Ozone Precursors, Source Regions, and the Rate and Efficiency of Ozone Production

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The DOE G-1 aircraft made flights on 14 days during the TexAQS 2000 study.

On 7 of those days,

(8/19, 8/21, 8/26, 8/29, 8/31, 9/6, 9/12)

the aircraft encountered O_3 plumes with concentrations in excess of 150 ppb. On several of these days, peak O_3 concentrations were in excess of 200 ppb.

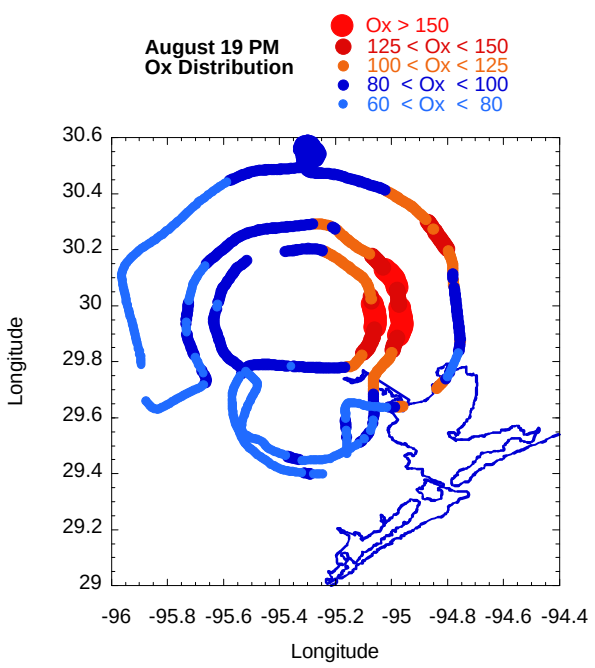
Where did these plumes occur?

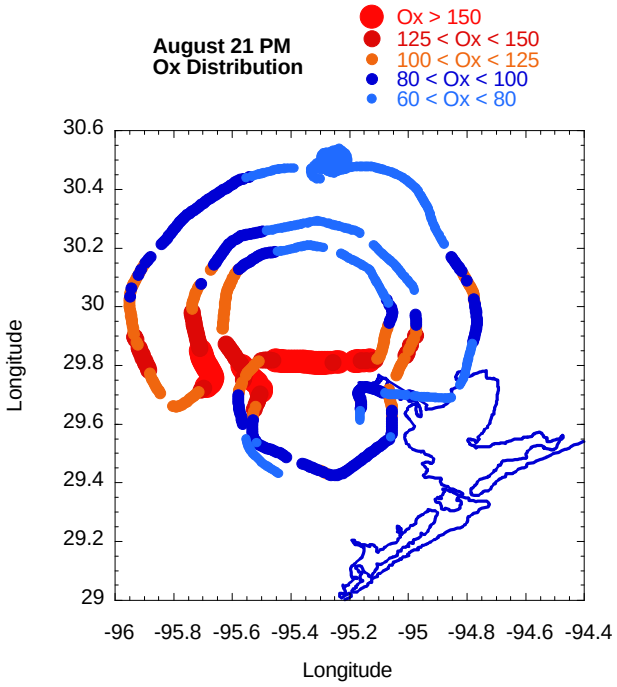
What were their characteristics?

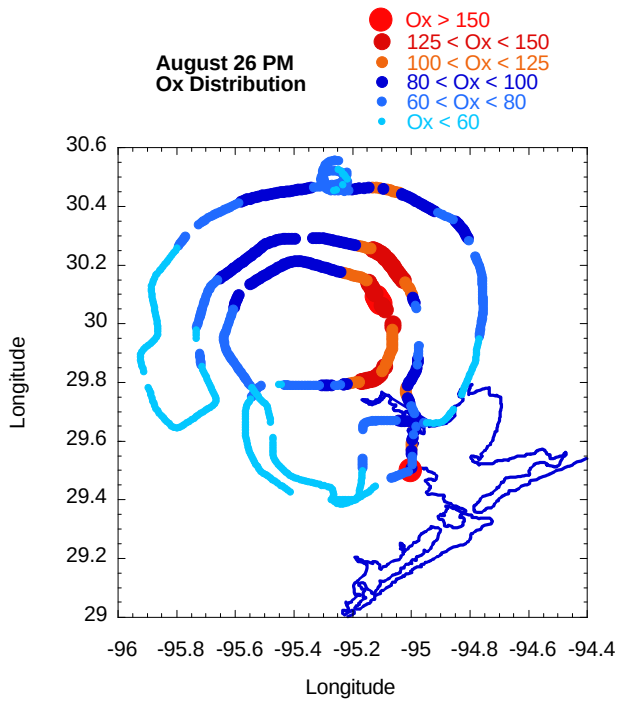
How rapidly were they formed?

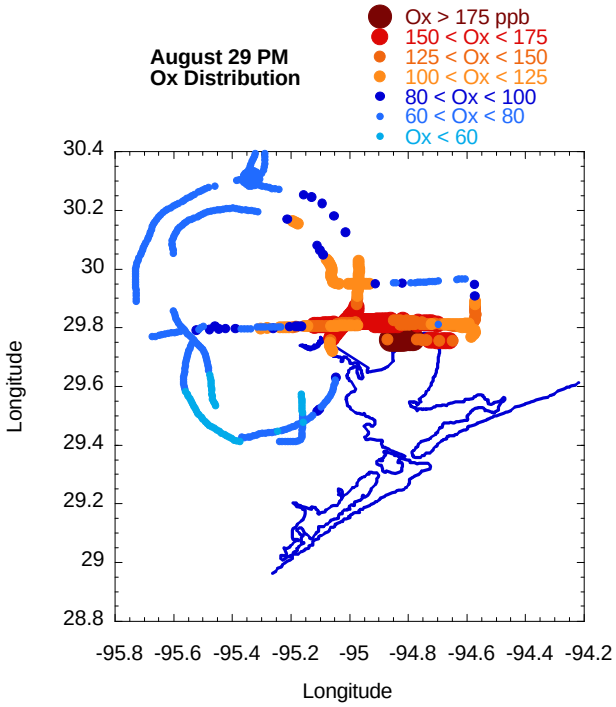
What were the sources of the precursors?

Geographic Distribution of O_3 Plumes





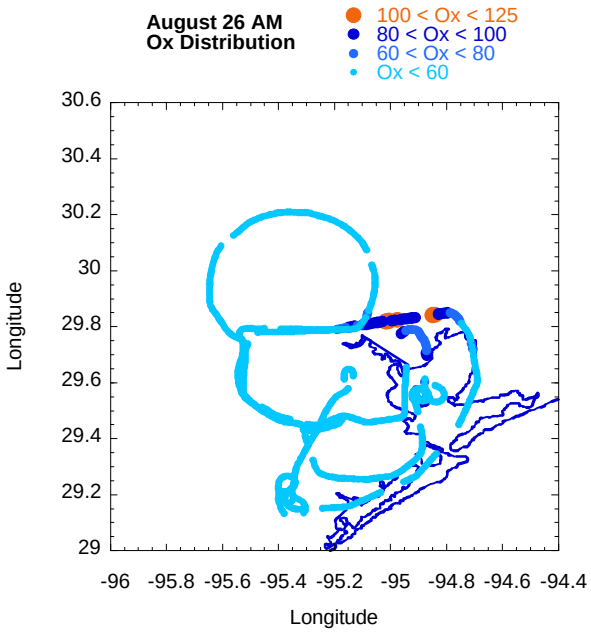


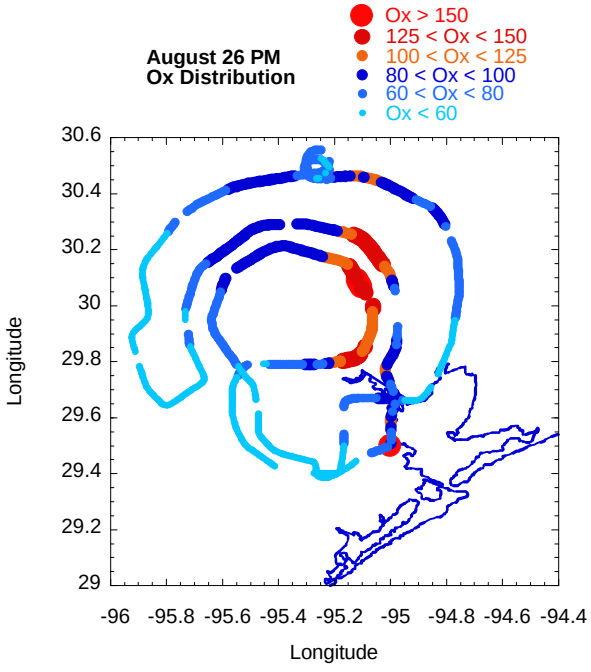


Ozone Plumes

What are their characteristics?

a. Rapid formation

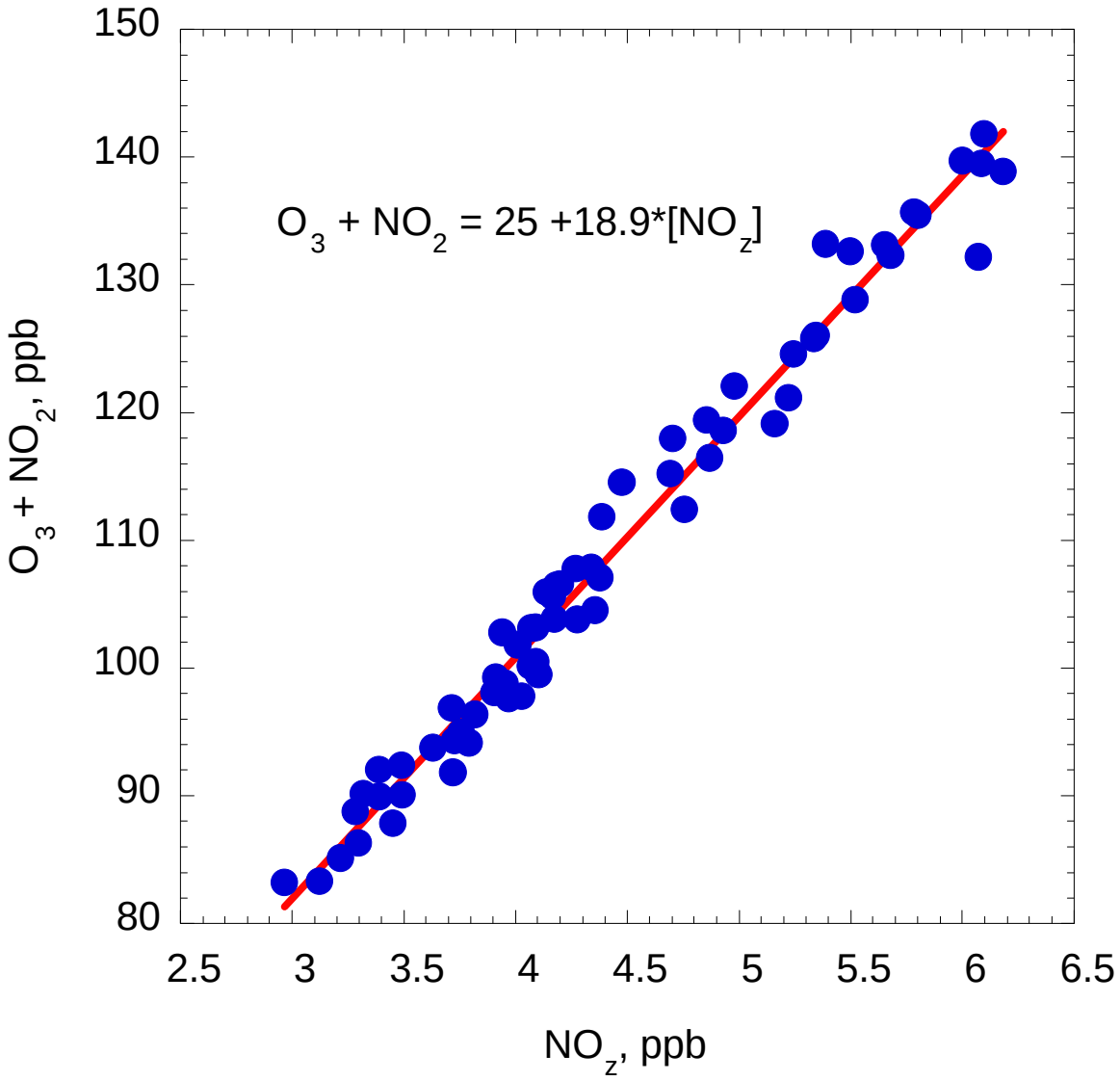




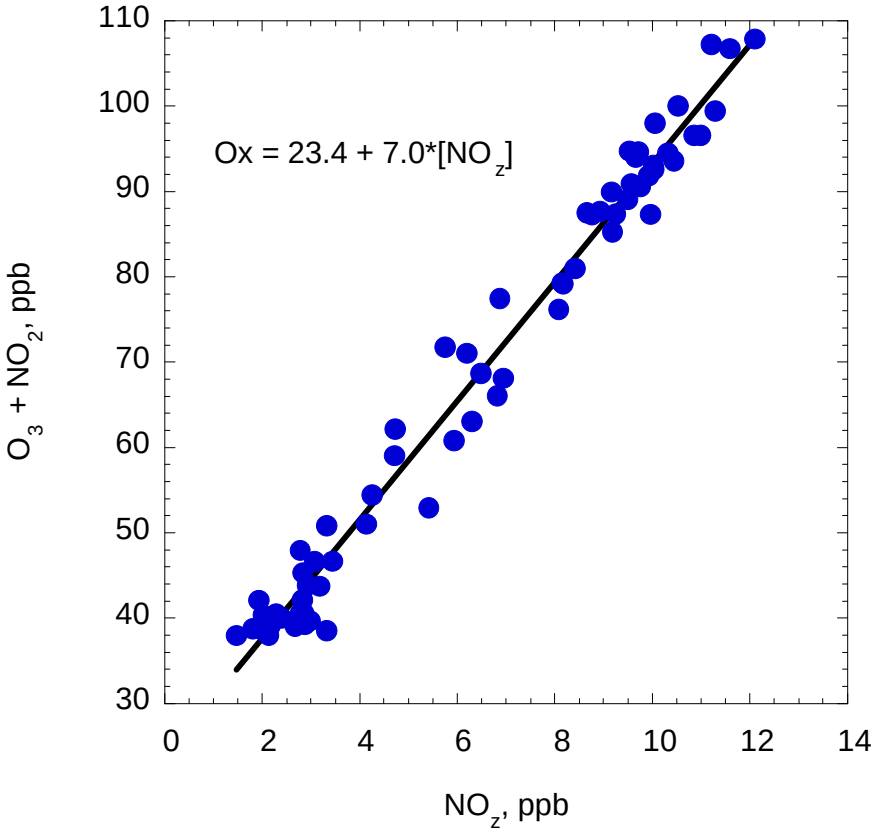
Ozone Plumes

What are their characteristics?

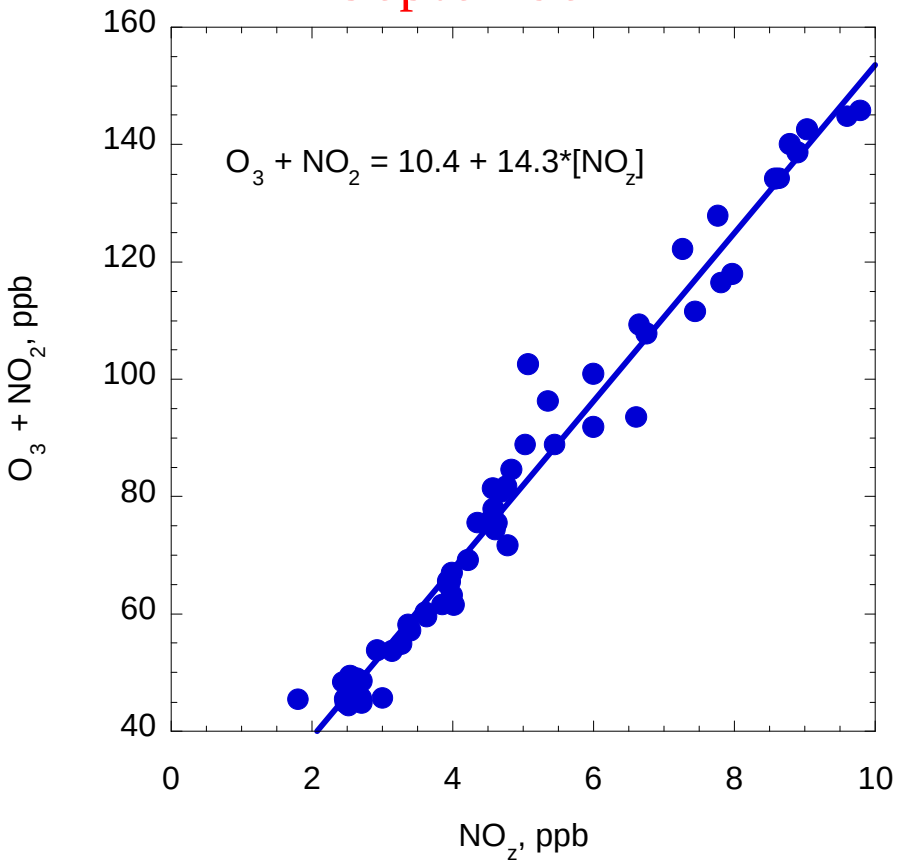
b. High O_3 production efficiencies, e.g, afternoon flight of 8/19



August 29 late morning



September 12

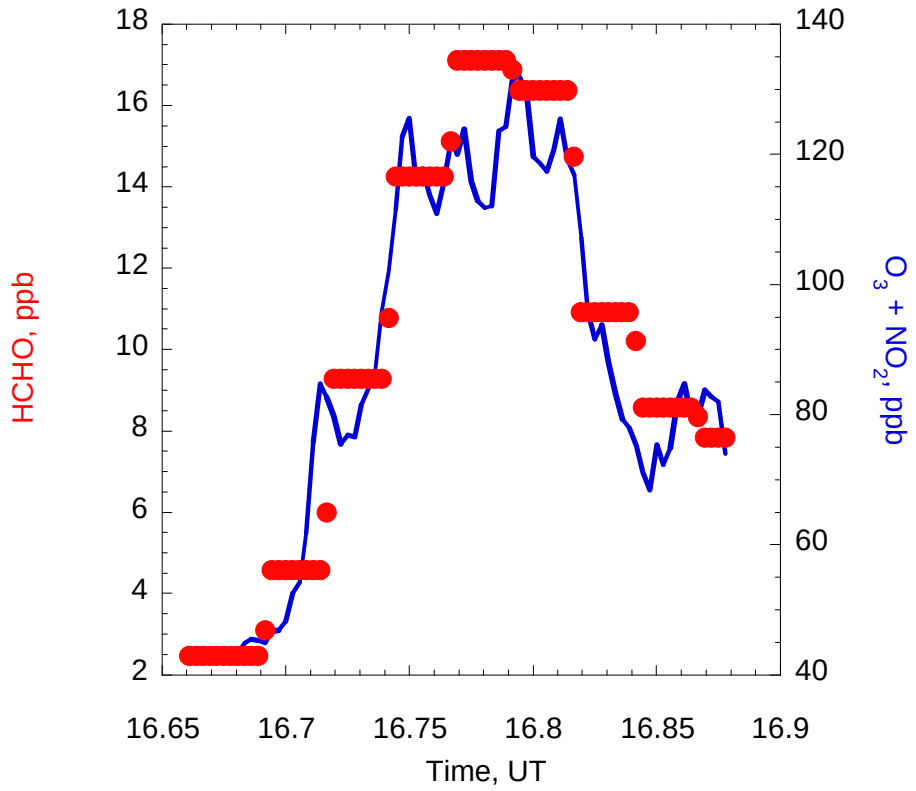


Ozone Plumes

What are their characteristics?

c. Frequently associated with high concentrations of secondary organic species such as HCHO.

For example- August 29th, late morning



HCHO is a product of HC oxidation. Suggests that O_3 spike associated with high initial HC concentrations, perhaps high concentrations of alkenes.

Ozone Plumes

How can we understand source of these localized regions of high O_3 concentration?

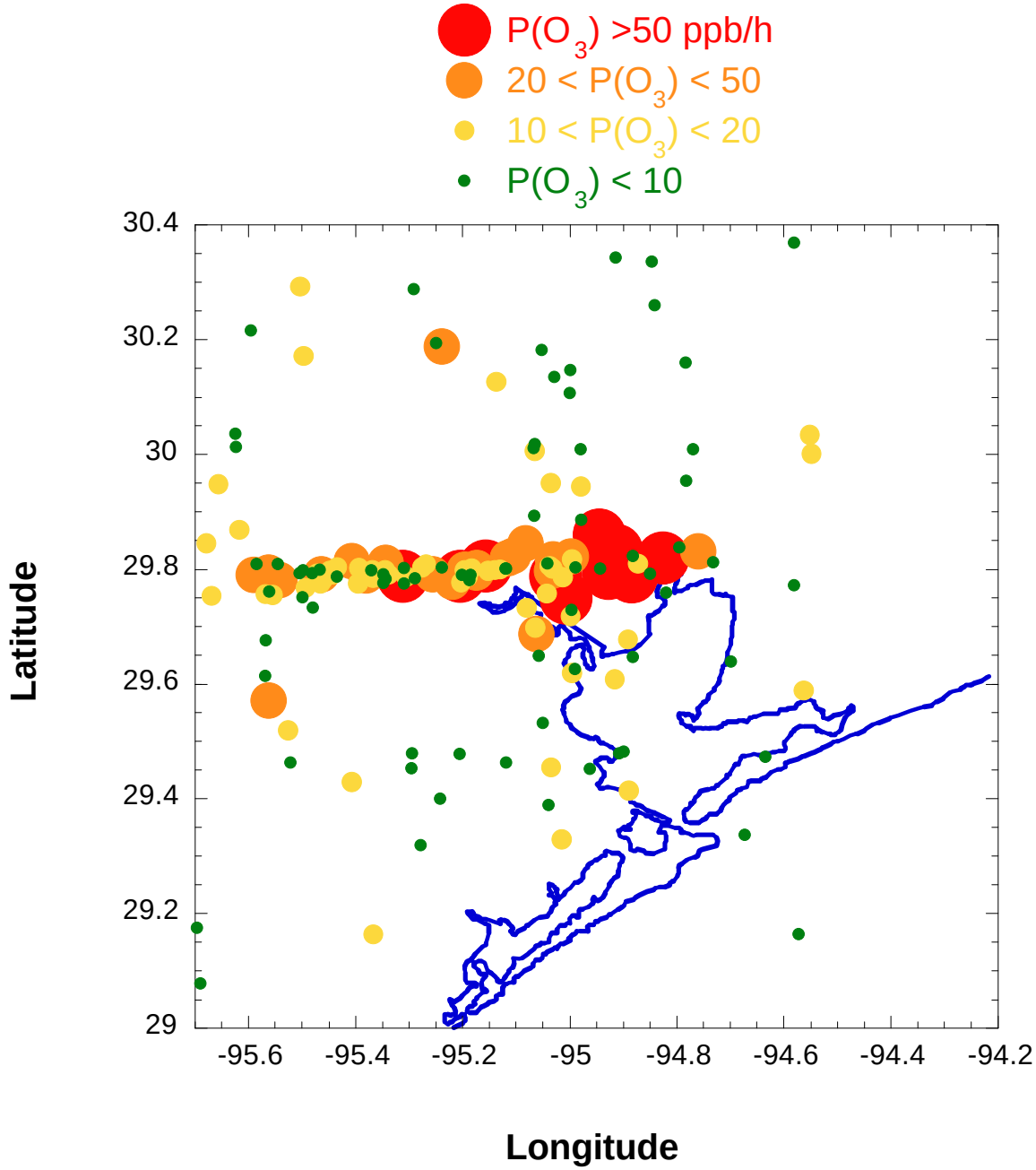
Examine $P(O_3)$- (constrained box model calculations)

Identify conditions and locations where $P(O_3)$ high.

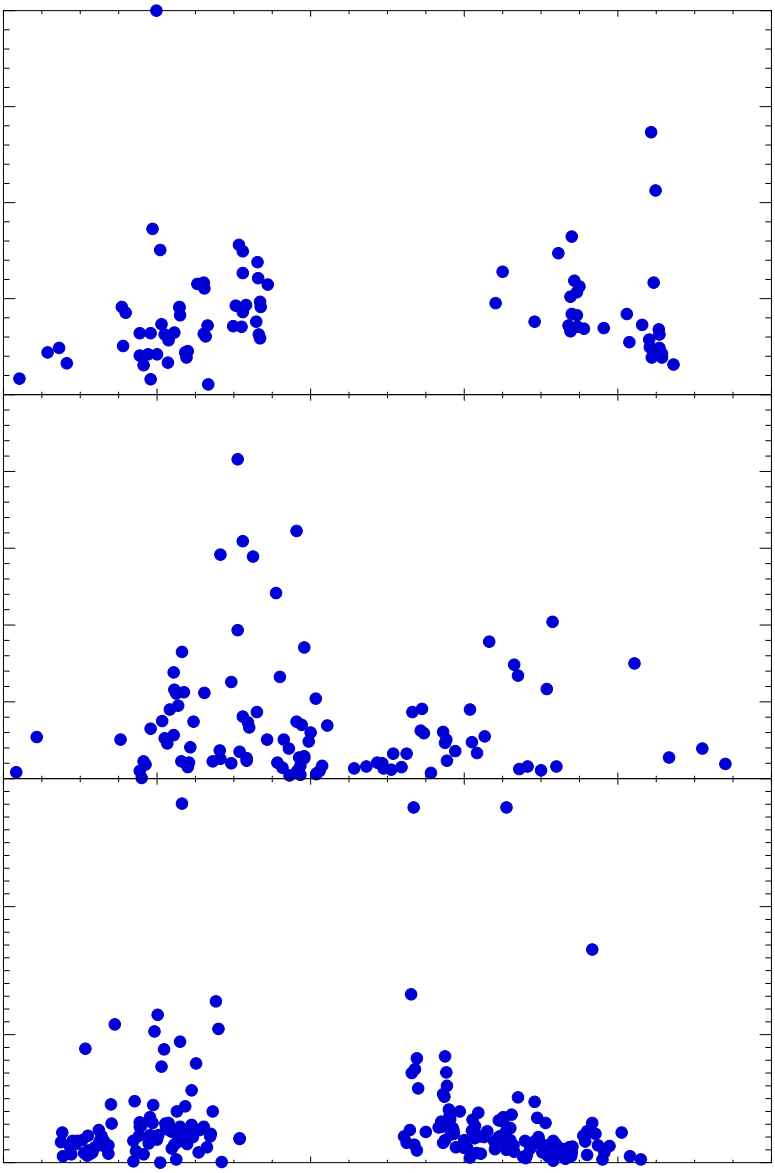
Identify compounds responsible for hydrocarbon reactivity.

Connect regions where $P(O_3)$ high to regions where high O_3 concentrations observed..

Geographic Distribution of $P(O_3)$



Comparison of $P(O_3)$ to other Cities



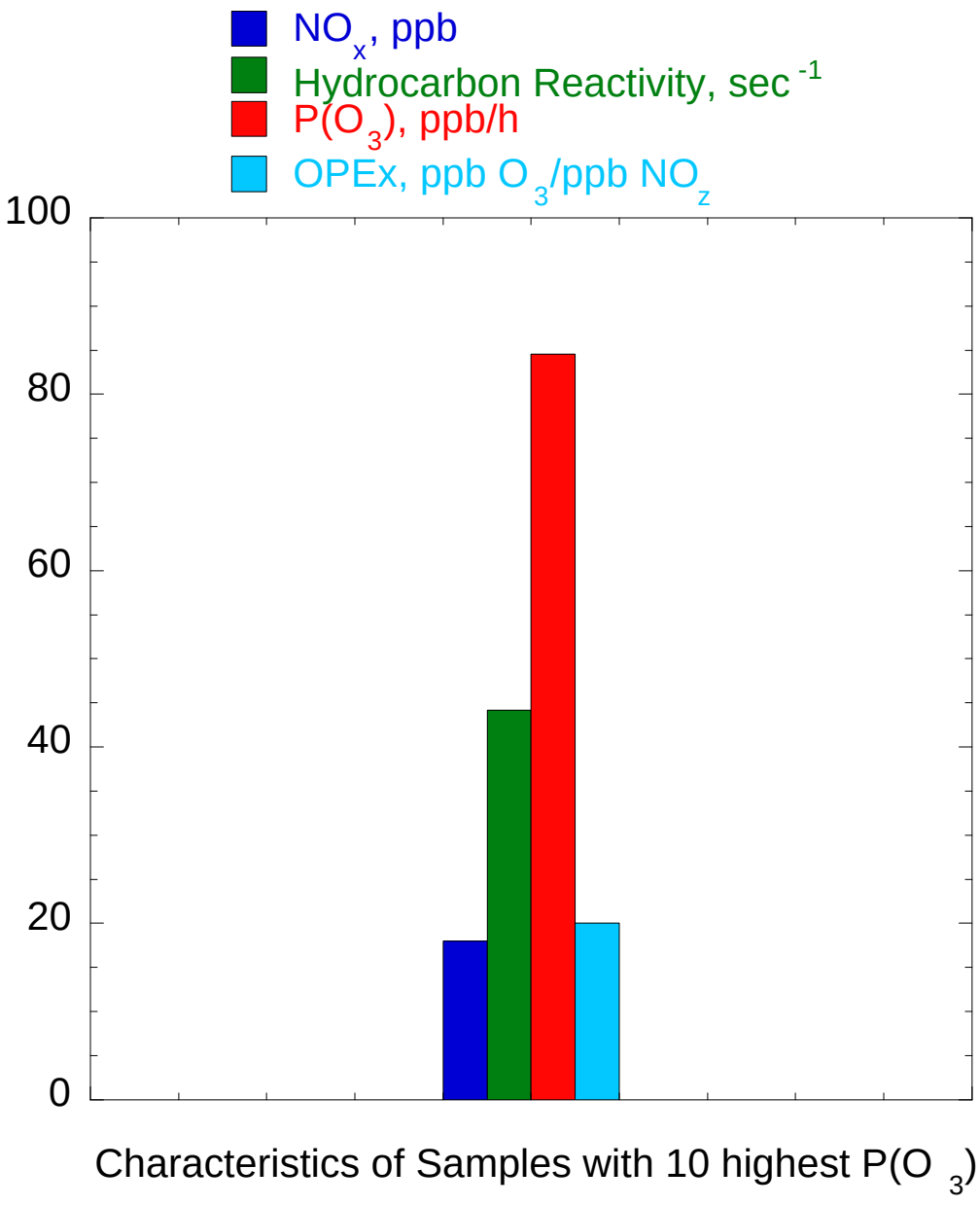
Comparison of $P(O_3)$

Summary-

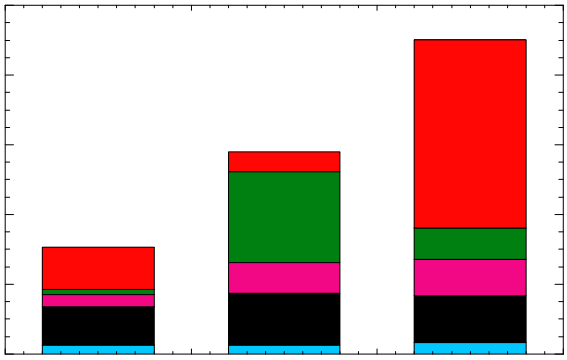
- *$P(O_3)$ can be very high in Houston, even relatively early in the morning.*
- *A number of extreme situations are observed where $P(O_3) > 50$ ppb/h*
- *$P(O_3)$ much higher than in Phoenix*
- *$P(O_3)$ overall higher than Nashville, but biggest difference is in the magnitude of the extreme events.*

What is the cause of these high production rates?

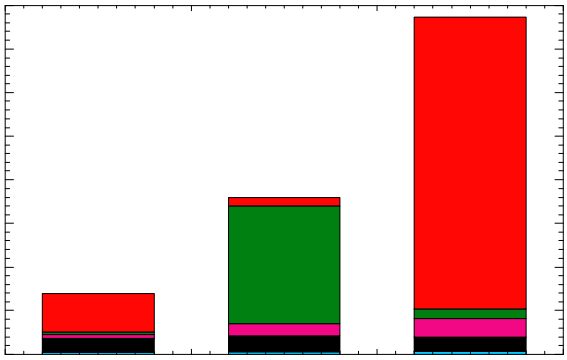
Characteristics of O_3 production when $P(O_3)$ high



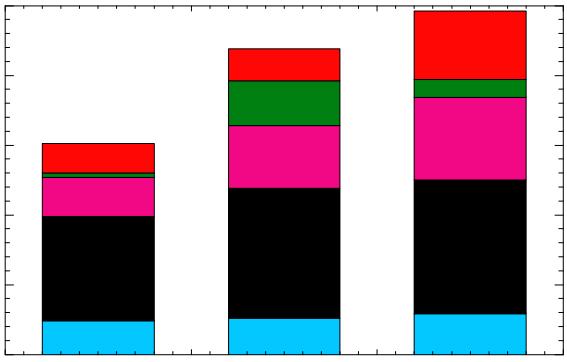
Comparison of Hydrocarbon Reactivities



Mean Reactivities

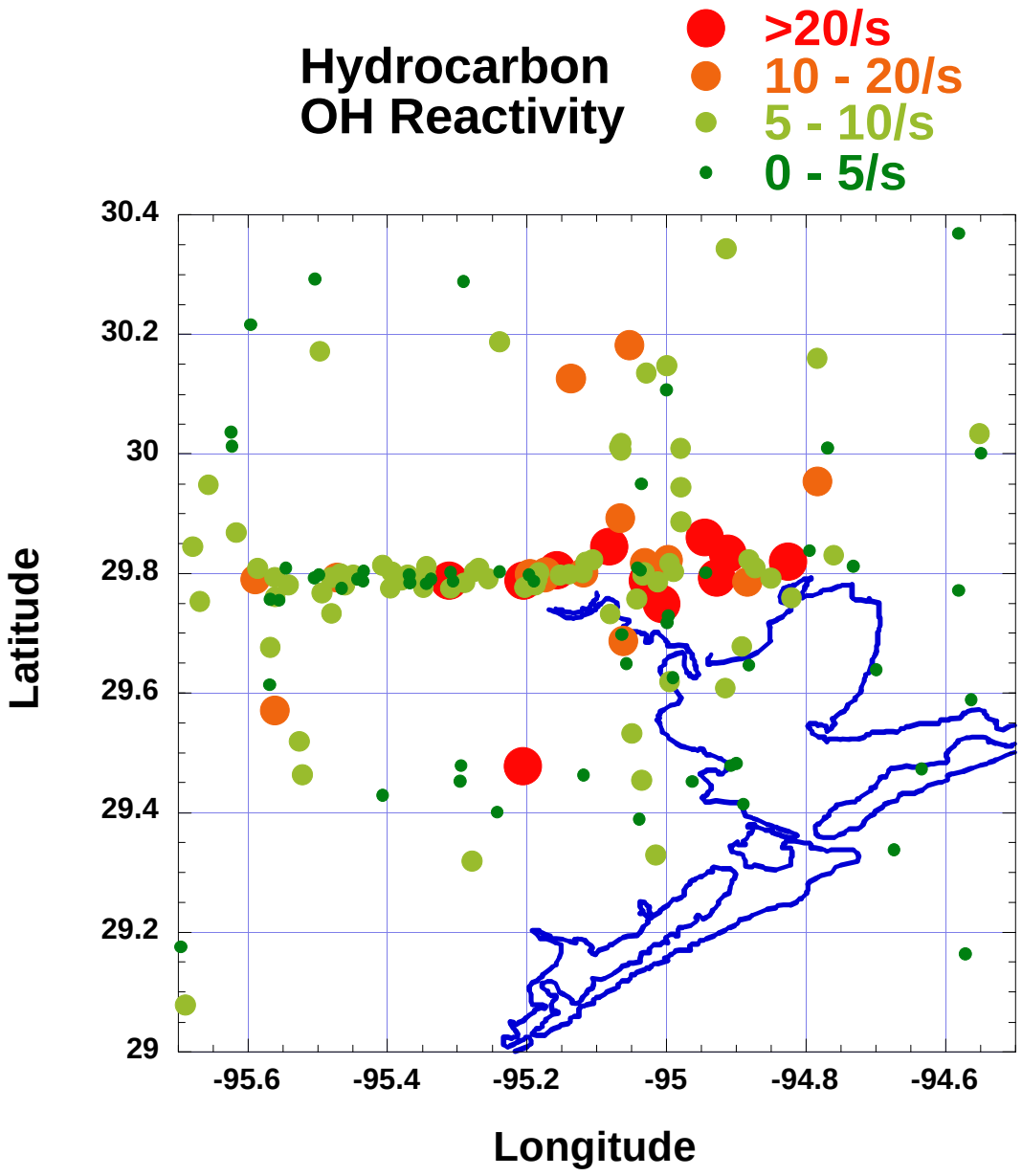


Highest 10%



Lowest 10%

Geographic Distribution of Hydrocarbon Reactivity



Hydrocarbon Reactivity

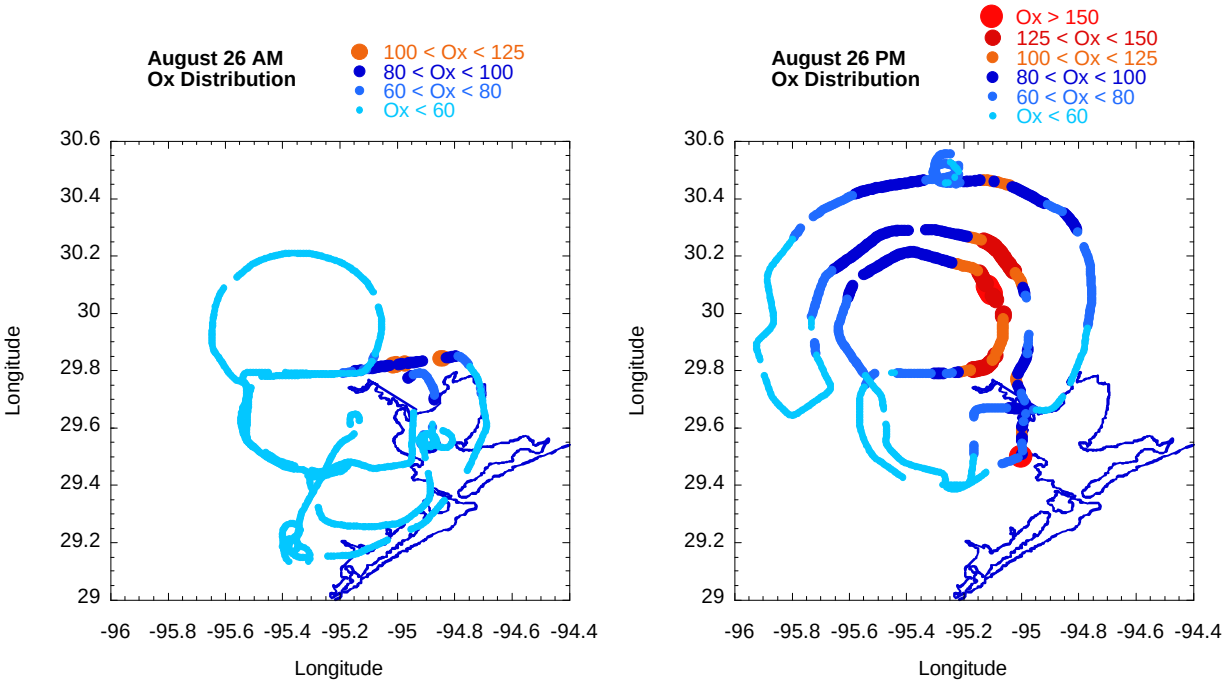
Conclusions

- *Average hydrocarbon reactivity in Houston is significantly higher than observed in either Nashville or Phoenix by a factor of 2-4x.*
- *This higher hydrocarbon reactivity is due to enhanced concentrations of NMNIHC*
- *Extreme hydrocarbon reactivities are caused by very large concentrations of NMNIHC. In contrast, extreme reactivities in Nashville are caused by isoprene.*
- *On average, biogenic hydrocarbons do not contribute significantly to O_3 formation in Houston.*
- *For the most part, the highest values of hydrocarbon reactivity were observed in and around the Ship Channel.*

August 26th Case Study

G-1 made two flights-0900-1200CDT

1400-1700 CDT



AM-Background O_3 concentrations ~ 30 - 40 ppb. Observed small O_3 plume NE of ship channel late in flight.

PM-Well defined O_3 plume exhibiting peak concentrations of ~160 ppb north of the Ship Channel.

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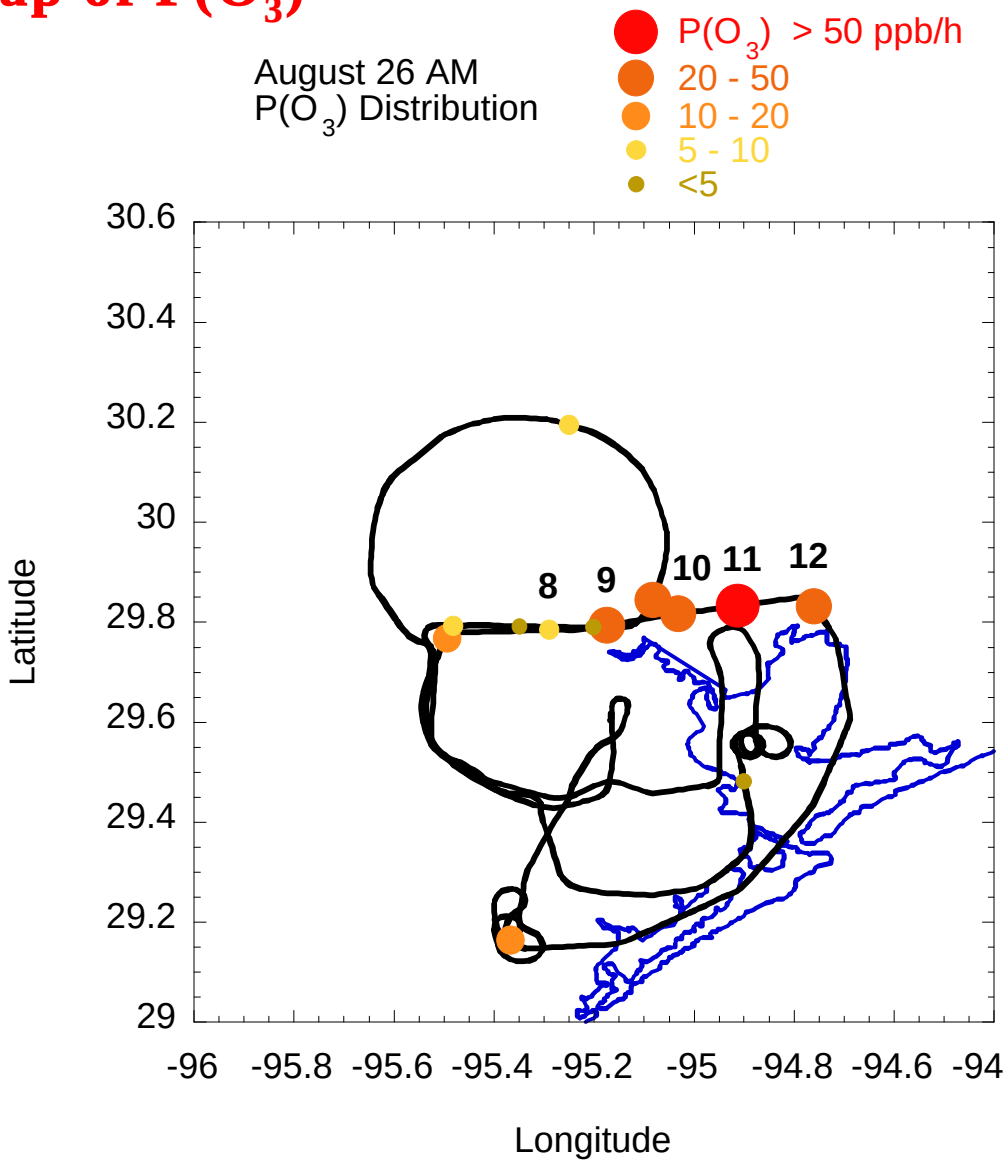
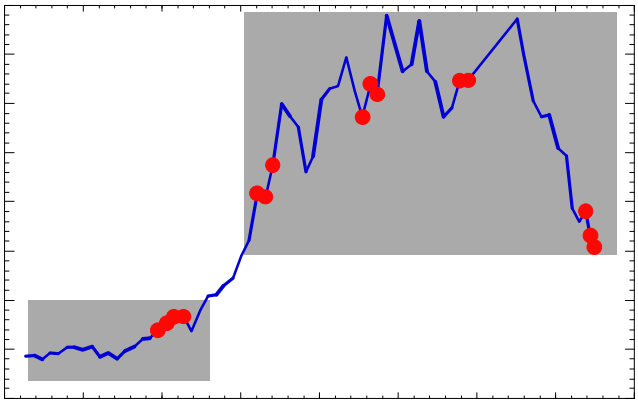
Map of $P(O_3)$

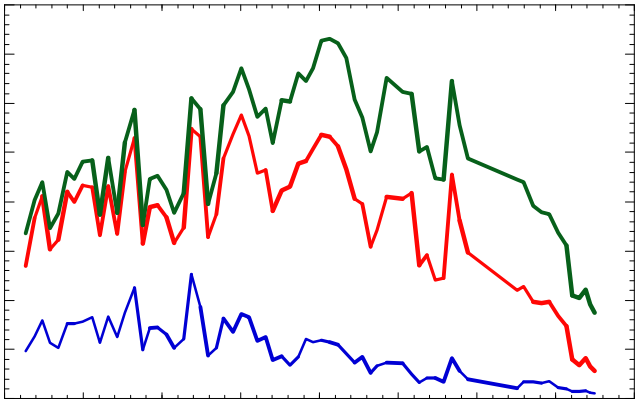


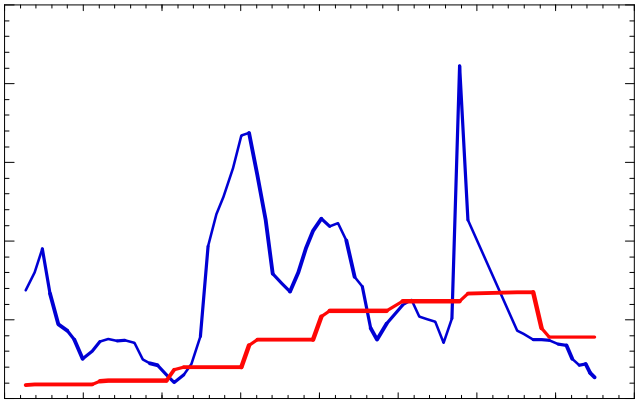
Examine the gradient in the trace gas concentrations and the instantaneous chemistry from the urban area through the industrialize ship channel.

August 26th Case Study

Trace gas concentrations morning flight-







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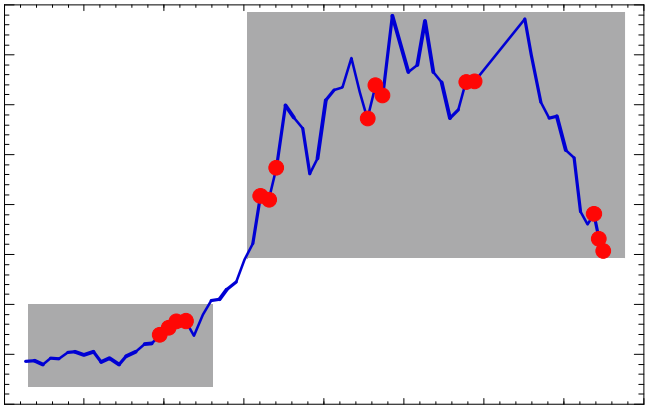
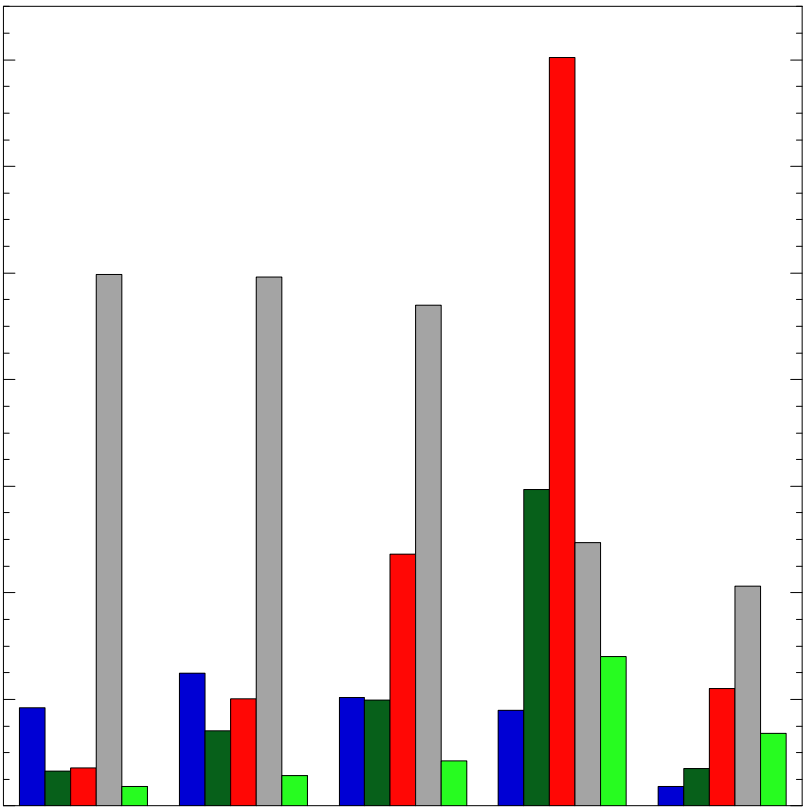
Instantaneous chemistry-





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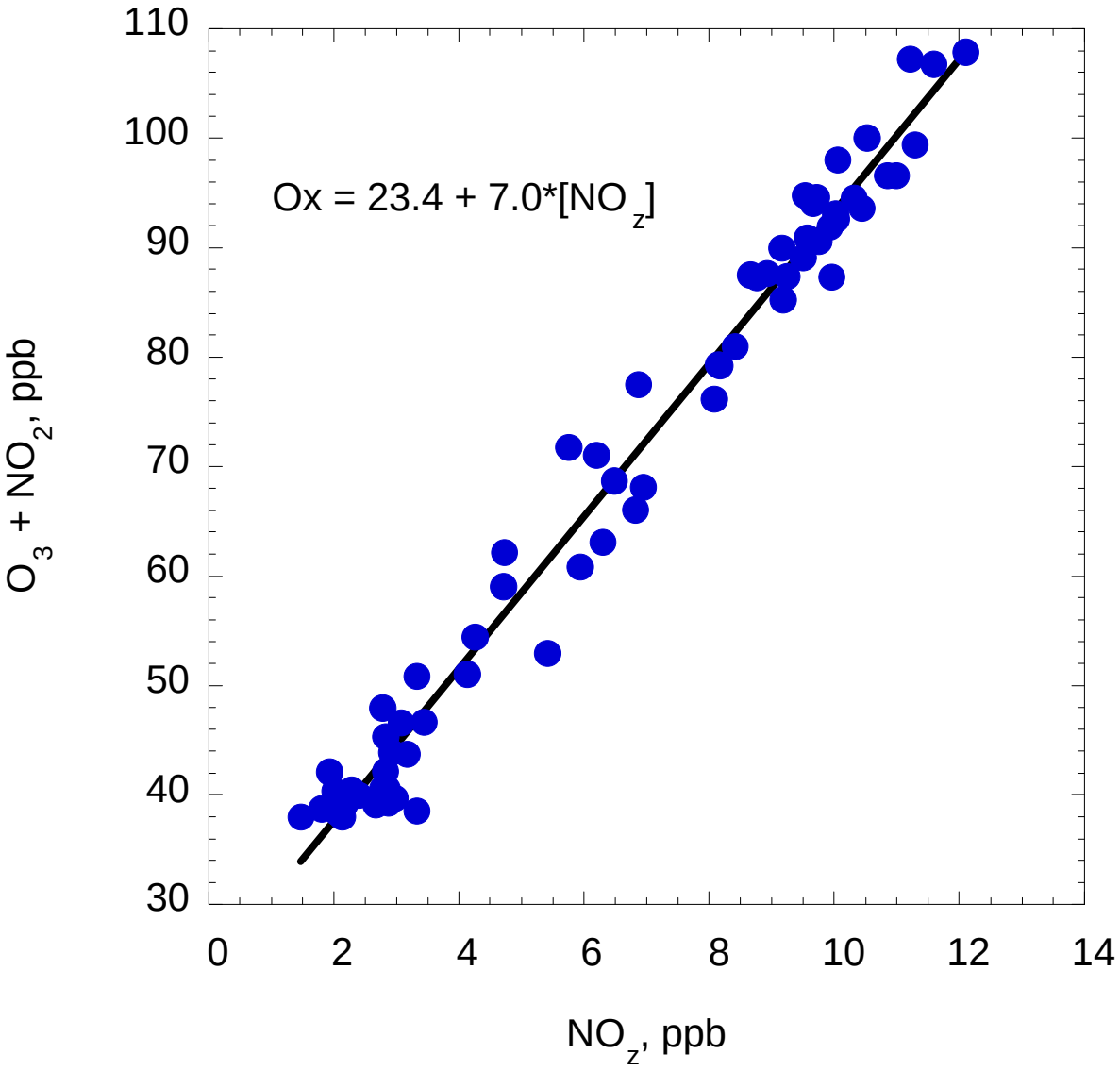
Integral Production efficiency-



August 26th Case Study

Summary, Morning Flight-

- *Background O_3 concentrations very low.*
- *NO_x concentrations in downtown Houston and in the Ship Channel region very similar.*
- *Ozone production rate and efficiency over the heart of Houston was low, and not much O_3 had been produced.*
- *Rate and efficiency of ozone production east of downtown Houston was very high, and significant ozone had already accumulated.*
- *This high rate and efficiency is driven by high HC reactivity.*
- *There was ample NO_x and HC east of Houston to generate substantial additional quantities of O_3.*

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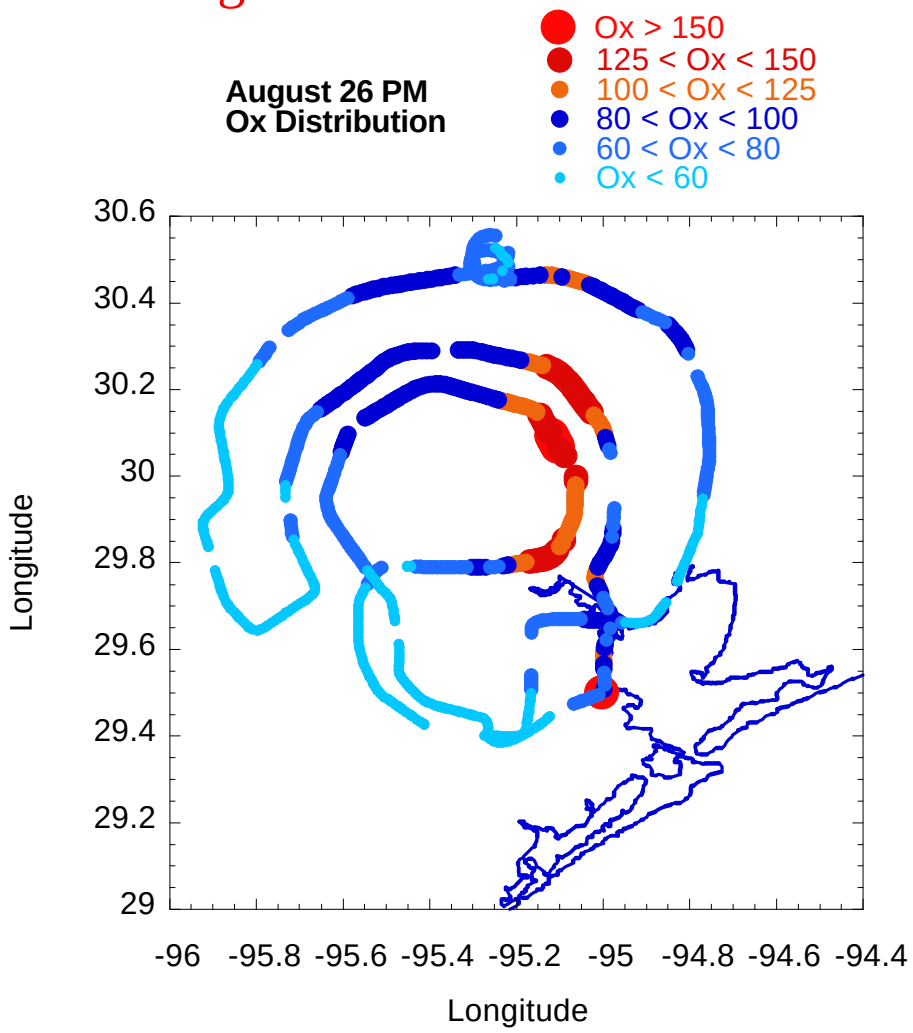
Afternoon Flight-



By mid-afternoon plume containing O_3 concentrations in excess of 150 ppb was observed to the northeast of Houston.

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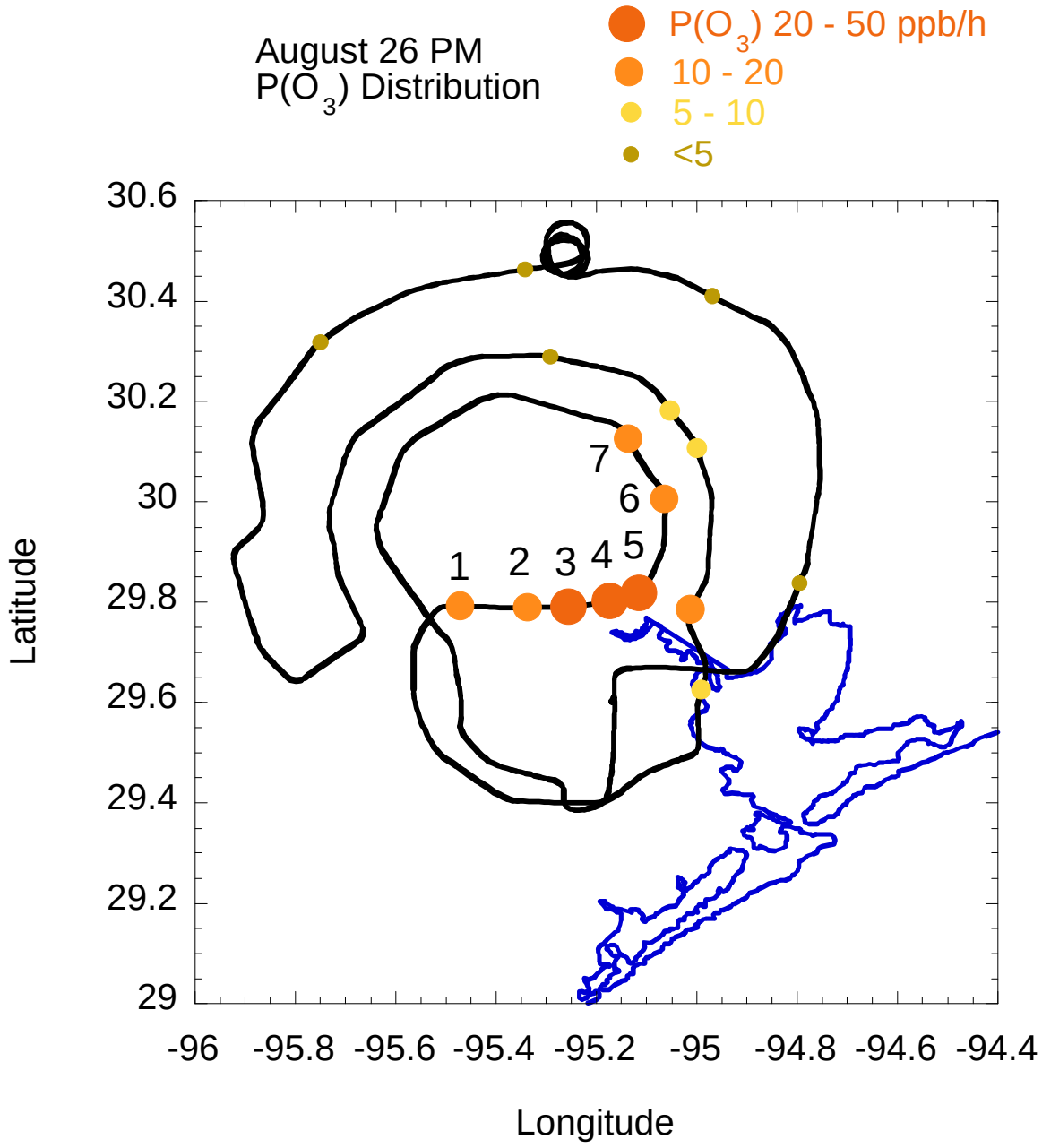
Afternoon Flight-



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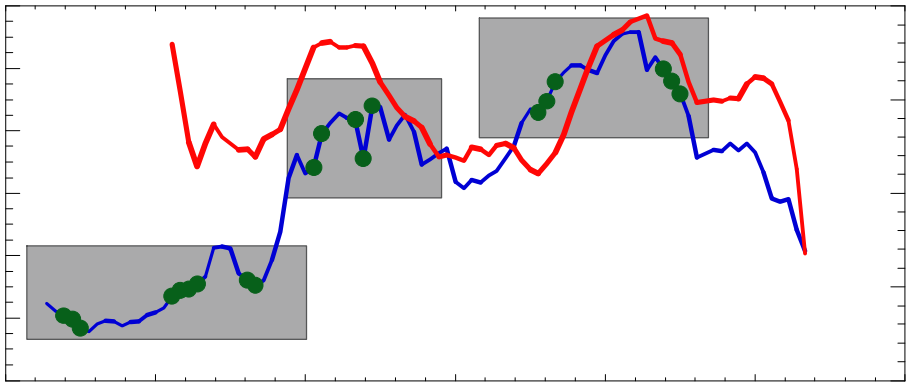
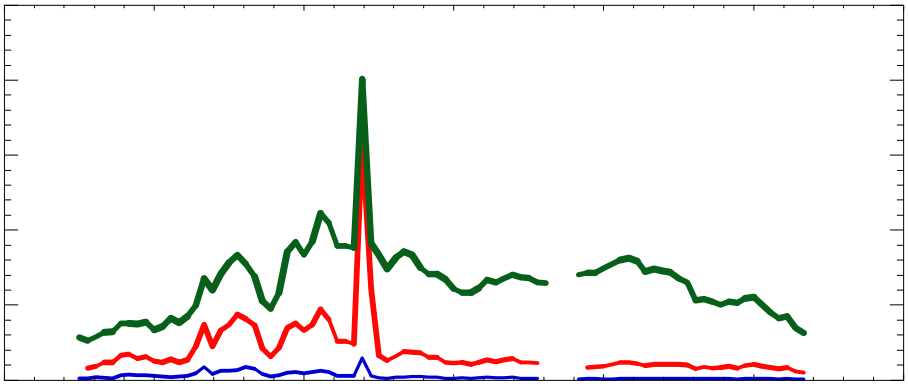
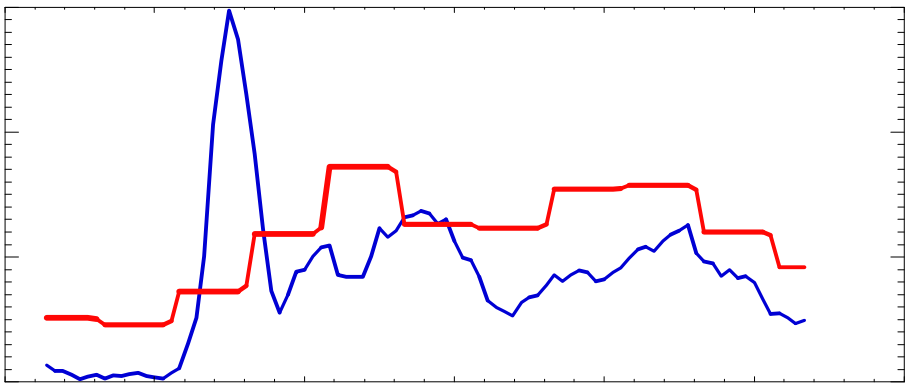
Afternoon Flight-







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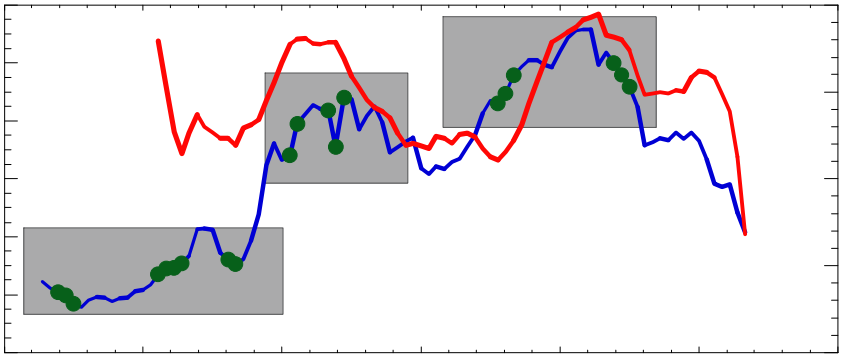
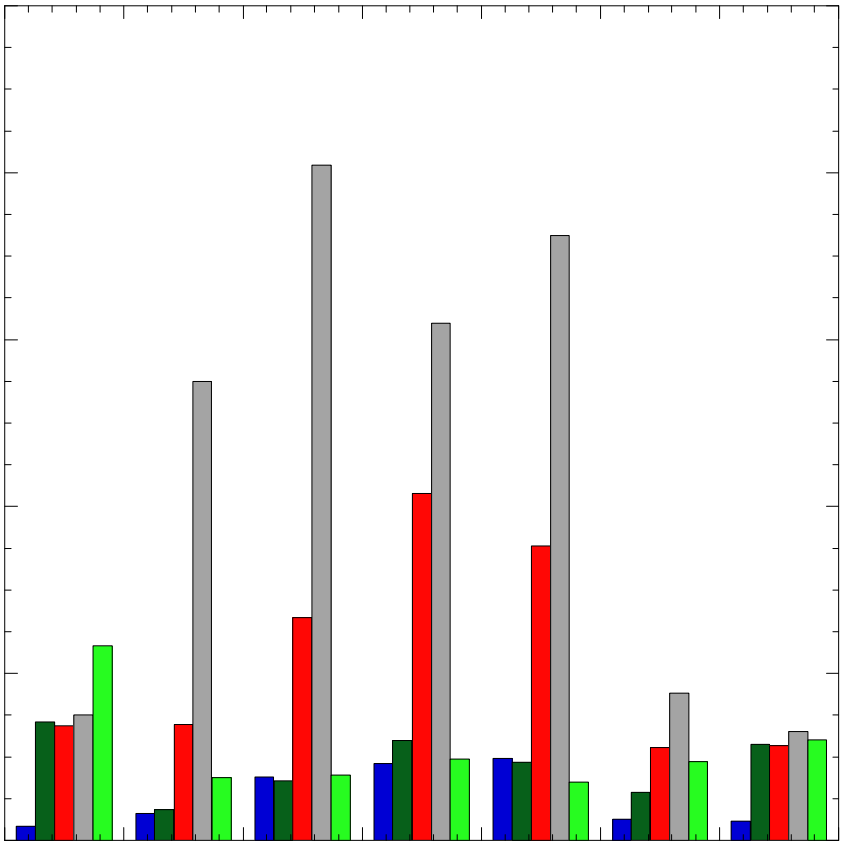
Afternoon flight-

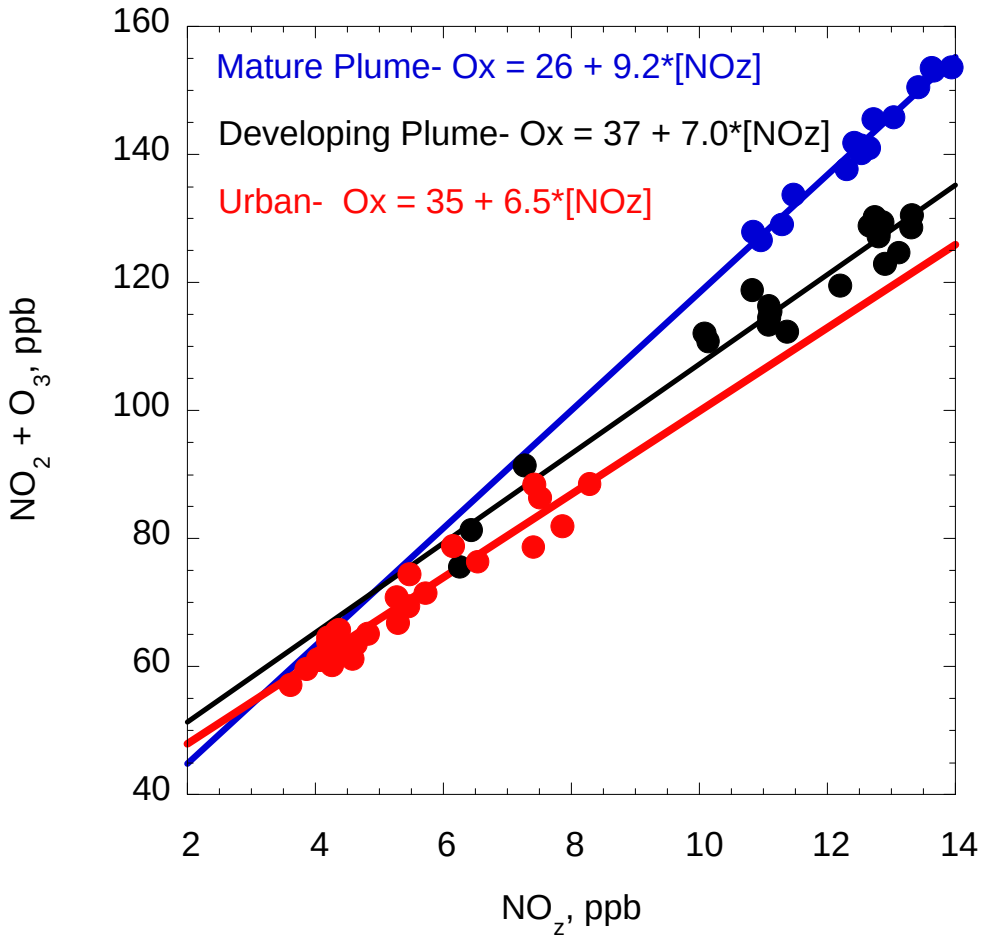




August 26th Case Study

Afternoon flight-

Comparison of Ozone Production Efficiencies



August 26th Case Study

Summary, afternoon flight-

- *Precursor concentrations, even in the Ship Channel, were lower than they were during the morning. Probably due to dilution and consumption of precursors.*
- *Except for the urban samples, $P(O_3)$ was lower than in the morning.*
- *Although lower than in the morning, $P(O_3)$ in the ship channel samples was still very high, with sufficient precursors to produce substantial quantities of additional ozone very efficiently.*
- *$P(O_3)$ was lowest in the region of highest O_3 concentrations due to the availability of NO_x and HC precursors.*

Summary of Study Findings

- *Geographically compact regions containing O_3 concentrations in excess of 150 ppb were frequently observed during TexAQS 2000.*

- *These regions of high ozone concentration were nearly always associated with the emissions of industrial facilities located in and around Houston.*

- *Ozone formation appeared to occur very rapidly and very efficiently. $P(O_3)$ values, on average, were 2-4 times those observed elsewhere in the country. Average efficiencies were nearly twice those observed in Nashville.*

Summary of Findings

- *The highest values of $P(O_3)$, ~150 ppb/h, were observed in the late morning in the vicinity of the Houston Ship Channel.*
- *These high values of $P(O_3)$ were attributable to unusually high concentrations of reactive hydrocarbons (frequently ethylene and propylene).*
- *Ozone formation rates and efficiencies in the Houston urban plume were lower than in the industrial plumes, and were similar to rates and efficiencies measured in urban areas elsewhere.*