>Description</th>
<th>Ozone Maxima</th>
<th>Number of cells</th>
<th>Number of cell-hours</th>
<th>Population</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical case</td>
<td>129</td>
<td>50</td>
<td>69</td>
<td>183,630</td>
</tr>
<tr>
<td>August 10 case</td>
<td>129</td>
<td>48</td>
<td>65</td>
<td>152,940</td>
</tr>
<tr>
<td>August 10 w/o McDonough</td>
<td>134</td>
<td>60</td>
<td>83</td>
<td>327,213</td>
</tr>
<tr>
<td>August 10 w/o Bowen</td>
<td>129</td>
<td>34</td>
<td>45</td>
<td>90,102</td>
</tr>
<tr>
<td>August 10 w/o Bowen &amp; McDonough</td>
<td>133</td>
<td>44</td>
<td>56</td>
<td>263,390</td>
</tr>
</tbody>
</table>

NOTE: “Number of cell-hours” is the number of cells that exceed ozone standard each hour summed throughout the day and “Population” is the total human population within cells experiencing ozone exceedances.

KEY CITATION:
2.2.6 Ambient Concentrations of VOC Compared to Emission Inventories

Aircraft-based and ground-level measurements of VOC during TexAQS 2000 revealed large discrepancies between direct measurements of air concentrations and emissions inventories of various VOC. Ambient measurements of the ratio of total VOC to NO\textsubscript{x}\textsuperscript{a} in industrial plumes, especially those near the Houston Ship Channel, were consistently factors of 2-15, and in some isolated instances even a factor of 50 or more higher, than the ratios reported in emission inventories. The most notable discrepancies between measured air concentrations and emissions inventories were for five low molecular weight alkenes – ethene, propene, butenes, pentenes and butadiene – but often also included low molecular weight alkanes and aromatic compounds.

Underestimates of fugitive VOC emissions, VOC emissions from flares, and VOC emissions from cooling towers are believed to be the most likely causes of differences between the observed VOC/NO\textsubscript{x}\textsuperscript{a} ratios and those for emissions inventories. Major finding of this research is summarized below.

- Measurements of ambient concentrations of VOC in the industrial areas of Houston, TX show large discrepancies compared to emissions inventories. Inventoried emissions are lower than measured concentrations.

KEY CITATION:
2.2.7 Spatial and Temporal Variability of VOC and NO\textsubscript{x} Emissions in Houston

Observations made by aircraft during 2001 indicate that plumes from petrochemical facilities are spatially heterogeneous – with NO\textsubscript{x}-rich regions, VOC-rich regions, and regions rich in both VOC and NO\textsubscript{x}. In addition, data on VOC/NO\textsubscript{x} ratios, taken over multiple years at ground monitoring stations in areas dominated by industrial sources, show substantial temporal variability. Because of this spatial and temporal heterogeneity, isolated measurements of VOC/NO\textsubscript{x} ratios must be interpreted with caution. Nevertheless, the ensemble of measurements made during TexAQS 2000 indicate that average VOC/NO\textsubscript{x} ratios observed in Houston industrial plumes are higher than the ratios documented in current emissions inventories.

Reliable data on the chemical species composition of VOC emissions are available at only a few locations in Houston; at these few locations, however, the annual average composition of VOC has remained relatively constant for a decade or more. While the annual average VOC composition may be reasonably well established, daily variability in VOC chemical species composition is remarkably large downwind of petrochemical facilities.

Ground observations in Houston, taken over a period of several years, and other data, suggest that VOC emissions show significant temporal variability. The implication of this finding is that VOC/NO\textsubscript{x} ratios will be variable, and thus individual plumes may have very different ozone formation potentials at different times. The extent to which this observed variability is caused by changes in emissions and/or changes in meteorological conditions such as wind direction, vertical mixing and atmospheric stability, has not been determined. Key finding is summarized below.

- VOC and NO\textsubscript{x} emissions in industrial areas of Houston, TX show substantial spatial and temporal variability.

**KEY CITATION:**
2.2.8 Variability of CO Emissions at Power Plants

Airborne plume data from power plants observed during the SOS Nashville ’95 and ’99 studies and the TexAQS 2000 Study suggest that data for NO\textsubscript{x}, SO\textsubscript{2}, and CO\textsubscript{2} collected by Continuous Emissions Monitoring Systems at major power plants are accurate to ± 10% on average. But fossil-fueled power plants also can be large point sources of CO. Aircraft measurements during TexAQS 2000 showed that CO emissions from several power plants near Houston powered by gas, coal, and lignite were 22 to 34 times higher than reported in emissions inventories. Furthermore, these significantly larger CO emissions were very variable temporally. Key finding from this research is shown below.

- NO\textsubscript{x}, SO\textsubscript{2}, and CO\textsubscript{2} emissions from fossil-fueled power plants are accurately estimated, but CO emissions show significant variability at some plants.

KEY CITATION:
2.2.9 Rapid Formation of Ozone in Houston

Back trajectory analysis of air parcels with very high ozone concentrations (150-250 ppb) during TexAQS 2000 showed substantial contributions of emissions from industrial source regions. The chemical composition of these air parcels was representative of industrial sources rather than typical urban sources.

Ground observations of VOC concentrations, taken over a period of several years, and aircraft data collected during the TexAQS 2000 Study, describe numerous episodes with very high VOC concentrations. The VOC chemical species observed at high concentrations varied greatly from episode to episode. But almost invariably, they originated from industrial rather than typical urban sources. The co-location of industrial sources of NO\textsubscript{x} and VOC emissions, in significantly larger amounts than previously known from emissions inventories, is the primary cause of rapid and efficient production of ozone downwind in the Houston metropolitan area. The principal gap in knowledge essential for effective management of ozone in Houston, TX is the substantial underestimate of reactive VOC from petrochemical sources in the existing emissions inventories.

- The uniquely rapid formation and accumulation of ozone in Houston, TX is caused primarily by photochemical processing of industrial emissions.

KEY CITATIONS:
2.2.10. Inverse Modeling of Emissions

Inverse modeling is a useful tool for reconciling emission inventories with direct measurements of air concentrations of precursor chemicals. Inverse methods minimize the difference between observed concentrations and concentrations obtained from air quality models. SOS applications of inverse methods include the temporal and spatial distribution of isoprene and CO emissions in the Atlanta area. Key findings of this investigation are outlined below.

- Isoprene emissions derived from inverse modeling were 2 to 10 times higher than any of the accepted emission estimates.
- Higher isoprene emissions significantly increase the concentration of ozone within the plumes of nitrogen oxides emitted from large point sources.
- Uncertainties in mixing height are not likely to be responsible for the underprediction of isoprene in air quality models.
- Inhomogeneities in the spatial distribution of emissions can severely limit the application of the inverse method.

![Figure 2.2.3](image)

Figure 2.2.3. Observed (solid circle) and model-simulated isoprene concentrations at an Atlanta monitoring station. Simulations are with (A) BEIS and (B) BEIS2 inventories: base case (open circles), and two inverse applications (square and triangles) (from Chang et al., 1996).

**KEY CITATIONS:**
2.2.11. Comparison of Trace Gas Concentrations and Emission Estimates

Assessing the accuracy of an emission inventory is a difficult but important step in establishing the overall accuracy of models that are used to determine ozone management strategies. A comparison between emission ratios and ambient concentrations in a source region is one of the few ways of making such an assessment. During the 1995 SOS Nashville Intensive, continuous measurements of CO, NO<sub>y</sub>, and SO<sub>2</sub> and twice-a-day samples of hydrocarbons were made at a Nashville downtown location. Ratios of morning concentrations of CO, NO<sub>y</sub> and VOC were compared with the corresponding ratios derived from emission estimates for the Nashville area. Key findings of this study are summarized below:

- Correlations between SO<sub>2</sub>, CO, and NO<sub>y</sub> indicated only a minor impact from power plant emissions. Plume-like excursions of high SO<sub>2</sub> occur less than 5% of the time.
- The observed morning ratios of VOC/CO, VOC/NO<sub>x</sub> and CO/NO<sub>x</sub> were 0.32 ppbC/ppb, 2.9 ppbC/ppb and 2.9 ppb/ppb, respectively.
- The 1990 NAPAP emission estimates can be brought into agreement with the observed values if the VOC emission rate is decreased by 30% while the 1995 SOS inventory will agree if the CO emission rate is increased by about 35%.
- In contrast to comparisons in other locations, no evidence of large (i.e., factor of 2 or greater) underpredictions of CO or VOC was found.

Table 2.2.2. Comparison of observed concentrations with corresponding quantities from emission estimates (after Kleinman et al., 1995).

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Observations</th>
<th>1990 NAPAP emissions</th>
<th>1995 SOS emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOC/CO</td>
<td>0.32 ppbC/ppb</td>
<td>0.46</td>
<td>0.42</td>
</tr>
<tr>
<td>VOC/NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>2.9 ppbC/ppb</td>
<td>4.1</td>
<td>2.9</td>
</tr>
<tr>
<td>CO/NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>9.3 ppb/ppb</td>
<td>9.1</td>
<td>6.9</td>
</tr>
</tbody>
</table>

KEY CITATION:
2.2.12 NO\textsubscript{x} Emission from Soils

Soil biogenic NO\textsubscript{x} emissions are an important part of the total global NO\textsubscript{x} budget. SOS recognized that non-traditional sources of NO\textsubscript{x} should be included as part of the oxides of nitrogen budget and therefore, SOS sponsored a series of projects to characterize the magnitude and the parameters that control biogenic emissions from soils. Key findings from this study are summarized below.

- A model of soil NO emissions was developed based on soil temperatures. This model explains over 80% of the variation in emissions (see Figure 2.2.4).
- The summertime contribution of soil NO to the overall NO\textsubscript{x} inventory averages 4.1% for the southeastern US with a high of 9.5 for Mississippi and a low of 2.2% for Florida.
- Urban-metropolitan soils are not an important source of soil NO\textsubscript{x}.
- For the Middle Tennessee non-attainment area, soil biogenic NO\textsubscript{x} contributes from 7 to 9.8% of the daily average NO\textsubscript{x} budget during the months of June through August. However, during the hottest July days the soil biogenic component can contribute over 17% of the total NO\textsubscript{x}.

KEY CITATIONS:


2.2.13 Natural Emissions of Non-methane VOC, CO, and NOx

Natural emissions are responsible for a major portion of the chemical species that determine tropospheric oxidant concentrations. These compounds include non-methane volatile organic compounds (NMVOC), carbon monoxide (CO) and nitric oxide (NO). Natural sources include soil microbes, vegetation, biomass burning and lightning. A review of current estimates of natural emissions is summarized below (see Table 2.3):

- Over 98% of the total annual NMVOC emissions are from vegetation, primarily foliage, and isoprene is the dominant compound with 35% of the total emissions.
- Natural emissions of alkane and aromatic compounds are very low and are greatly overestimated by earlier inventories.
- Sources of NMVOC emission from vegetation include chloroplasts, defense from specialized tissues, defense from unspecialized tissues, growth hormones, floral scents, cut and drying vegetation, and other. The total North America NMVOC flux is dominated by emissions from chloroplasts.
- Soil and lightning each contribute about half of the annual natural NO flux. Biomass burning and vegetation are each responsible for about half of the natural CO emissions.

Table 2.2.3. Annual above canopy fluxes of NO (Tg-N), NMVOC (Tg-C) and CO (Tg-N) from natural sources in North America (after Guenther et al., 2000).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vegetation</th>
<th>Soil</th>
<th>Lightning</th>
<th>Biomass Burning</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>0</td>
<td>0.9</td>
<td>0.9</td>
<td>0.3</td>
<td>2.1</td>
</tr>
<tr>
<td>CO</td>
<td>4</td>
<td>0.0</td>
<td>0</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>NMVOC</td>
<td>82.2</td>
<td>1.1</td>
<td>0</td>
<td>0.6</td>
<td>83.9</td>
</tr>
</tbody>
</table>

KEY CITATION:
2.2.14 Natural VOC Fluxes from Enclosure and Ambient Measurements

A major objective of SOS and SOS-affiliated field research has been the measurement of ambient concentrations of the various hydrocarbon species that play a significant role in the production and accumulation of photochemical oxidants in both urban and rural environments. Over 90% of the total VOC entering the atmosphere of the earth is of biogenic origin. In one project natural VOC were measured on tethered balloon platforms between 1985 and 1996; in another project biogenic VOC emissions were investigated at two forested sites in the southeastern US. Major conclusions are given below.

- Ambient measurements of isoprene and monoterpene emissions are within a factor of 2 of modeled estimates (see Figure 2.2.5).
- Concentrations of biogenic VOC decrease slowly with altitude in the mixed layer while surface layer concentrations show much more variability.
- Isoprene concentrations in the mixed layer remained fairly constant in the middle of the day, in contrast to isoprene concentrations at canopy-level, which continued to increase until evening.
- Daytime emissions, which increase with temperature and solar radiation, are balanced by changes in entrainment and oxidation.

**KEY CITATIONS:**


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![Figure 2.2.5. Typical observed diurnal isoprene and monoterpene emission (µg C g⁻¹ h⁻¹) patterns from (a) post oak, (b) loblolly pine, and (c) sweetgum trees. Leaf temperature T (degrees celsius) and photosynthetically active radiation (PAR) (10 µmol m⁻² h⁻¹) are shown for reference (from Guenther et al., 1996).](image)
2.2.15 Influence of Isoprene Emissions in Regional Ozone Modeling

The role of biogenic hydrocarbons in ozone formation has been the subject of considerable debate since the 1970s. In order to provide better emission inventory inputs into photochemical air quality models, an improved emission algorithm (BEIS2) for calculating biogenic emission rates was developed. The key features of this new and improved emission algorithm include:

• BEIS2 uses more temporally resolved environmental corrections (hourly versus monthly), more spatially resolved vegetative cover (county level versus 1° latitude/longitude grid cells), and more resolved vegetative emission factors (genus versus broad biome classes).
• Higher isoprene emissions are obtained with BEIS2, which are about a factor of 5 higher than BEIS1 during warm, sunny conditions.
• When BEIS2 is used with the RADM model, elevated concentrations of ozone went from being VOC-sensitive to NOx-sensitive across much of the RADM modeling domain.
• The new system yields better agreement with observations. Using BEIS2 in RADM resulted in mean near-surface isoprene predictions that were slightly lower (25%) than observed.

![Figure 2.2.5. Mean diurnal plot of isoprene concentrations observed and modeled near the surface of Scotia, Pennsylvania during July and August 1988. Data points represent the bin of 10 values (from Pierce et al., 1998).](image)

KEY CITATIONS:
2.2.16 Sources and Importance of Ammonia Emissions

Ammonia is the most abundant alkaline component in the atmosphere and a precursor of fine particulate matter when it is converted into ammonium nitrate and ammonium sulfate. Dry and wet deposition of gases as ammonia and ammonium ion contribute significantly to the acidification and eutrophication of terrestrial and aquatic ecosystems. As a result, research on ammonia emissions has become an emerging issue in the US. SOS undertook studies to characterize the location and strength of the ammonia sources at the state and county level. During the 1999 Nashville field study, ammonia emission maps were used to plan the trajectories of aircraft with instrumentation to measure ammonia concentrations in the atmosphere. Key findings of the SOS study on ammonia emissions are summarized below.

- The estimated ammonia emissions for the US are about 5 billion kg per year. The major sources include animal waste that account for about 75% of total emissions and fertilizer applications with 9%.
- Minor sources include industries (about 6%), motor vehicles (about 5%), sewage treatments (about 2%), and human populations (about 1%).
- During the last ten years, ammonia emissions have been increasing at a rate of about 1% per year.

Table 2.2.4. 1997 US Ammonia emissions (kg NH₃ yr⁻¹) and emission density (kg NH₃ mi⁻² yr⁻¹) (after Cardelino, 2000).

<table>
<thead>
<tr>
<th>Source category 1997-1987</th>
<th>Ammonia Emissions</th>
<th>Emissions density</th>
<th>Percent of Emissions</th>
<th>Percent trend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Animal waste</td>
<td>3,776,327,843</td>
<td>1,067.9</td>
<td>76.8</td>
<td>5.9</td>
</tr>
<tr>
<td>Fertilizer application</td>
<td>441,448,466</td>
<td>124.8</td>
<td>9.0</td>
<td>10.6</td>
</tr>
<tr>
<td>Human population</td>
<td>66,909,015</td>
<td>18.9</td>
<td>1.4</td>
<td>10.5</td>
</tr>
<tr>
<td>Motor vehicles</td>
<td>253,972,965</td>
<td>71.8</td>
<td>5.2</td>
<td>32.6</td>
</tr>
<tr>
<td>Industries</td>
<td>289,087,983</td>
<td>81.7</td>
<td>5.9</td>
<td>9.1</td>
</tr>
<tr>
<td>POTW</td>
<td>89,595,818</td>
<td>25.3</td>
<td>1.8</td>
<td>40.6</td>
</tr>
<tr>
<td>TOTAL</td>
<td>4,917,342,090</td>
<td>1,390.5</td>
<td></td>
<td>8.2</td>
</tr>
</tbody>
</table>

KEY CITATION:
2.3. OZONE FORMATION IN POWER PLANT PLUMES
James Meagher and Fred Fehsenfeld

Early efforts to decrease NO\textsubscript{x} emissions focused on motor vehicles and have resulted in dramatic improvements in automobile NO\textsubscript{x} emission rates. More recently, the EPA, in an effort to further decrease NO\textsubscript{x} emissions, has turned its attention to the electric utility sector. Fossil-fuel combustion for electricity generation contributes approximately 24% of U.S. manmade NO\textsubscript{x} emissions. In a series of regulatory actions intended to address both ground-level ozone and acid deposition, the EPA is requiring the electric utility industry to decrease power plant NO\textsubscript{x} emissions by approximately 3 million tons per year by 2003. This decrease constitutes almost 50% of 1997 electric utility NO\textsubscript{x} emissions, with the bulk of the decreases slated for eastern U.S. coal-fired power plants that have the greatest annual NO\textsubscript{x} emissions (see Figure 2.3.1).

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2.3. Ozone Formation in Power Plant Plumes

- What is the distribution of NO\textsubscript{x} emissions from fossil-fueled power plants?
- How is ozone made in power plant plumes?
- Do all power plants produce ozone with equal efficiency?
2.3.1 What is the distribution of NO\textsubscript{x} emissions from fossil-fueled power plants?

Thousands of fossil-fueled units located throughout the country contribute to electric utility NO\textsubscript{x} emissions. However, the emissions are not uniformly distributed, with a relatively small number of power plants producing a large fraction of the total. In 1997, the last year for which data are available, the fifty power plants with the largest NO\textsubscript{x} emissions account for approximately 36\% of the emissions, with the top 28 accounting for more than 25\%. The location of the fifty largest NO\textsubscript{x} sources is shown in Figure 2.3.1. For the most part, the largest NO\textsubscript{x} sources are located in rural areas in the eastern U.S., many in areas with the highest natural VOC emissions. This superposition provides a fertile environment for ozone formation. SOS has conducted several field studies in this region to better understand ozone formation and distribution in the NO\textsubscript{x} plumes from these power plants.

- Most of the largest utility sources of NO\textsubscript{x} are found in rural areas, which have high emissions of natural VOC.

Figure 2.3.1. The 50 largest NO\textsubscript{x} point sources in the U.S. (all are fossil-fueled power plants) for 1996 (after EPA, 1997). The annual emissions shown here can be compared to those for the Nashville urban area (Davidson county, population 1M), which are approximately 30,000 tons per year.

KEY CITATION:
2.3.2 How is ozone formed in power plant plumes?

Only one of the two major precursors required to make ozone (NO\textsubscript{x}) is emitted from power plants. In the presence of sunshine when the rapidly expanding NO\textsubscript{x} plume mixes with VOC present in the surrounding air, ozone is formed. The VOC that participate in the ozone formation can be either natural or man-made depending upon the location of the power plant. In the early stages of plume dilution, the NO\textsubscript{x} concentrations are extremely high. They are so high, in fact, that ozone already present in the atmosphere is actually consumed in the plume, and ozone concentrations in the plume are smaller than in the surrounding atmosphere (Figure 2.3.2). As the plume grows, eventually filling the mixed layer (Figure 2.3.3), NO\textsubscript{x} concentrations become smaller and ozone is produced. Ozone production continues until all the reactive NO\textsubscript{x} is consumed or the sun goes down.

Figure 2.3.2. Crosswind profiles of pollution in a power plant plume. Pollutant concentrations were measured on a NOAA research aircraft as it penetrated the power plant plume at three distances downwind.
2.3.3 Do all power plants produce ozone with equal efficiency?

The chemical processes that form ozone in the atmosphere are nonlinear, which means that any change in emissions will not be accompanied by a proportional change in amount of ozone formed. We must understand the nature of this nonlinear relationship if we are to know how much decrease in NO\textsubscript{x} emissions will be required to produce a desired decrease in ambient ozone concentrations or, alternatively, what will be the effect of introducing additional sources of NO\textsubscript{x}. SOS research has focused therefore on ways to estimate the efficiency with which ozone is being formed in power plants with different NO\textsubscript{x} emission rates. In this work we have calculated the Ozone Production Efficiency or OPE for a number of power plants on different days. The OPE is defined as the number of molecules of ozone formed per molecule of NO\textsubscript{x} emitted, which provides a direct comparison of two different sources in terms of their potential to form ozone.

Figure 2.3.3. Schematic of ozone formation in power plant plumes. A temperature inversion limits the transport of pollution out of the “mixed layer”.

The effect of NO\textsubscript{x} emission rate on ozone formation was determined using data collected in the plumes of several different coal-fired power plants located in close proximity to each other in the Southeast during the summer of 1995 (see Figure 2.3.3 for an illustration of the processes involved in ozone formation in power plant plumes). These plants had very different (more than a factor of 10) NO\textsubscript{x} emission rates and were located in a region of abundant forests with significant biogenic VOC (isoprene) emissions. Instrumented aircraft were used to study ozone production in the plumes of several different power plants on the same day (Ryerson et al., 1998) and different plants on different days (Gillani et al., 1998; Nunnermacker et al., 2000). The measured ozone production efficiencies ranged from 0.8 to 7.0. In each case, the plants with the
greatest NO\textsubscript{x} emission rates exhibited the lowest ozone production efficiencies. Model simulations of plume experiments produced somewhat higher OPEs (but lower than previous estimates) than were measured (Sillman, 2000).

The ozone production efficiency measured in these plumes varies from day to day due to changes in meteorological factors, (e.g., the temperature, the amount of sunlight, and the wind speed) that affect the abundance of isoprene in the atmosphere (Luria et al., 2000) and the rate of plume dilution. Therefore, a direct quantitative comparison between individual measurements is not possible. However, it is evident that the power plants with greater NO\textsubscript{x} emission rates produced ozone less efficiently in these studies, a direct manifestation of the nonlinear processes discussed above. Also, the data clearly demonstrate that, for large sources, the benefits of decreasing emissions of NO\textsubscript{x} are partially offset by an increase in the efficiency with which ozone is formed.

These findings are particularly important in light of the current U.S. focus on NO\textsubscript{x} reduction as the primary mechanism for ozone management. The observed inverse relationship between ozone production efficiency and NO\textsubscript{x} emission rate has significant implications for environmental policy and management strategies related to tropospheric ozone. In particular, the results discussed above provide new perspectives that should aid in the optimization of NO\textsubscript{x} emission management plans for current and planned fossil-fueled power plants.

Current strategies for NO\textsubscript{x} emission reductions inherently assume that “all NO\textsubscript{x} is created equal”. In order to minimize costs, EPA and the States often give industry a fair amount of flexibility in terms of how and where NO\textsubscript{x} emission reductions are achieved. This policy often results in controls being applied to the sources with the greatest NO\textsubscript{x} emissions where the cost per ton of NO\textsubscript{x} removed is lowest. EPA has recently issued a rule (under section 126 of the Clean Air Act) designed to minimize the impact of ozone formed in one state on states downwind. The rule calls for NO\textsubscript{x} emission reductions at 392 large NO\textsubscript{x} sources, mostly coal-fired power plants, located in 19 states (extending from Alabama to Rhode Island) and the District of Columbia using a “cap-and-trade” program. Under “cap-and-trade” the total NO\textsubscript{x} emission reduction is fixed, but trading of emissions within the affected states is allowed. Thus, a ton of emitted NO\textsubscript{x} is “valued” equally whether it comes from a large power plant in the South or a small one in the Midwest. Our results would suggest that the OPE will vary greatly among
the source types and locales being considered, and the resultant change in ambient ozone will be greatly affected by the choice of sources that are controlled under such a system.

The U.S. electric power industry is in the early stages of a massive restructuring designed to move the country away from a system of regional monopolies to a competitive market that provides open access for commercial and residential customers. The prospect of more open and competitive electricity markets has resulted in a renewed interest in distributed generation, many small (typically less than 30 MW) generating facilities located near the end user, as an alternative to large central generating stations. Incentives to promote distributed generation are included in electricity utility restructuring bills currently before the U.S. Congress. Although many technologies ranging from internal combustion engines to solar panels and fuel cells are being considered as candidates for Distributed Generation, small gas turbines appear to be the most attractive in the near term. These modern gas turbines have impressively low NO\textsubscript{x} emissions. However, reducing the emission density by spreading the NO\textsubscript{x} emissions over a larger area, especially one with abundant VOC emissions, creates a situation that is very favorable for ozone production. Under such a scenario, the SOS results suggest that, some of the benefits associated with these lower NO\textsubscript{x} emissions will be offset by higher ozone production efficiencies. Key finding of this work is summarized below.

- Ozone production efficiency was observed to have an inverse relationship with NO\textsubscript{x} emission rate. The implication is that, for large sources, the benefits of decreasing emissions of NO\textsubscript{x} are partially offset by an increase in the efficiency with which ozone is formed.

**KEY CITATIONS:**


2.4. OZONE FORMATION IN URBAN AND INDUSTRIAL AREAS

Peter Daum, Larry Kleinman, and David Allen

During the last eight years, SOS has conducted four major field programs centered on Nashville (1995 and 1999), Atlanta (1999), and Houston (2000). The objectives of these programs were diverse, but a common focus has been to understand the processes leading to elevated O$_3$ concentrations in urban areas, and also particulate matter formation in the case of Atlanta and Houston. An overview of the field campaigns is provided in Section 1.4.

Each of the cities visited by SOS has its own distinctive emissions characteristics and meteorological conditions. Conducting experiments in different venues is a deliberate strategy based on the belief that contrasts between regions constitute an important test of our understanding of the composite meteorological/chemical processes that lead to O$_3$ and PM formation and accumulation.

Results of the Nashville and Atlanta field campaigns in 1999 have been nearly completely analyzed and published. Analysis of SOS work in Houston during TexAQS2000 is ongoing, with publications in the peer-reviewed literature just emerging. Measurement capabilities have evolved since 1995. For example, in the later campaigns instruments were deployed to determine concentrations of free radicals (OH and HO$_2$), NO$_x$ compounds important to nighttime chemistry (NO$_3$ and HONO), VOC compounds with 1-second time resolution, size measurements of ultra-small aerosol particles, and composition measurements for single aerosol particles. These new instruments allow examination of photochemistry and aerosol production in unprecedented detail.
2.4.1 Industrial Plumes

The Houston-Galveston urban area presents a very unique situation with regard to its emissions source areas, in which areas along the coastal ship channel are dominated by a large concentration of petrochemical industrial plants. Much effort during TexAQS2000 was given to measurements that would elucidate the processes contributing to ozone formation and accumulation in the unique industrial plumes and surrounding areas.

1. Ozone is produced very rapidly and very efficiently downwind of areas dominated by industrial sources, compared to other areas in Houston and to other cities

   The rate of ozone production in and around the industrial source dominated areas in Houston can be very high; ozone formation rates ranging between 50 ppb/hr and 150 ppb/hr were measured on multiple days during the month-long Texas Air Quality Study 2000. These rates of ozone production are much higher than those observed in other urban areas, which are almost always less than 40 ppb/hr.

   In addition, the efficiency of ozone production in and downwind of the industrial source dominated areas in Houston can be very high, ranging from 10-20 molecules of ozone per molecule of reacted NO\textsubscript{x}. These efficiencies of ozone formation are much higher than those observed in other urban areas (typically 3-5), those observed in the Houston urban plume (approximately 5), or those observed in the plume of an isolated power plant in the region (approximately 2).

   Ozone production in the Houston urban plume was found to be slower and less efficient than in the composite industrial plume from the Ship Channel region and in plumes from isolated petrochemical facilities. The ozone formation rates and efficiencies observed in the Houston urban plume were similar to rates observed in other urban areas.

   Aircraft observations of ozone and ozone precursors from Houston, Nashville, New York, Phoenix, and Philadelphia show high VOC in Houston, leading to calculated ozone production rates that are 2 to 5 times higher than in the other four cities, even though NO\textsubscript{x} concentrations are comparable. The geographic distribution of VOC reactivity, its very high magnitude in comparison with other less industrial urban regions, and its high fraction of olefins indicate that industrial emissions are contributing in large measure to Houston’s very high ozone concentrations.

   Ozone production rates were calculated based on aircraft measurements for five cities, including Nashville in 1995 and Houston in 2000. 90% of the measurements made in Houston were similar to other cities with regard to NO\textsubscript{x} concentrations, VOC reactivity, and ozone production rate. 10% of Houston is very different, with high anthropogenic VOC reactivity and high ozone production rate. Samples with high ozone production rates had high concentrations of ethene, propene, and/or butenes, butanes, and aromatics and were in areas near industrial sources.
2. High rates and high efficiencies of ozone formation can be explained by co-located emissions of VOC and NO\textsubscript{x} from industrial sources

High rates and high efficiencies of ozone production in the industrial plumes are driven by high concentrations of reactive hydrocarbons in the presence of NO\textsubscript{x}. The industrial plumes exhibiting rapid and efficient ozone formation also tend to exhibit a complex spatial structure.

Aircraft measurements of formaldehyde, formaldehyde precursors, and ozone during TexAQS2000 in plumes from petrochemical facilities were higher than in plumes dominated by power plants and mobile source emissions (see Figure 2.4.1).

CH\textsubscript{2}O is produced as an intermediate in the oxidation of VOC; terminal alkenes such as isoprene, ethane, and propene are the most important precursors generally. Measured petrochemical ethene and propene concentrations were sufficient to explain CH\textsubscript{2}O and ozone concentrations in several Houston area plumes. OH-initiated terminal alkene oxidation is the dominant source of ozone in Houston, while other oxidants such as Cl radicals play a much smaller role.

Fig. 2.4.1. Mixing ratios of CH\textsubscript{2}O and other species in a cross section of the Houston plume acquired at 30.1° latitude on August 28th, showing distinct power plant (W. A. Parish), mobile source (Houston urban) and petrochemical (Ship Channel) dominated plumes (from Wert et al., 2003).

3. Chlorine can promote ozone formation in some urban areas

Chlorine was shown to enhance ozone production in chamber experiments with captured Houston air, although it appears not to be the dominant mechanism of ozone formation in Houston.

KEY CITATIONS:


2.4.2 Urban Plumes under Stagnation Conditions

Stagnation conditions are a major reason for the occurrence of very high O\textsubscript{3} concentrations. A classic case was observed in Nashville between July 11 –13, 1995 (see Figure 2.4.1). Ozone concentrations reached 138 ppb. Vertical cross sections determined by lidar showed that O\textsubscript{3} concentrations exceeded 120 ppb up to 2 km altitude, but that the O\textsubscript{3} hardly moved at all horizontally, instead forming a vertical column or dome of ozone over or near the city (see also Section 2.5). Findings related to urban plumes in stagnation conditions are shown below.

Figure 2.4.1. Map of O\textsubscript{3} interpolated from flight data on July 11, 1995 (from Valente et al., 1998).

1. O\textsubscript{3} formation is VOC-limited in extreme stagnation conditions. Observed indicator ratios show VOC-sensitive conditions in the Nashville urban plume (see Figure 2.4.2).

Figure 2.4.2. Total peroxide to NO\textsubscript{2} ratio for the afternoon of July 11, 1995. Map interpolated from aircraft observations. High O\textsubscript{3} area can be seen from preceding figure (from Valente et al., 1998).
• Under stagnation conditions, O$_3$ production in the Nashville urban plume starts out being VOC-limited in the morning and remains that way for the remainder of the day (see Figure 2.4.3).

Figure 2.4.3. Instantaneous O$_3$ production rate for downtown Nashville on July 11, 1995 as a function of the measured hydrocarbon to NO$_x$ OH reactivity ratio. P(O$_3$) calculated using a box model constrained by measured concentrations of stable species. The exhibited linear dependence is an indication of hydrocarbon sensitive O$_3$ formation. (from Daum et al., 2000).

• In the southeastern US, the highest O$_3$ concentrations occur under stagnation conditions. Model calculations and observations show that stagnation conditions promote VOC sensitivity. In Nashville the sensitivity of peak O$_3$ concentrations is somewhere in-between the strongly VOC-sensitive condition typical of Los Angeles and the strongly NO$_x$-sensitive condition typical of rural areas. In all likelihood, a dual control strategy is required. Such a strategy will have to take into account the role of biogenic VOC emissions that cannot be controlled.

2. Anthropogenic compounds (including CO) account for 2/3 of OH – VOC reactivity. As shown in Figure 2.4.4, much of the OH - VOC reactivity is apportioned to the anthropogenic component of emissions.

Figure 2.4.4. Apportionment of VOC OH reactivity for samples collected over downtown Nashville in the boundary layer on July 11, 1995 during a stagnation episode. Biogenic reactivity includes contributions from isoprene, methylvinylketone, methacrolein, and 40% of the formaldehyde. (from Daum et al., 2000).

KEY CITATIONS:
2.4.3 Urban Plumes under Advective Conditions

Winds usually limit the accumulation of pollutants in an urban area. Ozone that would be found within the city under stagnation conditions is advected away, thereby affecting a larger geographic area, albeit at lower concentration. Under advective conditions there are changes in photochemistry and optimum control measures. During the Nashville 1995 campaign there were several instances where the urban plume could be tracked over a several-hour travel time, thereby giving us a natural laboratory to follow the O₃ production process.

1. The amount of O₃ formed under stagnation and advective conditions was similar. The total amount of O₃ formed in an urban plume can be approximated as the product of NOₓ emissions times the O₃ production efficiency (OPEₓ equal the number of molecules of O₃ formed per molecule of NOₓ that reacts). OPEₓ under stagnation and advective conditions was observed to be about the same (see Table 2.4.1). Small power plants (i.e., Gallatin) have an OPEₓ similar to Nashville; large power plants (i.e., Paradise) have a lower OPEₓ. See also Section 2.2 on power plant plumes.

Table 2.4.1. O₃ production efficiencies in urban and power plant plumes.

<table>
<thead>
<tr>
<th>Date/Time(local)</th>
<th>Plume</th>
<th>OPEₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 11 / 1500</td>
<td>Nashville - stagnation</td>
<td>3.5</td>
</tr>
<tr>
<td>July 13 / 1430</td>
<td>Nashville - stagnation</td>
<td>4</td>
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<tr>
<td>July 13 / 1430</td>
<td>Nashville - stagnation</td>
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<tr>
<td>July 11 / 1500</td>
<td>Nashville - stagnation</td>
<td>4</td>
</tr>
<tr>
<td>July 18</td>
<td>Nashville - advective</td>
<td>3-4</td>
</tr>
<tr>
<td>July 3</td>
<td>Nashville - advective</td>
<td>3-4</td>
</tr>
<tr>
<td>July 7</td>
<td>Paradise</td>
<td>2</td>
</tr>
<tr>
<td>July 15</td>
<td>Gallatin</td>
<td>3</td>
</tr>
</tbody>
</table>

The total number of molecules of O₃ formed for each molecule of NOₓ emitted in the Nashville urban area was observed to be almost independent of ventilation. Under stagnation conditions, this O₃ occupies a small volume leading to very high concentrations. Good ventilation spreads the O₃ and may lead to impacts in rural areas.

2. Photochemistry was rapid in the Nashville urban plume. Within 2 hours travel time from the urban center, photochemistry had removed about half of the NOₓ and half of the anthropogenic hydrocarbons (Figure 2.4.5).

Figure 2.4.5. Decay rate of the NOₓ concentration in the Nashville urban plume under advective conditions. Measurements from July 3 and July 18, 1995. Decay rate is consistent with a 1/e lifetime for NOₓ of ~2.1 hrs, and an average OH concentrations of 10⁷/cm³ (from Nunnermacker et al., 1998).
3. **Biogenic VOCs become more important as the urban plume is advected into the rural surroundings.** As the urban plume moved into rural areas, the biogenic apportionment of hydrocarbons to O$_3$ production increased (Figure 2.4.6).

![Figure 2.4.6](image)

Figure 2.4.6. Estimated contribution of anthropogenic and biogenic hydrocarbons to O$_3$ production in the center of the Nashville urban plume. Left plot is the apportionment after transport of the urban plume approximately 2 hours downwind of Nashville. Right plot is the estimated contribution of hydrocarbon sources after approximately 4-6 hours reaction time. Data from G-1 flights of 7/3 and 7/18/1995 (after Nunnermacker et al., 1998).

4. **NO$_x$ control is favored under advective conditions.** Model calculations indicate a tendency for NO$_x$ sensitivity to increase and VOC sensitivity to decrease as the meteorological situation shifts from the stagnation conditions typical of extreme episodes to more typical advection conditions (Duncan and Chameides, 1998). Ozone over the urban center can still be VOC-sensitive, but in contrast to stagnation episodes, this is no longer where peak O$_3$ occurs.

**KEY CITATIONS:**


2.4.4 Ozone Transport from Urban to Rural Areas

Ozone that is formed in an urban area does not stay there. Even under extreme stagnation conditions, it is advected away within a day. Often, the advection occurs preferentially at night (see Section 2.5). As ozone has a relatively long atmospheric lifetime, ozone transported out of a city can contribute to a regional background. The next day’s photochemistry then has a higher base upon which to build. These processes were observed during the Nashville field campaigns. Model calculations show the implications on control strategies.

1. Transport of ozone from Nashville. Lidar cross sections and profiles and wind profiler data showed that the dome of ozone over Nashville during the July 11-13 stagnation episode mixed out and became part of the suburban and rural mixed layer the next day.

2. Impact of urban ozone at a suburban location. Of the 120 ppb O$_3$ recorded at suburban New Hendersonville (July 1, 1994), 80 ppb was due to entrainment of O$_3$ rich air from aloft – which was a remnant of the previous day’s photochemistry. An additional 40 ppb was added due to the current day’s urban plume (see Figure 2.4.7).

![Figure 2.4.7](image-url)

Figure 2.4.7. Ozone measured at New Hendersonville and other ground stations. Bottom panel shows calculated O$_3$ production rate. From 0700 to 1000 CST, July 1, O$_3$ increased from essentially 0 to 80 ppb, which can only be explained by entrainment since photochemical production was nil during this period. The further increase to 120 ppb is due to intense photochemical production in the Nashville urban plume as it passed over the New Hendersonville site (adapted from Baumann et al., 2000).
3. **Regional background and urban ozone can require different control measures.** Model calculations show that export of O$_3$ from a city is more sensitive to NO$_x$ emission decreases, even for cases where VOC emission controls more effectively decrease peak O$_3$ during pollution episodes (Duncan and Chameides, 1998).

4. **Ozone = Plume + Background.** Each day’s photochemistry builds on a background of O$_3$ that was created in previous days. Background O$_3$ is almost always NO$_x$-sensitive. It often cannot be attributed to a single source region. Plume O3, on the other hand, can be NOx- or VOC-sensitive. In a stagnation episode, the O$_3$ that is formed in the urban plume during the day of the episode can be very VOC-sensitive and even increase if NO$_x$ emissions are lessened. Thus, plume and background O$_3$ can require different control measures.

**KEY CITATIONS:**

