Ozone production rate and hydrocarbon reactivity in 5 urban areas: A cause of high ozone concentration in Houston

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[1] Observations of ozone (O_3) and O_3 precursors taken from aircraft flights over Houston, TX, Nashville, TN; New York, NY; Phoenix, AZ, and Philadelphia, PA show that high concentrations of reactive volatile organic compounds (VOCs) in the Houston atmosphere lead to calculated O_3 production rates that are 2 to 5 times higher than in the other 4 cities even though NO_x concentrations are comparable. Within the Houston metropolitan area, concentrations of VOCs and O_3 production rates are highest in the Ship Channel region; the location of one of the largest petrochemical complexes in the world. As a consequence the concentration of O_3 in the Houston metropolitan area has recently exceeded 250 ppb, the highest value observed in the U.S within the past 5 years.   *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry

1. Introduction

[2] In spite of 4 decades of progressively more stringent emission controls, approximately 1/3 of the population of the U.S. is exposed to ground level O_3 concentrations that exceed the health-based National Ambient Air Quality Standard (NAAQS) [*Environmental Protection Agency*, 2000]. Although elevated O_3 concentrations are a regional problem, the highest concentrations occur in major metropolitan areas. The Texas Air Quality Study (TexAQS) was conducted in the summer of 2000 to determine why Houston has frequent and severe exceedances of the NAAQS for O_3.

[3] Ozone production in the lower troposphere occurs by reaction of NO_x (NO + NO_2) and VOCs (volatile organic compounds, consisting mainly of hydrocarbons) in the presence of sunlight [e.g., *National Research Council*, 1991]. Control of O_3 is accomplished by identifying the sources of NO_x and VOCs, quantifying their contribution to O_3 production, and then reducing emissions of either NO_x or VOCs or both. Ozone precursors are ubiquitous in urban areas, the major source categories being on and off-road vehicles, power plants, and solvent use [*Environmental Protection Agency (EPA)*, 2000]. Houston, in addition to having the usual urban mix of anthropogenic and biogenic [*Chameides et al.*, 1988] emission sources, is exposed to emissions from nearby petrochemical facilities. A comparison between Houston and 4 other cities (Nashville, TN [*Daum et al.*, 2000]; New York, NY [*Kleinman et al.*, 2000]; Phoenix, AZ [*Fast et al.*, 2000; *Kleinman et al.*, 2001], and

Philadelphia, PA [*Fast et al.*, 2002]) where the Atmospheric Chemistry Program of the Department of Energy (DOE) has conducted aircraft based field campaigns, reveals very high concentrations of VOCs, specifically reactive olefins, along with high concentrations of NO_x in the industrial Houston Ship Channel region. Based on the observed concentration of O_3 precursors we are able to calculate the local rate of O_3 production, $P(O_3)$. A key feature of $P(O_3)$ determined from observations is that it is independent of emission estimates and their associated uncertainties [*Henry et al.*, 1997; *EPA*, 2000, 2001]. We find that most of Houston resembles other urban areas as to the concentration of O_3 precursors and O_3 production rate. The industrial Houston Ship Channel region, however, has a distinctive chemistry, with elevated concentrations of anthropogenic hydrocarbons causing $P(O_3)$, at a given NO_x concentration, to be several-fold greater than elsewhere.

2. Observations and Calculations

[4] The DOE G-1 aircraft has been used to sample, O_3, O_3 precursors, and photochemical oxidation products in a series of urban plume studies. Measurement techniques have been described elsewhere [*McLaren and Singleton*, 1996; *Lee et al.*, 1998; *Kleinman et al.*, 2000]. Aircraft sampling was conducted mostly at 500–1000 m altitude, within the atmospheric boundary layer, typically in the mid-morning and mid-afternoon. Flight patterns in each city were designed to sample in clean background air; over urban and industrial areas with high NO_x and VOC emission rates, and downwind of these sources in regions where O_3 is expected to be formed.

[5] For each city, constrained steady state (CSS) box model calculations [*Kleinman et al.*, 2001] using a chemical mechanism based on *Stockwell et al.* [1990] were performed to determine the rate of O_3 production, $P(O_3)$. Inputs to the CSS model are observed concentrations of O_3, NO, CO, HCHO, speciated VOCs, H_2O_2, and organic peroxides; photolysis rate constants as determined from a UV radiometer and a radiative transfer code; and observed temperature, pressure and dew point. The number of calculations is limited by VOC observations which are obtained from whole air samples collected in canisters [*McLaren and Singleton*, 1996]. Calculations yield 1) the concentrations of rapidly reacting species (NO_2, OH, HO_2, and RO_2s (organic peroxy radicals)) which are nearly in steady state with the observed mixture of trace gases, and 2) the production and loss rates of all species, including those which have been constrained. Calculations reported here are similar to those done for Nashville [*Daum et al.*, 2000], New York City [*Kleinman et al.*, 2000], and Phoenix [*Kleinman et al.*, 2001], except that actinic flux which controls the rate of photolysis reactions has been set to 90% of it's clear sky value, thereby removing cloud cover as a cause of inter-city differences. Our

Table 1. Summary of O_3 Monitoring Data, Aircraft O_3 Observations, and Calculated O_3 Production Rates for 5 Cities

City	Monitoring Data[a]		Aircraft Observations				CSS Calculations		
	# Days $O_3 > 120$ ppb	Max. O_3 (ppb)	Dates (m/yy)	# flights	# flights $O_3 > 120$ ppb	Max. O_3 (ppb)	# Calc.	Median $P(O_3)$ (ppb h^{-1})	90th % $P(O_3)$ (ppb h^{-1})
Nashville	1	124	6/95–7/95	17	3	146	81	6.2	15.2
NYC	5	138	7/96	13	0	119	67	4.3	14.7
Phoenix	1	123	5/98–6/98	24	0	101	117	3.5	7.6
Philadelphia	2	162	7/99–8/99	20	1	147	131	11.3	22.3
Houston	38	225	8/00–9/00	18	9	211	206	11.3	39.1

[a] Monitoring data is for the entire year in which each field campaign was conducted and for regions that are approximately coincident with the aircraft sampling [*EPA, 2001*].

analysis focuses on the chemical consequences of having high concentrations of both NO_x and VOCs in an air mass. Meteorological factors are not considered, although they play a crucial role in controlling the accumulation of O_3 precursors in an air mass and in translating the instantaneous value of $P(O_3)$ into an amount of O_3 eventually produced.
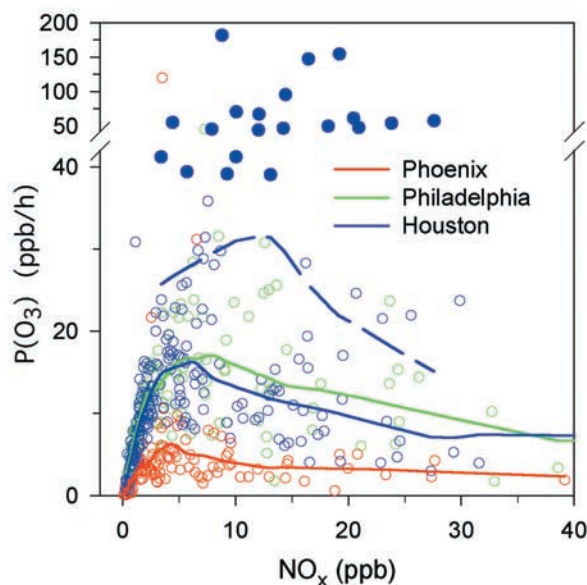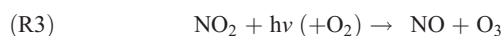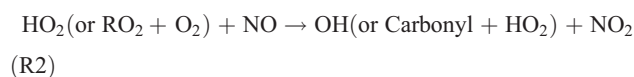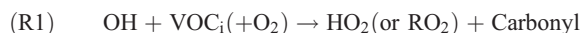
3. Results

[6] An inter-city comparison of observed O_3 concentration and calculated O_3 production rate is given in Table 1. Monitoring data shows that both the peak O_3 concentration (251 ppb in 1999) and the number of O_3 NAAQS exceedances in Houston are significantly higher than in the other 4 cities [*EPA, 2000, 2001*]. Ozone data from the G-1 aircraft parallels the inter-city trends deduced from surface monitoring sites and captures the high surface values recorded in Houston. Median $P(O_3)$ is the same in Philadelphia and Houston consistent with O_3 production in most of the Houston metropolitan area being caused by typical urban emissions. Effects of an atypical emission source are evident in the 90th percentile value for $P(O_3)$ in Houston which is double that in Philadelphia, 3-fold higher than Nashville, and New York City, and 5-fold higher than Phoenix.

[7] Pollution conditions are often defined in terms of NO_x concentration [*Chameides et al.,* 1992; *Kleinman,* 1994] and Figure 1 shows $P(O_3)$ for Houston, Philadelphia, and Phoenix in terms of this metric. Nashville and NYC (not shown in Figure 1) are similar to Houston and Philadelphia for NO_x concentrations up to 6 ppb. Above 6 ppb data are sparse. In the high $P(O_3)$ Houston samples, indicated by solid blue circles, $P(O_3)$ is greater than that calculated for all but 2 of the Phoenix and Philadelphia samples. The range of NO_x concentrations observed in these 3 cities is similar and is clearly not the cause of the higher $P(O_3)$ in Houston.

[8] $P(O_3)$ is expected to increase at low NO_x, reach a maximum, and then decrease at high NO_x [*Sillman et al.*, 1990]. This behavior is understood in terms of the dual role of NO_x in photochemical O_3 production: NO_x is a catalyst yielding O_3 from photolysis of NO_2 produced from reactions of peroxy radicals with NO. However, at high NO_x concentration, the reaction $OH + NO_2 \rightarrow HNO_3$ inhibits O_3 production. Figure 1 shows that $P(O_3)$ has the expected behavior for Phoenix, Philadelphia, and for those Houston samples with $P(O_3)$ below the 90th percentile value. For this data subset, $P(O_3)$ vs. NO_x is similar in Houston and Philadelphia. Phoenix has lower $P(O_3)$ primarily because the prevailing dry atmosphere leads to a much lower rate of radical production [*Daum et al.*, 2000]. The highest 10 percentile $P(O_3)$ samples in Houston follow a different pattern in that $P(O_3)$ remains high at high NO_x. The joint occurrence of high $P(O_3)$ and high NO_x suggests that rapid O_3 production can occur for many hours before dilution and oxidation deplete the air mass of NO_x. Extremely high concentrations of O_3 can result.

[9] To determine the reason for the high $P(O_3)$ Houston samples, we compare the composition and reactivity of VOCs in

5 cities as measured from the G-1 at mid-boundary layer altitude. The specific categories of compounds that we consider are anthropogenic hydrocarbons, biogenic hydrocarbons, CO, HCHO, and CH_4. VOCs, broadly defined here to include CO, participate in the O_3 forming sequence of reactions as illustrated below:

(R1) $OH + VOC_i(+O_2) \rightarrow HO_2(or\ RO_2) + Carbonyl$

$HO_2(or\ RO_2 + O_2) + NO \rightarrow OH(or\ Carbonyl + HO_2) + NO_2$
(R2)

(R3) $NO_2 + h\nu\ (+O_2) \rightarrow\ NO + O_3$

Figure 1. Ozone production rate calculated from CSS model as a function of NO_x concentration for Phoenix, Philadelphia, and Houston. Open circles are individual $P(O_3)$ determinations for all Phoenix and Philadelphia samples. Houston samples with $P(O_3)$ in the lower 90th percentile are given by open circles; samples in the top 10th percentile by solid blue circles. Solid lines are Lowess (Locally WEighted regression Scatterplot Smoothing) fit to $P(O_3)$. Houston Lowess fit omits $P(O_3)$ above the 90th percentile value. For clarity the NO_x scale is truncated at 40 ppb omitting a single data point for Houston and Philadelphia. Dashed line is a Lowess fit to the high $P(O_3)$ Houston calculations, re-calculated with an anthropogenic VOC mixture based on Philadelphia VOC composition as explained in text.
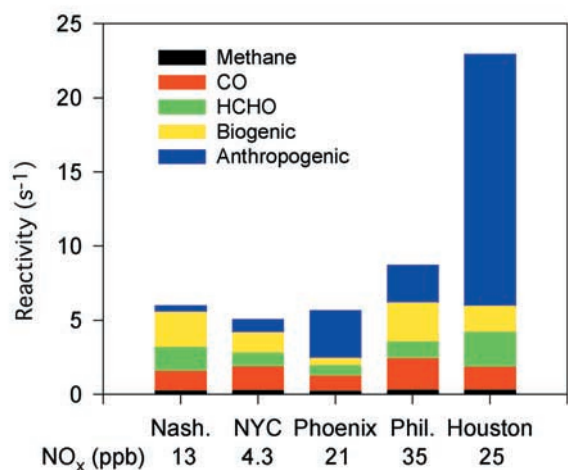
Figure 2. VOC reactivity for 5 cities, averaged over a set of samples with $P(O_3)$ equal or above the 90th percentile values shown in Table 1. One Houston and one Phoenix VOC sample have been removed as outliers with biogenic reactivity (primarily from terpenes) an order of magnitude greater than the 2nd highest value. NO_x concentration is averaged over near-source samples as defined in text.

Essentially all chemical production of O_3 in the troposphere occurs by reactions R1–R3, although there are a great many variations (including primary sources for peroxy radicals) depending on the exact nature of the VOC that is being oxidized [*Atkinson*, 2000]. At NO_x concentrations greater than a few ppb, R1 is a rate limiting step and $P(O_3)$ can be approximated by

$$P(O_3) \approx \sum k_i Y_i [OH] [VOC_i] \qquad (1)$$

where square brackets indicate concentration, k_i is the rate constant of R1 for VOC_i, and Y_i is a stoichiometric factor, usually equal to 1 or 2 depending on whether an OH or HO_2 radical is produced in R2 [*Sillman*, 1995; *Tonnesen and Dennis*, 2000]. Equation 1 cannot be used to determine $P(O_3)$ based only on VOC measurements because OH is highly variable. However, (1) is a good starting point for an inter-city comparison of VOCs. Our measure of VOC reactivity is $k_i[VOC_i]$ [*Lee et al.*, 1998; *Golden et al.*, 2000]. Y's are ignored because they are relatively independent of location and VOC mixture [*Tonnesen and Dennis*, 2000]. Reactivity as defined here is the inverse of the lifetime of OH radical with respect to reaction with a VOC. Summation over individual compounds yields the reactivity of a class of compounds, or total reactivity.

[10] A 5 city comparison of VOC reactivity is shown in Figure 2. For each city we have averaged VOC reactivity over a set of samples with $P(O_3)$ equal or above the 90th percentile values shown in Table 1. The high $P(O_3)$ Houston samples used in Figure 2 coincide with the samples that did not follow the expected $P(O_3)$ vs. NO_x behavior in Figure 1 (solid blue circles). The anthropogenic contribution of VOC reactivity in Houston is much greater than in the other 4 cities, yielding a total VOC reactivity for Houston that is triple that of Philadelphia. Because VOC reactivity in Houston is high, so also is the ratio of VOC reactivity to $[NO_2]$. As a consequence, radical propagation through R1 is favored relative to termination by $OH + NO_2$ and $P(O_3)$ does not have the expected decrease at high NO_x. Within the anthropogenic category, major contributors in Houston are ethene, propene, and butenes with an average concentration of 16, 8, and 2.5 ppb, respectively, accounting together for 60% of the anthropogenic

reactivity, with individual samples ranging from 4 to 91%. The remaining 40% is split among many alkanes and aromatic compounds, some of which can be present in extremely high concentration.

[11] Sampling strategies could conceivably account for inter-city differences, if observations in Houston were made unusually close to emission sources. To evaluate this possibility we have calculated an average NO_x concentration for each city using near-source samples, defined as the 10% having the highest NO_x concentration. According to this metric, aircraft flights in NYC and Nashville were indeed in cleaner air than in Houston, but not so clean that it would explain a factor of 20–40 difference in anthropogenic VOC reactivity. Sampling in Houston, Philadelphia, and Phoenix was done under comparable conditions.

[12] Figure 2 suggests that high $P(O_3)$ is associated with high anthropogenic VOC reactivity in Houston. A causal component of this relation is demonstrated by re-calculating the high $P(O_3)$ Houston samples using observed NO_x from Houston, but replacing observed VOCs with (lower) values obtained from a VOC to NO_x ratio determined from the Philadelphia data set. Figure 1 shows that the re-calculated Houston $P(O_3)$ has been significantly reduced to values comparable to the upper envelope of the Philadelphia samples and has a well defined peak at intermediate NO_x concentration. The re-calculated $P(O_3)$ is above the Philadelphia Lowess curve primarily because of high rates of radical production.

[13] The geographic distribution of VOC point source emissions [*EPA*, 2001], VOC reactivity, and $P(O_3)$ is shown in Figure 3 for a section of the Houston metropolitan area where there was extensive aircraft sampling. An urban downtown region is located to the west; in the center and towards the east is the industrial Ship Channel. Most of the VOC point sources also emit NO_x ensuring that these O_3 precursors will be well-mixed. The majority of samples with high VOC reactivity are located near the Ship Channel or north of Galveston Bay, within 1 hour travel time (at a wind speed of 6 m s^{-1}) of the emission region shown in Figure 3a. The spatial distribution of reactivity due to ethene, propene, and butenes (not shown) is even more strongly peaked in the east.

[14] $P(O_3)$ depends on VOC reactivity but also depends on NO_x, sunlight, and radical precursors [*Sillman*, 1995; *Daum et al.*, 2000] and thus it is not expected that there would be a simple linear relation between $P(O_3)$ and VOC reactivity. However, Figures 3b
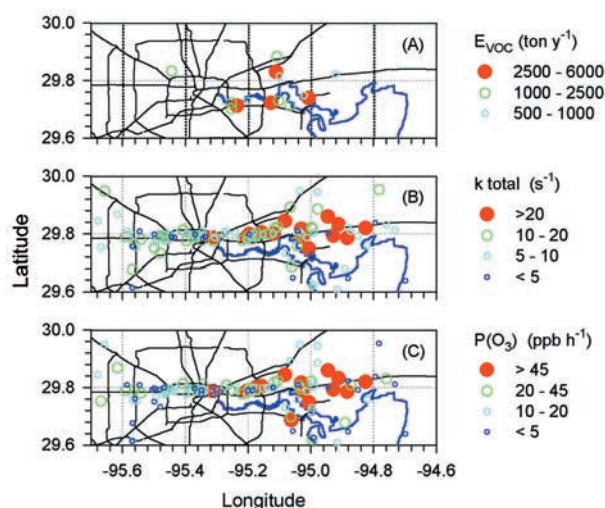
Figure 3. Map of section of Houston metropolitan area. Blue line indicates Galveston Bay and the Ship Channel extending to the west. Black lines are major roads. The Houston downtown area is located within the 2 loop roads. (a) VOC point source emissions, (b) total VOC reactivity, and (c) $P(O_3)$.

and 3c show that almost all of the samples with reactivity greater than 20 s^{-1} have P(O$_3$) greater than 45 ppb h^{-1}.

4. Conclusions

[15] Ozone concentrations observed in the high P(O$_3$) samples shown in Figure 3c reach 135 ppb. These samples have high concentrations of NO$_x$ and VOCs (Figures 1 and 3b) and are observed early enough in the day so that rapid O$_3$ production can continue for several hours leading to extremely high O$_3$ concentrations. The geographic distribution of VOC reactivity, its very high magnitude in comparison with other less industrial urban regions, and its high fraction of olefins show that industrial emissions are contributing in large measure to Houston's very high O$_3$ levels. A significant question is whether our VOC observations are consistent with emission inventory estimates [*Henry et al.*, 1997]. As was the case 15 years ago when the importance of biogenic emissions was being debated [*Trainer et al.*, 1987; *Chameides et al.*, 1988] a necessary prelude to formulating an O$_3$ control strategy for Houston, and possibly for other areas with similar industrial facilities, will be to obtain an accurate emission inventory consistent with ambient atmospheric measurements.

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