

## A comparative study of ozone production in five U.S. metropolitan areas

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[1] We present observations of  $O_3$  and  $O_3$  precursors measured at mid boundary layer altitude during field campaigns in Nashville, Tennessee (1995), New York City, New York (1996), Phoenix, Arizona (1998), Philadelphia, Pennsylvania (1999), and Houston, Texas (2000). Ozone production rates  $P(O_3)$  and their sensitivity to  $NO_x$  and volatile organic carbons (VOCs) are calculated using observed concentrations as inputs to a steady state box model. City to city comparisons are made to illustrate common features of urban photochemistry and features that are unique to specific cities. Ozone production rates vary from nearly zero to  $155 \text{ ppb h}^{-1}$ . Differences in  $P(O_3)$  depend on precursor concentrations, namely, radical sources,  $NO_x$  and VOCs. Under conditions where  $P(O_3)$  is greater than  $25 \text{ ppb h}^{-1}$ , there is a potential to produce enough same-day  $O_3$  to transform a typical regional background into a severe  $O_3$  episode. Six such cases were observed, in Nashville, Philadelphia, and Houston, with elevated  $O_3$  concentrations in the afternoon (130–211 ppb) following a morning in which  $P(O_3)$  was  $25\text{--}140 \text{ ppb h}^{-1}$ . High  $P(O_3)$  occurs when  $NO_x$  concentrations are  $5\text{--}25 \text{ ppb}$  and OH-VOC reactivity is above  $5 \text{ s}^{-1}$ . These conditions are infrequent, and aside from a common dependence on calm winds, reasons vary from city to city. In Nashville, high  $P(O_3)$  was observed during a stagnation event over downtown and under the circumstance that an air mass with a high concentration of isoprene encountered a  $NO_x$  source. In Houston,  $NO_x$  and light olefins are coemitted from petrochemical facilities leading to the highest  $P(O_3)$ s of the five cities studied. High values of  $P(O_3)$  did not occur in Phoenix because of low radical production, caused mainly by a dry atmosphere, and a low VOC to  $NO_x$  ratio. The sensitivity of  $P(O_3)$  to its precursors varied from  $NO_x$  limited in rural samples to VOC limited near emission sources. In Philadelphia, and especially Phoenix, the highest  $O_3$  production rates occurred under VOC-limited conditions. In Nashville, New York City, and Houston the high- $P(O_3)$  samples were near the ridge line where  $P(O_3)$  responds somewhat to VOC reductions but is insensitive to  $NO_x$  changes.

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### 1. Introduction

[2] The  $O_3$  in a photochemical smog episode can be broken up into components formed over different time-scales and space scales [Logan, 1989; National Research Council, 1991; Sillman, 1993]. Within the United States, about 10 to 30 ppb is from Northern Hemisphere midlatitude background sources [Fiore et al., 2002]. Another 20 to 70 ppb is a regional background, defined

as  $O_3$  covering a several hundred kilometers distance, formed on the day or days preceding a high- $O_3$  event. To these components is added “same-day”  $O_3$  formed on the day that the episode occurs. Usually, same-day  $O_3$  will be in the form of a plume associated with discrete urban or point source emissions. Typically, it is the addition of same-day  $O_3$  that transforms a high regional background into values that exceed the 120 ppb 1 hour National Ambient Air Quality Standard (NAAQS). In extreme situations, same-day  $O_3$  can contribute 100–200 ppb to ambient levels. Time series of  $O_3$  concentrations at monitoring sites suggest that much of the added increment of  $O_3$

during an episode day can be formed in just a few hours. In order to have a large increment of O<sub>3</sub> formed in a short time period, the rate of O<sub>3</sub> production must be rapid. As a corollary, O<sub>3</sub> production rates provide a pathway to understanding high-O<sub>3</sub> events. It has been argued that O<sub>3</sub> control strategies should be focused on reducing O<sub>3</sub> production rates in regions where they are high [Tonnesen and Dennis, 2000].

[3] In this article we examine O<sub>3</sub> precursors and O<sub>3</sub> production rates derived from observations that we have made during field campaigns conducted in five metropolitan areas in the United States: Nashville, Tennessee (1995); New York City, New York (1996); Phoenix, Arizona (1998); Philadelphia, Pennsylvania (1999); and Houston, Texas (2000). Ozone production rates, denoted as P(O<sub>3</sub>), are determined from constrained steady state (CSS) box model calculations that use as input concentrations and parameters observed from mid boundary layer altitude aircraft flights. Data are from the Department of Energy (DOE) G-1 aircraft, augmented by observations made from the Tennessee Valley Authority (TVA) helicopter during the 1995 Nashville campaign. This study builds on and expands the scope of a previous five city comparison which had as its focus the occurrence of very high olefin concentrations in Houston and the consequent high rates of O<sub>3</sub> production [Kleinman *et al.*, 2002a].

[4] Our goal is to determine the chemical features in each city that most affect the O<sub>3</sub> production rate and its sensitivity to NO<sub>x</sub> (NO + NO<sub>2</sub>) and VOCs (volatile organic compounds). Most of the graphs and tables in this study compare results among the five cities. We do this to illustrate the range of conditions observed in different metropolitan areas and to show distinctive features that could impact O<sub>3</sub> control measures. Sampling dates, hours of operation, and flight patterns differed somewhat from city to city. A challenge is to compare photochemistry in the five cities in a way that is not unduly influenced by experimental protocols. To some extent the same problem occurs even when comparing monitoring data in which city to city differences can be caused by differences in the number and location of monitors. Our analyses focus on the consequences of having a particular combination of O<sub>3</sub> precursors. How this combination came into being depends on emissions, meteorology, and chemical processing prior to our observations. These topics, though important, are secondary to our objective of characterizing O<sub>3</sub> production rates.

[5] Sections 2 and 3 present experimental and calculational methods. The presentation of results from the five-city study begins in section 4 with a brief overview of each field campaign. Aircraft data on O<sub>3</sub> precursors, namely, radical sources, NO<sub>x</sub>, and VOCs are presented in section 5. Section 6 shows calculated results, P(O<sub>3</sub>) and L<sub>N</sub>/Q which gives the sensitivity of P(O<sub>3</sub>) to its precursors. The five cities are similar in some respects but at the same time have pronounced differences due to meteorology and emission patterns. In section 7 we discuss diurnal trends and the occurrence of high O<sub>3</sub> production rates on the mornings of high-O<sub>3</sub> days. We describe the impacts on O<sub>3</sub> production from high isoprene concentrations in Nashville, the dry atmosphere and low VOC reactivity in Phoenix, and emissions of light olefins

from petrochemical facilities in Houston. Conclusions are presented in section 8.

## 2. Experimental Setup

[6] The primary data sets used in this article are from the DOE G-1 aircraft. Table 1 provides a list of the trace gases that were measured. Most of the instrumentation has been discussed in a series of articles which make use of the G-1 data set. Over the 6 year period between Nashville in 1995 and Houston in 2000, there were evolutionary changes to the instruments as well as some problems which resulted in missing measurements. That will be the focus of this section.

[7] All VOC samples discussed here were collected in Summa electropolished canisters and analyzed by GC-FID at York University [Rudolph, 1999]. Although the basic procedures remained nearly unchanged for the five field programs, there were changes in columns which resulted in a modest enlargement of the number and molecular weight of the species that were quantified. Terpenes were first quantified in the 1998 Phoenix data set. Species quantified in the 1995 Nashville campaign accounted for 88% of the hydrocarbon reactivity measured in Houston. A subset of the VOC canisters collected in Houston and Phoenix were found to have leaky fittings [Kleinman *et al.*, 2003a]. Because of suspected contamination we have removed 23 samples out of a total of 234 Houston samples and 7 out of 124 Phoenix samples from further consideration.

[8] In 1999, a shorter inlet was adapted for the NO<sub>y</sub> detector to minimize loss of HNO<sub>3</sub> and other “sticky” compounds. In the new inlet a heated Mo converter is mounted 10 cm outside of the aircraft fuselage. Ambient air is drawn through a small pinhole in the quartz housing. Improvements were made to the NO-O<sub>3</sub> chemiluminescence reactor cell and photomultipliers resulting in improved sensitivity and signal-to-noise ratio. The NO<sub>2</sub> channel in the NO/NO<sub>2</sub>/NO<sub>y</sub> detector was damaged during transit prior to the 1999 Philadelphia program. In its place we use NO<sub>2</sub> concentrations calculated from a photochemical model. On the basis of comparisons between observed and calculated NO<sub>2</sub> from the preceding field program in Phoenix (NO<sub>2</sub> calculated = 1.09 NO<sub>2</sub> observed) and based on measurements in newly emitted plumes in Philadelphia where we assume that NO<sub>x</sub> ≈ NO<sub>y</sub>, we estimate that the calculated values for NO<sub>2</sub> in Philadelphia are within 25% of the actual value as long as NO<sub>x</sub> is greater than about 2 ppb.

## 3. O<sub>3</sub> Photochemistry and Calculations

[9] Ozone production depends on free radical sources, NO<sub>x</sub>, and VOCs [e.g., Seinfeld and Pandis, 1997]. In this section we describe the construction of these composite quantities from the aircraft observations. We also describe the constrained steady state box model calculations that use those observations as input.

### 3.1. O<sub>3</sub> Precursors

[10] In presenting our observations, we will treat radical precursors, NO<sub>x</sub>, and VOCs as three variables which pro-

**Table 1.** G-1 Chemical Instrumentation

Species	Method	$\sim 3\sigma$ Limit of Detection/Response Time <sup>a</sup>
O <sub>3</sub>	UV absorption	5 ppbv (precision)/10 s
NO	O <sub>3</sub> chemiluminescence	10 pptv/<10 s
NO <sub>2</sub>	photolysis/O <sub>3</sub> chemiluminescence	50 pptv/<10 s
NO <sub>y</sub>	Mo catalyst/O <sub>3</sub> chemiluminescence	100 pptv/<10 s
CO	nondispersive IR absorption	20 ppbv/20 s
Hydrocarbons	canister collection/GC analysis	5 ppt C/30 s
HCHO	HPLC/DNPH derivatization	80 pptv/1 min
H <sub>2</sub> O <sub>2</sub> and organic peroxides	scrubber/selective derivatization/fluorescence detection	$\sim 60$ pptv/1 min
SO <sub>2</sub>	pulsed fluorescence	<1 ppbv/10 s

<sup>a</sup>Data from the continuous instruments (all except hydrocarbons and HCHO) are first averaged over 10 s intervals. HCHO is assumed to be constant between measurement intervals. With the exception of peak O<sub>3</sub> concentrations shown in one figure, data are subsequently averaged to match the hydrocarbon collection time periods. HPLC/DNPH is high-performance liquid chromatography/dinitrophenylhydrazine.

vide a reasonably complete description of O<sub>3</sub> photochemistry. This is only an approximation, which most notably ignores the specific chemical properties of different VOCs and radical precursors (which are considered in the CSS calculations). As our determination of O<sub>3</sub> precursors is based on measurements, it is limited by the number and types of compounds that are observed.

[11] Radical precursors are substances which can be photolyzed or undergo thermal reactions producing free radicals. This definition specifically excludes reactions which cycle free radicals as opposed to creating new free radicals. We will denote the sum total rate of radical production by  $Q$  which will have units of ppb h<sup>-1</sup>. The most important radical sources are usually



Because of very high alkene concentrations, ozonolysis reactions,



are a significant radical source in some Houston samples.  $Q$  also contains several smaller terms including photolysis of H<sub>2</sub>O<sub>2</sub> and organic peroxides. Observations in urban areas suggest that HONO can be the predominant radical source early in the day [Alicke *et al.*, 2003]. Photolysis of HONO is not included in  $Q$  (nor in the CSS calculations) because it was not measured. At the times of our observations, mainly from midmorning to mid afternoon, HONO is expected to be a lesser contributor to radical production with the possible exception of surface locations in high-NO<sub>x</sub> environments [Ren *et al.*, 2003]. For lack of observations, photolysis of CH<sub>3</sub>CHO and other carbonyl compounds are also not counted in  $Q$ .

[12] NO<sub>x</sub> is defined as NO + NO<sub>2</sub>. Except for Philadelphia, both NO and NO<sub>2</sub> are observed quantities. As previously described NO<sub>2</sub> measurements were not available in Philadelphia; there NO<sub>x</sub> is the sum of measured NO and calculated NO<sub>2</sub>.

[13] VOCs are broadly defined to include most of the species which react with OH radical, producing a peroxy

radical which can then go on to convert NO to NO<sub>2</sub>, leading to O<sub>3</sub> production. Our definition of a VOC includes CH<sub>4</sub>, CO, oxygenated hydrocarbons such as HCHO, anthropogenic hydrocarbons, and biogenic hydrocarbons. Our measure of VOCs is based on OH reactivity:

$$\text{VOC}_R = \sum k_i[\text{VOC}_i], \quad (1)$$

where  $k_i$  is the rate constant for



Reaction rate constants are from Atkinson *et al.* [1997], or from structure-reactivity relations of Kwok and Atkinson [1995]. As with the determination of a radical production rate, the calculation of VOC<sub>R</sub> is limited by what is measured, with two exceptions. Concentrations of methyl vinyl ketone (MVK) and methacrolein (MACR) are estimated to be 250% and 110% of isoprene; a steady state mixture generated by OH kinetics, i.e., the formations rates of these compounds by OH oxidation of isoprene is equal to their destruction rate by OH oxidation [Paulson and Seinfeld, 1992]. Lewis *et al.* [2000] have observed that GC-FIDs such as used here can be missing a significant fraction of the total ambient hydrocarbons. Closure experiments have been performed in which an observed disappearance rate of OH radical is compared to calculations based on the total reactivity determined from (1) using observed VOC concentrations [Kovacs *et al.*, 2003; Martinez *et al.*, 2003]. In some near-source environments, agreement is good suggesting that the usual array of C<sub>2</sub>–C<sub>10</sub> hydrocarbons contains most of the OH reactivity. However, in aged air masses, there is OH reactivity not picked up by the usual hydrocarbon canister measurements. Because of different chemical environments in the five cities it is possible that they are affected to different extents by the additional VOC reactivity present in the ambient atmosphere, but not in our measurements.

### 3.2. CSS Model

[14] The CSS box model determines the concentrations of NO<sub>2</sub> and free radicals that are in steady state with the observed mixture of trace gases [Kleinman *et al.*, 2002b]. The chemical mechanism in the model is based on the RADM2 anthropogenic set of reactions [Stockwell



**Table 2.** Properties of O<sub>3</sub> Photochemistry as a Function of L<sub>N</sub>/Q<sup>a</sup>

L <sub>N</sub> /Q	Properties of O <sub>3</sub> Photochemistry
Near 0	low NO <sub>x</sub> regime, peroxide formation, NO <sub>x</sub> sensitive O <sub>3</sub> formation, P(O <sub>3</sub> ) ≈ Q <sup>1/2</sup> [NO]
1/2	crossover point between NO <sub>x</sub> and VOC, sensitive O <sub>3</sub> production, P(O <sub>3</sub> ) ≈ Q <sup>2/3</sup> [NO] <sup>1/3</sup> VOC <sub>R</sub> <sup>1/3</sup>
2/3	ridge line: ∂P(O <sub>3</sub> )/∂[NO <sub>x</sub> ] = 0, P(O <sub>3</sub> ) ≈ Q <sup>3/4</sup> VOC <sub>R</sub> <sup>1/2</sup>
Near 1	high NO <sub>x</sub> regime, NO <sub>x</sub> formation, VOC sensitive O <sub>3</sub> formation, P(O <sub>3</sub> ) ≈ Q VOC <sub>R</sub> /[NO <sub>2</sub> ]

<sup>a</sup>P(O<sub>3</sub>) is the chemical production rate of O<sub>3</sub>. L<sub>N</sub>/Q is the fraction of radicals removed by reactions with NO<sub>x</sub>. VOC<sub>R</sub> is the VOC-OH reactivity defined in (1). Q is the production rate of free radicals.

*et al.*, 1990] and the isoprene reactions given by *Paulson and Seinfeld* [1992]. Measured concentrations of O<sub>3</sub>, H<sub>2</sub>O, NO, CO, speciated hydrocarbons, HCHO, SO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and organic peroxides are used as model inputs. In addition the model uses observed pressure, temperature, and actinic flux as determined from an Eppley radiometer and a radiative transfer program [*Madronich*, 1987]. Actinic flux is adjusted to 90% of its clear-sky value thereby ignoring cloud cover as a source of variability. Because hydrocarbons are determined from discrete canister samples, the number of calculations is limited by the number of samples. Model inputs are averaged over the time needed to fill a hydrocarbon canister (~30 s).

[15] Calculations yield the rate of O<sub>3</sub> production, P(O<sub>3</sub>), determined as the rate at which peroxy radicals react with NO, and pathway information on radical removal. There are two families of reactions that remove free radicals, namely radical-radical reactions such as those that form peroxides, and radical-NO<sub>x</sub> reactions such as OH + NO<sub>2</sub> → HNO<sub>3</sub>. L<sub>N</sub> is the rate of the second pathway and L<sub>N</sub>/Q is the fraction of radicals removed by reactions with NO<sub>x</sub>. This variable forms the basis of an indicator species method for determining the sensitivity of O<sub>3</sub> production to changes in NO<sub>x</sub> and VOCs [*Sillman*, 1995]. Properties of O<sub>3</sub> formation as a function of L<sub>N</sub>/Q are given in Table 2. Further discussion of L<sub>N</sub>/Q and an explicit formula are provided in *Kleinman et al.* [2001] and *Kleinman* [2004].

[16] The accuracy of photochemical box models such as that used here has been addressed by Monte Carlo uncertainty analysis [e.g., *Thompson and Stewart*, 1991] and in conjunction with closure experiments that compare measured and observed OH and HO<sub>2</sub> radical concentrations [e.g., *Martinez et al.*, 2003]. Accuracy assessments depend on conditions and vary from study to study. As a representative number we note the assessment by *Martinez et al.* [2003] of a 50% 2σ uncertainty in calculated OH and HO<sub>2</sub>. The uncertainty in P(O<sub>3</sub>) should be comparable. These estimates ignore the possibility of incomplete chemistry that might explain the divergence between calculated and observed peroxy radical concentration under high-NO<sub>x</sub> conditions [*Thornton et al.*, 2002].

#### 4. Field Programs

[17] Field campaigns in Nashville and Houston were part of the Southern Oxidants Study (SOS). Campaigns in New York City (NYC) and Philadelphia were part of NARSTO-NE, and the campaign in Phoenix was done in cooperation with the Arizona Department of Environmental Quality (ADEQ). These studies varied in size and scope with the SOS campaigns involving tens of institutions and hundreds

of investigators. The Philadelphia study was also a multi-investigator project but with a smaller scope than either Nashville or Houston. NYC and Phoenix were primarily DOE National Lab projects with infrastructure help from Electric Power Research Institute (EPRI) and ADEQ, respectively. These five field studies have generated numerous publications and many valuable results which we can not hope to adequately summarize here.

[18] Table 3 provides summary information about the G-1 observation during field campaigns in Nashville [*Hübner et al.*, 1998; *Daum et al.*, 2000a, 2000b; *Lee et al.*, 1998; *Nunnermacker et al.*, 1998, 2000; *Weinstein-Lloyd et al.*, 1998], New York City [*Kleinman et al.*, 2000], Phoenix [*Fast et al.*, 2000; *Kleinman et al.*, 2002b, 2003b; *Nunnermacker et al.*, 2004], Philadelphia [*Fast et al.*, 2002; *Kleinman et al.*, 2004], and Houston [*Kleinman et al.*, 2002a; *Daum et al.*, 2003, 2004; *Berkowitz et al.*, 2004a, 2004b]. For some of the field programs, in particular the SOS affiliated campaigns in Nashville and Houston and the NARSTO-NE affiliated campaign in Philadelphia, the information gathered from the G-1 flights is a small fraction of the total gathered by the many other participants in these studies. Many of the 1995 Nashville papers can be found in the Southern Oxidants Study Nashville/Middle Tennessee Ozone Study (SOS) special issues of *Journal of Geophysical Research* (103 (D17), 1998 and 105 (D7), 2000) and are summarized by *Cowling et al.* [1998, 2000]. The NYC and Philadelphia field campaigns were affiliated with NARSTO-NE, an overview of which is described by *Solomon et al.* [2000]. Among the outputs from NARSTO-NE are three papers that describe the evolution of O<sub>3</sub> episodes along the NE coastal region of the U.S [*Ryan et al.*, 1998; *Zhang et al.*, 1998; *Seaman and Michelson*, 2000]. Other papers which specifically address O<sub>3</sub> production and VOCs in Houston include those of *Roberts et al.* [2001], *Karl et al.* [2003], *Ryerson et al.* [2003], *Wert et al.* [2003], and *Jiang and Fast* [2004].

[19] Figure 1 shows a composite flight track for the G-1 in each of the five field campaigns, indicating the locations where VOC samples were collected and P(O<sub>3</sub>) was calculated. Ozone production rates in the top 10% for each city are indicated with bolder symbols. Flight patterns were often repeated, especially in Phoenix and Philadelphia, which shows up in Figure 1 as a multistranded line, representing, in some cases more than 20 traverses along nearly identical ground tracks. For four cities we have plotted on a 4 km grid NO<sub>x</sub> emissions obtained from a 1999 simulation using the SMOKE model. Phoenix emissions are from a 1996 ADEQ inventory. Sampling in Nashville and NYC is seen to be mainly outside of the population centers with high NO<sub>x</sub> emission rates. In contrast, a significant portion of the flight time in Phoenix,

**Table 3.** Field Programs

City	Dates	Flights	Constrained Steady State Calculated
Nashville, Tennessee	June–July 1995	17	81
New York City, New York	July 1996	13	67
Phoenix, Arizona	May–June 1998	24	110
Philadelphia, Pennsylvania	July–August 1999	20	131
Houston, Texas	Aug.–Sept. 2000	18	186

Philadelphia, and Houston was directed at sampling over high-emission rate regions.

[20] High P(O<sub>3</sub>) samples, not surprisingly, are mainly located near high-emission rate regions. For Phoenix and Philadelphia these samples are concentrated near the city centers. Houston has four out of 18 located near a major collection of roads in the downtown area. The other 14 (with the highest values of P(O<sub>3</sub>)) are located near the industrial Ship Channel. The Nashville high-P(O<sub>3</sub>) samples are situated in a ring around the city, which reflects the absence of VOC sampling by the G-1 over the city itself. In the NYC campaign, the highest P(O<sub>3</sub>)s are observed over central New Jersey, downwind of the Philadelphia metropolitan area.

#### 4.1. Characteristics of O<sub>3</sub> Production in the Five Cities

[21] A general indication of pollution conditions is provided in Figure 2 which summarizes the maximum values of O<sub>3</sub> observed on each G-1 flight.

##### 4.1.1. Nashville

[22] Nashville is a city of 1/2 million people in a metropolitan area of 1 million people, relatively isolated from other large urban areas. There are nearby regions with high isoprene emissions, particularly to the west [Goldan *et al.*, 2000]. The city's NO<sub>x</sub> emissions of 40 kton yr<sup>-1</sup> (Davidson County) are a factor of 7 less than that of four coal fired power plants located 40 to 120 km away. Power plants are not colocated with VOC sources. Because O<sub>3</sub> production depends on mixing VOCs into a plume, usually from distributed biogenic sources, peak O<sub>3</sub> concentrations may not be all that high. However, power plant NO<sub>x</sub> emissions are large and eventually a large quantity of O<sub>3</sub> is produced (see e.g., Ryerson *et al.* [2001] for O<sub>3</sub> production efficiency) which can contribute to an elevated regional background.

[23] Ozone episodes in the southeastern United States in general and in Nashville in particular occur during periods with low winds where high regional concentrations can accumulate over a several day period [Schichtel and Husar, 2001]. The highest O<sub>3</sub> concentrations observed during the 1995 campaign were in a localized blob which sat over downtown Nashville for 3 days, 11–13 July [Valente *et al.*, 1998; Daum *et al.*, 2000a]. Even though there was a 3 day period with calm winds, peak O<sub>3</sub> concentrations depended on same-day photochemistry as a multiday buildup was moderated by an inertial oscillation of the winds at night which dispersed pollutants but contributed to higher regional O<sub>3</sub> levels [Banta *et al.*, 1998; McNider *et al.*, 1998; Baumann *et al.*, 2000].

##### 4.1.2. Northeast Corridor: New York City and Philadelphia

[24] Both cities are large urban areas surrounded by a high-population suburban sprawl. They have a mixture of

emission sources consisting of a vehicle dominated urban component plus utility and industrial sources. There are nearby areas with high isoprene emission rates. These two cities are part of the northeast corridor, a heavily populated industrialized area stretching from Washington, D. C., to Boston, Massachusetts. Ozone episodes often occur when winds are from the SW in an along-corridor direction. Interregional transport in many episodes accounts for NAAQS O<sub>3</sub> exceedances 100 km or more downwind of the major urban centers. Effects of transport were seen in the NYC campaign where the highest O<sub>3</sub> concentrations were observed over Long Island and Connecticut, about 100 km from NYC [Kleinman *et al.*, 2000]. An O<sub>3</sub> episode that occurred during the Philadelphia campaign was atypical in that winds were stagnant on the morning of the day with highest O<sub>3</sub> concentration, causing peak levels to be located near emission hot spots [Kleinman *et al.*, 2004]. Ozone episodes have been observed to depend upon a regional background of 80–100 ppb O<sub>3</sub> transported into the area from the west or NW. Same-day O<sub>3</sub> formed on the peak day of an episode can contribute another 80–100 ppb resulting in O<sub>3</sub> levels of 175 ppb [Ryan *et al.*, 1998; Zhang *et al.*, 1998]. A major difference between the NYC and Philadelphia campaigns was that most of the NYC sampling was done over suburban areas, while the Philadelphia study focused on high-emission rate areas. Peak levels of O<sub>3</sub> during the NYC campaign were significantly lower than in Philadelphia (Figure 2). Along the Northeast corridor, O<sub>3</sub> levels in 1996 were lower than in 1995.

##### 4.1.3. Phoenix

[25] Phoenix is in a metropolitan area of 3 million people, surrounded by mountains on three sides and located in a desert, relatively remote from other large urban areas. Emissions are dominated by vehicles with only a small admixture from large point sources. Vegetation is sparse and biogenic emissions are low. Mixing heights are about 3 km in contrast to the 1–2 km heights typical in the other four cities. The Phoenix campaign took place before the peak O<sub>3</sub> season which occurs during July and August under different flow conditions and with significantly higher absolute humidity than observed during May and June.

##### 4.1.4. Houston

[26] Houston is a large metropolitan area with 4 million people and has the usual assortment of urban emission sources. The Houston metropolitan area also contains one of the largest conglomerations of petrochemical plants in the world. Many of these facilities are located on the Ship Channel, a body of water that is about 30 km long extending from Galveston Bay, almost into downtown Houston. Ozone concentrations recorded in Houston in the past 6 years are generally the highest in the United States (Environmental Protection Agency, AIRData database,

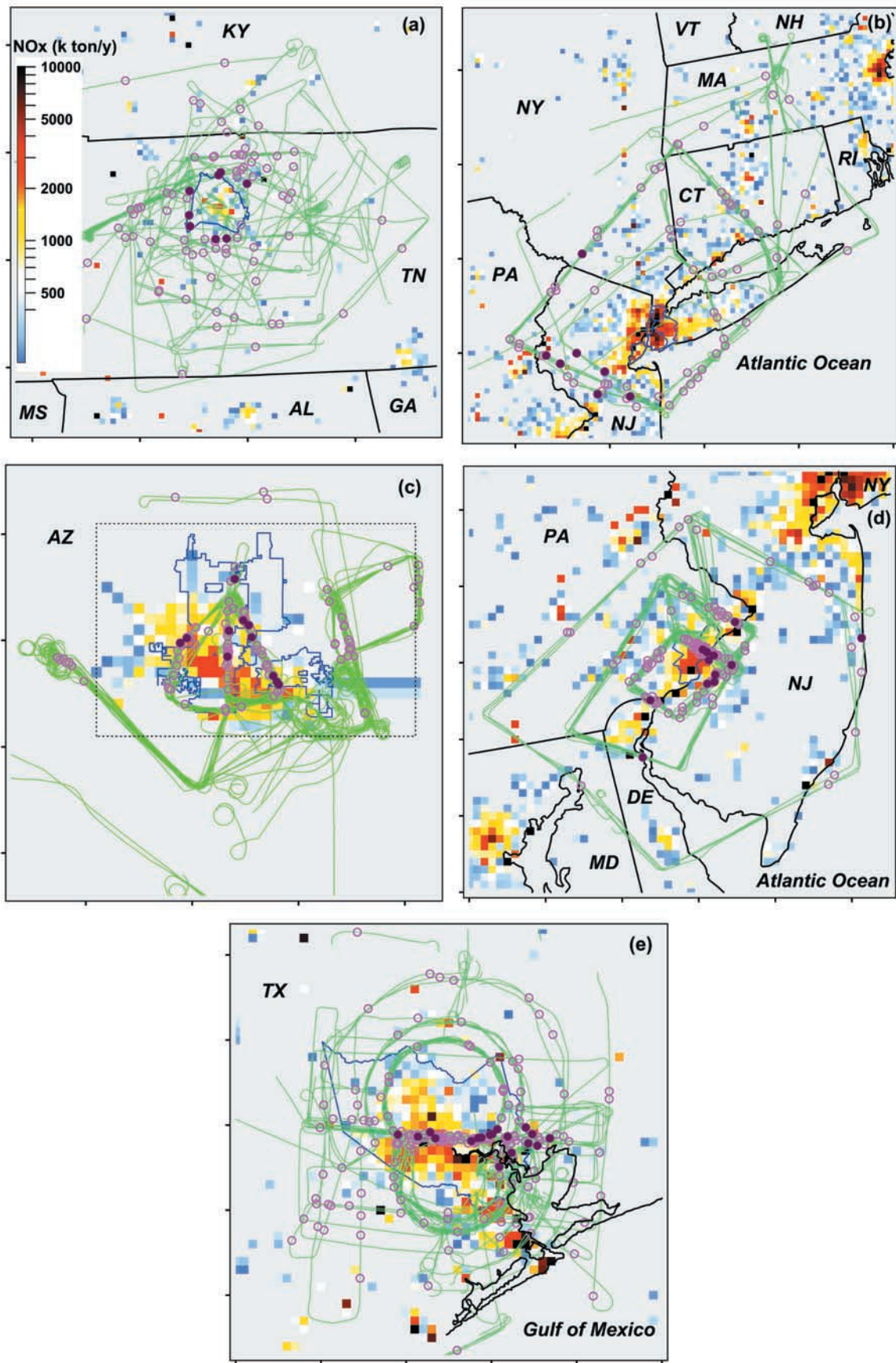
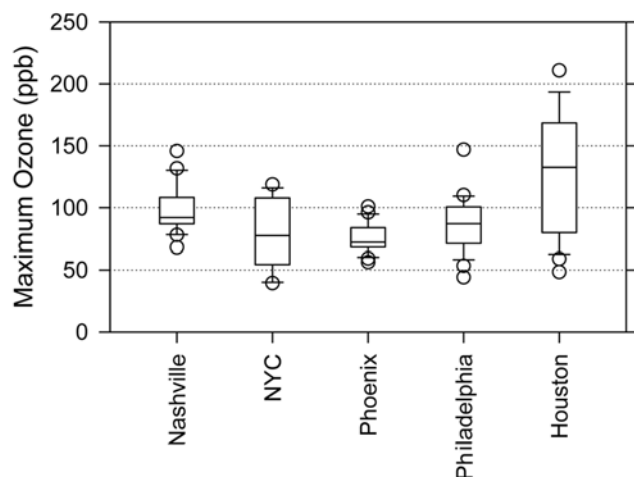


Figure 1





**Figure 2.** Box plot showing the distribution of values for the peak O<sub>3</sub> concentration observed on each G-1 aircraft flight during five field campaigns. Box shows median value and interquartile range (25th to 75th percentile of distribution). Caps indicate 10th and 90th percentiles; circles indicate points outside of the 10th to 90th percentile range.

available at [www.epa.gov/air/data](http://www.epa.gov/air/data), 2004). Figure 2 shows that the Texas campaign captured many high-O<sub>3</sub> events and indicates the uniqueness of these concentrations relative to other cities. Extreme O<sub>3</sub> concentrations are typically seen at only a few monitoring sites at a time which show large rapid changes in O<sub>3</sub>. These O<sub>3</sub> episodes have been linked to very high olefin emissions from petrochemical facilities [Kleinman et al., 2002a; Daum et al., 2003, 2004; Ryerson et al., 2003; Wert et al., 2003]. Many of these same facilities have high NO<sub>x</sub> emission rates. Impacts from these point sources are particularly severe on days where there is a flow reversal of the land bay breeze causing a period of stagnation which allows O<sub>3</sub> precursors to accumulate [Nielson-Gammon, 2002]. Locations north of the Ship Channel have high biogenic emission rates.

## 5. Five-City Intercomparison: Ozone Precursors

[27] In this section we examine city to city differences in the chemical and physical variables that control ozone production. Because we will be using the CSS model to determine how P(O<sub>3</sub>) depends on its precursors, we restrict our attention to measurements that have been made at the

times and locations where VOC samples were taken and where other model inputs are also available. Calculations are mostly at mid boundary layer height; sample altitudes are below 1000 m msl except in Phoenix where a 2000 m msl ceiling is imposed. Table 3 gives the resulting number of data points meeting these criteria. Figure 1 gives the geographic distribution of our data set in relation to city boundaries and emission sources.

[28] Frequency distributions are used to compare the range of values for a single concentration or parameter. On the basis of these frequency distributions, data subsets with low (bottom 10%), median (central 20%), and high (top 10%) values of radical production rate and VOC reactivity are singled out for closer inspection.

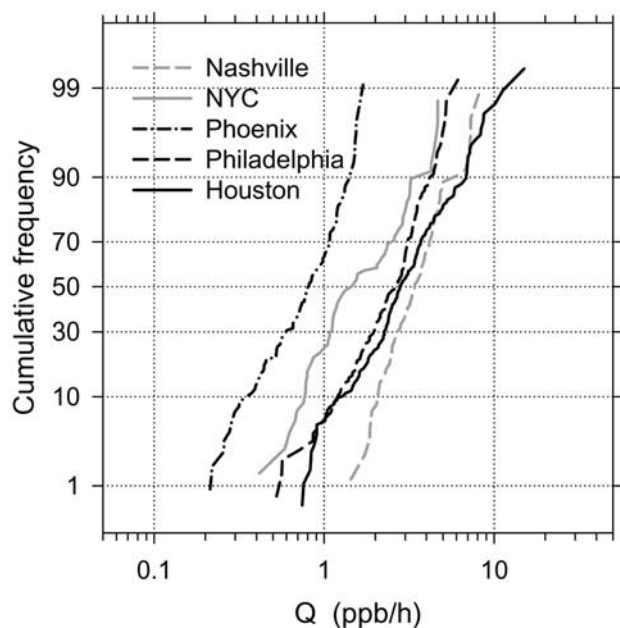
### 5.1. Radical Production Rate

[29] A frequency distribution for Q is shown in Figure 3. Houston and Nashville have the highest rates of radical production and Phoenix the lowest. In Figure 4 we show the contributions of the processes generating radicals for data subsets with high median and low values of Q. On average, O<sub>3</sub> photolysis accounts for 59% of radical production, HCHO photolysis for 26%, and all other sources combined for 14%. Ozone + olefin reactions are particularly important in the high-Q Houston samples. We note that Figures 3 and 4 give a lower bound to Q as there are radical precursors that are not being measured.

[30] As O<sub>3</sub> photolysis is a dominant term, city to city differences in Q depend strongly on the O<sub>3</sub> contribution to Q, which will be called Q(O<sub>3</sub>). Figure 5 illustrates the city to city difference in j(O<sup>1</sup>D), O<sub>3</sub>, and H<sub>2</sub>O that determine radical production from O<sub>3</sub> photolysis. Figure 5 uses the high-Q subset, but similar considerations apply to the rest of the samples. Radical production in Phoenix from O<sub>3</sub> is low primarily because of low water vapor concentration and secondarily because of low O<sub>3</sub> concentration. In Nashville, the high Q points have particularly high water vapor concentration (volume mixing ratio 0.028–0.031), while in Houston the high Q points have particularly high O<sub>3</sub> concentration (average = 130 ppb).

[31] A possible confounding issue in comparing the photochemistry in five cities is that the field programs were conducted at different times of the spring and summer and flights occurred at different times of the day. For this reason, we need to determine to what extent sample to sample and city to city differences in photochemistry are caused by differences in solar intensity and actinic flux versus differences in precursor concentrations. Figures 6 and 7 address

**Figure 1.** NO<sub>x</sub> emission maps showing G-1 ground track and locations of volatile organic carbon (VOC) samples for (a) Nashville, (b) New York city (NYC), (c) Phoenix, (d) Philadelphia, and (e) Houston field campaigns. Emission rates are displayed on a log scale in kt yr<sup>-1</sup> per 4 by 4 km grid cell. Emission data for Nashville, NYC, Philadelphia, and Houston are from a Saturday, 31 July 1800 UTC simulation from the SMOKE model. Phoenix emissions are for a weekday at 1800 UTC from a July 1996 inventory compiled by the Arizona Department of Environmental Quality and are limited to the area inside the dashed box in Figure 1c. Tic marks are spaced 80 km apart in Nashville and NYC and 40 km apart in Phoenix, Philadelphia, and Houston. The emission scale ranges from 300 to 10,000 t yr<sup>-1</sup>, with higher rates truncated to 10,000 and lower rates not displayed. State borders are shown in black, city or county borders are shown in blue, and the G-1 ground track for flight segments below 1000 m altitude (2000 m in Phoenix) are shown in green. Open circles indicate locations where VOC samples were collected and constrained steady state (CSS) calculations were performed. Darker solid circles indicate CSS calculations that had P(O<sub>3</sub>) in the top 10 percentile for that city. Data used for the diurnal cycle discussion in section 7.1 are from the right-side triangle in Phoenix and the inner box of Philadelphia.



**Figure 3.** Frequency distribution for radical production rate during five field campaigns. Data are confined to the times and locations where CSS calculations were performed. Figure 1 shows locations, and Table 3 indicates number of data points and dates for each field campaign.

that question by showing a five-city comparison of the frequency distribution of solar zenith angle and  $j(\text{O}^1\text{D})$ , respectively. Of the several  $j$  values used in the CSS calculations we have chosen to look at  $j(\text{O}^1\text{D})$  because of its importance as a source of radicals. Also, because  $j(\text{O}^1\text{D})$  depends on short-wavelength UV which is primarily absorbed in the stratosphere, it is more sensitive to solar zenith angle than the other  $j$  values.

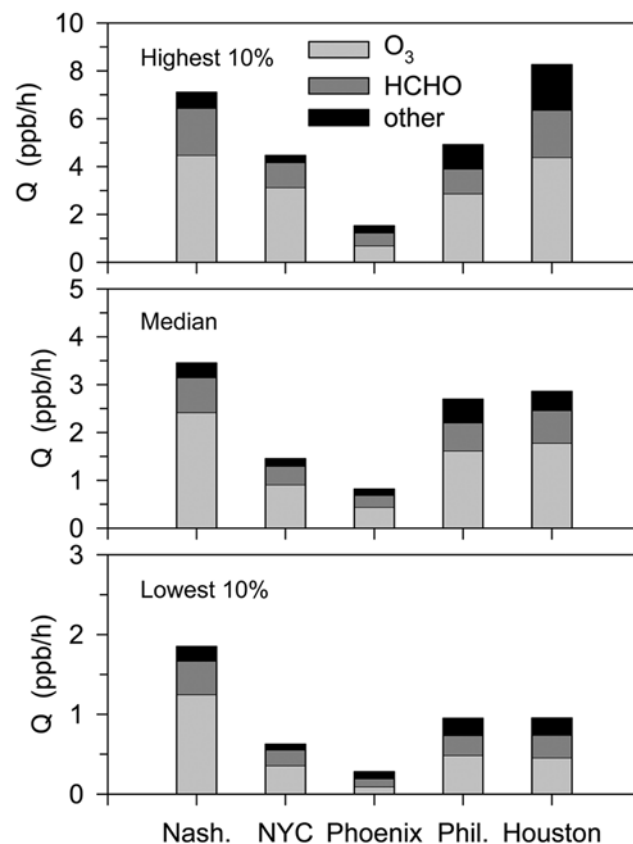
[32] Within a given field program, time of day is the most important determinant for  $j(\text{O}^1\text{D})$ . The range of values for solar zenith angle and  $j(\text{O}^1\text{D})$  within a city reflects a general sampling strategy of flights in the midmorning and mid afternoon, except in Nashville and NYC where some of the flights straddled local solar noon. The Phoenix flights tended to start earlier and end later than elsewhere causing a greater variation in solar zenith angle and  $j(\text{O}^1\text{D})$ . For samples closest to noon in each city, i.e., above the 70th percentile in Figure 7, there is about a 35% spread in  $j(\text{O}^1\text{D})$  from city to city. The variability increases at lower percentiles primarily because of low values for Phoenix samples collected in early morning or late afternoon.

[33] It might be expected that  $j(\text{O}^1\text{D})$  acting as a surrogate for other  $j$  values, time of day, and season would be the principal source of variations in  $Q$  within and between cities. This turns out not to be the case. Regarding city to city variability, the parameter that shows the least variability in Figure 5 is  $j(\text{O}^1\text{D})$ . A comparison of Figures 3 and 7 shows that the city to city range of  $j(\text{O}^1\text{D})$  is only 1/4 that of  $Q$ , except for Phoenix. Regarding within-city variability, a linear regression of  $Q$  versus  $j(\text{O}^1\text{D})$  shows that the fraction of variability in  $Q$  explained by  $j(\text{O}^1\text{D})$  in Nashville, NYC, Phoenix, Philadelphia, and Texas, is 0.16, 0.08, 0.81, 0.26,

and 0.26, respectively. Even though Figure 7 shows that there is a several-fold variation in  $j(\text{O}^1\text{D})$  within each city, the primary cause of variability in radical production rate is due to other causes, except in Phoenix where samples were taken in the early morning and late afternoon. Thus we judge time of day and season to be of secondary importance in explaining city to city and within-city differences in  $Q$ .

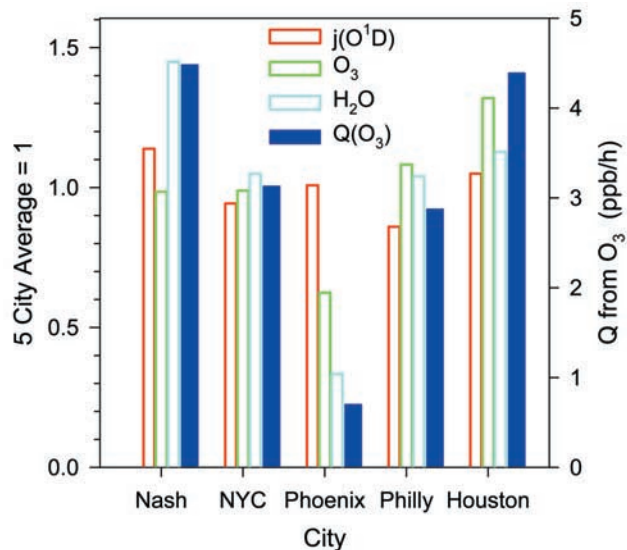
## 5.2. NO<sub>x</sub>

[34] A five-city comparison for the frequency distributions of NO<sub>x</sub> is given in Figure 8. Concentrations range from several tens of parts per trillion, characteristic of the unpolluted boundary layer, to about 100 ppb occurring in power plant plumes. These distributions reflect inherent features of the cities and also city to city differences in sampling strategies. The high ends of the distributions are controlled by a few encounters with high concentration NO<sub>x</sub> plumes. Over the central 80% of the frequency distributions, the five cities split into 2 groups: Nashville and NYC have low NO<sub>x</sub> while Phoenix, Philadelphia, and Houston have high NO<sub>x</sub>. NYC is grouped with Nashville rather than with the other three large high-NO<sub>x</sub> cities as might have been expected, because most of the sampling in NYC was done 50–150 km away from the high-emission rate area



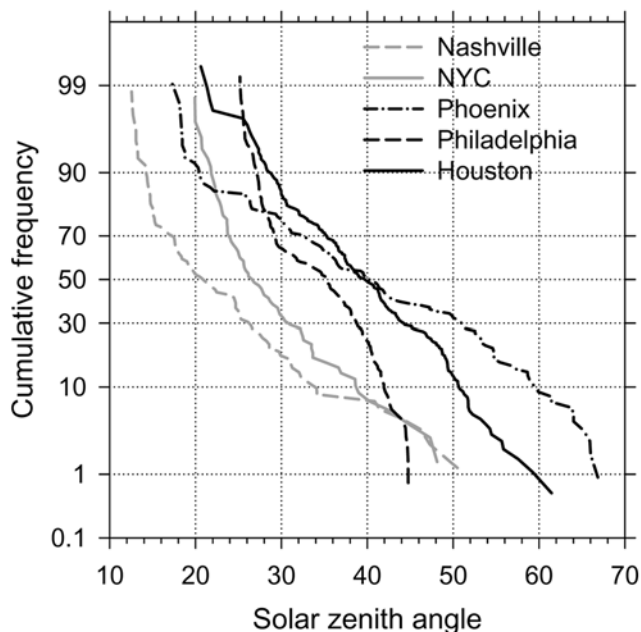
**Figure 4.** Components of radical production rate,  $Q$ , for five cities. “Other” category includes photolysis of peroxides and O<sub>3</sub>-olefin reactions. Data subsets have (top) high values for  $Q$  (top 10% of distribution), (middle) median values of  $Q$  (central 20% of distribution), and (bottom) low values of  $Q$  (bottom 10% of distribution).



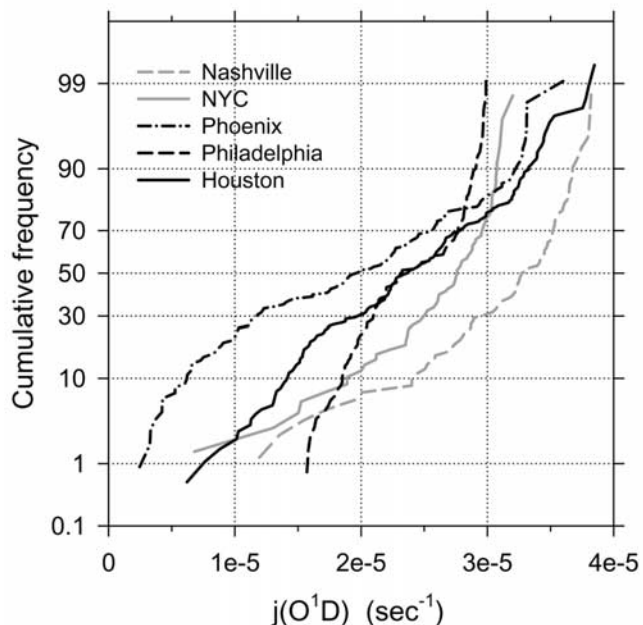


**Figure 5.** Radical production rate from O<sub>3</sub> photolysis, Q(O<sub>3</sub>), for high-Q samples (top 10% of distribution) in five cities. Right-side scale gives absolute magnitude of Q(O<sub>3</sub>) in ppb h<sup>-1</sup>. Left-hand scale gives relative magnitude of j(O<sup>1</sup>D), O<sub>3</sub>, and H<sub>2</sub>O with the five-city average for each factor defined as one. Q(O<sub>3</sub>) is proportional to the product of these three factors.

(Figure 1). In contrast the flights in Phoenix, Philadelphia, and Houston emphasized sampling over regions with high emission rates. If we accept NO<sub>x</sub> as a general indicator of pollution conditions, the sampling in Phoenix, Philadelphia, and Houston is sufficiently similar to allow an intercity comparisons without undue distortion from sampling differences. However, comparisons between the low-NO<sub>x</sub>



**Figure 6.** Frequency distribution for solar zenith angle during five field campaigns. Format is the same as Figure 3.

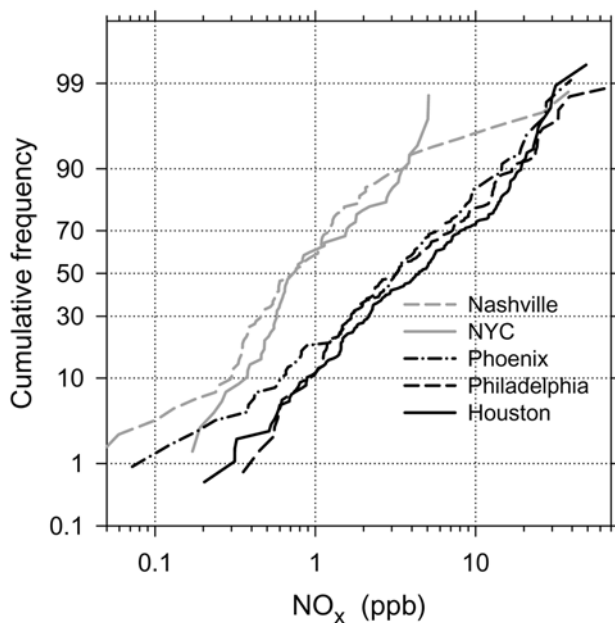


**Figure 7.** Frequency distribution for j(O<sup>1</sup>D) during five field campaigns. Format is the same as Figure 3.

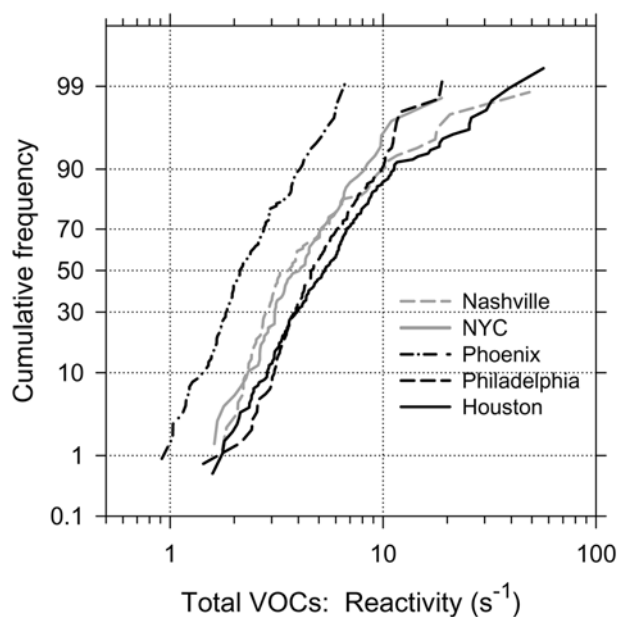
and high-NO<sub>x</sub> cities will have to take into account different sampling strategies.

**5.3. VOCs**

[35] Figures 9 and 10 show the frequency distribution of total VOC reactivity (VOC<sub>R</sub>) and the anthropogenic HC component, respectively. In total reactivity, Phoenix stands out as having low values; the other four cities are tightly grouped except at the high end of the frequency distribution



**Figure 8.** Frequency distribution for NO<sub>x</sub> concentration during five field campaigns. Format is the same as Figure 3.



**Figure 9.** Frequency distribution for total OH-VOC reactivity ( $\text{VOC}_R$ ) during five field campaigns. OH reactivity is defined in equation (1) and includes contributions from all species that react with OH-producing peroxy radicals. Format is the same as Figure 3.

where very high reactivities are observed in Houston and to a lesser extent Nashville. The anthropogenic and total distributions look very different because in most cases total VOC reactivity arises primarily from compounds other than anthropogenic hydrocarbons. Anthropogenic HC reactivity in Figure 10 shows an order of magnitude difference between cities. Nashville and NYC are at the low end, as they were for  $\text{NO}_x$ , because most of the sampling was done a distance away from the urban centers. Philadelphia and especially Houston have the highest values of OH reactivity from anthropogenic hydrocarbons.

[36] In Figure 11 we examine the classes of compounds contributing to VOC reactivity for high-, median- and low-reactivity samples. The average  $\text{NO}_x$  concentrations for each data subset in each city are given above the reactivity bars. In clean air, represented by the lowest 10% reactivity samples, 50–80% of the reactivity comes from  $\text{CH}_4$  and CO.  $\text{NO}_x$  concentrations are low but on average still significantly higher (by as much as an order of magnitude) than found in the above-boundary layer samples that were parsed out of the data set. In the median VOC samples, the  $\text{CH}_4 + \text{CO}$  contribution to reactivity has decreased to less than 40% except in Phoenix. Biogenic contributions are higher, both in a relative and absolute sense, with Phoenix again being the exception. The Houston median samples and to a lesser extent the Philadelphia median samples are showing increased contributions from anthropogenic hydrocarbons. In the 90th percentile samples there are extreme differences between the five cities. This percentile ranking in Nashville and NYC has picked out samples taken in rural high-isoprene areas with low  $\text{NO}_x$  concentration. Consistent with the  $\text{NO}_x$  concentrations, the high-reactivity samples in Phoenix, Philadelphia, and Houston are obtained close to

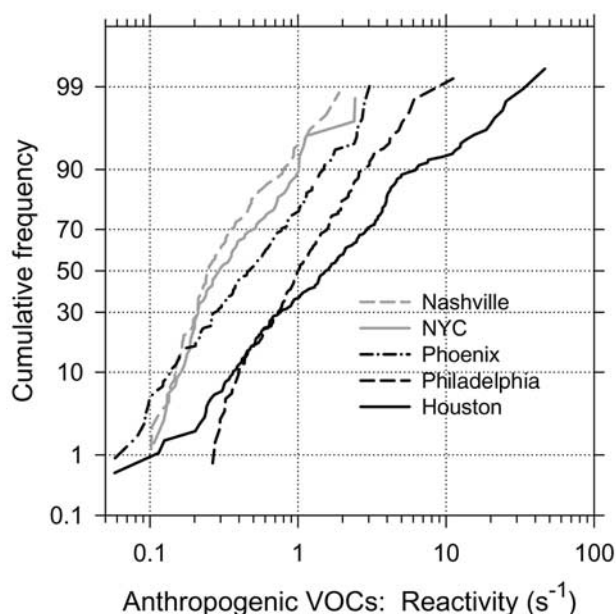
anthropogenic emission sources. Yet these three cities differ qualitatively in VOC reactivity. In Phoenix, anthropogenic hydrocarbon reactivity and the VOC to  $\text{NO}_x$  ratio are much lower than in the other high- $\text{NO}_x$  cities. The Philadelphia high-reactivity samples have a range of compositions, but most have significant anthropogenic and biogenic components. Houston has high VOC reactivity caused by high anthropogenic hydrocarbons. All of the 90th percentile Houston samples have moderate to high  $\text{NO}_x$ , the range being 4.4 to 24 ppb.

[37] The individual compounds and classes of compounds contributing to anthropogenic hydrocarbon reactivity are shown in Figure 12. High-reactivity samples from Houston have a unique composition, because of the large fraction of reactivity from ethene, propene, and butenes.

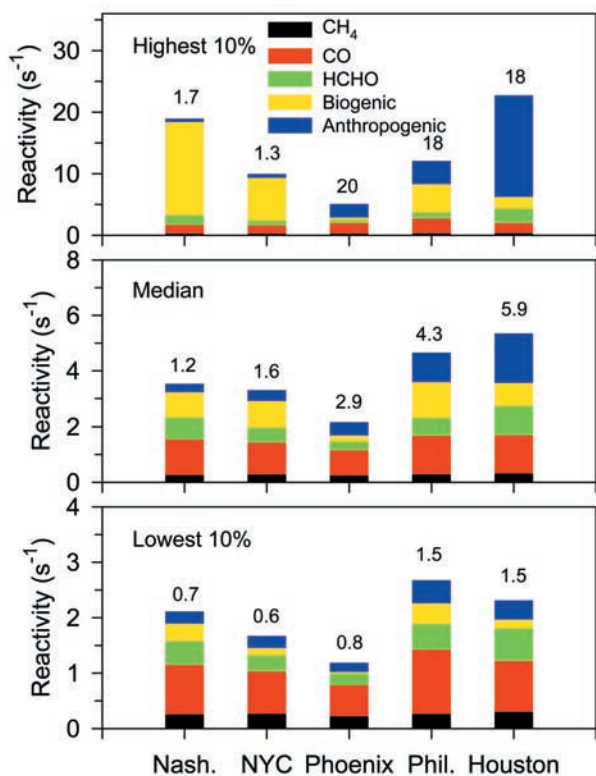
## 6. Five-City Intercomparison: Ozone Production Rate

[38] Ozone production rates have been calculated with the CSS model yielding the frequency distributions shown in Figure 13. As previously described, measurements of radical precursors and VOCs are incomplete. Table 2 indicates how missing radical sources and VOC reactivity impact calculated values of  $\text{P}(\text{O}_3)$ . Except for low  $\text{NO}_x$  conditions where  $\text{P}(\text{O}_3)$  is insensitive to  $\text{VOC}_R$ , missing observations will cause an underestimate of  $\text{P}(\text{O}_3)$ , the magnitude of which is difficult to estimate without additional information.

[39] Within a city,  $\text{P}(\text{O}_3)$  varies by 1 to 2 orders of magnitude, reflecting similarly large variations in  $Q$ ,  $\text{NO}_x$ , and VOCs. Looking across the graph at a constant percentile, there is a several-fold city to city difference in  $\text{P}(\text{O}_3)$ . Over most of the distribution,  $\text{P}(\text{O}_3)$  are in the order: Philadelphia > Nashville > NYC > Phoenix. Houston's



**Figure 10.** Frequency distribution for OH reactivity of anthropogenic hydrocarbons during five field campaigns. OH reactivity is defined in equation (1). Format is the same as Figure 3.



**Figure 11.** Components of OH-VOC reactivity ( $VOC_R$ ) for five cities. Data subsets have (top) high values for  $VOC_R$  (top 10% of distribution), (middle) median values of  $VOC_R$  (central 20% of distribution), and (bottom) low values of  $VOC_R$  (bottom 10% of distribution). Average  $NO_x$  concentration in ppb is indicated for each data subset. In calculating the averages, one point with extremely high  $NO_x$  has been omitted from the Philadelphia high- $VOC_R$  subset.

$P(O_3)$  is almost identical to Philadelphia's in the lower half of the distribution. Between the 70th and 90th percentiles,  $P(O_3)$  in Houston is 15–35% higher than in Philadelphia. Above the 90th percentile,  $P(O_3)$  in Houston is 40% to more than 300% greater than in Philadelphia. Our task is to understand the  $P(O_3)$  values in Figure 13 in relation to the precursor results presented in the preceding section.

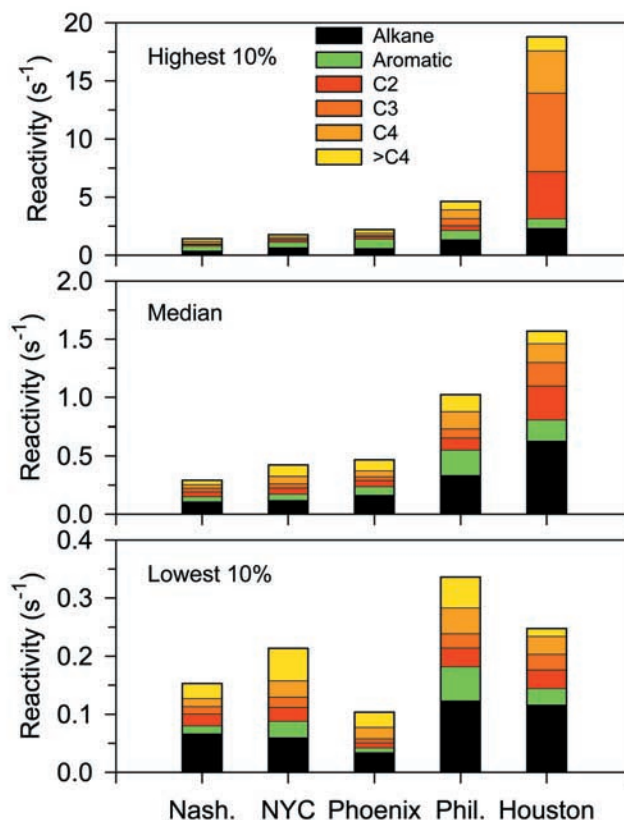
### 6.1. O<sub>3</sub> Isopleth Style Diagrams

[40] In Figure 14 we use a two-dimensional representation in the style of an O<sub>3</sub> isopleth diagram to show how  $P(O_3)$  depends on total VOC reactivity and  $NO_x$  concentration [Seinfeld and Pandis, 1997]. Total VOC reactivity is used as an independent variable instead of anthropogenic hydrocarbon concentration since  $P(O_3)$  depends on the former more than the latter [Chameides et al., 1992; Thielmann et al., 2001]. In a conventional O<sub>3</sub> isopleth diagram the independent variable, O<sub>3</sub>, is obtained from a model calculation which can be repeated for any range of  $NO_x$  and VOCs. In our case we have discrete sample points so that only a portion of each graph is filled in. Furthermore, unlike a conventional isopleth diagram, our data set has three dimensions so that points which occupy the same place on the 2-D graph can have different

values of  $Q$ . The more polluted samples in these plots fall within the range of values reported by Chameides et al. [1992] for urban/suburban sites, namely, 5–100 ppb  $NO_x$  and 4–50 s<sup>-1</sup> VOC reactivity (20–250 ppb C propylene equivalents). Samples with the highest 10% values of  $P(O_3)$  in each city are identified in Figure 14 by drawing a bolder border around the data point.

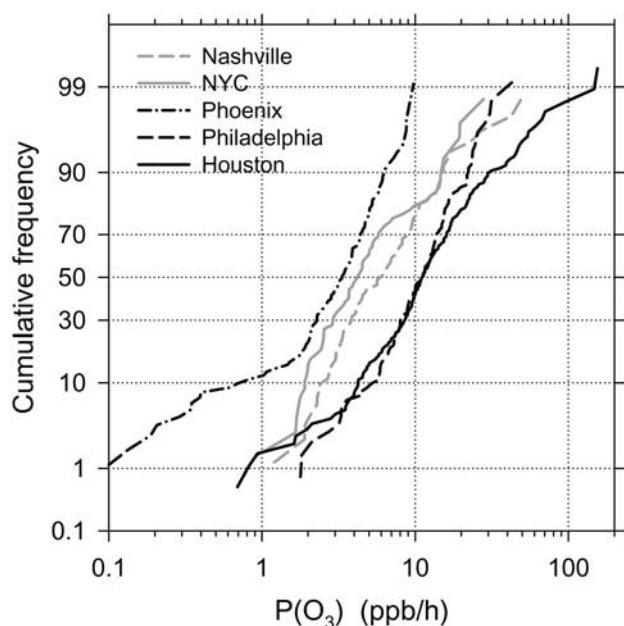
[41] In Nashville and NYC, there is virtually no correlation between  $NO_x$  and VOC reactivity, because VOC reactivity is influenced strongly by biogenic emissions occurring mainly from regions without  $NO_x$  sources. High  $NO_x$  points in Nashville are primarily due to traverses through power plant plumes which are not significant sources of VOC reactivity. For Phoenix, Philadelphia, and Houston, the sample data points lie more or less along an upward sloping line, indicating a collocation of  $NO_x$  and VOC sources such that air masses with high concentrations of one pollutant tend to have high concentrations of the other.

[42] Diagonal lines with constant values of the ratio of VOC reactivity to  $NO_x$  concentration have been added to



**Figure 12.** Categories of hydrocarbons contributing to OH-VOC reactivity of anthropogenic hydrocarbons for five cities. Data subsets have (top) high values for anthropogenic hydrocarbon reactivity (top 10% of distribution), (middle) median values (central 20% of distribution), and, (bottom) low values (bottom 10% of distribution). High-olefin proportion in low-reactivity subset is partially an artifact, formed in the canisters [Ramacher et al., 1997].





**Figure 13.** Frequency distribution for O<sub>3</sub> production rate, P(O<sub>3</sub>), calculated from CSS model during five field campaigns. Format is the same as Figure 3.

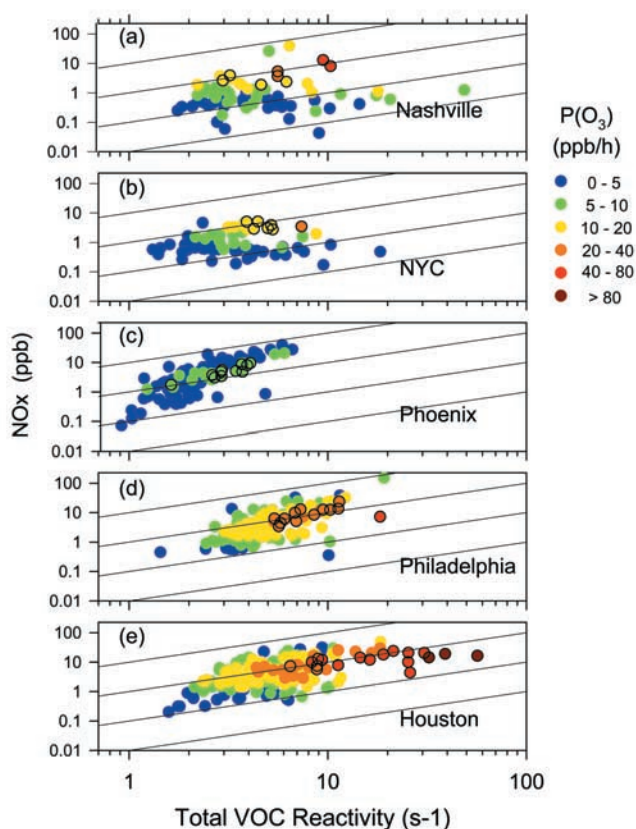
Figure 14. These isolines differ from each other by a factor of 10 showing that the entire data set spans 3 orders of magnitude in VOC reactivity to NO<sub>x</sub> ratio. For Phoenix and Philadelphia and for Houston samples with  $k < 10 \text{ s}^{-1}$ , the VOC<sub>R</sub> to NO<sub>x</sub> ratio increases in the low-concentration samples. This trend is particularly apparent in the Phoenix data sets. In previous Phoenix studies it was found that the low-concentration samples resemble the high-concentration ones subject to chemical aging caused by reactions with OH radical and subject to dilution with relatively clean background air [Kleinman *et al.*, 2002b, 2003b]. Both processes tend to remove NO<sub>x</sub> at a faster rate than VOC reactivity.

[43] A vertical cross section through Figure 14d, depicted in Figure 15, shows how P(O<sub>3</sub>) depends on NO<sub>x</sub> concentration. On the basis of theory and O<sub>3</sub> isopleth calculations (see Table 2 and, e.g., Sillman *et al.* [1990] and Seinfeld and Pandis [1997]) we expect that P(O<sub>3</sub>) increases with NO<sub>x</sub> at low NO<sub>x</sub> concentration, reaches a maximum, and then decreases at still higher values of NO<sub>x</sub>. This behavior can be traced back to the two effects that NO<sub>x</sub> has on photochemistry. NO<sub>x</sub> is an essential catalyst for O<sub>3</sub> production, but at high concentration its role as a reactant that removes free radicals dominates. In constructing Figure 15 we have selected a subset of P(O<sub>3</sub>) calculations from Philadelphia which have a relatively narrow range of VOC<sub>R</sub> and Q. Except for some scatter which can be explained by the finite range of VOC<sub>R</sub> and Q, P(O<sub>3</sub>) has the expected dependence on NO<sub>x</sub> concentration. In this case P(O<sub>3</sub>) has a maximum value at a NO<sub>x</sub> concentration of 6 ppb. Similar graphs can be drawn for different VOC<sub>R</sub> and for different cities. At a higher VOC<sub>R</sub>, the P(O<sub>3</sub>) maximum shifts to higher NO<sub>x</sub> concentration and vice versa. Figure 15 also shows values of L<sub>N</sub>/Q from which we can see that the P(O<sub>3</sub>) maximum occurs when L<sub>N</sub>/Q ≈ 2/3 as predicted [Kleinman *et al.*,

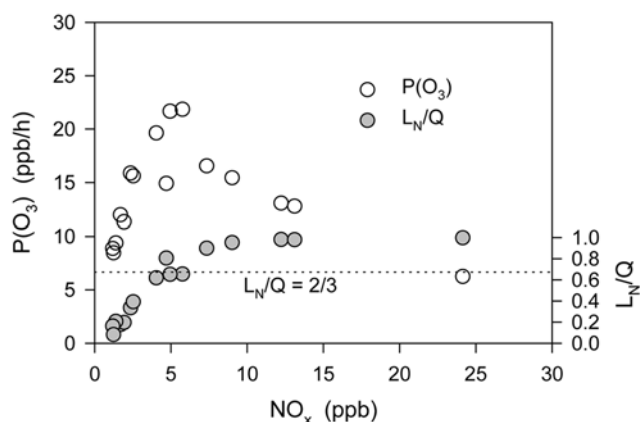
1997; Kleinman, 2004]. This maximum is analogous to the O<sub>3</sub> ridge line appearing in an O<sub>3</sub> isopleth diagram.

[44] A maximum in P(O<sub>3</sub>) with respect to NO<sub>x</sub> is not apparent in most of the vertical cross section that can be constructed from Figure 14. Either there are too few points to define the P(O<sub>3</sub>) versus NO<sub>x</sub> curve or the points are all situated on one side or the other of the P(O<sub>3</sub>) maximum. The P(O<sub>3</sub>) maximum can be best visualized in Philadelphia and Houston because there are points above and below it (at higher and lower NO<sub>x</sub>). In Phoenix, most of the data are on the high-NO<sub>x</sub> side of the P(O<sub>3</sub>) maximum, where P(O<sub>3</sub>) decreases as NO<sub>x</sub> is increased. Data points are more scattered in Nashville and NYC, but the qualitative appearance is that the expected P(O<sub>3</sub>) maximum lies above most of the data points.

[45] By looking at L<sub>N</sub>/Q we can get a more direct answer to the questions of where data points lie in relation to the P(O<sub>3</sub>) maximum and whether P(O<sub>3</sub>) is NO<sub>x</sub> or VOC limited. Figure 16 shows values of L<sub>N</sub>/Q for the five-city data set,

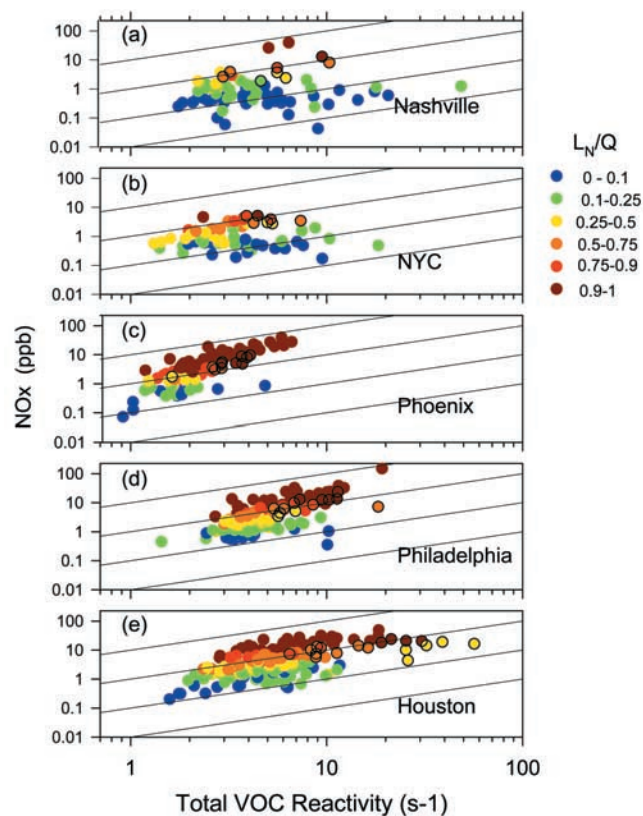


**Figure 14.** Ozone production rates for five cities displayed as color-coded symbols as a function of VOC<sub>R</sub> and NO<sub>x</sub> concentration: (a) Nashville, (b) NYC, (c) Phoenix, (d) Philadelphia, and (e) Houston. Plots are in the style of an O<sub>3</sub> isopleth diagram. Data are ordered from low values of P(O<sub>3</sub>) to high values, so high-P(O<sub>3</sub>) samples in some cases are hiding low-P(O<sub>3</sub>) samples underneath. Points with the same value of NO<sub>x</sub> and VOC<sub>R</sub> can differ by having different values of Q. Samples having high values of P(O<sub>3</sub>) in each city (top 10% of distribution) are indicated by circles with a bold outline. Isolines of constant VOC<sub>R</sub>/NO<sub>x</sub> are shown by diagonal lines.



**Figure 15.**  $P(\text{O}_3)$  and  $L_N/Q$  versus  $\text{NO}_x$  concentration for Philadelphia samples with  $\text{VOC}_R = 5\text{--}7 \text{ s}^{-1}$  and  $Q = 2\text{--}4 \text{ ppb h}^{-1}$ . These data points correspond to a thin vertical slice of Figure 14d, with a relatively narrow range of  $\text{VOC}_R$  and  $Q$ . Theory predicts that  $P(\text{O}_3)$  should have a peak value at  $L_N/Q = 2/3$ , where  $\partial P(\text{O}_3)/\partial[\text{NO}_x] = 0$ , indicated by the dotted line.

presented in the same O<sub>3</sub> isopleth style format as the  $P(\text{O}_3)$  results in Figure 14. We have seen from Figure 15 that the  $P(\text{O}_3)$  maximum where  $\partial P(\text{O}_3)/\partial[\text{NO}_x] = 0$  occurs at  $L_N/Q = 2/3$ , which falls within the range of the orange



**Figure 16.**  $L_N/Q$  (fraction of radicals removed by reaction with  $\text{NO}_x$ ) for five cities displayed as color-coded symbols as a function of  $\text{VOC}_R$  and  $\text{NO}_x$  concentration.  $L_N/Q$  is determined from CSS calculations. Plots are in the style of an O<sub>3</sub> isopleth diagram using the same format as Figure 14.

**Table 4.** Characteristics of High-, Median-, and Low- $P(\text{O}_3)$  Samples

Parameter <sup>a</sup>	City				
	Nashville	NYC	Phoenix	Philadelphia	Houston
<i>High-<math>P(\text{O}_3)</math> Samples<sup>b</sup></i>					
$P(\text{O}_3)$ , $\text{ppb h}^{-1}$	20	17	8.3	25	49
$\text{O}_3$ , ppb	83	66	57	90	89
$Q$ , $\text{ppb h}^{-1}$	5.9	3.2	1.4	4.6	6.9
$\text{NO}_x$ , ppb	3.8	3.5	4.8	8.5	12.6
$\text{VOC total}$ , $\text{s}^{-1}$	5.6	5.0	2.9	7.2	17.7
$\text{VOC anthropogenic}$ , $\text{s}^{-1}$	0.37	0.88	1.12	2.0	11.3
$L_N/Q$	0.64	0.64	0.94	0.81	0.67
<i>Median-<math>P(\text{O}_3)</math> Samples<sup>b</sup></i>					
$P(\text{O}_3)$ , $\text{ppb h}^{-1}$	5.9	4.2	3.3	11.2	11.1
$\text{O}_3$ , ppb	71	42	60	64	72
$Q$ , $\text{ppb h}^{-1}$	3.3	1.1	0.76	2.4	2.7
$\text{NO}_x$ , ppb	0.83	0.83	3.8	2.1	2.7
$\text{VOC total}$ , $\text{s}^{-1}$	3.1	2.3	2.1	4.0	4.3
$\text{VOC anthropogenic}$ , $\text{s}^{-1}$	0.26	0.29	0.46	0.92	1.3
$L_N/Q$	0.12	0.26	0.96	0.39	0.49
<i>Low-<math>P(\text{O}_3)</math> Samples<sup>b</sup></i>					
$P(\text{O}_3)$ , $\text{ppb h}^{-1}$	2.2	1.7	0.34	3.3	3.3
$\text{O}_3$ , ppb	66	36	58	64	47
$Q$ , $\text{ppb h}^{-1}$	2.5	1.1	0.29	1.7	1.7
$\text{NO}_x$ , ppb	0.33	0.28	0.56	0.61	0.64
$\text{VOC total}$ , $\text{s}^{-1}$	4.3	3.5	1.7	3.3	3.6
$\text{VOC anthropogenic}$ , $\text{s}^{-1}$	0.19	0.19	0.20	0.64	0.42
$L_N/Q$	0.04	0.07	0.04	0.11	0.07

<sup>a</sup>Median values over data subset. See Table 2 for nomenclature.

<sup>b</sup>High subset has top 10% of frequency distribution, median has central 20%, and low has bottom 10%.

symbols in Figure 16. According to Table 2 the transition between  $\text{NO}_x$  and VOC-limited chemistry occurs at  $L_N/Q = 1/2$ , at the interface between the yellow and orange symbols in Figure 16. Most of the Nashville and NYC data sets is  $\text{NO}_x$  limited; most of Phoenix is VOC limited, and Philadelphia and Houston are mixed. Most of the high- $P(\text{O}_3)$  subset in Phoenix and about half of the high  $P(\text{O}_3)$  subset in Philadelphia is strongly VOC limited (brown symbols with  $L_N/Q > 0.9$ ). The other cities have a wider range of  $L_N/Q$  values for their high  $P(\text{O}_3)$  subsets.

## 6.2. High-, Median-, and Low- $P(\text{O}_3)$ Samples

[46] In Table 4 we examine the conditions that lead to high-, median-, and low- $\text{O}_3$  production rates in the five cities. Values in Table 4 are medians over a data subset. A few instances are noted where the median values do not give a representative picture of conditions because a parameter has a bimodal or very wide distribution.

[47] The dominant type of low  $P(\text{O}_3)$  samples is from an unpolluted low- $\text{NO}_x$  rural environment. Low  $P(\text{O}_3)$  can also occur under high- $\text{NO}_x$  and low- $Q$  conditions and there is one such sample in Phoenix, four in Philadelphia, and five in Houston. These samples only slightly affect the median values reported in the low- $P(\text{O}_3)$  portion of Table 4. In all cases except Phoenix, net  $\text{O}_3$  production rates (not shown) are significantly positive and if maintained over a full day, which requires continued emission inputs, could give rise to a 10–20 ppb increase in  $\text{O}_3$  concentration.  $P(\text{O}_3)$  in Phoenix is lower than elsewhere primarily because of low  $Q$ , due in part to low water vapor and in part to samples taken early in the morning or late in the afternoon. Anthropogenic

**Table 5.** Precursor Limits for Samples With High P(O<sub>3</sub>)

P(O <sub>3</sub> ), ppb h <sup>-1</sup>	Q, ppb h <sup>-1</sup>	NO <sub>x</sub> , ppb	VOC <sub>R</sub> , s <sup>-1</sup>	Fraction <sup>a</sup>
>25	>3	5–24	>5	33/35
>30	>3.5	7–24	>6	21/23
>40	>3.5	7–24	>8	17/18
>50	>5.5	8–24	>10	8/9
>60	>6	10–21	>15	6/6

<sup>a</sup>Number of samples meeting Q, NO<sub>x</sub>, and VOC<sub>R</sub> criteria divided by total number of samples with P(O<sub>3</sub>) greater than stated rate. See Table 2 for nomenclature.

hydrocarbons contribute little to the total VOC reactivity except in Philadelphia.

[48] The median P(O<sub>3</sub>) samples differ from the low P(O<sub>3</sub>) cases in having higher values of most pollutants, especially NO<sub>x</sub>. There is a wide city to city range in L<sub>N</sub>/Q; all of the Nashville samples are low NO<sub>x</sub>, all but one of the Phoenix samples are high NO<sub>x</sub>, and the other three cities have both low- and high-NO<sub>x</sub> samples in the median P(O<sub>3</sub>) category. As with the low-P(O<sub>3</sub>) samples, Philadelphia and Houston are quite similar in P(O<sub>3</sub>) and precursors. Phoenix has more NO<sub>x</sub> than either Philadelphia or Houston, which combined with its low rate of radical production and its lower VOC reactivity causes it to be in a high-NO<sub>x</sub> state where the increased NO<sub>x</sub> leads to lower P(O<sub>3</sub>). In all five cities most of the VOC reactivity comes from compounds other than anthropogenic hydrocarbons.

[49] The high-P(O<sub>3</sub>) samples in Table 4 are identified on the two-dimensional diagrams for P(O<sub>3</sub>) and L<sub>N</sub>/Q in Figures 14 and 16, from which one can see the range of NO<sub>x</sub> concentration and VOC reactivity in this data subset. For all five cities, radical production rate, NO<sub>x</sub> concentration, and VOC reactivity are higher in the high-P(O<sub>3</sub>) subset as compared with the median P(O<sub>3</sub>) subset. Nashville, NYC, and Philadelphia have comparable P(O<sub>3</sub>); Phoenix is much lower and Houston is a factor of 2 higher. High-P(O<sub>3</sub>) samples in Nashville and NYC have high concentrations of biogenic hydrocarbons, while the distinctive feature of Houston is the very high reactivity from anthropogenic hydrocarbons [Kleinman *et al.*, 2002a]. Table 4 indicates that in the high-P(O<sub>3</sub>) samples, L<sub>N</sub>/Q is near the ridge line for Nashville, NYC, and Houston and above the ridge line for Phoenix and Philadelphia. Individual values of L<sub>N</sub>/Q in Nashville, NYC, and Houston, however, vary between 0.25 and 0.97.

[50] In Table 5 we summarize the minimum Q, NO<sub>x</sub> and VOC<sub>R</sub> found in samples with high P(O<sub>3</sub>). Samples contrib-

uting to Table 5 have a wide range of L<sub>N</sub>/Q, but most are VOC limited. For example, 30 out of 35 samples with P(O<sub>3</sub>) > 25 ppb h<sup>-1</sup> have L<sub>N</sub>/Q > 0.5.

## 7. Discussion

[51] In many respects Philadelphia is our base case, a large urban area, with nearby utilities and industrial sites that contribute but do not overwhelm the urban emissions. New York City probably has many features in common with Philadelphia, but a direct comparison based on our data set is difficult because of differences in sampling strategy. Nashville is notable for its high isoprene emissions and large power plants, Phoenix has very low humidity and a low VOC<sub>R</sub>/NO<sub>x</sub> ratio, and Houston has high concentrations of light olefins from the nearby petrochemical industry. In this section we discuss these very prominent differences along with two common features, namely diurnal trends and the occurrence of high-P(O<sub>3</sub>) conditions on the morning of a high-O<sub>3</sub> day.

### 7.1. Morning to Afternoon Photochemical Development

[52] Of the five cities, Phoenix and Philadelphia are best suited for examining morning to afternoon trends in photochemistry. In both cities morning and afternoon flights repetitively covered a common area near the urban centers as illustrated in Figures 1c and 1d. Results based on samples taken in those regions are shown in Table 6. Concentrations follow a typical diurnal pattern in which emitted pollutants, NO<sub>x</sub> and VOCs, decrease during the day because of a deepening boundary layer and photochemistry, while O<sub>3</sub> which is a product of the photochemistry increases. The NO<sub>x</sub> to NO<sub>y</sub> ratio decreases in the afternoon showing that the afternoon air masses are more aged than those from the morning [Kleinman *et al.*, 2003b]. Morning and afternoon

**Table 6.** Diurnal Evolution of Photochemistry

Parameter <sup>a</sup>	Phoenix		Philadelphia	
	Morning	Afternoon	Morning	Afternoon
CSS calculations	34	23	57	34
Time, LST	1018	1529	1047	1326
Altitude, m	1067	1052	440	581
O <sub>3</sub> , ppb	55	69	61	84
H <sub>2</sub> O (v mix ratio)	0.020	0.019	0.007	0.006
NO <sub>x</sub> /NO <sub>y</sub>	0.50	0.42	0.43	0.16
Q, ppb h <sup>-1</sup>	1.1	0.74	2.2	3.4
NO <sub>x</sub> , ppb	4.5	3.4	6.0	2.3
VOC <sub>R</sub> , s <sup>-1</sup>	2.6	2.4	5.1	4.6
P(O <sub>3</sub> ), ppb h <sup>-1</sup>	4.6	4.2	10.1	12.7
L <sub>N</sub> /Q	0.96	0.93	0.90	0.37

<sup>a</sup>Median values over data subset. See Table 2 for nomenclature.



**Table 7.** High O<sub>3</sub> Events

City	Date <sup>a</sup>	Location	Morning <sup>b</sup>				Afternoon <sup>c</sup>		Morning-Afternoon <sup>d</sup>	
			Time, LST	O <sub>3</sub> , ppb	P(O <sub>3</sub> ), ppb h <sup>-1</sup>	L <sub>N</sub> /Q	Time, LST	O <sub>3</sub> , ppb	ΔO <sub>3</sub> , ppb	ΔO <sub>3</sub> /Δt, ppb h <sup>-1</sup>
Nashville	11 July	south side of city	0950 <sup>e</sup>	74	32	0.94	1441	130	56	12
	11 July	10 km NW of city	1049 <sup>e</sup>	76	35	0.39			54	14
Philadelphia	31 July	SW of city	0950	78	8	1.00	1314 (1330)	147 (161)	83	23
	31 July	NE of city	0956	69	25	0.95	1445 (1430)	138 (151)	82	18
	31 July	NE of city	0957	66	25	0.95			85	19
	31 July	NE of city	1041	70	31	0.92			81	16
Houston	26 Aug.	Ship Channel	0904	40	48	0.96	1352	152	112	24
	26 Aug.	Ship Channel	1018	81	50	0.94			71	20
	26 Aug.	Ship Channel	1020	82	140	0.49			69	20
	29 Aug.	Ship Channel	0958	72	54	0.94	1554	211	139	23
		Ship Channel	1001	74	61	0.97			137	23
		Ship Channel	1046	108	67	0.72			103	20
	12 Sept.	Ship Channel, O <sub>3</sub> max west side of city	1048	48	55	0.29	1448	148	100	25

<sup>a</sup>References are as follows: Nashville [Daum *et al.*, 2000a], Philadelphia [Kleinman *et al.*, 2004], Houston 26 August [Daum *et al.*, 2004], Houston 29 August [Daum *et al.*, 2003], Houston 12 September [Berkowitz *et al.*, 2004a].

<sup>b</sup>Peak values of P(O<sub>3</sub>) in source regions contributing to afternoon O<sub>3</sub> maximums are given. See Table 2 for nomenclature.

<sup>c</sup>Peak O<sub>3</sub> concentration is given. Values in parentheses are from surface observations at Chester, Pennsylvania (161 ppb), and Bristol, Pennsylvania (151 ppb).

<sup>d</sup>ΔO<sub>3</sub>/Δt is ratio of the change in O<sub>3</sub> occurring between the morning P(O<sub>3</sub>) determination and the afternoon O<sub>3</sub> maximum. Surface values of O<sub>3</sub> are used for Philadelphia.

<sup>e</sup>Nashville morning observations and calculations are from TVA helicopter.

values of P(O<sub>3</sub>) are comparable. This is in contrast to NO<sub>x</sub>-limited rural areas where P(O<sub>3</sub>) decreases by a large factor in the afternoon because of a corresponding decrease in NO<sub>x</sub> concentration [Kleinman *et al.*, 1995]. Median values of L<sub>N</sub>/Q in both cities indicate strongly VOC-limited chemistry in the morning.

[53] Photochemistry in Philadelphia proceeds more rapidly than in Phoenix causing a larger morning to afternoon decrease in NO<sub>x</sub>/NO<sub>y</sub>. While the median afternoon Philadelphia sample has made a transition to being NO<sub>x</sub> limited (L<sub>N</sub>/Q < 0.5), the median Phoenix sample is still strongly VOC limited. The transition from VOC to NO<sub>x</sub>-limited conditions depends mainly on a decrease in NO<sub>x</sub> concentration. This decrease can occur by atmospheric dilution [Honoré *et al.*, 2000] or photochemical processing. The latter pathway is stoichiometrically limited by the radical production rate since it requires one radical to remove one molecule of NO<sub>x</sub>. Although the transition to NO<sub>x</sub>-limited conditions depends also on VOC reactivity, ventilation, and the rate at which NO<sub>x</sub> increases from emissions, the stoichiometric constraint in conjunction with a low radical production rate is one reason why Phoenix stays VOC limited in the afternoon.

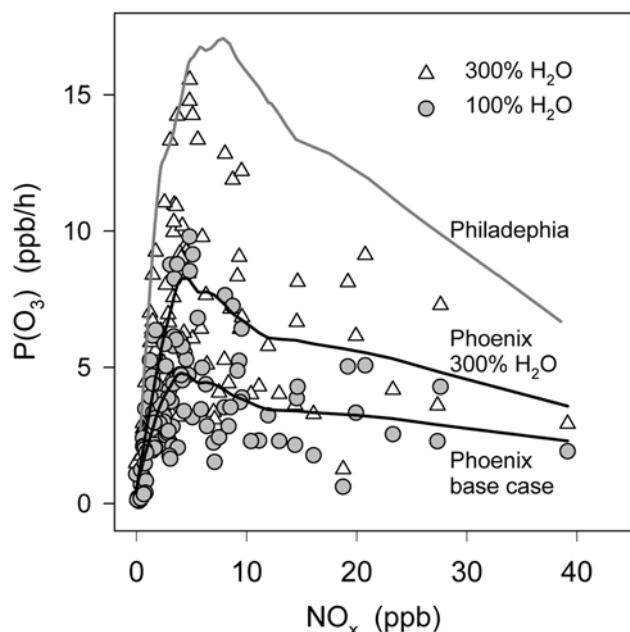
## 7.2. High-O<sub>3</sub> Events are Preceded by High P(O<sub>3</sub>)

[54] From the five field campaigns we have six cases in which P(O<sub>3</sub>) was calculated during a morning flight followed by the observation of high O<sub>3</sub> concentrations later in the day, during an afternoon flight. Morning and afternoon observations, however, are not related to each other in a strict Lagrangian sense. Instead, the morning and afternoon measurements are of an air mass observed in two stages of its diurnal evolution. Table 7 summarizes the morning and afternoon observations and calculations. The last column in this Table, ΔO<sub>3</sub>/Δt, is the time rate of change of O<sub>3</sub> over the period between the morning and

afternoon observations, a qualitative metric for O<sub>3</sub> production during midday hours. We note that our morning observations are taken after the photochemistry is well under way and that the afternoon observations do not necessarily capture the peak O<sub>3</sub>. All of the cases in Table 7 are described more fully in papers dealing with those specific episodes. In brief, a defining feature of the high-O<sub>3</sub> events in Table 7 was poor ventilation allowing pollutants to accumulate. In Nashville stagnation was caused by a synoptic-scale high-pressure cell [McNider *et al.*, 1998], in Philadelphia by the interaction of a mesoscale low with the Appalachian lee trough [Kleinman *et al.*, 2004], and in Houston by flow reversal of the land-bay breeze [Nielson-Gammon, 2002; Daum *et al.*, 2003, 2004].

[55] Same-day O<sub>3</sub> increase varies from ~50 ppb in the Nashville episode up to 140 ppb on 29 August in Houston. Except for the SW Philadelphia plume, P(O<sub>3</sub>) varied from 25 to 140 ppb h<sup>-1</sup>. The P(O<sub>3</sub>) determination SW of Philadelphia happened to coincide with extremely high NO<sub>x</sub> concentration (>100 ppb) because of local sources almost directly underneath the flight path of the G-1. Under reasonable assumptions, P(O<sub>3</sub>) outside of the local NO<sub>x</sub> plume is about 30 ppb h<sup>-1</sup>. With this revision, each of the six high-O<sub>3</sub> events occurs after a morning of photochemistry in which P(O<sub>3</sub>) are equal to or greater than 25 ppb h<sup>-1</sup>. All of the P(O<sub>3</sub>) calculations, except two in Houston (with very high anthropogenic VOC reactivity) and one in Nashville (with high isoprene concentration), indicate that O<sub>3</sub> is being produced under VOC-limited conditions with L<sub>N</sub>/Q greater than 0.5, in many cases approaching 1. As Table 6 shows, high values of L<sub>N</sub>/Q are typical for morning samples taken in high-concentration source regions.

[56] The calculated morning P(O<sub>3</sub>) are as much as a factor of 7 greater than the average rate of O<sub>3</sub> increase i.e., ΔO<sub>3</sub>/Δt. Factors that could explain this discrepancy



**Figure 17.**  $P(\text{O}_3)$  as a function of  $\text{NO}_x$  for Phoenix samples with actual water vapor concentration and after water vapor was increased by 300%. Curves give Lowess fit to data points. For comparison, the Lowess fit to Philadelphia data points is also shown.

are chemical loss processes, dilution, and the depletion of  $\text{O}_3$  precursors. The last factor is expected to be particularly significant in Houston as the very high  $P(\text{O}_3)$  (i.e.,  $140 \text{ ppb h}^{-1}$ ) cannot be sustained as a plume is advected away from the point sources that supplied reactive olefins. The difference between  $P(\text{O}_3)$  and  $\Delta\text{O}_3/\Delta t$  is smallest in Philadelphia, where plume transport is occurring along the I95 corridor which can provide a continuous supply of  $\text{NO}_x$  and VOCs. Our data set supports the conclusion that high  $P(\text{O}_3)$  is a necessary condition for the occurrence of  $\text{O}_3$  episodes. High  $P(\text{O}_3)$ , however, is not a sufficient condition as there are examples in which elevated  $P(\text{O}_3)$  occurs only in a small area because of local emissions, or cases where ventilation dilutes the  $\text{O}_3$  over a large area.

### 7.3. Phoenix: Dry With Low VOC Reactivity

[57] Among Phoenix's distinctive features is very low atmospheric humidity. A sensitivity calculation was performed in which the water vapor concentration in the Phoenix samples was increased by 300%, bringing it up to the average value observed in the other four cities [Kleinman, 2004]. Figure 17 shows calculated values of  $P(\text{O}_3)$  before and after the water vapor increase. By far the largest effect of the water vapor increase is to triple radical production from photolysis of  $\text{O}_3$ . This translates into a less than threefold increase in  $Q$ , as  $Q(\text{O}_3)$  represents about 70% of the total. On average,  $P(\text{O}_3)$  increased by 58%. Individual samples show more or less of an increase depending on the values for  $Q(\text{O}_3)/Q$  and where the sample is in the low- $\text{NO}_x$  to high- $\text{NO}_x$  continuum (see Table 2).

[58] Increasing  $\text{H}_2\text{O}$  by 300% still leaves Phoenix with a lower  $P(\text{O}_3)$  than the other two high- $\text{NO}_x$  cities. This is due to two factors: Phoenix still (with 300%  $\text{H}_2\text{O}$ ) has a low radical

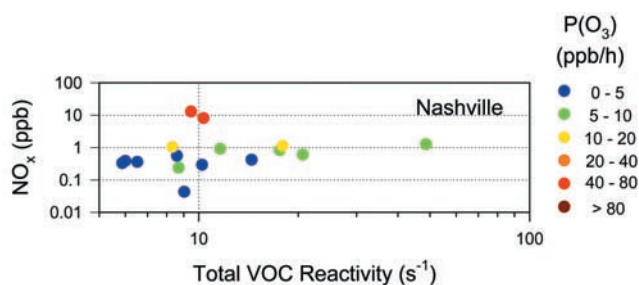
production rate because of low concentrations of  $\text{O}_3$  and HCHO and, on average, higher solar zenith angles (Figure 6). Also Phoenix has a  $\text{VOC}_R/\text{NO}_x$  ratio about a factor of 2 lower than in Philadelphia or Houston (Figures 8 and 9). Table 2 shows that the effect of this ratio on  $P(\text{O}_3)$  varies from no effect in the low  $\text{NO}_x$  regime to a direct proportionality in the high- $\text{NO}_x$  regime. Figure 16 indicates a predominance of high- $\text{NO}_x$  samples in Phoenix.

[59] Several factors contribute to the low  $\text{VOC}_R/\text{NO}_x$  ratio in Phoenix. Sparse vegetation results in low concentrations of biogenics and contributes to low concentrations of HCHO [Lee et al., 1998], an oxidation product of isoprene. Anthropogenic hydrocarbon reactivity in Phoenix is about a factor of 2 lower than in Philadelphia or Houston (leaving aside the very high reactivity Houston samples), even though  $\text{NO}_x$  concentrations are similar (Figures 8 and 10). There appear to be large city to city differences in anthropogenic emissions: either a large admixture of VOCs not associated with  $\text{NO}_x$  in Philadelphia and Houston or VOC lean emissions from mobile sources in Phoenix.

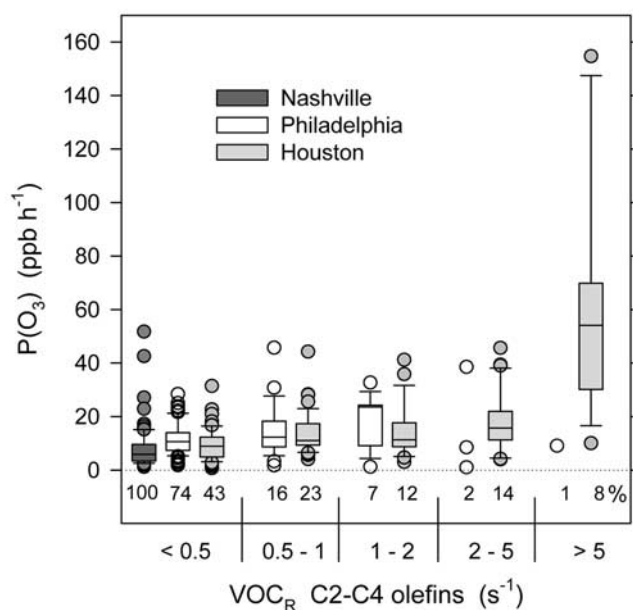
### 7.4. Effects of Isoprene in Nashville

[60] Isoprene plays an important role in  $\text{O}_3$  formation in rural areas [Trainer et al., 1987], cities [Chameides et al., 1988], and power plant plumes [Luria et al., 2000; Ryerson et al., 2001]. It is very reactive ( $k_{\text{OH}} = 9.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ) so that even levels below ppb can dominate the overall OH-VOC reactivity. Of the five cities studied, isoprene concentrations were highest in Nashville, characteristic of conditions in the southeastern United States. Figure 11 shows that the high-reactivity Nashville samples are dominated by biogenics. Isoprene concentrations in Nashville ranged from 0.01 ppb to 10.2 ppb with a median of 0.2 ppb and an average of 0.6 ppb. A frequency distribution given by Nunnermacker et al. [1998] provides a pictorial representation of how the average is dominated by samples at the high-concentration end of the distribution.

[61] Figure 18 is an  $\text{O}_3$  isopleth style plot for  $P(\text{O}_3)$  restricted to Nashville samples in which isoprene plus equilibrium MVK and MACR supplies more than half of the total VOC reactivity. The 16 points on this graph fall into two categories: 14 samples have low  $\text{NO}_x$  concentration (0.6–1.3 ppb) while two have high  $\text{NO}_x$  concentration (8 and 13 ppb). The later two points have much higher  $P(\text{O}_3)$ ,



**Figure 18.** Ozone production rates for Nashville displayed as color-coded symbols as a function of  $\text{VOC}_R$  and  $\text{NO}_x$  concentration. Data points are a subset of those shown in Figure 14 in which isoprene plus oxidation products, methyl vinyl ketone and methacrolein, contribute more than 50% of the total OH reactivity.



**Figure 19.** Box plot showing range of  $P(\text{O}_3)$  for samples from Nashville, Philadelphia, and Houston as a function of OH reactivity from the light olefins, ethene, propene, and butenes (1-butene, i-butene, *cis*-2-butene, *trans*-2-butene, and 1,3 butadiene). Box shows median value and interquartile range (25th to 75th percentile of distribution). Caps indicate 10th and 90th percentiles; circles indicate points outside of the 10th to 90th percentile range. Four Philadelphia samples with OH reactivity  $>2 \text{ s}^{-1}$  are indicated by circles. Two Nashville samples with light olefin reactivity equal to 0.6 and  $0.7 \text{ s}^{-1}$  have been grouped with the lowest reactivity subset. The percent of samples in each category is provided beneath the box plot.

52 and  $43 \text{ ppb h}^{-1}$ , respectively. The samples with low  $\text{NO}_x$  all have  $L_N/Q$  below 0.15 and to a good approximation,  $P(\text{O}_3)$  is proportional to  $Q^{1/2} [\text{NO}_x]$ , i.e., independent of VOC reactivity, as is typical of rural conditions. The high- $\text{NO}_x$  samples have  $L_N/Q = 0.74$  and  $0.93$ , respectively, and are in a regime where  $P(\text{O}_3)$  is almost proportional to  $\text{VOC}_R$ . The two high- $\text{NO}_x$  samples were taken on the western edge of the Nashville urban area. Goldan *et al.* [2000] present emission data and VOC observations indicating high emission rates and ambient isoprene in that region. Although our samples by no means provide a statistically representative geographic coverage, according to our data set it was uncommon to have very high  $P(\text{O}_3)$  because of the co-occurrence of  $\text{NO}_x$  and isoprene. A sampling strategy focusing on high isoprene emission rate regions near  $\text{NO}_x$  sources might have reached a different conclusion.

[62] Isoprene has another effect, which does not appear in the calculation of an instantaneous  $\text{O}_3$  production rate. Observations and calculations indicate that  $\text{O}_3$  production efficiency increases with VOCs in general [Lin *et al.*, 1988; Kleinman *et al.*, 2002b] and isoprene in particular [Luria *et al.*, 2000; Ryerson *et al.*, 2001]. Even though isoprene in a low  $\text{NO}_x$  environment may not cause  $\text{O}_3$  to be produced faster, it has the effect of lowering OH radical concentra-

tion, causing the  $\text{NO}_x$  to last longer and ultimately produce more  $\text{O}_3$ .

### 7.5. Effects of Reactive Olefins in Houston

[63] Observations made during the TexAQS 2000 field campaign showed extremely high concentrations of light olefins emitted from the conglomeration of petrochemical plants located on the Ship Channel as well as from isolated plants located approximately 50 km south of the city [Kleinman *et al.*, 2002a; Daum *et al.*, 2003, 2004; Karl *et al.*, 2003; Ryerson *et al.*, 2003; Wert *et al.*, 2003]. Petrochemical plants contain large  $\text{NO}_x$  point sources because of the requirements of these facilities for electric power, process heat, and the flaring of excess hydrocarbons [Ryerson *et al.*, 2003; Environmental Protection Agency, National Emission Inventory (NEI) database, available at [www.epa.gov/air/data/](http://www.epa.gov/air/data/), 2004]. The co-occurrence of high concentrations of reactive hydrocarbons and  $\text{NO}_x$  is what sets Houston apart from the other four cities in regard to  $\text{O}_3$  production rates and  $\text{O}_3$  concentration.

[64] In Figure 19, we explicitly show the relation between  $P(\text{O}_3)$  and light olefin reactivity for Nashville, Philadelphia, and Houston. Data are binned according to OH reactivity of the light olefins, ethylene, propylene, and butenes ( $\text{VOC}_R(\text{C}2-\text{C}4)$ ). Numbers below the box plots indicate the percentage of samples in each category. High concentrations of reactive olefins are a unique occurrence in Houston with the exception of one sample taken in Philadelphia near petrochemical facilities located on the Delaware River [Kleinman *et al.*, 2004]. The highest values of  $P(\text{O}_3)$  are seen to be from Houston samples with  $\text{VOC}_R(\text{C}2-\text{C}4) > 5 \text{ s}^{-1}$ . That this is a causal relation has been demonstrated by redoing the Houston CSS calculations with a VOC mixture characteristic of Philadelphia [Kleinman *et al.*, 2002a]. Because  $P(\text{O}_3)$  depends also on  $Q$  and  $\text{NO}_x$ , high-VOC reactivity does not guarantee high  $P(\text{O}_3)$ , as can be inferred by the wide range of  $P(\text{O}_3)$  in each reactivity bin. Figure 19 also shows that some samples achieve high  $P(\text{O}_3)$  ( $>40 \text{ ppb h}^{-1}$ ), without a large contribution to reactivity from light olefins. In most of these cases, including the two Nashville points discussed in the previous section, there is high biogenic VOC reactivity. Without an admixture of hydrocarbons, beyond the normal traffic dominated urban source, peak values of  $P(\text{O}_3)$  are about  $25\text{--}30 \text{ ppb h}^{-1}$ .

## 8. Conclusions

[65] The concentrations of  $\text{O}_3$  and  $\text{O}_3$  precursors were measured by aircraft at mid boundary layer altitude during five field campaigns conducted in Nashville, New York City, Phoenix, Philadelphia, and Houston. A steady state box model using observed concentrations as input gives the production rate of  $\text{O}_3$ ,  $P(\text{O}_3)$ , and the sensitivity of this rate to  $\text{NO}_x$  and VOCs. A wide range of pollutant conditions were encountered causing  $P(\text{O}_3)$  to vary between nearly 0 and  $155 \text{ ppb h}^{-1}$ . Conditions for  $\text{O}_3$  production vary from strongly  $\text{NO}_x$  limited to strongly VOC limited.

[66] There are intrinsic differences between cities and other differences that result from different sampling strategies. Sampling in Nashville and NYC was done primarily 50–150 km from the city centers, whereas in Phoenix,



Philadelphia, and Houston, sampling was concentrated in areas with high emission rates. As a consequence there is a factor of 5 difference in NO<sub>x</sub> concentration between the low and high-NO<sub>x</sub> cities. Low-NO<sub>x</sub> conditions lead to a predominance of NO<sub>x</sub>-limited samples in Nashville and NYC, while near-source sampling in the other three cities favors VOC sensitive P(O<sub>3</sub>). We believe that the following conclusions are qualitatively valid even though quantitative details may be contingent on a sampling strategy:

[67] 1. Radical production rates in Phoenix are on average one third of that observed in the other four cities. The primary reason is low atmospheric humidity which has the direct affect of reducing radical production from O<sub>3</sub> photolysis.

[68] 2. VOC-OH reactivity is primarily due to compounds other than anthropogenic hydrocarbons. Only in Houston is there an appreciable subset of samples (22%) in which more than half of total reactivity is from anthropogenic hydrocarbons.

[69] 3. The highest isoprene concentrations were observed in the Nashville campaign, primarily in locations without significant sources of NO<sub>x</sub>. Photochemistry in most of the high-isoprene regions is typical of low-NO<sub>x</sub> rural areas. Addition of NO<sub>x</sub> as seen in two Nashville samples caused P(O<sub>3</sub>) to increase several-fold to 40–50 ppb h<sup>-1</sup>.

[70] 4. P(O<sub>3</sub>) in Phoenix is a factor of 3 lower than in Philadelphia and Houston, the other two high-NO<sub>x</sub> cities. This difference is due to a low radical production rate and a low VOC<sub>R</sub>/NO<sub>x</sub> ratio in Phoenix. The latter factor is caused by the near absence of biogenic emissions and VOC lean anthropogenic emissions.

[71] 5. Ten percent of the Houston samples have very high P(O<sub>3</sub>), between 30 and 155 ppb h<sup>-1</sup>. These samples are taken in regions influenced by petrochemical facilities and are characterized by concentrations of C<sub>2</sub>–C<sub>4</sub> olefins that are significantly greater than in other cities—with the exception of one sample similarly affected by a petrochemical plant near Philadelphia. Petrochemical facilities also have high NO<sub>x</sub> emission rates enhancing the potential for rapid O<sub>3</sub> formation.

[72] 6. Morning and afternoon values of P(O<sub>3</sub>) within emission source regions are comparable, as determined from repetitive flight patterns in Phoenix and Philadelphia. Morning photochemistry is VOC limited. By the afternoon Philadelphia makes a transition to NO<sub>x</sub>-limited conditions but Phoenix stays VOC limited, in part because of the difficulty of reacting away morning NO<sub>x</sub> because of a low radical production rate.

[73] 7. High-O<sub>3</sub> events are preceded by periods of high P(O<sub>3</sub>). Six high-O<sub>3</sub> events were observed (one in Nashville, two on the same day in Philadelphia, and three in Houston) in which the same air mass was sampled in the morning and afternoon. The same-day increase in O<sub>3</sub> varied between 50 and 140 ppb, with afternoon concentrations between 130 and 211 ppb. Morning values of P(O<sub>3</sub>) were 25 to 140 ppb h<sup>-1</sup>.

[74] Since high-O<sub>3</sub> events in the afternoon are preceded by a morning of rapid O<sub>3</sub> formation, the high-P(O<sub>3</sub>) cases take on an importance out of proportion to their frequency. In each city, with the exception of Phoenix, there is a common pattern in which rapid O<sub>3</sub> production (>25 ppb h<sup>-1</sup>) requires moderate to high NO<sub>x</sub> concentration (~5–25 ppb) along with a VOC reactivity above 5 s<sup>-1</sup>. These values are modest

by urban ground level sampling standards [e.g., *Chameides et al.*, 1992] but are relatively uncommon during our mid boundary layer flights. They are most often seen during periods of poor ventilation. Most of the samples with P(O<sub>3</sub>) around 25 ppb h<sup>-1</sup> were VOC limited. Samples in this NO<sub>x</sub>-VOC<sub>R</sub> category were not observed in Phoenix, but even if they had been P(O<sub>3</sub>) would have been suppressed by the low rate of radical production. Ozone production rates that are significantly higher (>40 ppb h<sup>-1</sup>) require something unusual in the way of VOC reactivity, which in the cases that we have encountered is primarily caused by biogenic emissions of isoprene or industrial emissions of light olefins. The extra dose of VOC reactivity tilts these samples toward the transition regime where there is equal sensitivity to NO<sub>x</sub> and VOC<sub>R</sub>. Unfortunately, that is also the regime where P(O<sub>3</sub>) is least sensitive to emission changes.

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