NO_x and VOC Sensitive O_3 Production

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Box model calculations constrained by G-1 observations

- O_3 Production rates and sensitivities
- Comparison with other cities

H_2O_2 and NO_z observations

Some supporting results

- Lei et al., Characterizing ozone production ..., ACP, 2007
- Volkamer et al., Oxidative capacity of the Mexico City ..., ACPD, 2007
- Tie et al., Characterization of chemical oxidants ... AE, 2007
- Shirley et al., Atmospheric oxidation ... ACP, 2006

ftp://ftp.asd.bnl.gov/pub/ASP Field Programs/

Low and High NO_x Chemistry

Low NO_x

$P(O_3) \propto Q^{1/2}$ [NO]
All radicals removed by peroxides, *i.e.* $2\ HO_2 \rightarrow H_2O_2$
$\partial\, ln P(O_3)/\partial\, ln [NO] = 1$
$\partial\, ln P(O_3)/\partial\, ln [VOC] = 0$

High NO_x

$P(O_3) = Y\ Q\ (VOC/NO_2)_{OH\ reactivity}$
All radicals removed by NO_x, *i.e.* $OH + NO_2 \rightarrow HNO_3$
$\partial\, ln P(O_3)/\partial\, ln [NO] = -1$
$\partial\, ln P(O_3)/\partial\, ln [VOC] = 1$

Q = radical production rate
Y = number peroxy radicals from OH + VOC (~ 1.6 ± 6%)

Why Ln/Q?

Ln = radical removal rate by NO_x
Q = radical formation rate

Ln/Q = 0: Low NO_x, $P(O_3)$ is NO_x limited

Ln/Q = 1/2: $P(O_3)$ has equal sensitivity to NO_x & VOCs

Ln/Q = 2/3: Ridge line, $\partial P(O_3)/\partial[NO_x] = 0$

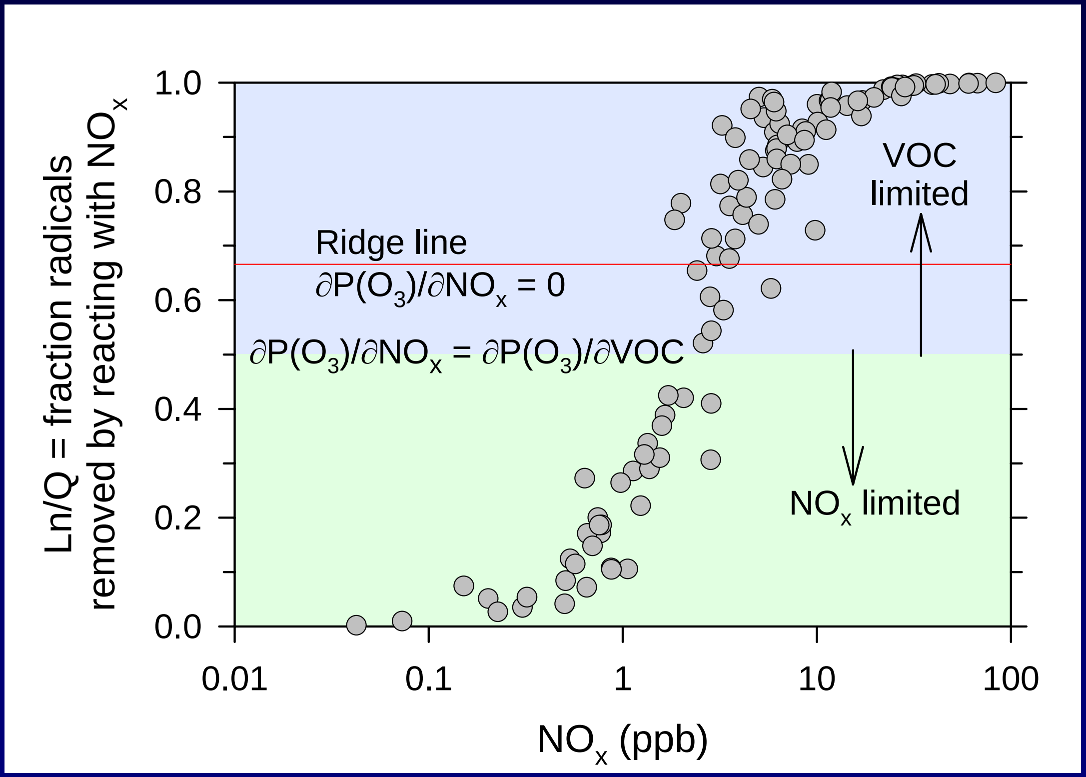
Ln/Q = 1: High NO_x, $P(O_3)$ is VOC limited

Ln/Q = f ($[NO_x]^2$ ☟ $(NO_2/VOC)_{reactivity}$ ☟ 1/Q)

VOC limited chemistry from:

High NO_x, low VOC to NO_x ratio, low Q

High and Low NO_x Chemistry



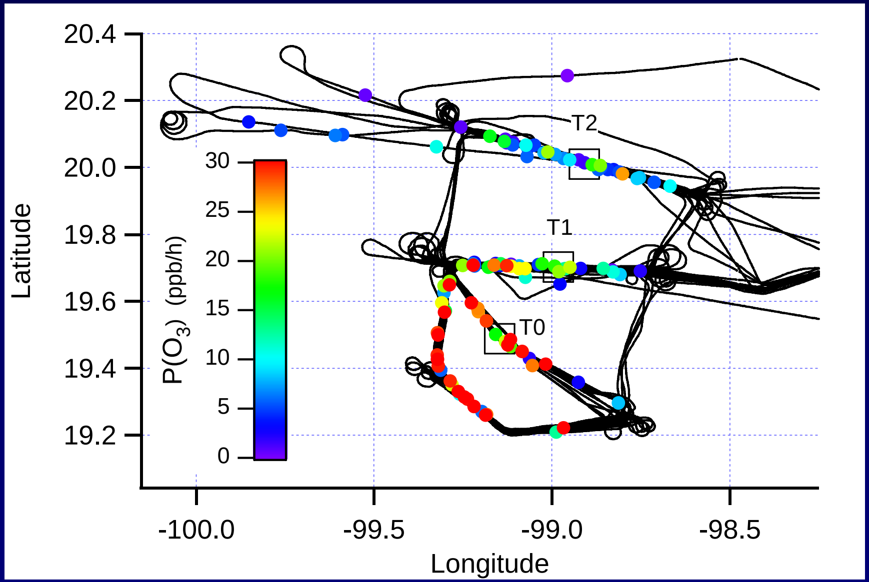
$P(O_3) = Y\ Q\ (VOC/NO_2)_{reactivity}$
High NO_x chemistry

$P(O_3) \propto Q^{1/2}\ [NO]$
Low NO_x chemistry

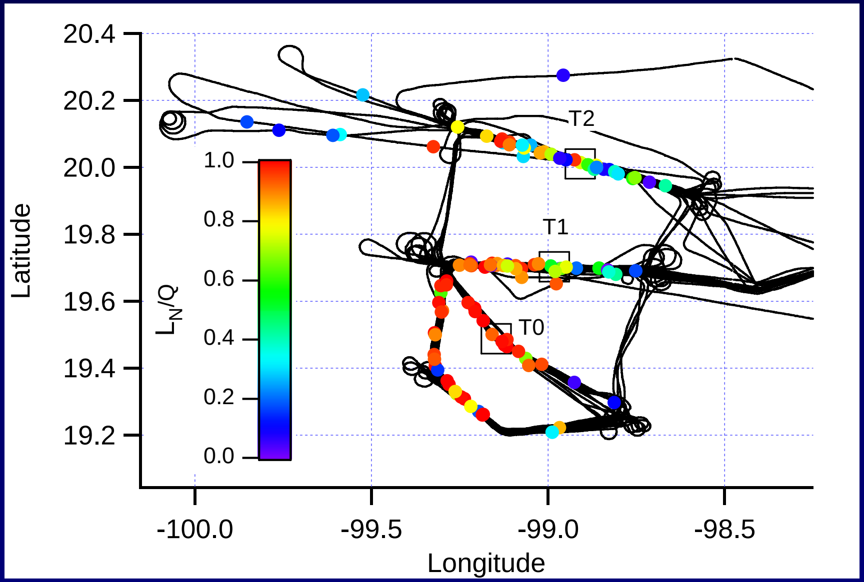
- If NO_x > ~5 ppb, O_3 production is VOC limited
- If NO_x < ~2 ppb, O_3 production is NO_x limited

Location, Location, Location

Ozone Production Rate



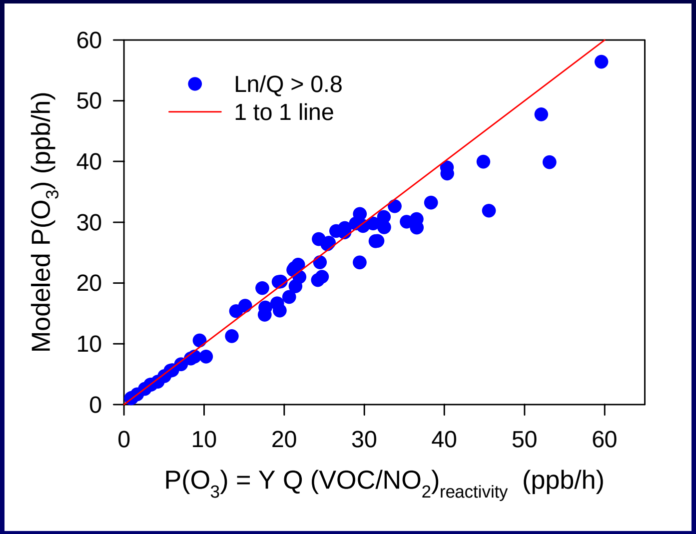
$Ln/Q = R+NO_x$/radical production rate



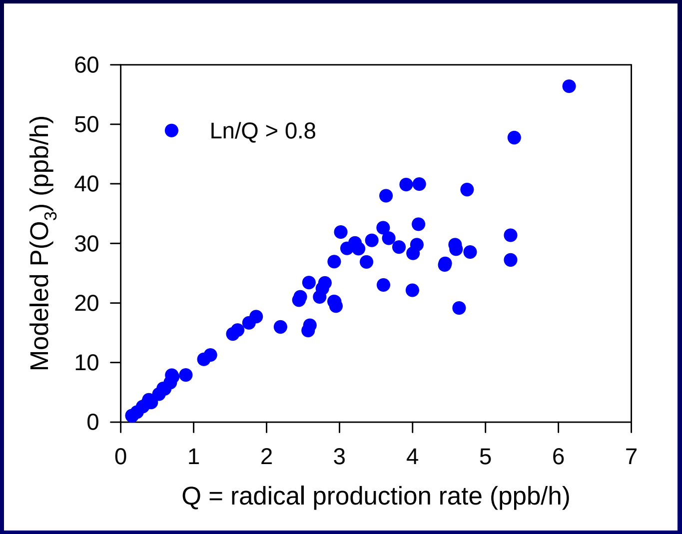
- Highest $P(O_3)$ over City. Lower $P(O_3)$ over T1 and T2.
- City is VOC limited. Ln/Q near 1.

High NO_x Formula

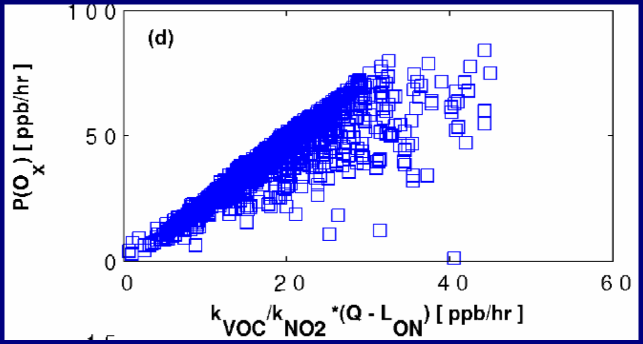
Test of Formula

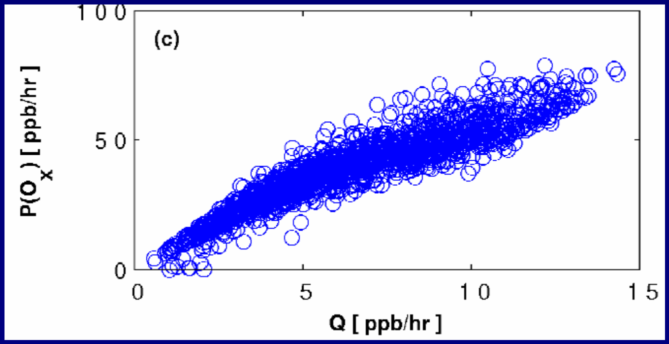


$P(O_3)$ depends mainly on Q

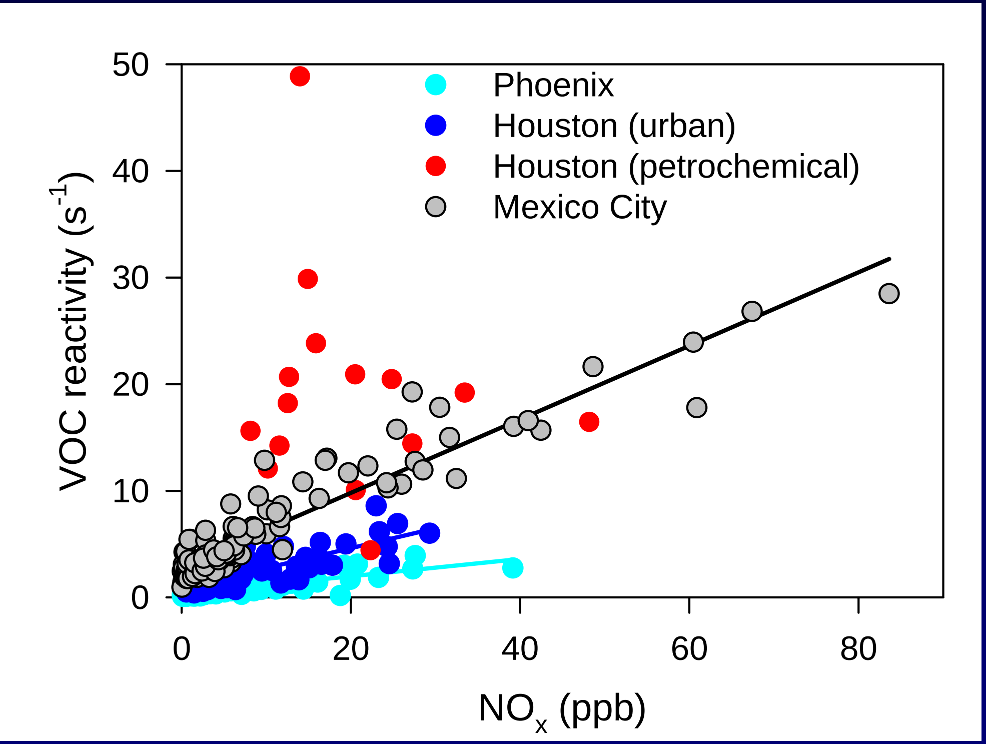


Eulerian model results of Lei et al (2007), low and high NO_x





3+ City Comparison



VOC to NO_x ratio

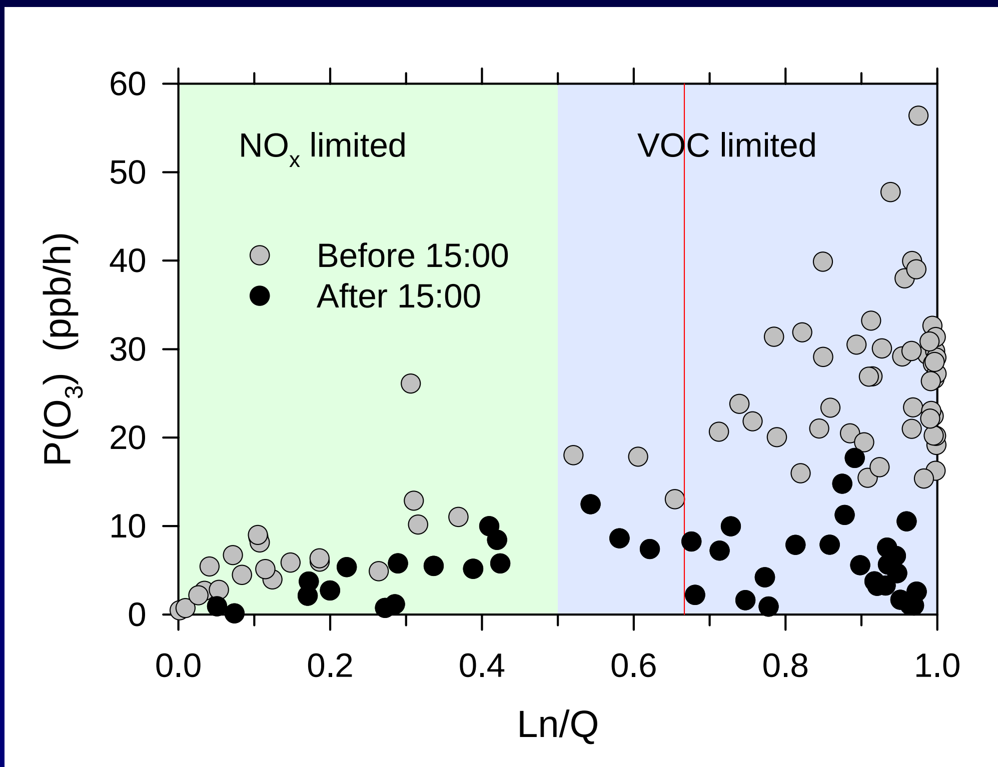
Mexico City > Houston (urban) > Phoenix

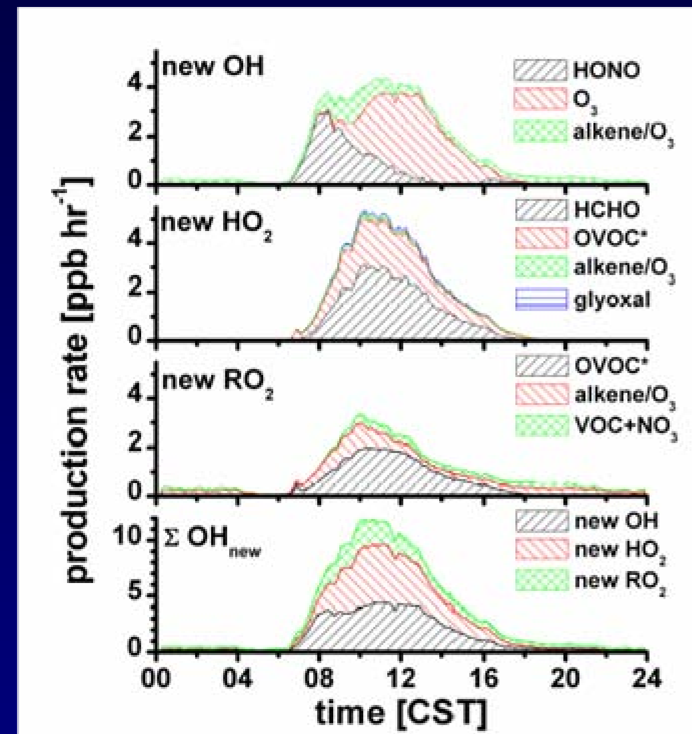
by itself this would make Mexico City less VOC limited

but: $[NO_x]$ very high and "extra" NO_x^2 dependence in Ln/Q

High ratio for Houston (petrochemical) yields mixed sensitivities

Highest $P(O_3)$ from VOC Limited Conditions





$P(O_3)$ = Y ☝ Q ☝ $(VOC/NO_2)_{reactivity}$

$P(O_3)$ variability mostly due to Q

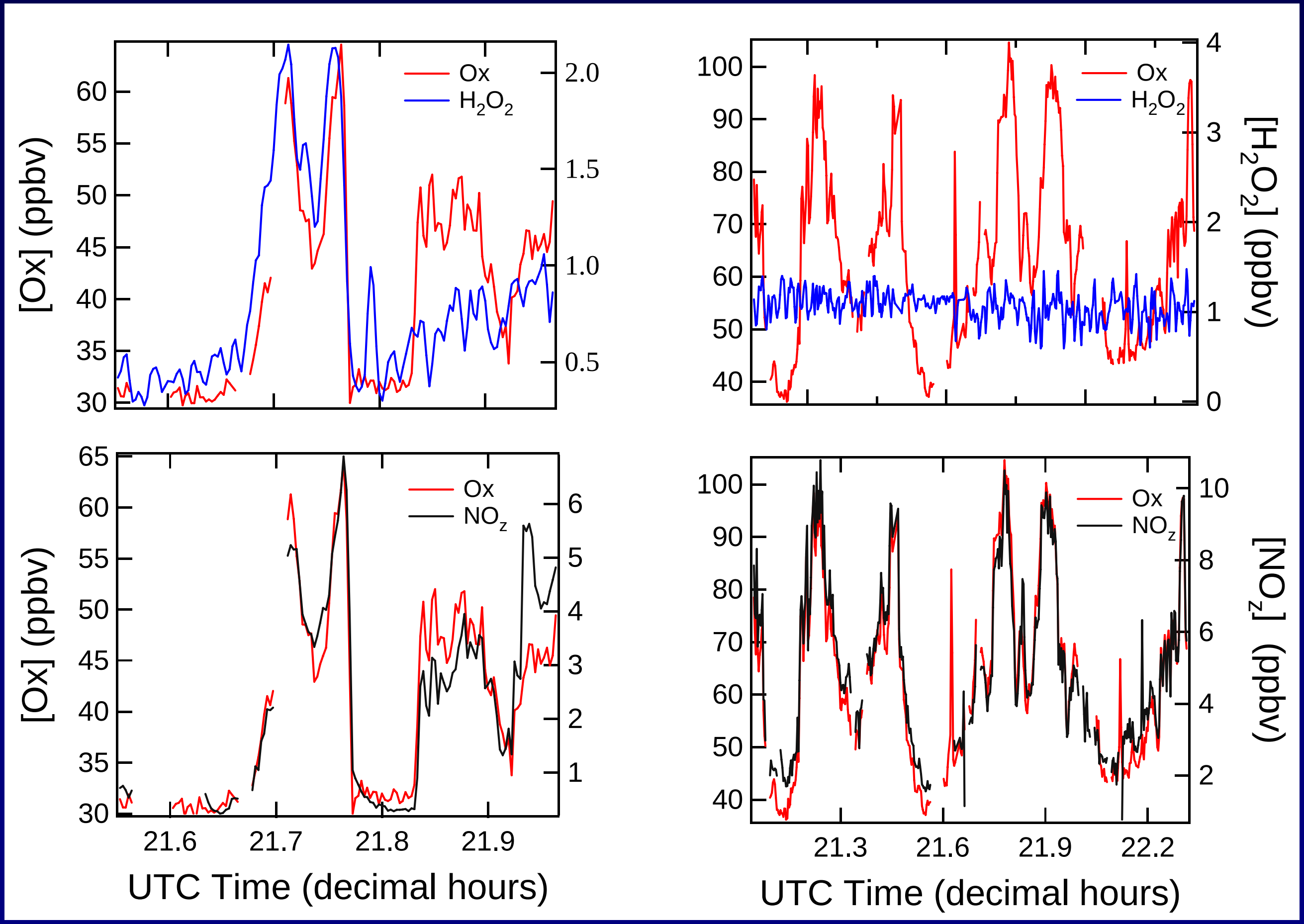
More than O_3 and HCHO for Q

Volkamer et al., ACPD, 2007

Peroxide Formation in the Source Region

March 19, 2006
Two plumes show H_2O_2 production

March 20, 2006
No H_2O_2 production in the plumes.
Overall, **fifty** plumes had **no** H_2O_2 formation



Conclusions

- O_3 in source region is VOC sensitive

  Ln/Q near 1

  ★ In O_3 plumes, NO_z formed but not H_2O_2

  Eulerian model calculations for 2003

  Lei et al, 2007; Tie et al 2007; and ...

  HO_x loss primarily OH + NO_2

  Shirley et al, 2006

- VOC/NO_2 reactivity ratio higher than other cities

  G-1; Shirley et al 2006; and ...

- Radical production rates dominate P(O_3) variability

  Not just O_3 and HCHO

  Volkamer et al, 2007