10.5 OZONE PRECURSORS, SOURCE REGIONS, AND O_3 FORMATION DURING THE TEXAQS 2000 STUDY

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The DOE G-1 aircraft made flights on 14 days during the TexAQS 2000 study. On 7 of those days, the aircraft encountered highly localized plumes exhibiting O_3 concentrations in excess of 150 ppb; on some days, peak O_3 concentrations were in excess of 200 ppb. These ozone plumes were rapidly formed with an efficiency (O_3 per NO_x molecule consumed) much higher (7-20) than observed in other urban areas (3-4), and were frequently associated with high concentrations (>20 ppb) of secondary hydrocarbon species such as formaldehyde. Back trajectory analysis showed that the plumes were invariably associated with emissions from one or more of the large industrial complexes clustered about the Houston Ship Channel and Galveston Bay. Very high hydrocarbon reactivities were found in the vicinity of these facilities during morning flights. These hydrocarbon reactivities, in combination with local NO_x emissions, were large enough to support instantaneous O_3 production rates as high as 200 ppb/h. It is hypothesized that the combination of nitrogen oxides and hydrocarbon emissions emanating from this complex of industries provided a potent mixture of chemicals that caused the rapid formation of very high concentrations of ozone which, depending on the prevailing meteorology, could cause exceedance of the NAAQS ozone standard anywhere in the Houston metropolitan area.

These features of O_3 formation in Houston are well illustrated by flights conducted by the G-1 aircraft on August 26, 2001. Two flights were made, one in the morning (0800-1100 CST) and one during the afternoon (1300-1600 CST). During the morning flight O_3 concentrations were generally 30-40 ppb except for a small O_3 plume of ~100 ppb observed north of the ship channel late in the flight. During the afternoon a well defined O_3 peak exhibiting peak concentrations of 160 ppb was observed north of the Ship Channel. The geographic distribution of O_3 for both the morning and afternoon flights is shown in Figure 1. Calculations of

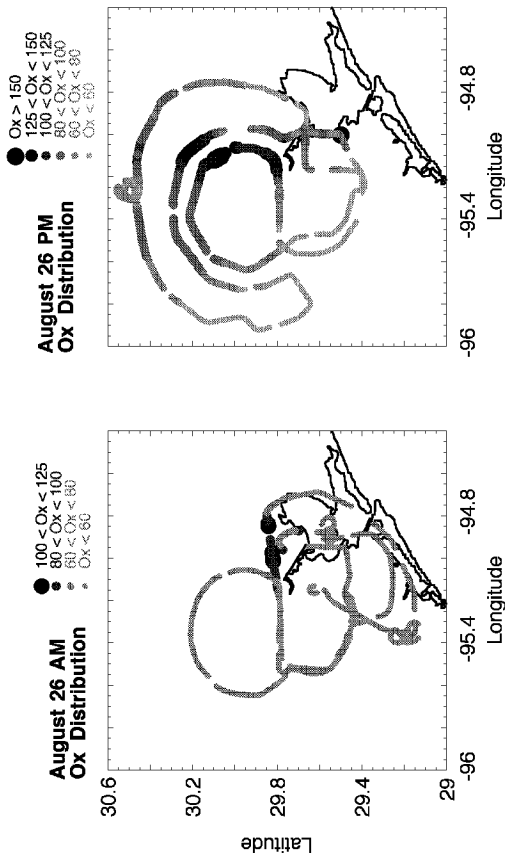

Figure 1. Geographic distribution of ozone for the G-1 Flights of 8/26/2000. Left panel ozone distribution during the morning flight. Right panel geographic distribution during the afternoon flight.

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the instantaneous ozone formation rate (constrained box model calculation) using data collected during the morning flight, reveal a very active photochemistry driven principally by emissions from the Houston Ship Channel. Results of these calculations are shown in Figure 2 for a transect that the G-1 made W-E from downtown Houston through the industrialized region surrounding the Houston Ship Channel. The top panel of Figure 2 shows the O_3 concentration and the times at which the hydrocarbon canister samples were collected. The location of the urban area and the industrial area surrounding the Houston Ship Channel are indicated by the shaded areas. Note that O_3 concentration over the urban area is much lower than it is over the Ship Channel. The lower panel of Figure 2 shows the results of the box model calculations for each of the hydrocarbon samples. Five parameters relevant to O_3 production are shown, precursors (NO_x concentration and hydrocarbon reactivity); the instantaneous ozone production rate $P(O_3)$; the % of the radicals being terminated by the OH + NO_2 -→ HNO_3 reaction (an indicator of NO_x or VOC sensitive O_3 production); and, the instantaneous O_3 production efficiency with respect to NO_x, OPEx.

Clear differences in the rate and efficiency of ozone formation between the urban and the Ship Channel samples are exhibited in Figure 2. $P(O_3)$ is relatively low (~7 ppb h^{-1}) over the urban area and the efficiency is modest (OPEx ~4), but to the east over the industrialized region surrounding the Ship Channel production rates and efficiencies are much higher. The maximum $P(O_3)$ of is ~140 ppb h^{-1} with an OPEx of ~30 is calculated for hydrocarbon sample #11. Since the NO_x concentrations (with the exception of sample #12) are similar for both the urban and Ship Channel samples, it must be concluded that the large differences between the urban and Ship channel $P(O_3)$ values must be due to differences in hydrocarbon reactivity. Indeed, Figure 2 shows that the Ship Channel samples exhibit much higher hydrocarbon reactivities than the urban sample. For sample # 11, which has the highest value of $P(O_3)$, the hydrocarbon reactivity is more than a factor of 10 higher than it is in the urban area. The high hydrocarbon reactivities associated with ship channel samples not only have the effect of making $P(O_3)$ very high but they also have the effect of making the OPEx very high. The highest OPEx shown in Figure 2 is associated with the hydrocarbon sample that exhibits the highest value of $P(O_3)$. These high hydrocarbon reactivities also have the effect of shifting O_3 production from the hydrocarbon sensitive regime towards the NO_x sensitive regime even though the NO_x concentrations are nearly 20 ppb. .Note also that samples in the Ship Channel region have the potential for generating substantial quantities of additional O_3 as both the hydrocarbon and the NO_x concentrations are still very high despite the fact that nearly 60 ppb of O_3 above background has already been produced.

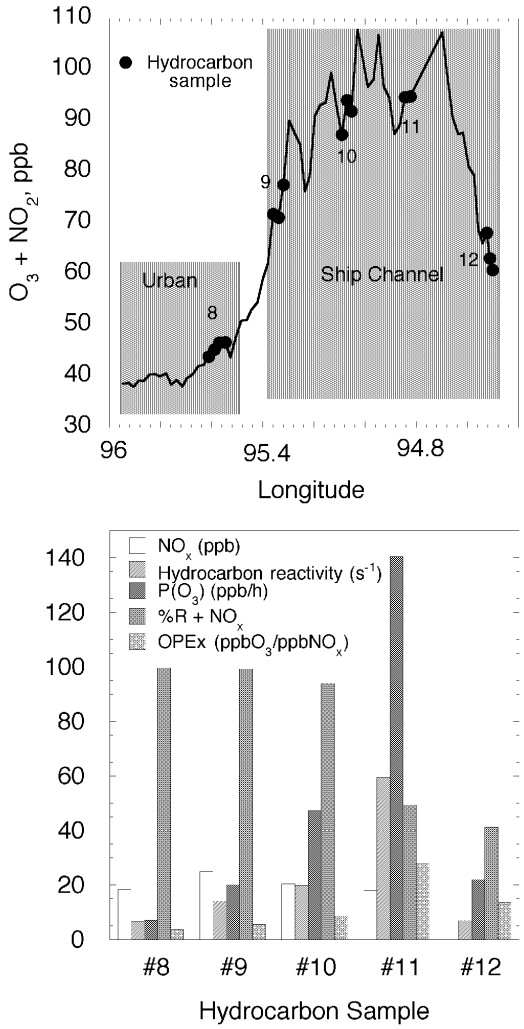

Figure 2. Upper panel: Ozone concentration during an east-to-west transect across the Houston urban plume and through the industrialized area surrounding the Houston Ship Channel during late morning August 26, 2000. Dots indicate the locations where hydrocarbon samples were collected. Lower Panel: Results of box model calculations constrained by observed concentrations of NO_x, hydrocarbons and other stable species.

Weak southerly winds advected the air that was over the Ship Channel during the late morning flight to the north during the afternoon (B. Lambeth, private communication), where it was sampled by the G-1 during the afternoon flight, Figure 1. Peak O_3 concentrations were 150 ppb, Figure 3, about 50 ppb in excess of the maximum concentration observed during the morning flight and about 100 ppb above the afternoon background O_3 concentration. As indicated in

hydrocarbon reactivity were much lower than they were in the morning, consistent with their consumption during O_3 formation, and to dilution. Although precursor concentrations were much lower than they were during the morning, O_3 was still being produced at a rate of ~10 ppb/h, but had shifted from hydrocarbon to NO_x limited production. The overall O_3 production as determined by the slope of an O_3/NO_z plot of the mature plume data was 9.2, Figure 4. This production efficiency is about a factor of two higher than observed in a typical urban plume, and is consistent with hydrocarbon concentrations in excess of those typically found in urban air.

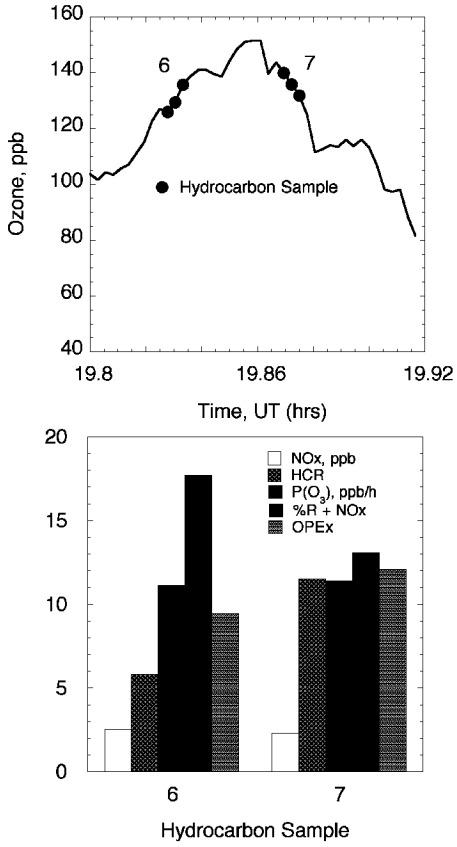

Figure 3. Upper panel: Ozone concentration measured during mid-afternoon in a plume that had been transported from the Ship Channel on August 26, 2000. Upper panel: Ozone concentration and location of hydrocarbon samples. Dots indicate locations where hydrocarbon samples were collected. Lower panel- Results of results of box model calculations as per Figure 3.

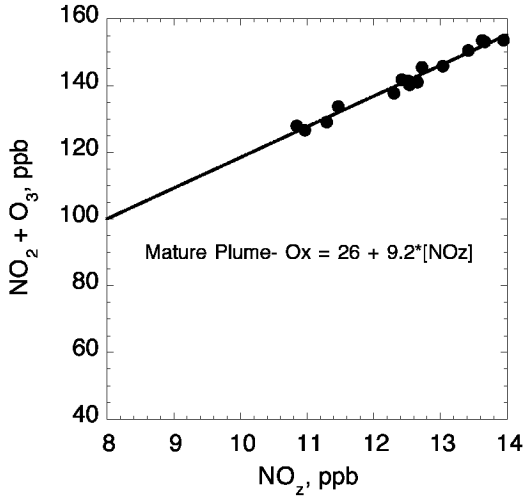

Figure 4. Ozone production efficiency plot for the mature plume observed on the afternoon G-1 flight of August 26, 2000.

The association of emissions from the Houston Ship Channel and other industrial complexes in the Houston area with plumes of high O_3 concentration as observed on the August 26th flights was typical. Plumes of high O_3 concentration were observed on seven flights during the program. In each case, back trajectory analysis associated these plumes with either Ship Channel emissions or emissions from other industrial sources elsewhere in the area. While sources in the ship channel emit both NO_x and hydrocarbons, the NO_x concentrations alone would not cause the appearance occurrence of these plumes of high O_3, as O_3 formation in the Houston urban plume and the surrounding background area are NO_x limited.

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