Chamber Evaluation of Process Diagnostics and Photochemical Indicators

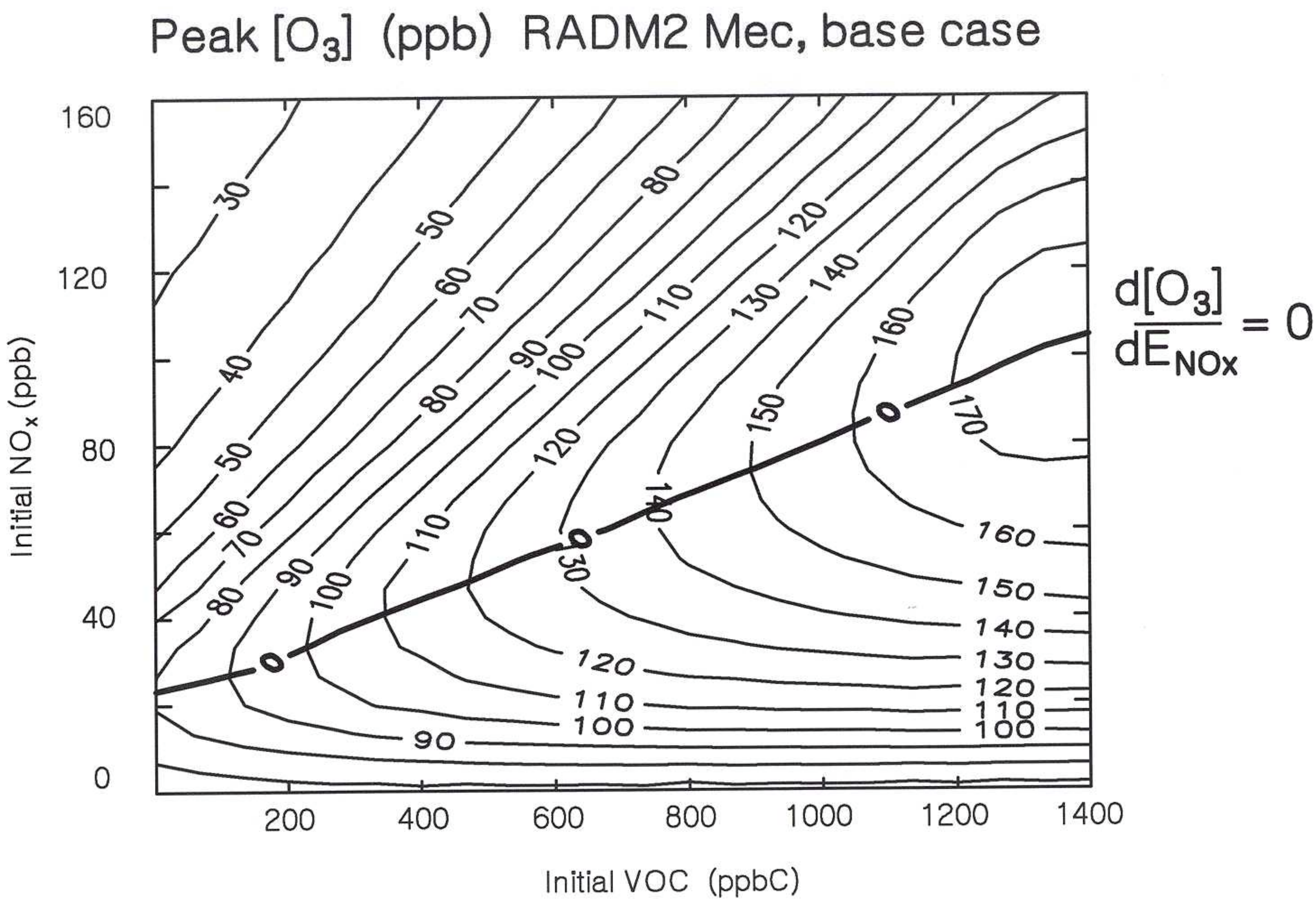
August 2, 2005

Gail Tonnesen, Chao Jung-Chien, Bill Carter

University of California, Riverside
Bourns College of Engineering
Center for Environmental Research and Technology

Outline

- **Process Diagnostics**
  - Chemistry Review
  - Local Diagnostics
  - Cumulative Diagnostics
- **Indicators of [O_3] and P(O_x) Sensitivity**
  - Theoretical Derivation
- **Chamber Evaluation of Indicators**


Peak [O3] (ppb) RADM2 Mec, base case
Initial NOx (ppb)
Initial VOC (ppbC)
$\frac{d[O_3]}{dE_{NOx}} = 0$

Definitions

$NO_x = NO + NO_2$

$NOX = NO_x + (NO_3 + 2\ N_2O_5 + HONO + \ldots)$

$NO_z = HNO_3 + RNO_3 + NO_3^- + PAN$

$NO_y = NOX + NO_z$

$HO_x = OH + HO_2 + RO_2$

Definitions

$$O_x = O_3 + NO_2 + PAN + O^1D + O^3P + 2\ NO_3 + 3\ N_2O_5$$

$$P_G(O_x) = k(HO_2 + RO_2)NO$$

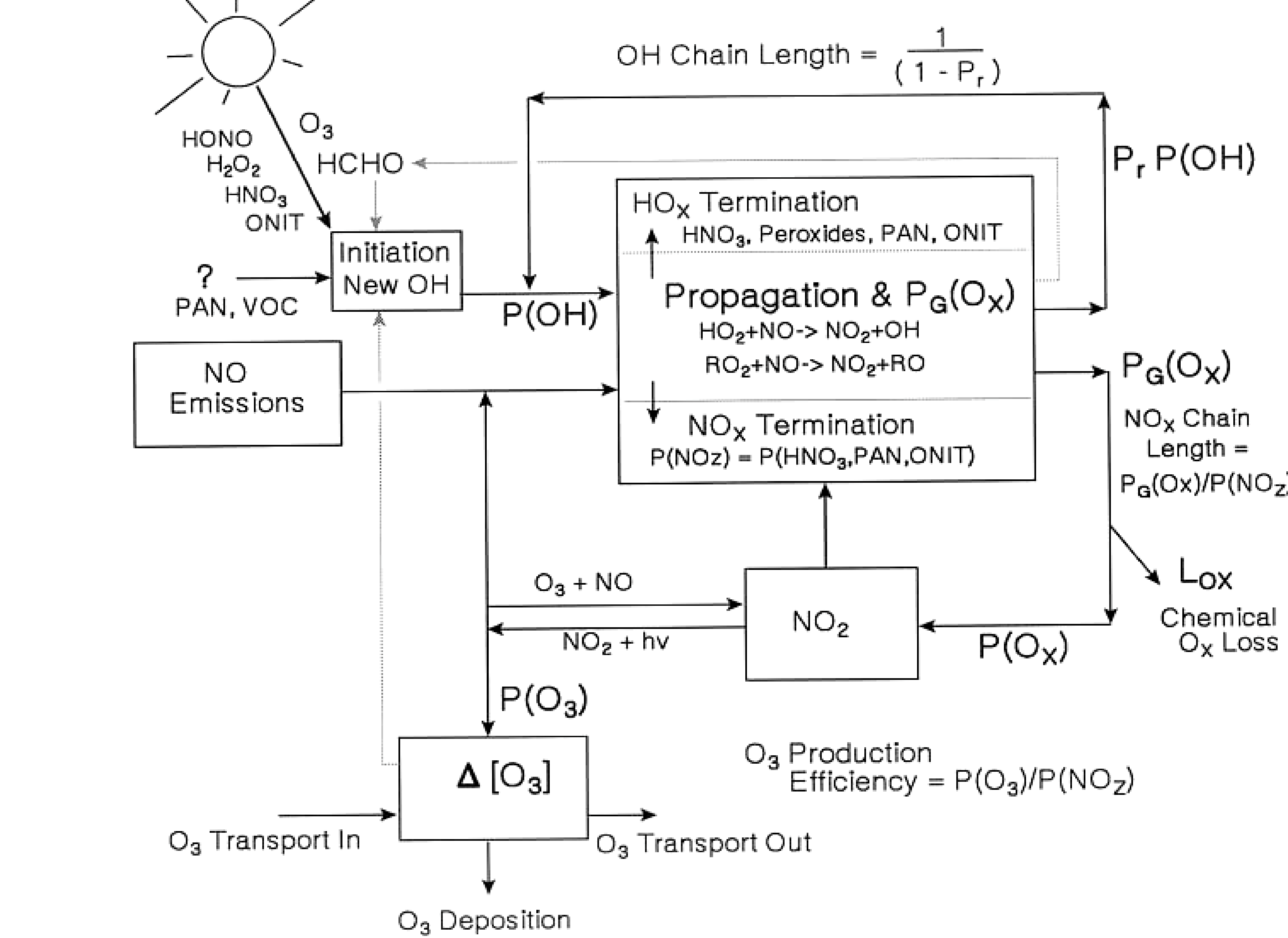
$$P(O_x) = P_G(O_x) - \text{Chemical Loss of Ox}$$

$$= P(O_3) + \text{oxidation of NO}$$

$$[O_3] = \int P(O_3)dt + [O_3]_{initial}$$

$$[O_3] = [O_x] - [NO_z]$$

- For urban environments oxidation of NO is a significant component of the system reactivity. Must consider sensitivity of total Ox to understand O3 sensitivity.



OH Chain Length = 1 / (1 - Pr)
O3
HONO
H2O2
HNO3
ONIT
HCHO
Pr P(OH)
HOx Termination
HNO3, Peroxides, PAN, ONIT
Initiation
New OH
?
PAN, VOC
P(OH)
Propagation & PG(Ox)
HO2+NO-> NO2+OH
RO2+NO-> NO2+RO
NO
Emissions
PG(Ox)
NOx Termination
P(NOz) = P(HNO3,PAN,ONIT)
NOx Chain
Length =
PG(Ox)/P(NOz)
Lox
Chemical
Ox Loss
O3 + NO
NO2
NO2 + hv
P(Ox)
P(O3)
Δ [O3]
O3 Production
Efficiency = P(O3)/P(NOz)
O3 Transport In
O3 Transport Out
O3 Deposition

Model Evaluation

- Local Diagnostics
  - Instantaneous reaction rates at a given site.
  - Examples: P(OH), $P(O_3)$, $P(O_x)$, $P(O_x)/P(NO_z)$
  - Cannot get production rates from time-series at a site because air is flowing through the site.
- Cumulative Trajectory Diagnostics
  - cumulative history of reaction rates and other loss processes in an air parcel integrated over hours or days.
  - Examples: $[H_2O_2]$, $[HNO_3]$, $[O_3]$, $[O_3]/[NO_z]$

Data Needs for Local Diagnostics

- **Radical Initiation:**
  - J-values & HCHO, O_3, H_2O, HONO, H_2O_2, PAN
- **OH Chain Length:**
  - NO, NO_2, speciated HC, total RO_2, O_3
- **Radical Termination:**
  - NO_2 & OH, HO_2 & RO_2, NO & RO_2, O_3
- **NO_x Termination, $P(NO_z)$:**
  - NO_2 & OH, NO & RO_2, RCO_3, NO_3,N_2O_5, H_2O
- **$P_g(O_x)$:**
  - NO, HO_2, RO_2.

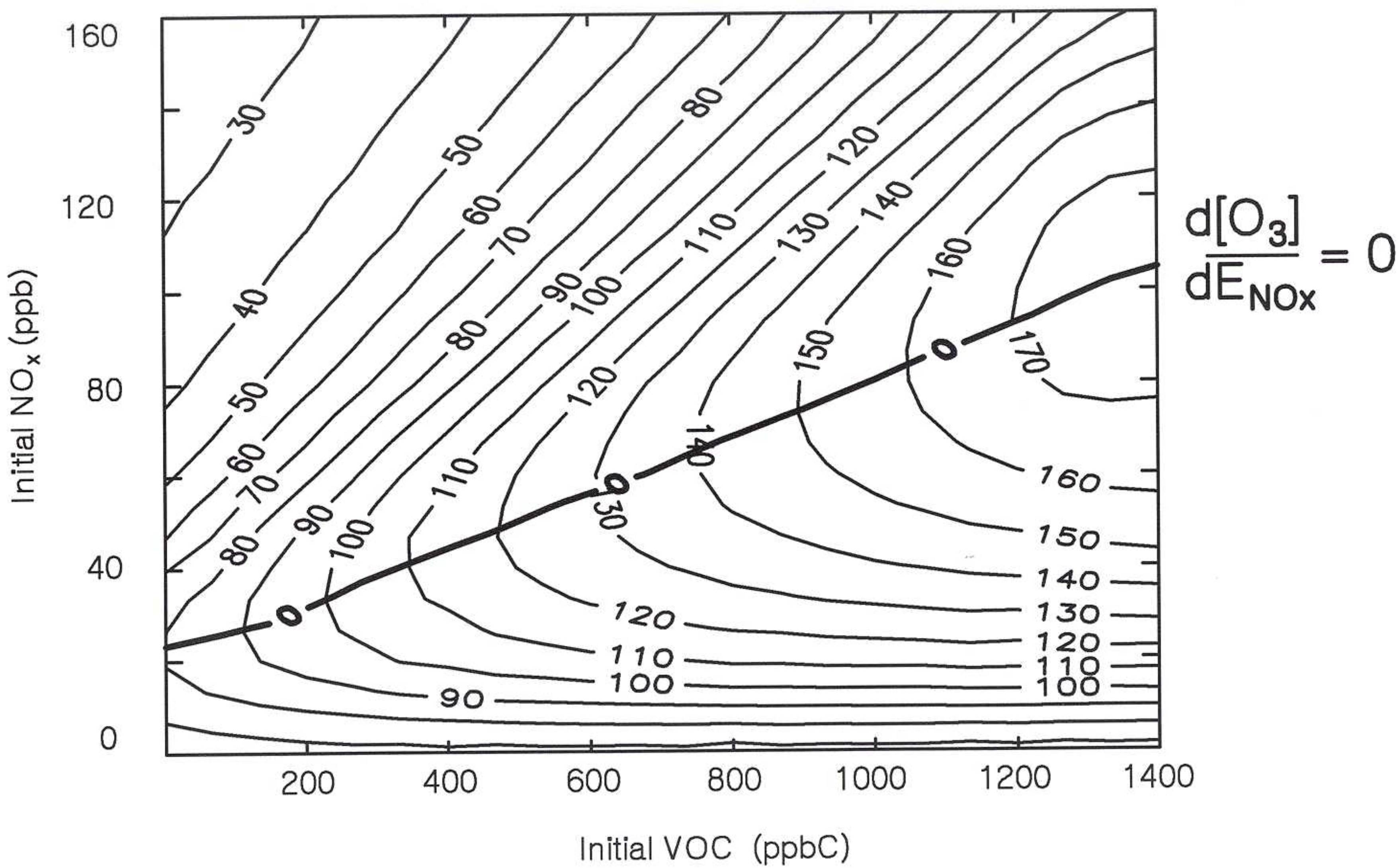
Data Needs for Cumulative Diagnostics

- **Radical Initiation & Termination (approximate):**
  - (2 peroxides + NO_z)
  - 2 peroxides/NO_z
- **OH Chain Length (approximate):**
  - O_3 / (2 peroxides + NO_z)
- **NO_x Termination, P(NO_z):**
  - HNO_3, speciated RNO_3, NO_3^-, PAN
- **P(O_3), P(O_x):**
  - O_3, & O_3 +NO_2 + NO_z

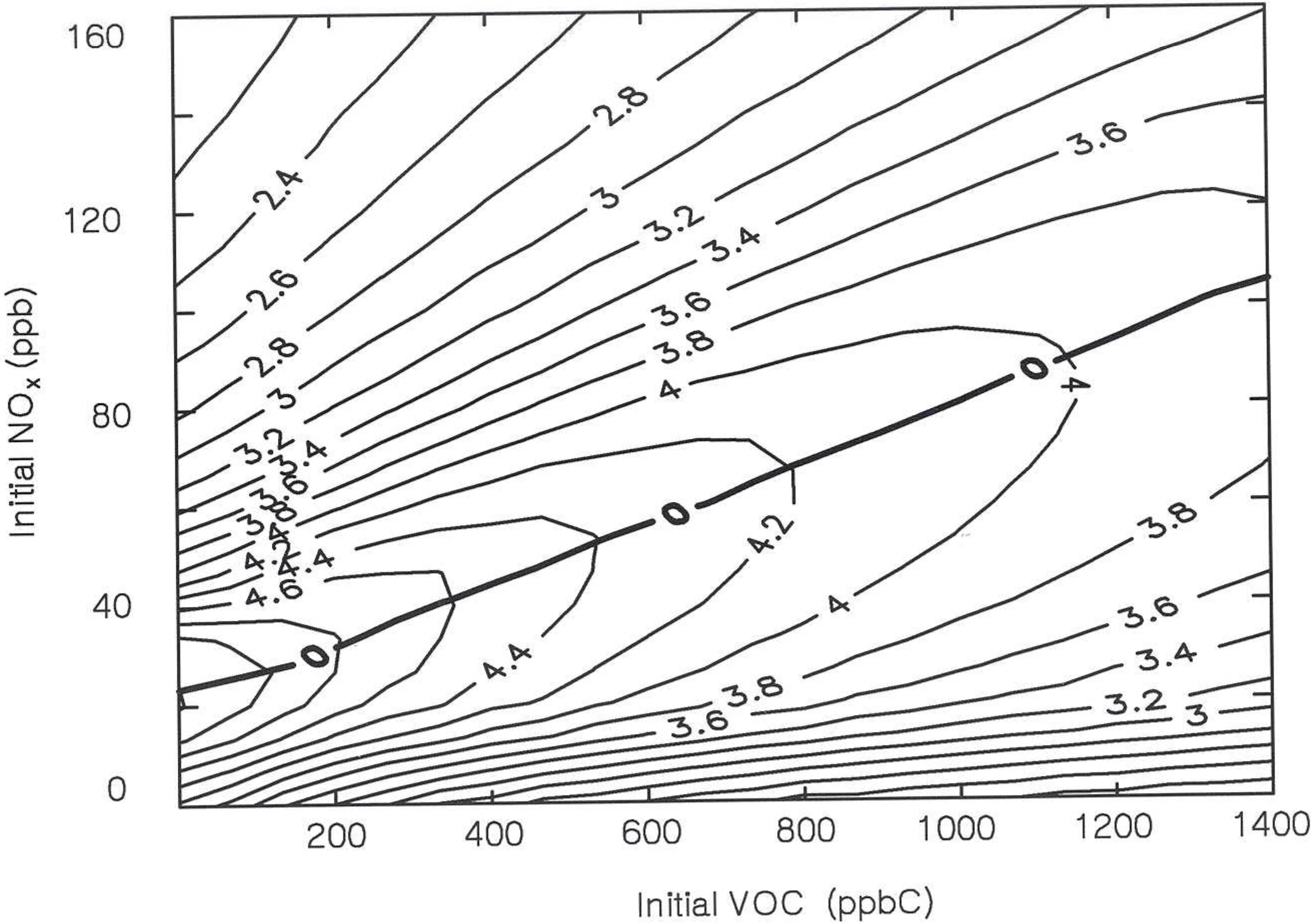
Indicators of O_3 Sensitivity

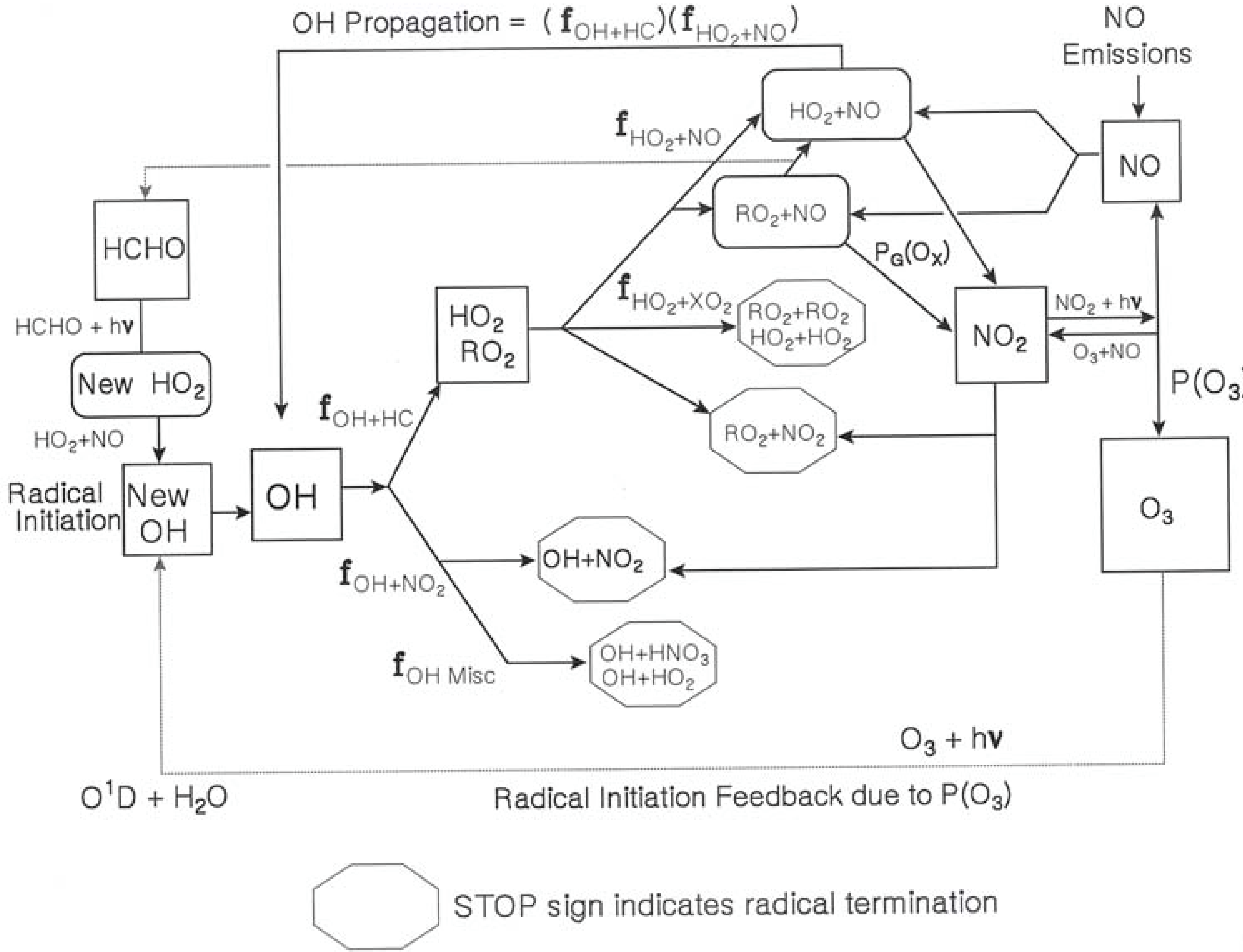
- Desire species or ratios that consistently assume different values under conditions of NO_x-sensitive and VOC-sensitive ozone.
- Theoretical derivations include:
  - Johnson (1984): max potential O_3 for a given NO_x level.
  - Milford et al., (1994): NO_y
  - Sillman (1995), Kleinman (1994): steady-state radical budgets.
  - Cardelino & Chameides (1994), Kleinman: constrained SS model
  - Tonnesen and Dennis (1997): radical propagation efficiency.

Peak $[O_3]$ (ppb) RADM2 Mec, base case



OH Chain Length (8 AM to 7 PM ave.)





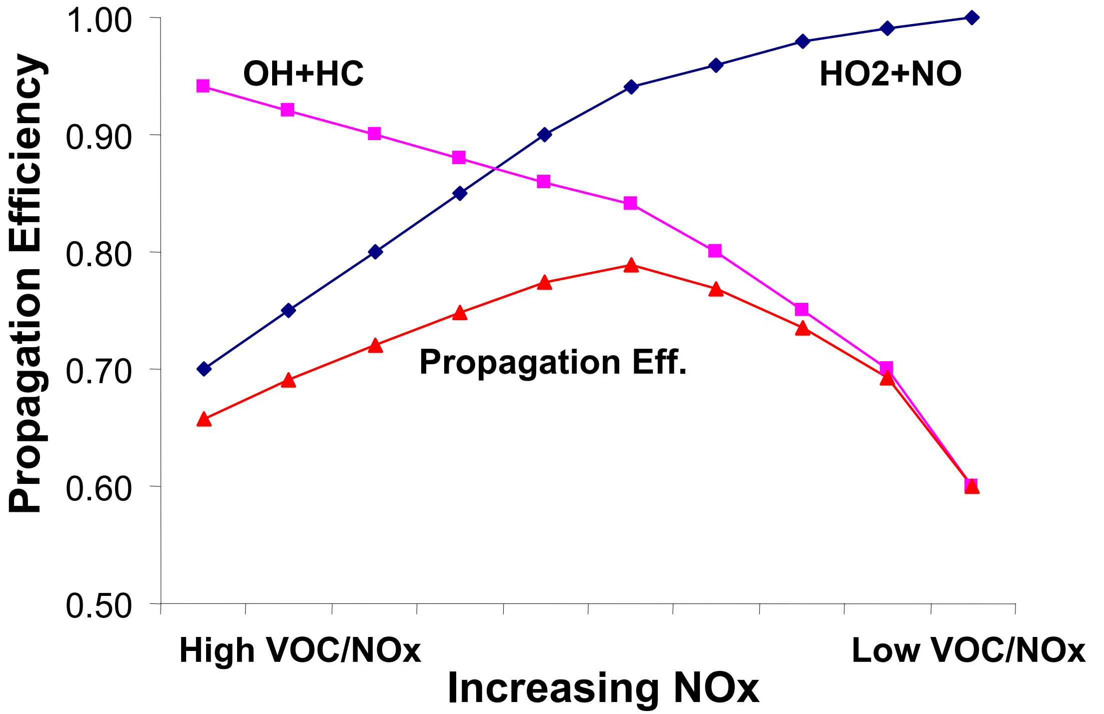
OH Propagation = (f_{OH+HC})(f_{HO_2+NO})
NO Emissions
HO_2+NO
NO
f_{HO_2+NO}
RO_2+NO
HCHO
$P_G(O_X)$
$f_{HO_2+XO_2}$
RO_2+RO_2
HO_2+HO_2
NO_2 + hv
HCHO + hv
HO_2
RO_2
NO_2
O_3+NO
New HO_2
$P(O_3)$
f_{OH+HC}
RO_2+NO_2
HO_2+NO
Radical Initiation
New OH
OH
O_3
$OH+NO_2$
f_{OH+NO_2}
$OH+HNO_3$
$OH+HO_2$
$f_{OH\ Misc}$
O_3 + hv
$O^1D + H_2O$
Radical Initiation Feedback due to $P(O_3)$
STOP sign indicates radical termination

OH Propagation Efficiency

- Derivation based on analysis of radical propagation efficiency.

$$OH: \quad f_{OH+HC} + f_{OH+NO2} + f_{OH+misc} = 1$$

$$HO_2: \quad f_{HO2+NO} + f_{HO2+RO2} + f_{HO2+misc} = 1$$

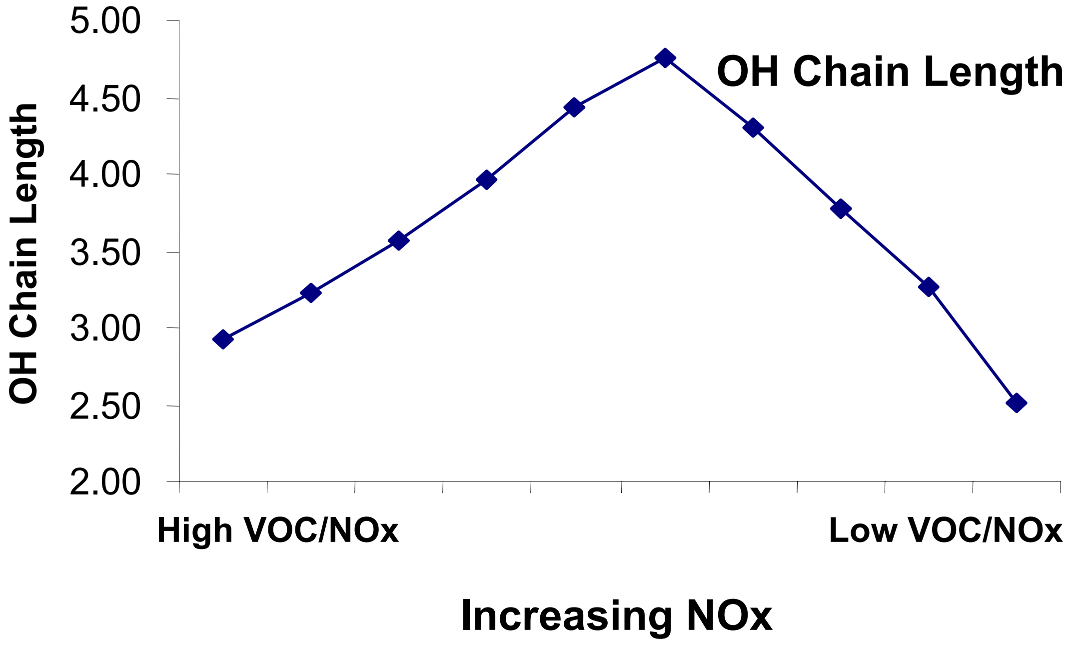


Propagation Efficiency ≈ $(f_{OH+HC})(f_{HO2+NO})$

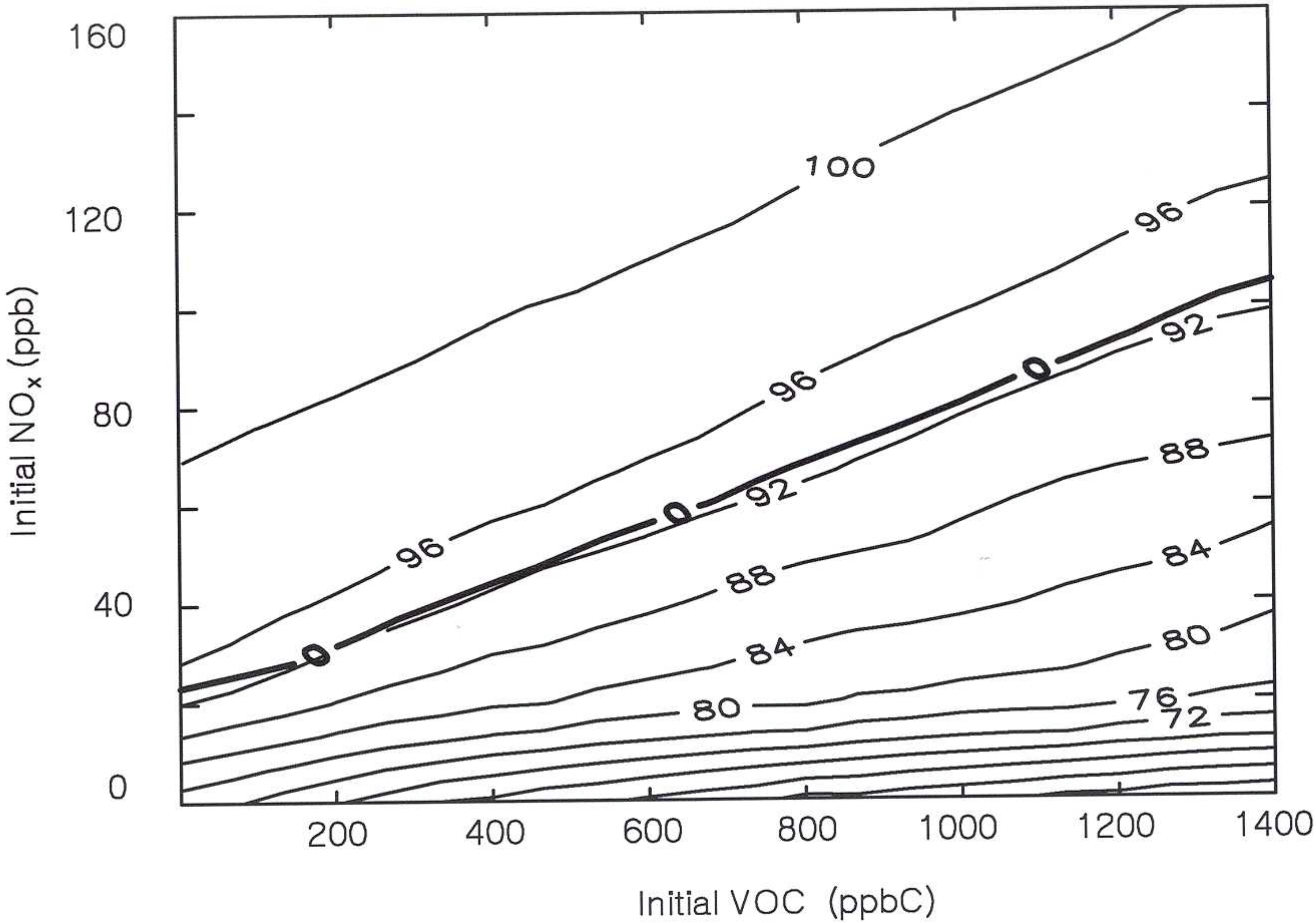
OH Chain Length

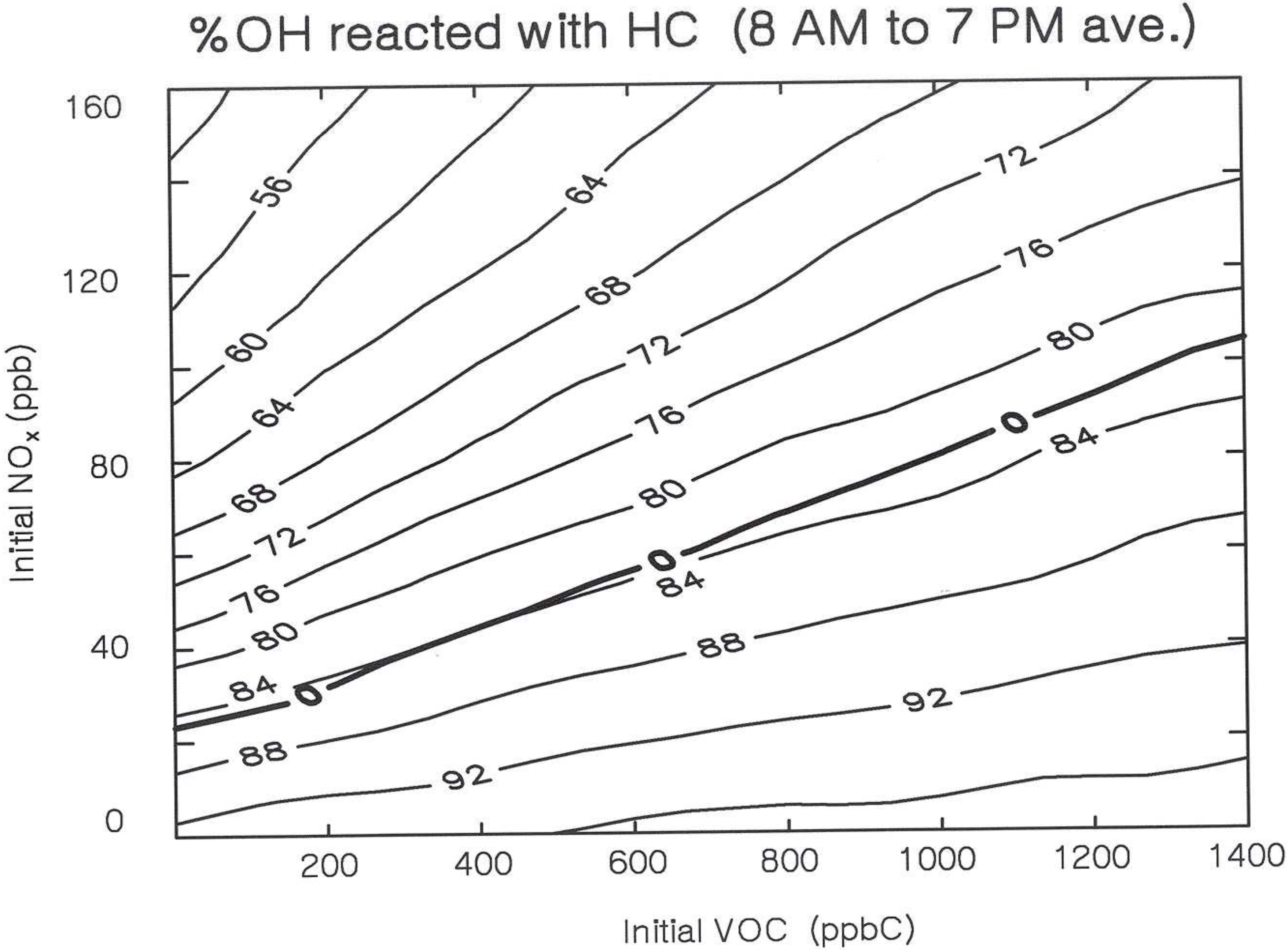
Chain Length = $Pr + Pr^2 + Pr^3 + Pr^4 + \ldots = 1 / (1 - Pr)$

Chain length increases rapidly with small increase in Prop



% HO_2 reacted with NO (8AM to 7 PM ave.)




%OH reacted with HC (8 AM to 7 PM ave.)
Initial NOx (ppb)
Initial VOC (ppbC)
0
40
80
120
160
200
400
600
800
1000
1200
1400
56
60
64
68
72
76
80
84
88
92
0

Indicators of O_3 Sensitivity

- Ridgeline for both peak $[O_3]$ and $P(O_x)$:

$$\partial P(O_x)/\partial E_{NOx} = 0$$

$$\partial [O_3]/\partial E_{NOx} = 0$$

- Caveats: No *a priori* estimate of indicator ratio:
  - transition values determined numerically using models.
  - Uncertainty in "misc" radical reactions contributes to uncertainty in this method (assumed to be small).

Indicators of $P(O_x)$ Sensitivity

$k_{HO2}\ NO /(k_{HO2}\ NO + k_{HO2}\ (RO_2 + HO_2))$

$\sum k_{OH}\ HC_i /(\sum k_{OH}\ HC_i + k_{OH}\ NO_2)$

$k_{HO2}\ HO_2^2 / k_{OH}\ NO_2 \cdot OH$ (or simply use HO_2)

$O_3/(NO_2+NO)$

Indicators of $[O_3]$ Sensitivity

$H_2O_2/(HNO_3 + NO_3^-)$

$(O_3 - background)/(HNO_3 + NO_3^-)$

$H_2O_2/(O_3 + NO_2)$

$HCHO/NO_2$

Extent Parameter

$O_3/(NO+NO_2)$

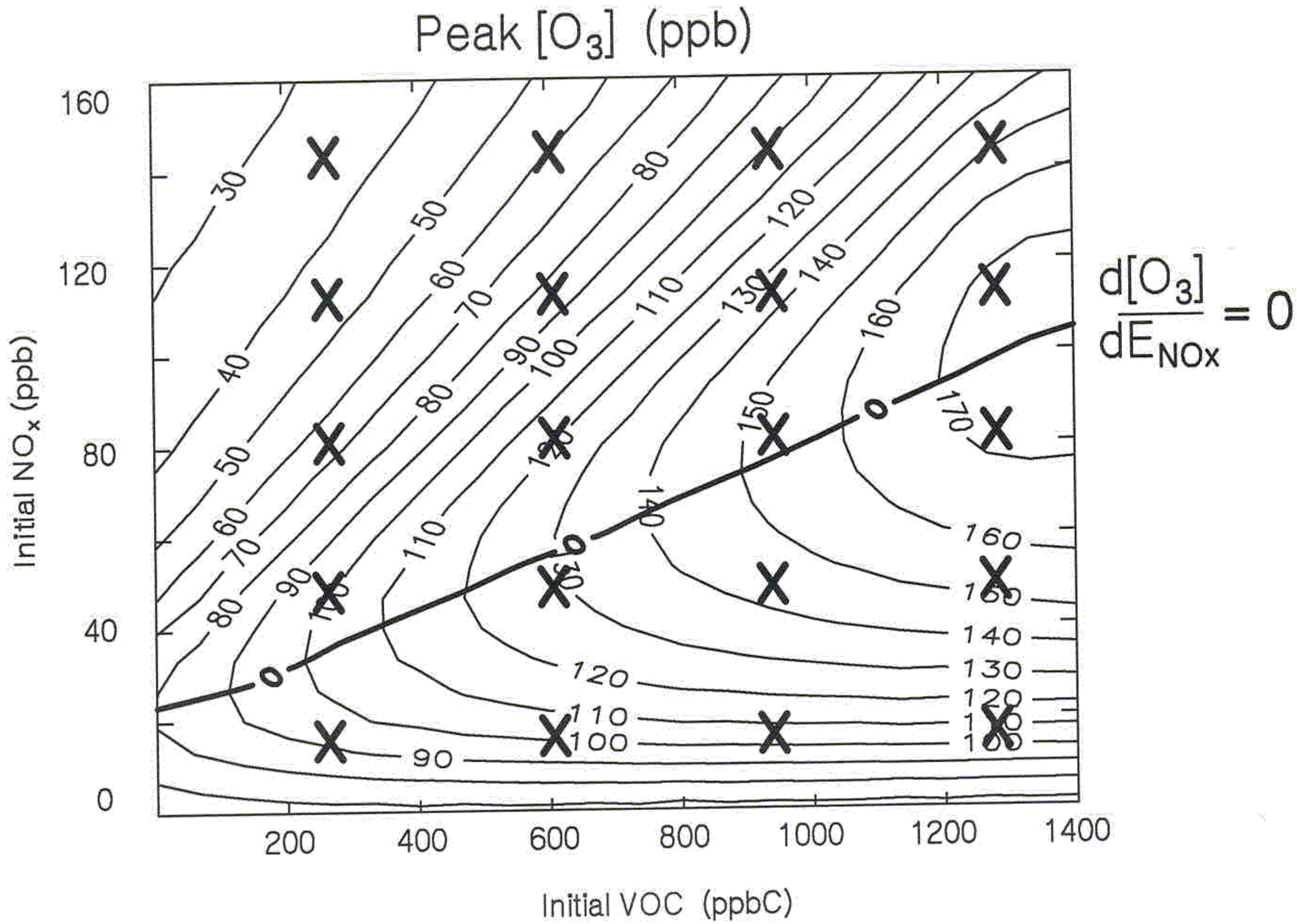
Indicators

- Strong Theoretical Basis for Use.
  - But based on models with large uncertainties.
- Best method for Assessing O3 Sensitivity
  - But models sensitivity experiments show mixed results.
  - Question remain about robustness and discriminating power.
- Research Need: Experimental validation of the indicator concept using:
  - Chamber experiments to evaluate indicators in a controlled setting.
  - Field Experiments.

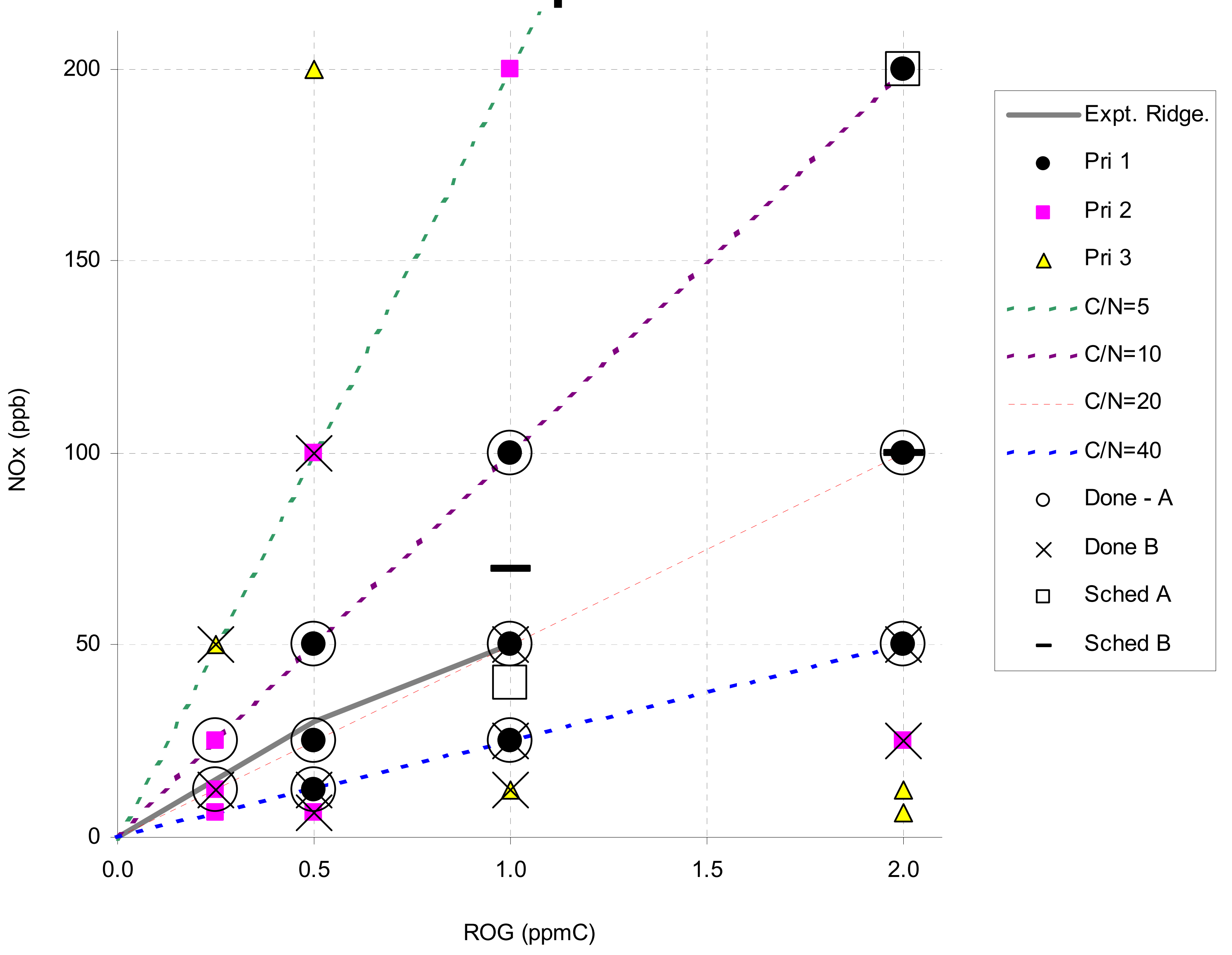
Chamber Empirical Evaluation

- Evaluation of diagnostics in chamber experiments
  - Local and Cumulative diagnostics can be compared directly in a chamber.
  - Existing chamber data base lacks the measurement needed to quantify HO_x and NO_y budgets.
  - Need a low NO_x chamber.
  - Wall effects still a problem.

Goal: experiments over a matrix of VOC/NOx pairs across the O3 Isopleth Surface

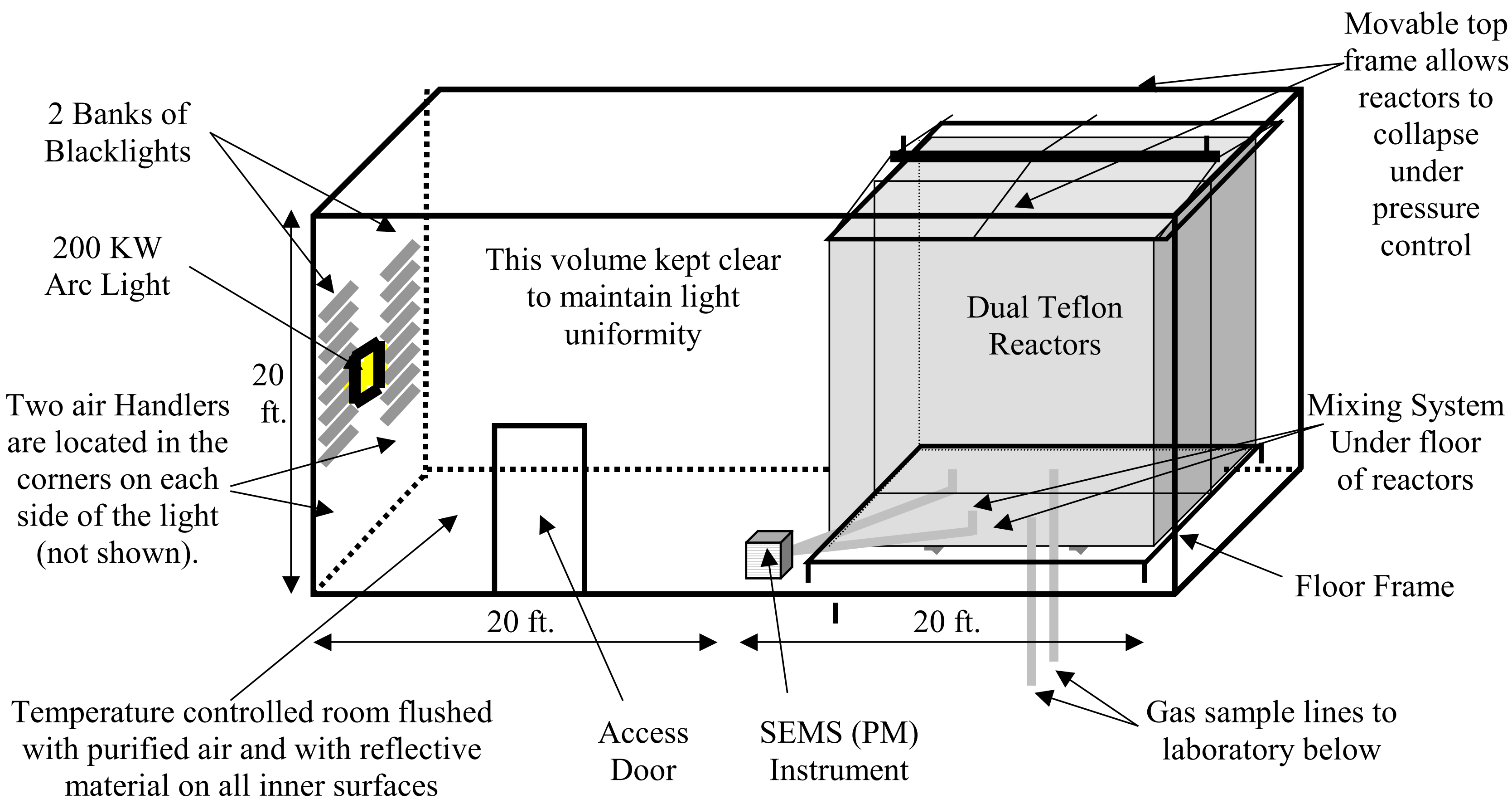


Actual Experimental Matrix



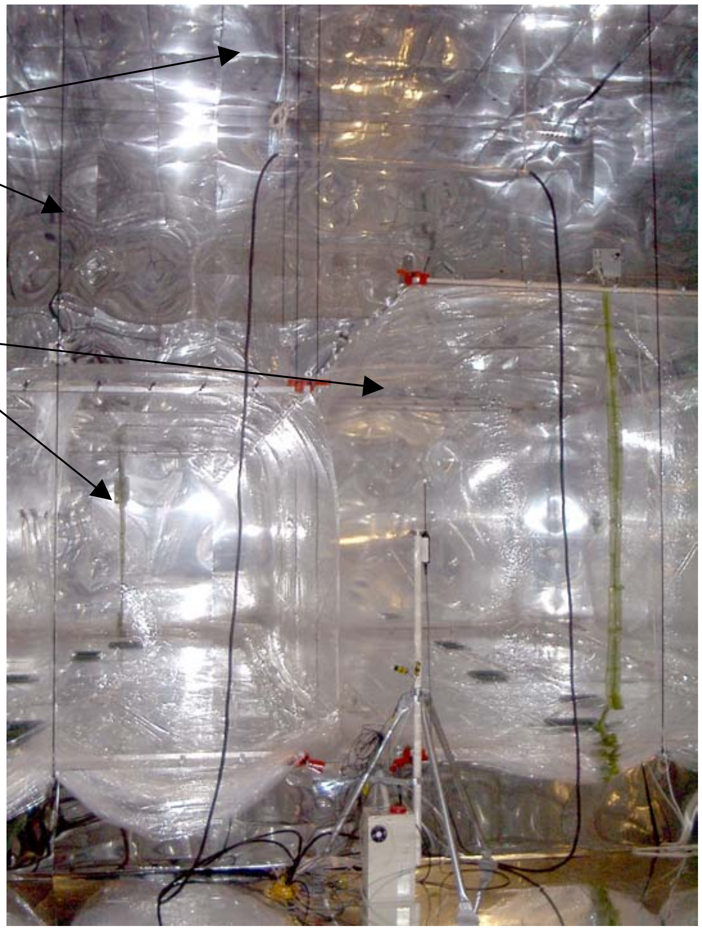
UCR EPA Chamber Facility

DIAGRAM OF UCR EPA CHAMBER



PHOTOGRAPHS OF CHAMBER AND LIGHTS

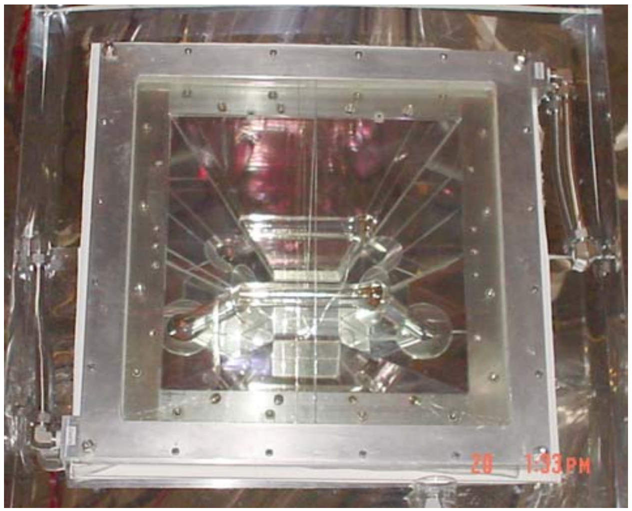
Looking Towards Reactors (from light)



Looking Towards Lights and Air Inlet

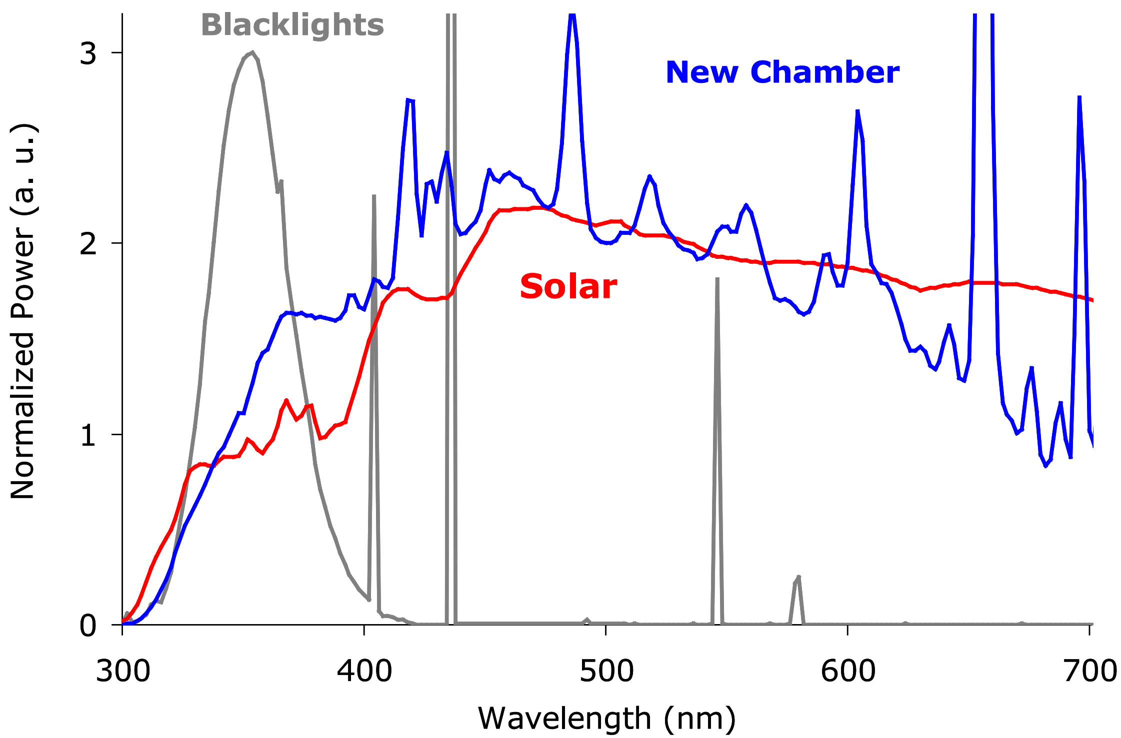
Collapsing reactors hang from suspended frame

Argon Arc Lamp



Water Cooled Reflector
and Filter Window
(60 cm x 60 cm)

Filtered Argon Arc Spectrum



Analytical Instrumentation

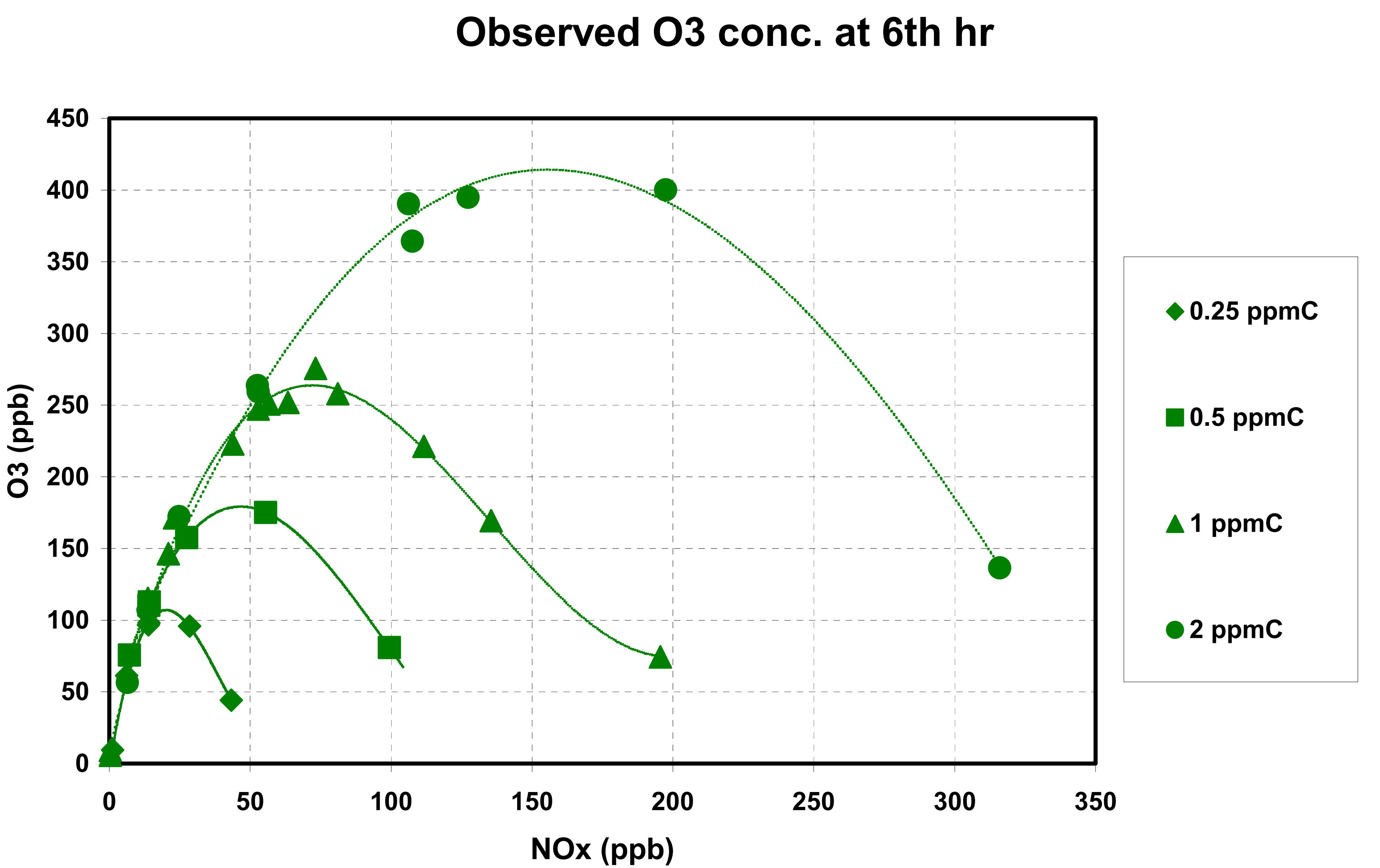
Ozone, CO, NO, NO_y, Humidity, Temperature, Total Hydrocarbons	Commercial Ambient Monitoring Instruments
Hydrocarbons	2 GC-FID, GC-ECD
NO (20 ppt MDL)	ECO Physics Chemiluminescence Analyzer
NO_2 and PAN	2 Luminol-GC Instruments
Computerized Data Acquisition and Reactor Control System	
NO_2 (<0.2 ppb MDL) **HNO_3 (1–2 ppb MDL)** **HCHO (0.5-1 ppb MDL)** **H_2O_2 (1–2 ppb MDL)**	**2 Dual Channel Mid-IR TDLAS Systems**
Light Spectrum	Spectroradiometer
Light Intensity	Spherical Irradiance Sensor Quartz Tube $J(NO_2)$ Monitor

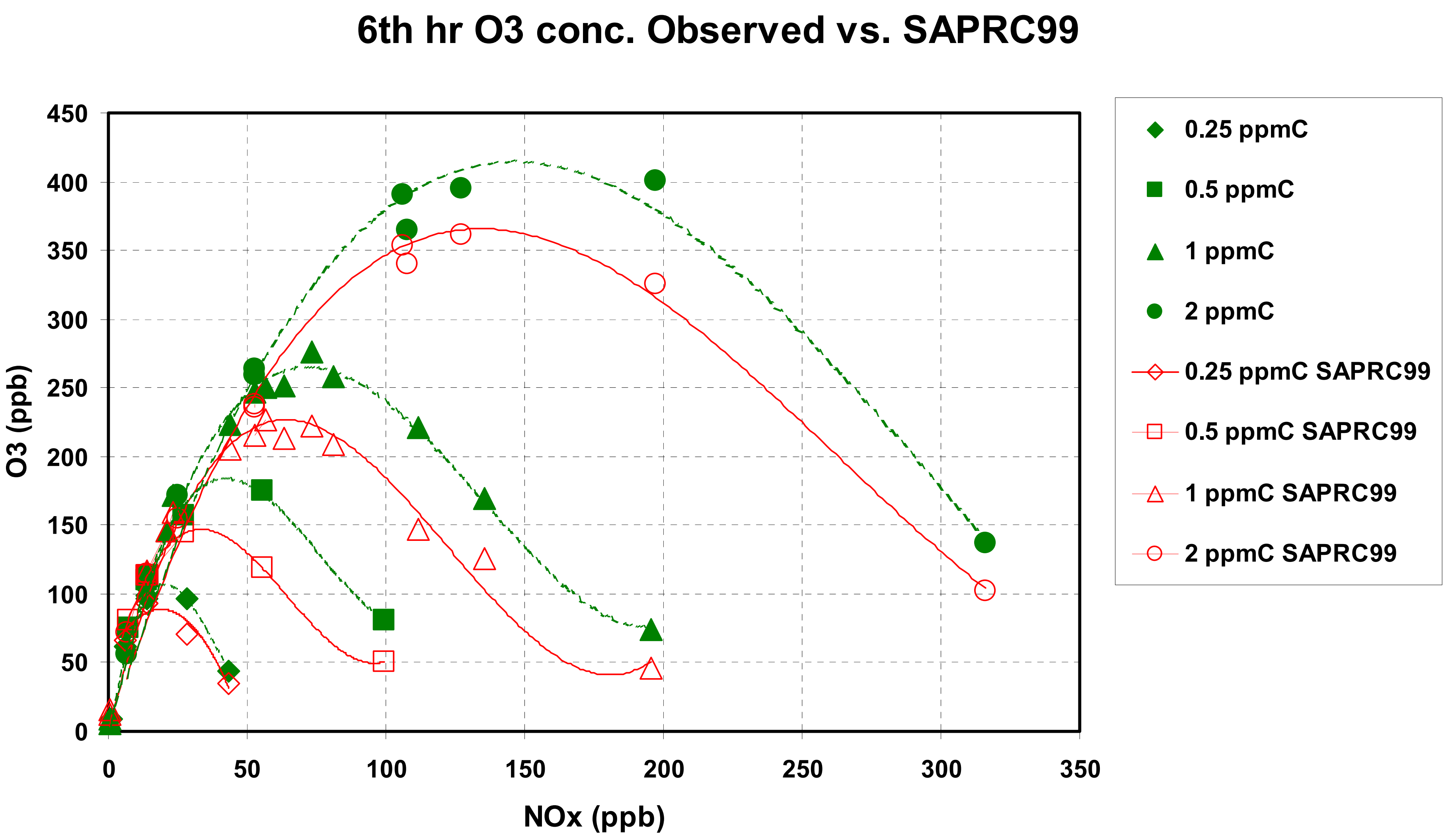
Analytical Instrumentation (2)

- Bill Brune's (PSU) Laser Induced Flouresence instrument:
  - Measures OH, HO2 and direct measure of VOC reactivity.
  - LIF detector was located in side A of the Chamber so HOx data is available for 50% on experiments.

Experimental Plan

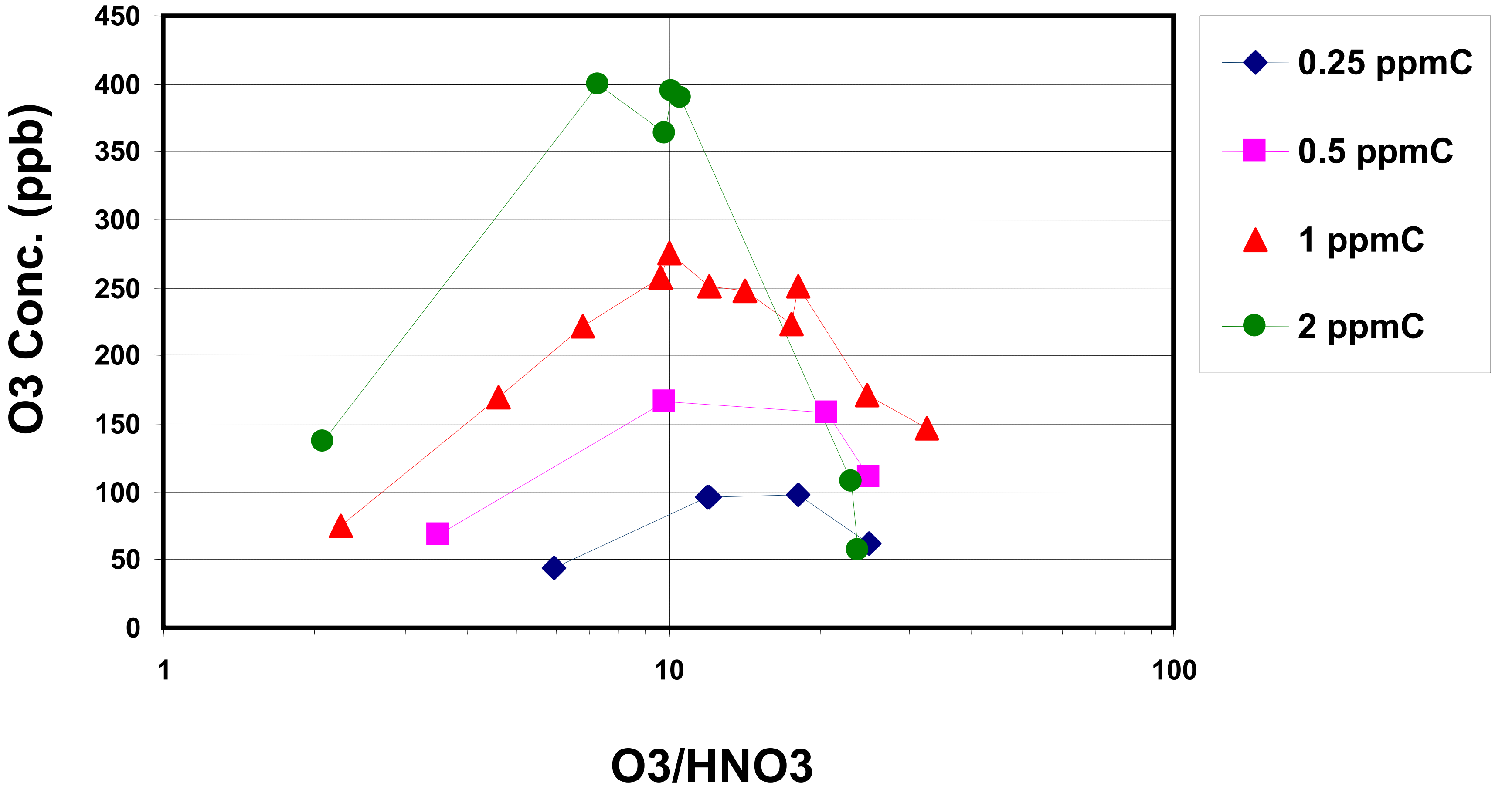
- Measure direct reactivity as P(Ox) and compare with indicators of P(Ox) sensitivity to VOC and NOx.
- Measure O3 concentration and compare to indicators of peak O3 sensitivity to VOC and NOx:
  - Evaluate results at the end of 6 hours.
- Perform mass budget analysis by comparing integral of reactions rates to changes in species conc.
- Compare with model simulations.


Observed O3 conc. at 6th hr
O3 (ppb)
0
50
100
150
200
250
300
350
400
450
NOx (ppb)
0
50
100
150
200
250
300
350
0.25 ppmC
0.5 ppmC
1 ppmC
2 ppmC

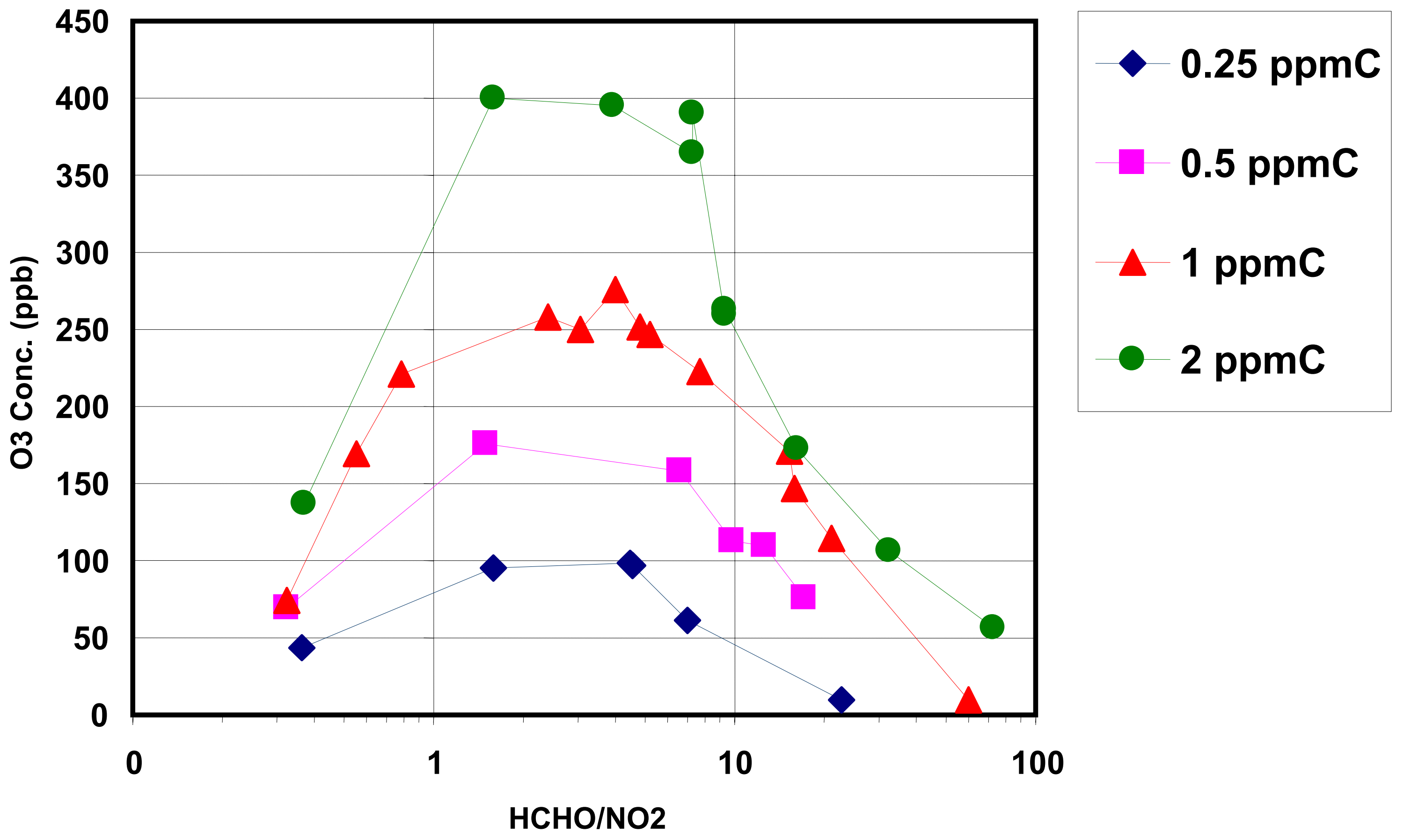

6th hr O3 conc. Observed vs. SAPRC99
O3 (ppb)
NOx (ppb)
0
50
100
150
200
250
300
350
400
450
0
50
100
150
200
250
300
350
0.25 ppmC
0.5 ppmC
1 ppmC
2 ppmC
0.25 ppmC SAPRC99
0.5 ppmC SAPRC99
1 ppmC SAPRC99
2 ppmC SAPRC99

O3/HNO3

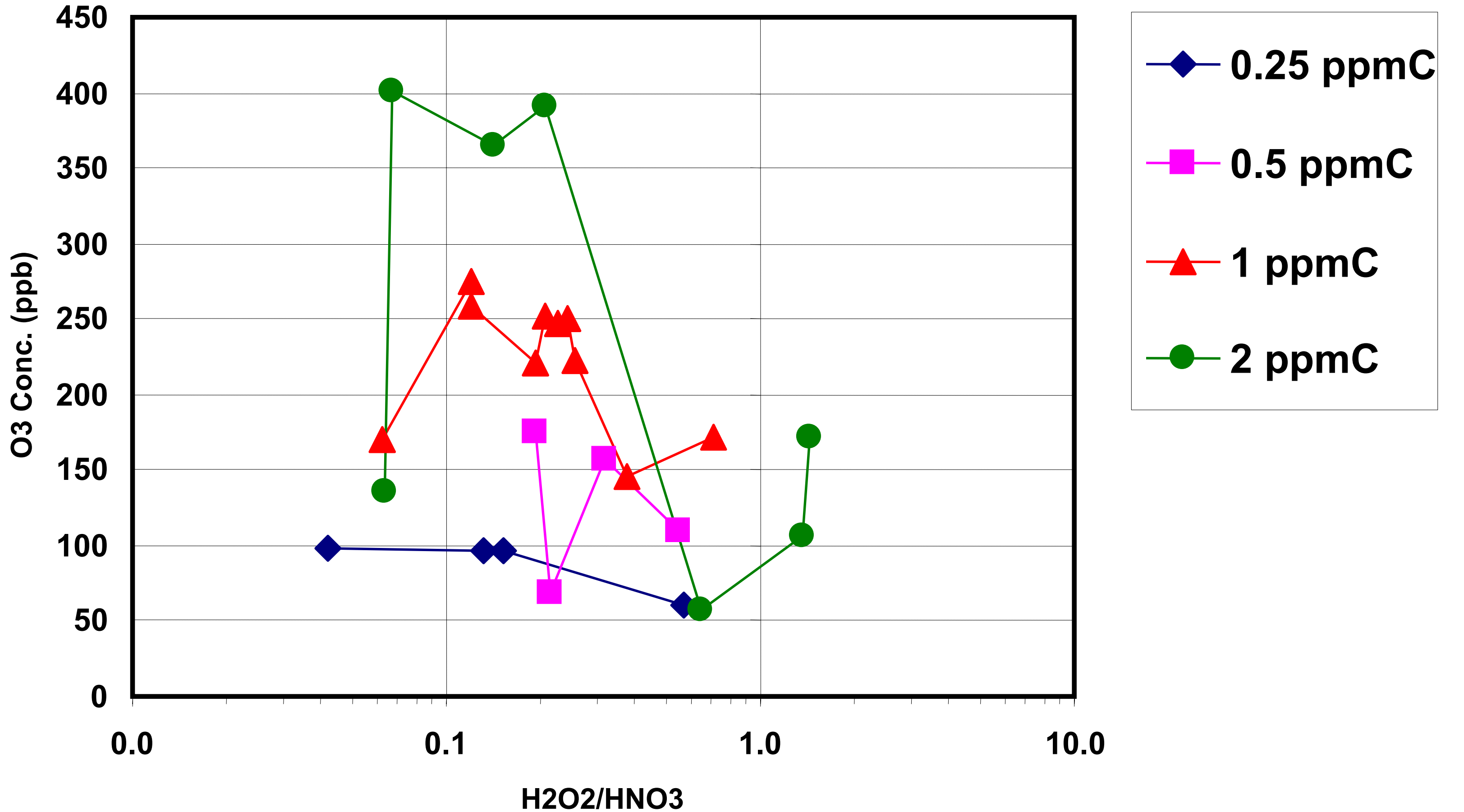
Notes: background O3 =0, and no aerosol nitrate formed in chamber.



HCHO/NO2


450
400
350
300
250
200
150
100
50
0
O3 Conc. (ppb)
0
1
10
100
HCHO/NO2
0.25 ppmC
0.5 ppmC
1 ppmC
2 ppmC

H2O2/HNO3



450
400
350
300
250
200
150
100
50
0
O3 Conc. (ppb)
0.0
0.1
1.0
10.0
H2O2/HNO3
0.25 ppmC
0.5 ppmC
1 ppmC
2 ppmC

Summary of [O3] Sensitivity Results

- Results generally consistent with previous model sensitivity studies:

Indicator Ratio	Experimental Range	Model Range
O_3/HNO_3:	8 to 12	about 9
$HCHO/NO_2$:	2 to 4	about 2
H_2O_2/HNO_3:	0.06 to 0.11	0.07 to .15 dd

- Slight trends in ratios as VOC conc changes for O_3/HNO_3 and for H_2O_2/HNO_3.

Caveats in Interpretation of Results

- Cannot exactly reproduce VOC in each experiment:
  - "constant" VOC series varies by +/-10%
  - Looking for algorithms to interpolate data.
- Problem with high noise in TDL H2O2 measurements.
- No background O3 in chamber, this might bias results relative to ambient air.

Work in Progress

- Working up data for HOx and P(Ox) sensitivity.
- Budget analysis of measured and modeled species.
- Still need to evaluate O3/NOx ratios.
- SAPRC99 under predicts O3 at low VOC/NOx
  - Need to refit the SAPRC to fit new chamber data.

Application in ambient air

- O_3/HNO_3 and $HCHO/NO_2$ seem useful
  - However, in ambient air we need to measure the sum $HNO_3+NO_3^-$
- H_2O_2 is too difficult to measure.
- O_3/NO_x is most accessible, still need to evaluate up the chamber data.
- Still need to evaluate reactivity weighted ratio of VOC to NOx.