Diagnostic Modeling with G-1 Obs.

- Plume Evolution

  L_N/Q (fraction radicals removed by NO_x)

  describes transition from:
  source-like VOC sensitive to
  background-like NO_x sensitive

- Ozone Production Efficiency

  $OPEx = \Delta O_3/\Delta NO_z$
  $OPEr = \Delta O_3/(\Delta NO_z + 2\Delta peroxide)$

  How much O_3 is produced?
  An observable to test models against

- Future Directions

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Why L_N/Q?

Radical Source = Radical sink

$Q = L_N(\text{radical}+NO_x) + L_R(\text{radical}+\text{radical})$

L_N/Q = fraction radicals removed by NO_x

An Old Result:

L_N/Q tells us all about $P(O_3)$ sensitivity

$d\ln P(O_3)/d\ln[NO] = (1-3/2L_N/Q)/(1-/2L_N/Q)$

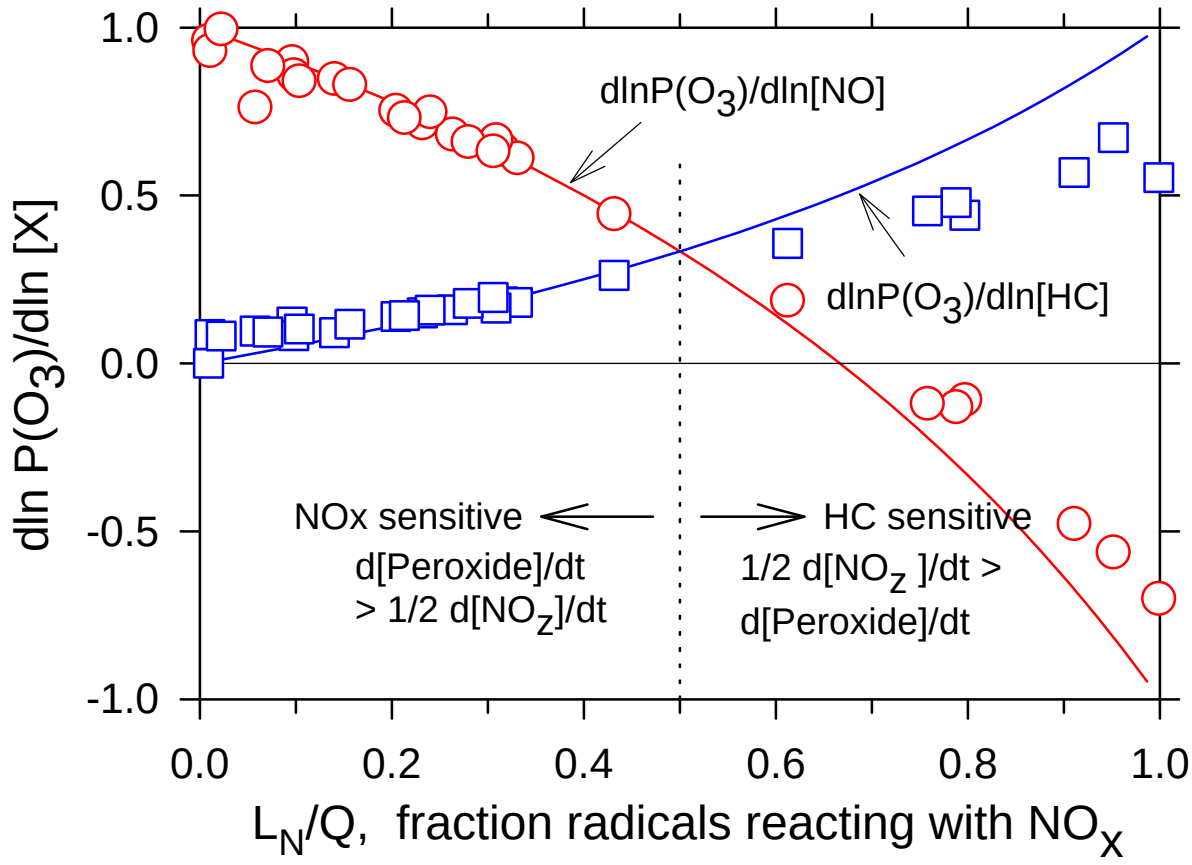
$d\ln P(O_3)/d\ln[VOC] = 1/2L_N/Q/(1-1/2L_N/Q)$

A New Result

L_N/Q is a simple analytic function of NO_x, VOCs, and Q

$P(O_3)$ Sensitivity Depends Only on L_N/Q

(Old Result)



Data points are CSS calculations from SOS 95

Solid lines are analytic results

L_N/Q Depends on NO_X, VOCs, Q

(New Result)

$$L_N/Q = -\alpha/2 + (\alpha^2 + 4\alpha)^{1/2}/2$$

$$\alpha = (k_1[NO_2]\, k_3\gamma[NO]/(k_2[VOC]))^2\, (1/(2\, Q\, k_{eff}))$$

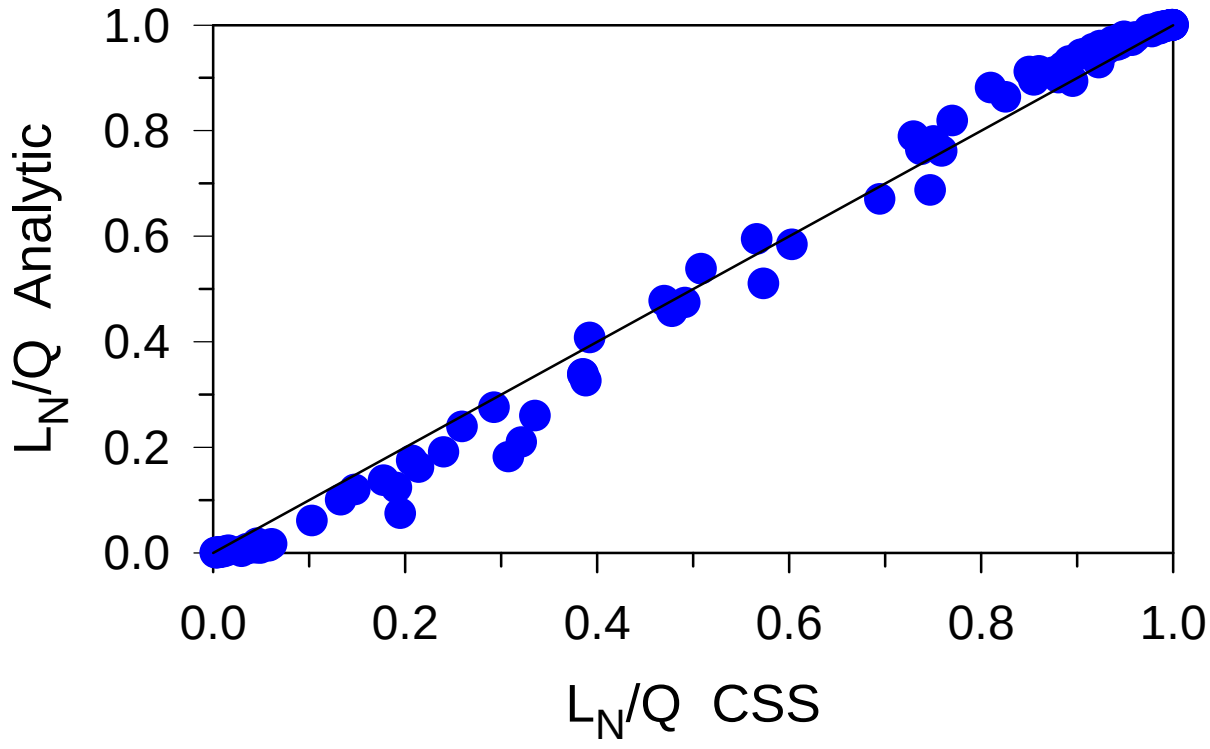
k_1: $OH + NO_2 \rightarrow HNO_3$
k_2: $OH + VOC \rightarrow HO_2$ or RO_2
k_3: $HO_2 + NO \rightarrow NO_2$
k_{eff}: Peroxy + Peroxy $\rightarrow$ Peroxide

L_N/Q is a monotonic increasing function of:

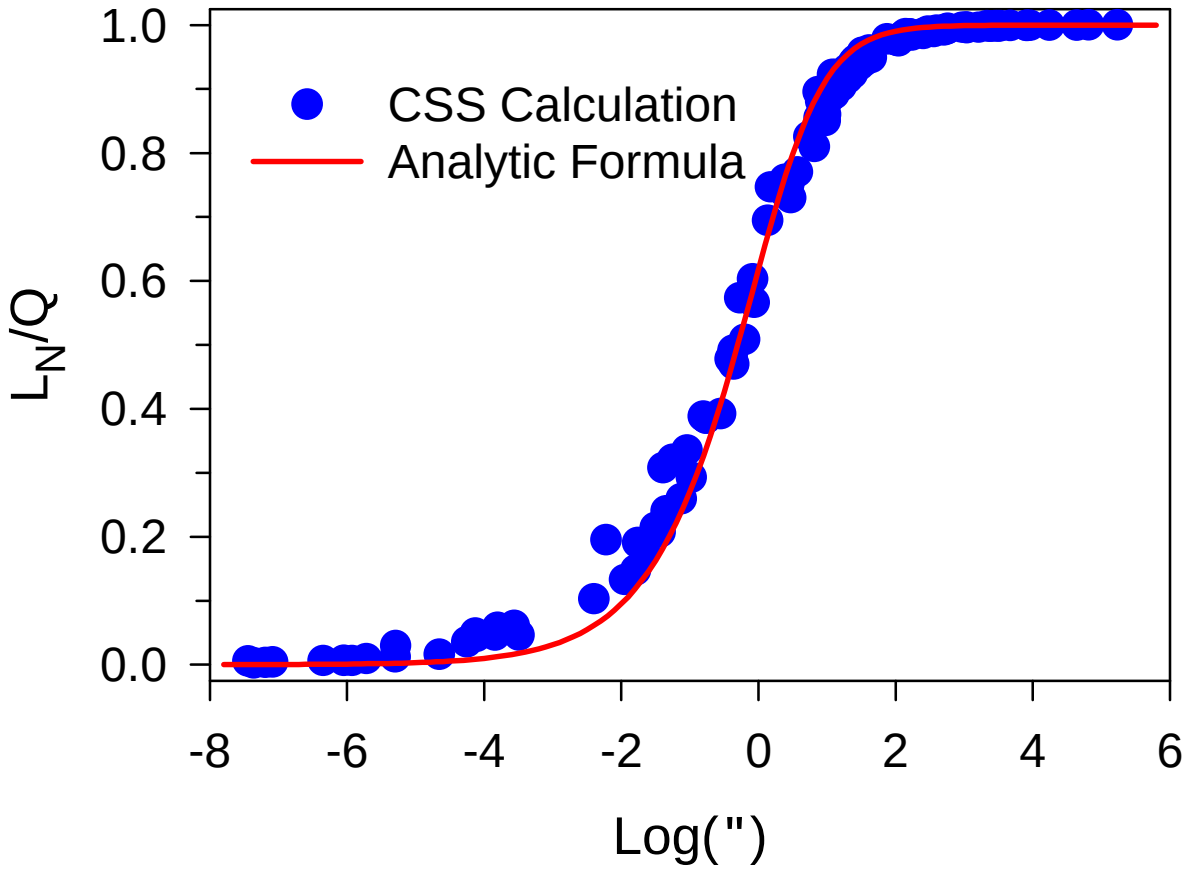
$$([NO_X]^4/[VOC]^2)/Q$$

Test of L_N/Q Analytic Formula

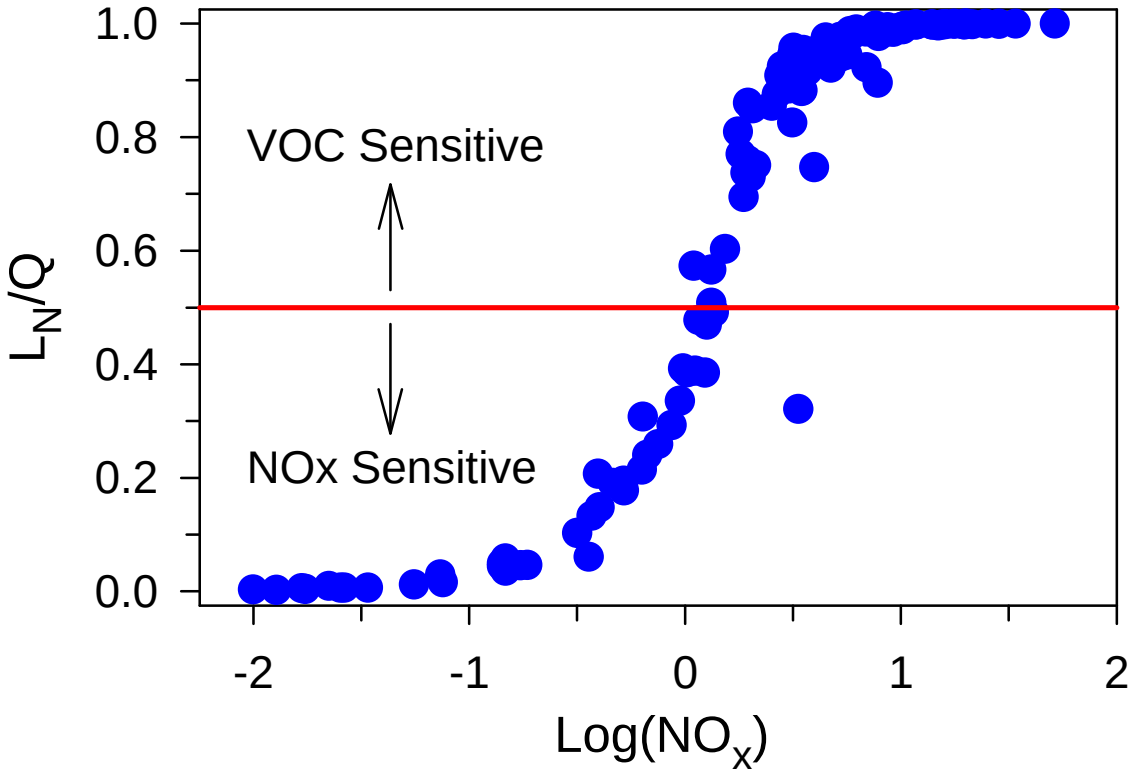
Data from Phoenix



L_N/Q Depends on $([NO_X]^4/[VOC]^2)/Q$



L_N/Q Depends Mainly on NO_X
(Phoenix data)



Note very sharp transition at NO_x =1ppb from VOC to NO_x sensitive chemistry

PLUME EVOLUTION

L_N/Q Depends on $(NO_X)^2 * (NO_X/VOC)^2 * 1/Q$

- OH Chemistry: Decreases NO_X and (NO_X/VOC)
- Dilution: Decreases NO_X and (NO_X/VOC)
- O_3 Production: Increases Q

For all 3 reasons a plume evolves from VOC sensitive to NO_X sensitive chemistry

Ozone Production Efficiency

$OPE_x = \Delta O_x/\Delta NO_z$ and
$OPE_R = \Delta O_x/\Delta(NO_z + 2\ peroxide)$

Number of molecules O_3 formed per NO_x molecule oxidized, or per Radical used

Determined from observed O_3+NO_2 and NO_z in a plume – most often as a regression slope

Is this OK?

Great Correlations

Why?

Values vary from place to place

What does this tells us about chemistry and control measures?

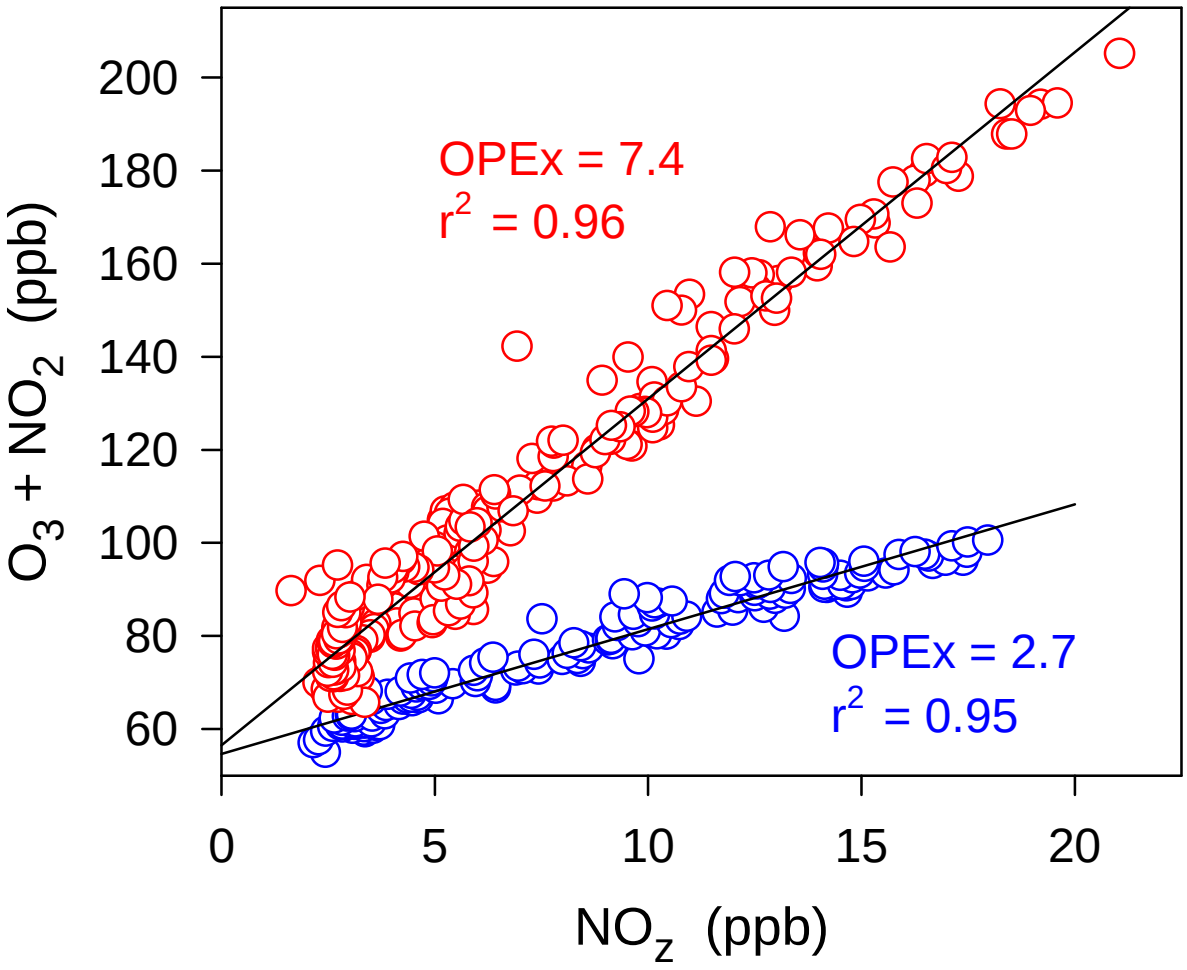
CSS calculations give us $P(O_x)/P(NO_z)$

Can OPE_x be determined from local calculations?

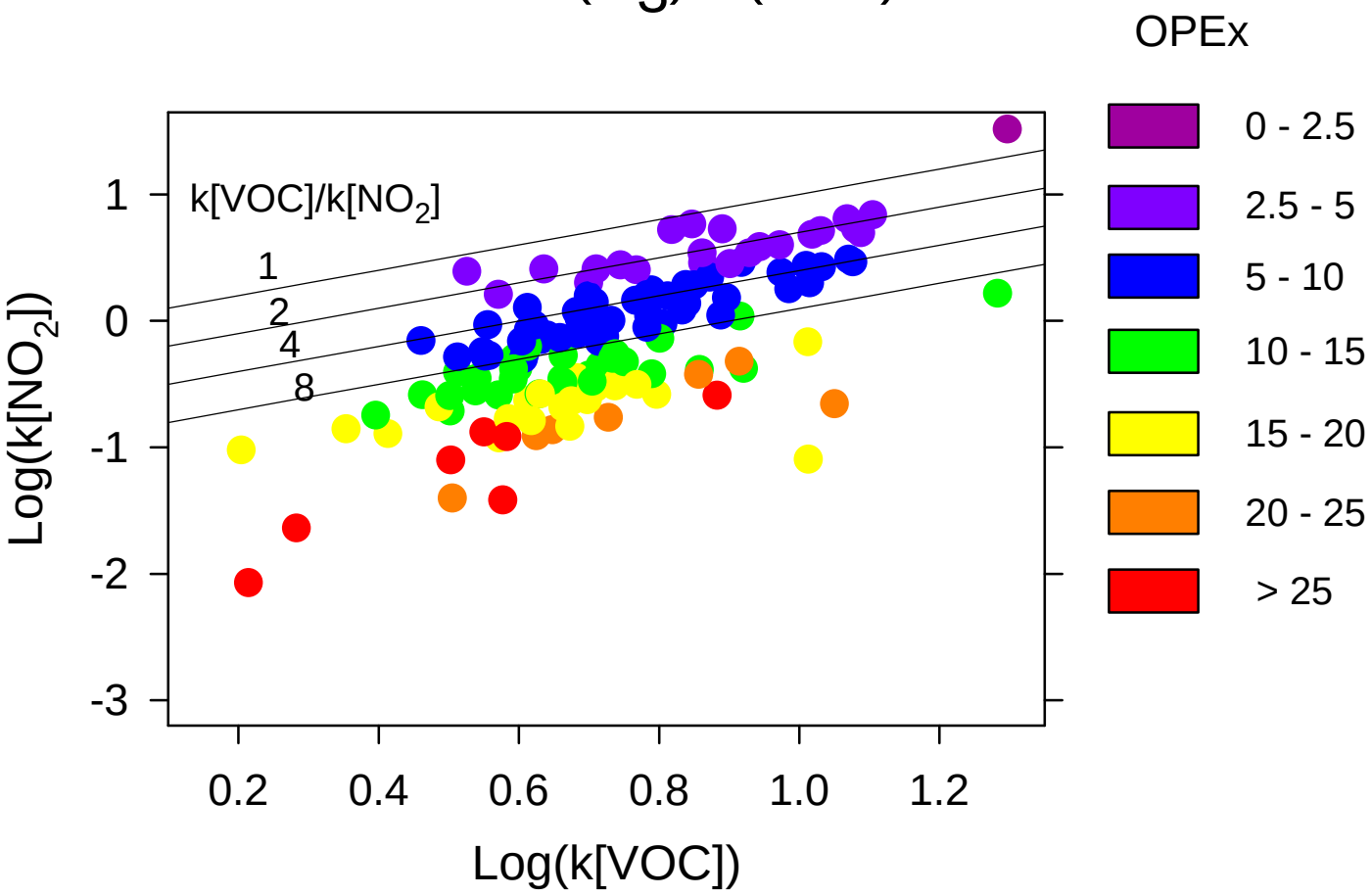
Ozone Production efficiency

Texas 821 PM 2000

Phoenix 601 PM 1998



Philadelphia
OPEx = $P(O_3)/P(NOz)$



VOCs = All

Future Directions

Use Eulerian Model Output from PNNL

Surrogate reality to augment G-1

True Lagrangian "experiment"

Emission controls

Relation between integrated quantity (ie, O_3) and instantaneous quantity (ie, $P(O_3)$)

Use NCAR Master Mechanism

Role of secondary organics for oxidants and aerosols