Chamber Evaluation of Photochemical Indicators of Ozone Sensitivity to VOC and NOx

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Indicators of O_3 Sensitivity

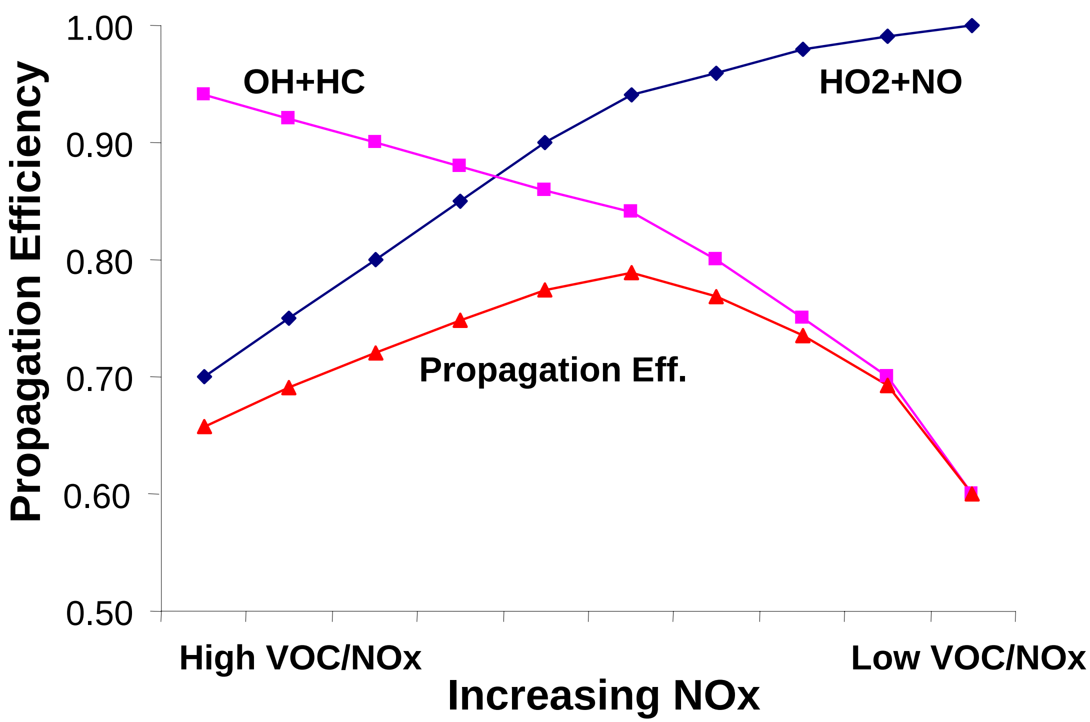
- Desire species or ratios that consistently assume different values under conditions of NO_x-sensitive and VOC-sensitive ozone.
- Theoretical derivations include:
  - Johnson (1984): max potential O_3 for a given NO_x level.
  - Milford et al., (1994): total NO_y
  - Sillman (1995), Kleinman (1994):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

OH Propagation Efficiency

- Derivation based on analysis of radical propagation efficiency.

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

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

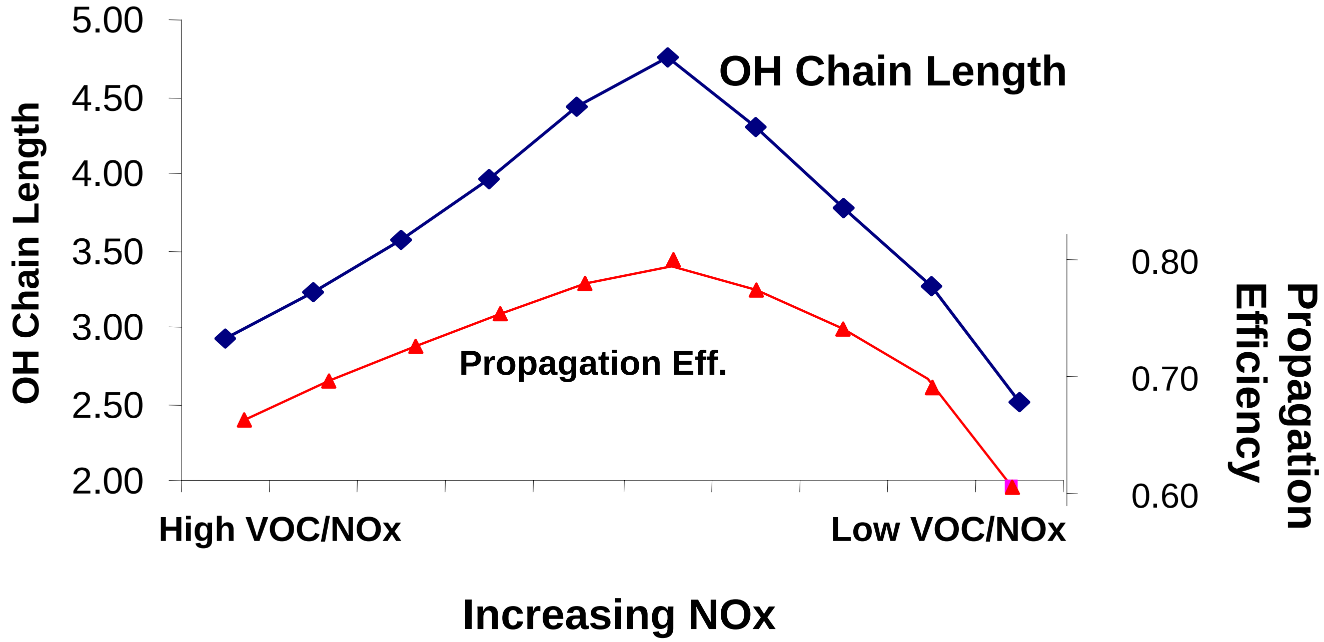


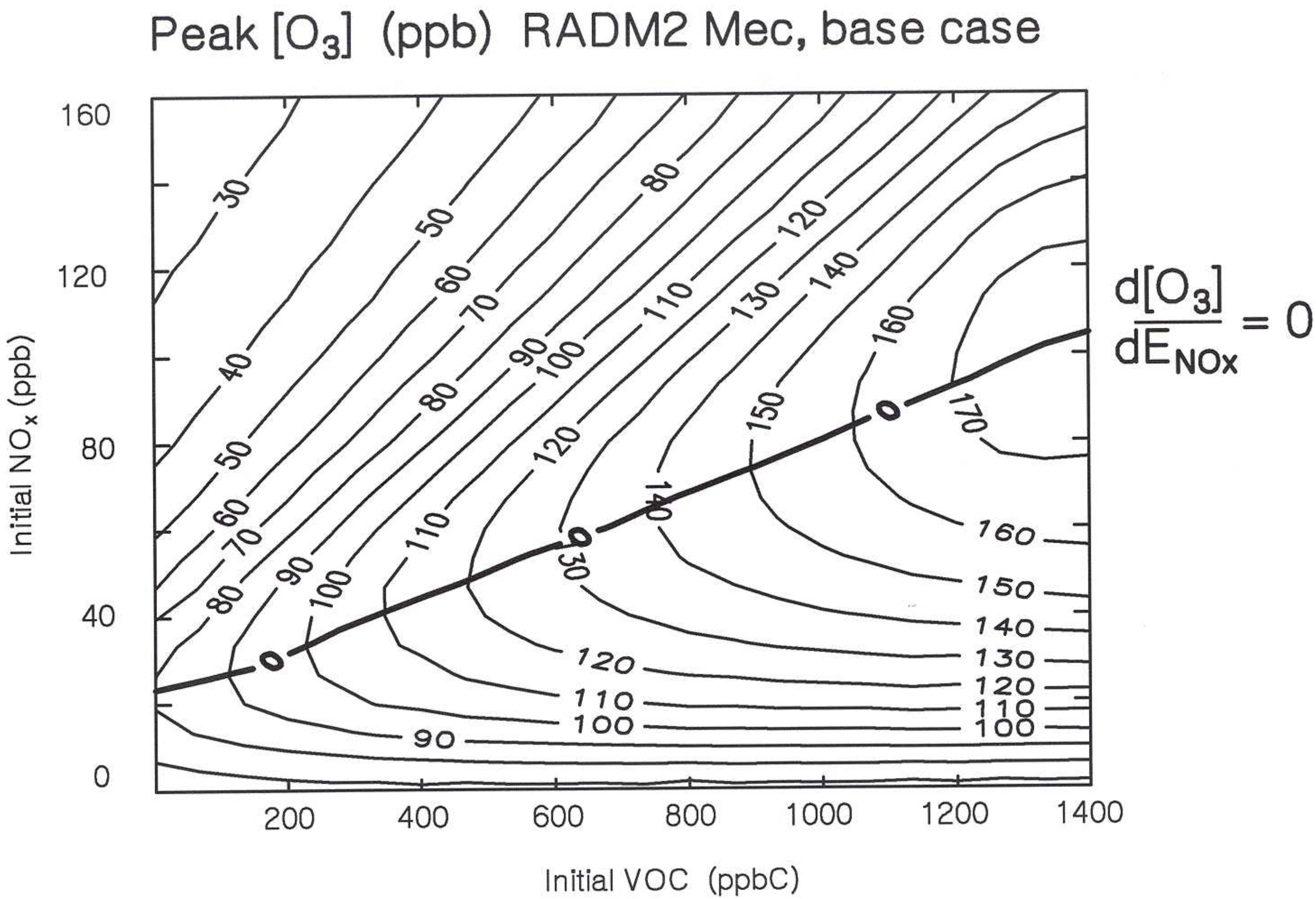
Propagation Efficiency ≈ $(f_{OH+HC})(f_{HO2+NO})$

OH Chain Length

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

Chain length increases rapidly with small increase in Prop





Peak [O3] (ppb) RADM2 Mec, base case
Initial NOx (ppb)
Initial VOC (ppbC)
0
40
80
120
160
200
400
600
800
1000
1200
1400
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
d[O3]/dENOx = 0

Indicators of O_3 Sensitivity

- Unique values of each indicator are associated with the ridgeline for both peak $[O_3]$ and $P(O_x)$:

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

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

- No *a priori* estimate of indicator ratio – transition values determined numerically using models.

Indicators of [O_3] Sensitivity

$H_2O_2 /(HNO_3 + NO_3^-)$

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

$H_2O_2 /(O_3 + NO_2)$

$HCHO/NO_2$

$O_3 /(NO+NO_2)$

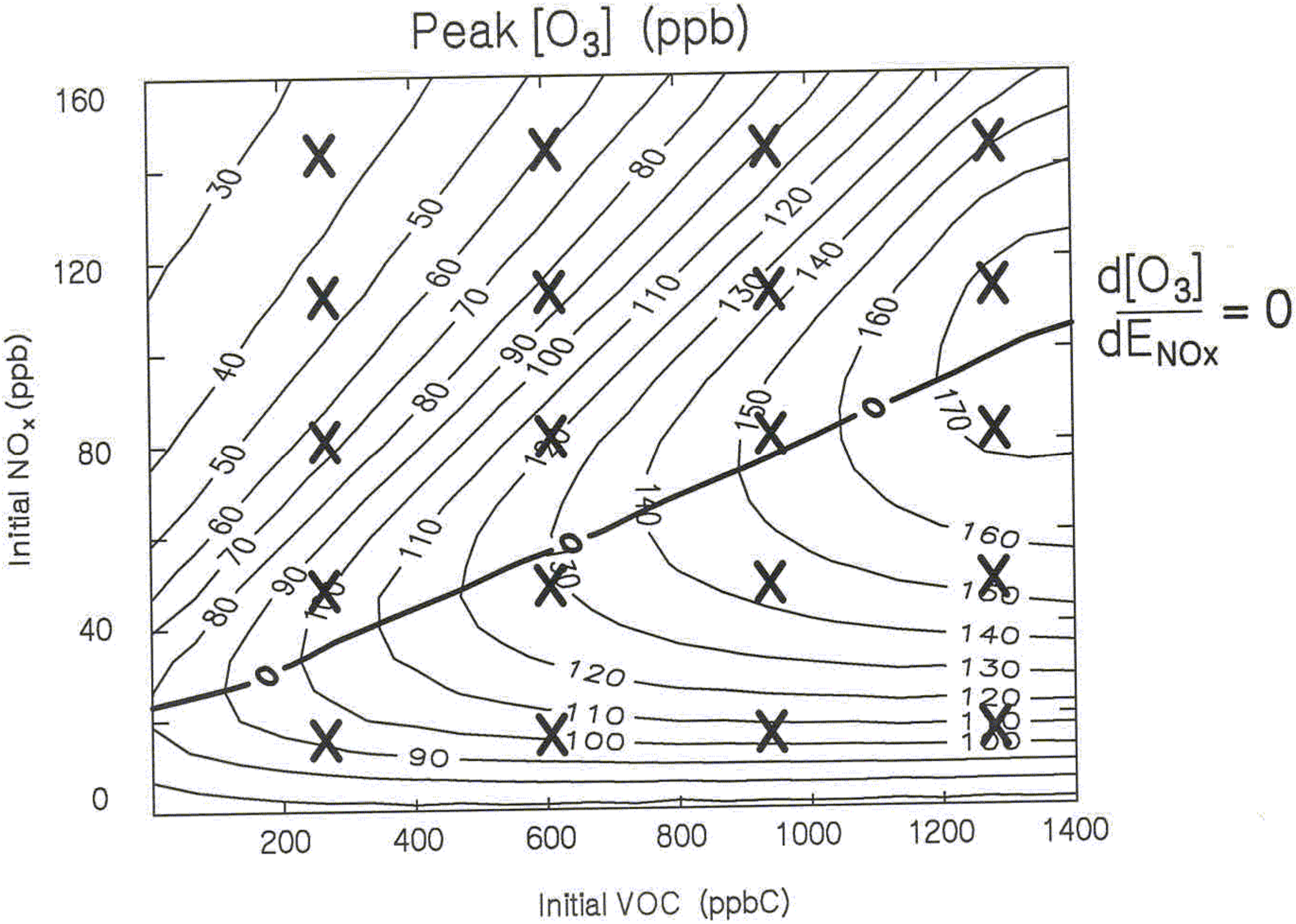
Motivation for this Study

- Strong Theoretical Basis for Use.
  - But based on models with large uncertainties.
- Best method for assessing O_3 sensitivity
  - But models sensitivity experiments show mixed results.
  - Question remain about robustness and discriminating power.
- Experimental validation of the indicator concept is needed using chamber experiments to evaluate indicators in a controlled setting.

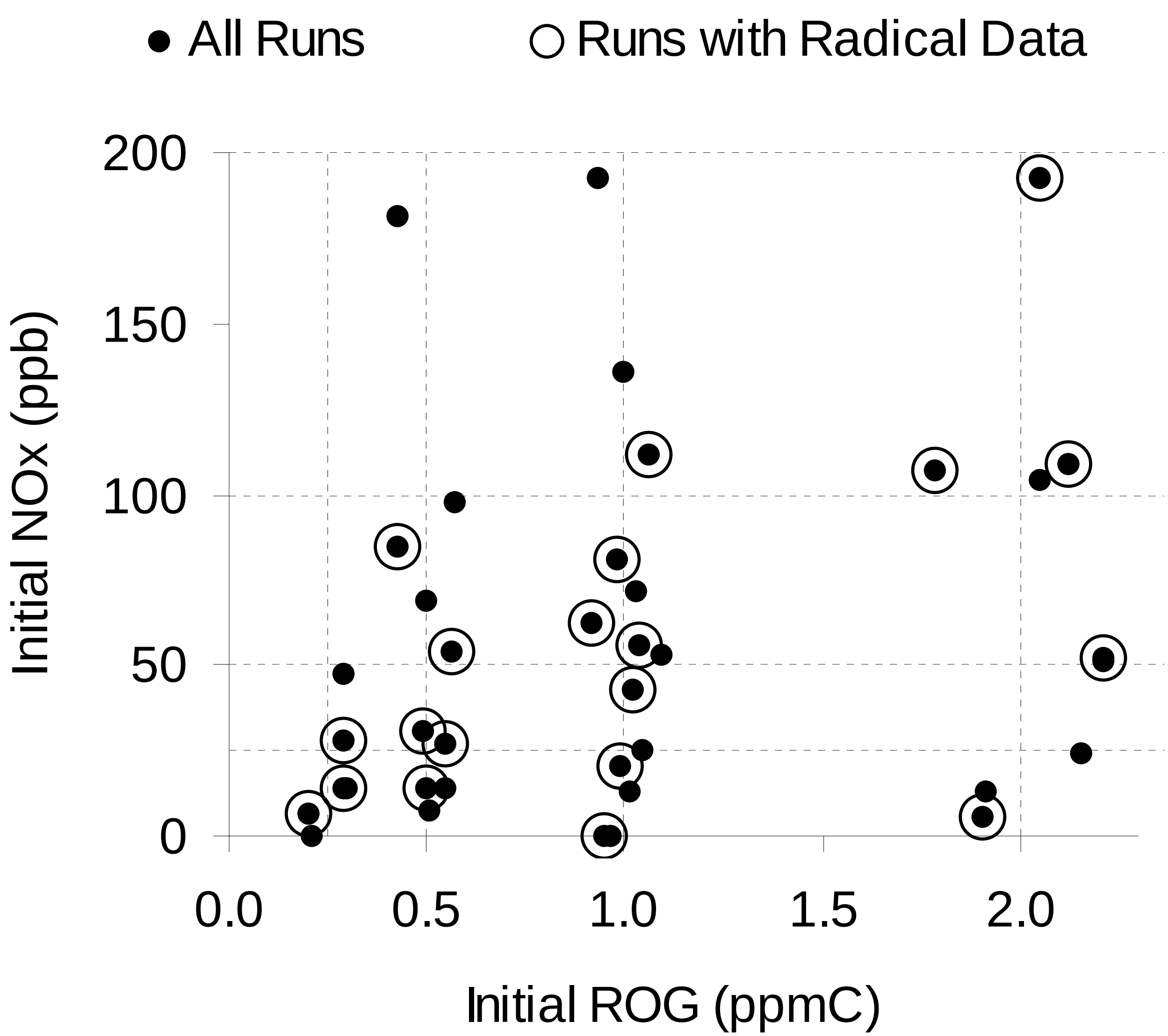
Chamber Empirical Evaluation

- Evaluation of indicators in chamber experiments:
  - Measure the values of each indicator for a range of VOC and NOx levels, and determine if a unique value of each indicator is associated with the O_3 ridgeline.
  - 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 concern, but these are reduced in the UCR's EPA chamber, and are included in the chamber wall mechanism.

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



Actual Experimental Matrix



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
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)

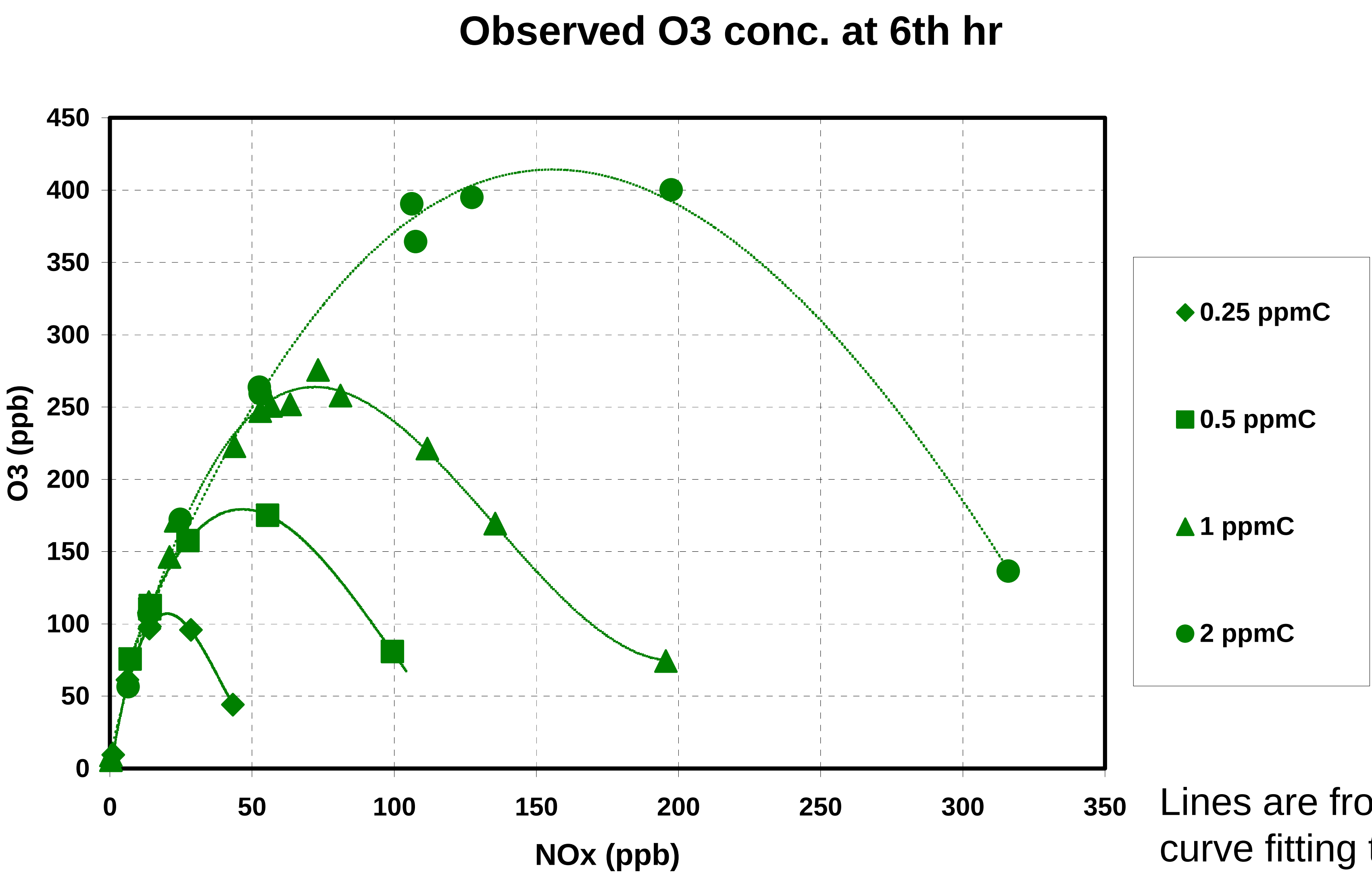
- Bill Brune's (PSU) Laser Induced Flouresence instrument:
  - Measures OH, HO_2 and direct measure of VOC reactivity.
  - LIF detector was located in side A of the Chamber so HOx data is available for 50% on experiments.
  - Detection limits

    OH: 0.01 pptv

    HO2: 0.1 pptv

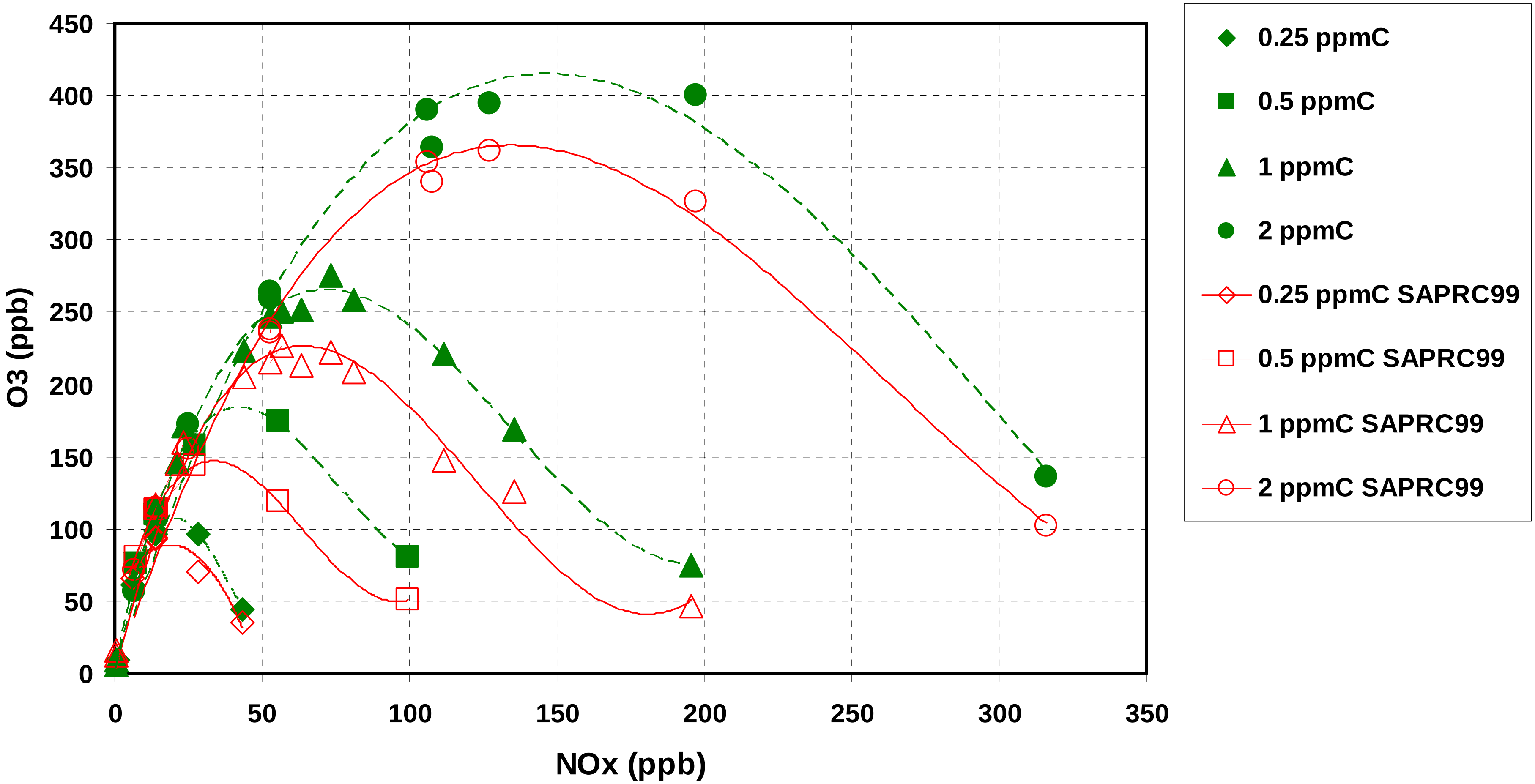
Experimental Plan

- Measure direct reactivity as P(Ox) and compare with indicators of P(Ox) sensitivity to VOC and NOx.
- Measure O_3 concentration and compare to indicators of peak O_3 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.



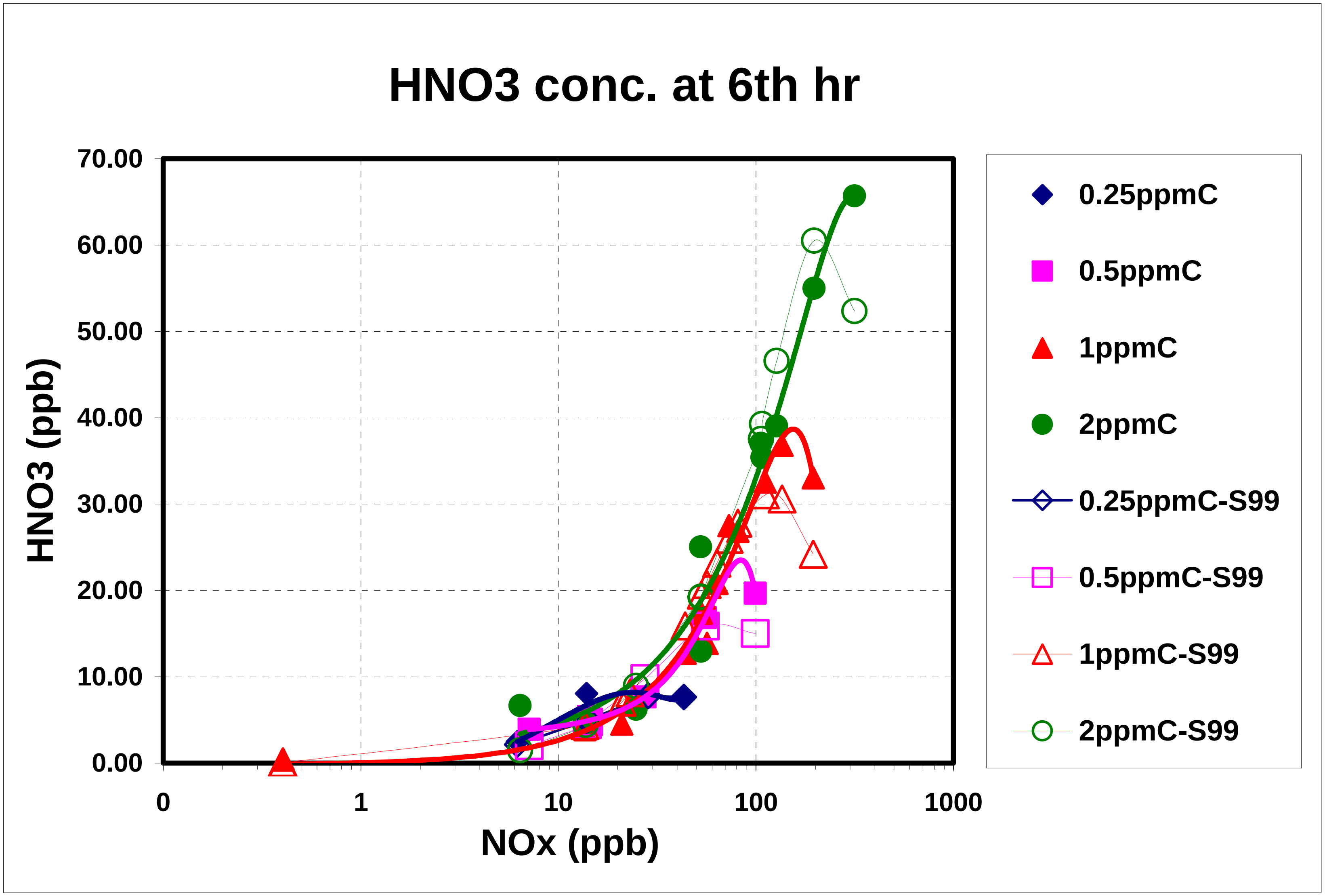
Lines are from curve fitting to data.

O3 Chamber vs. SAPRC99 Model at 6th hr

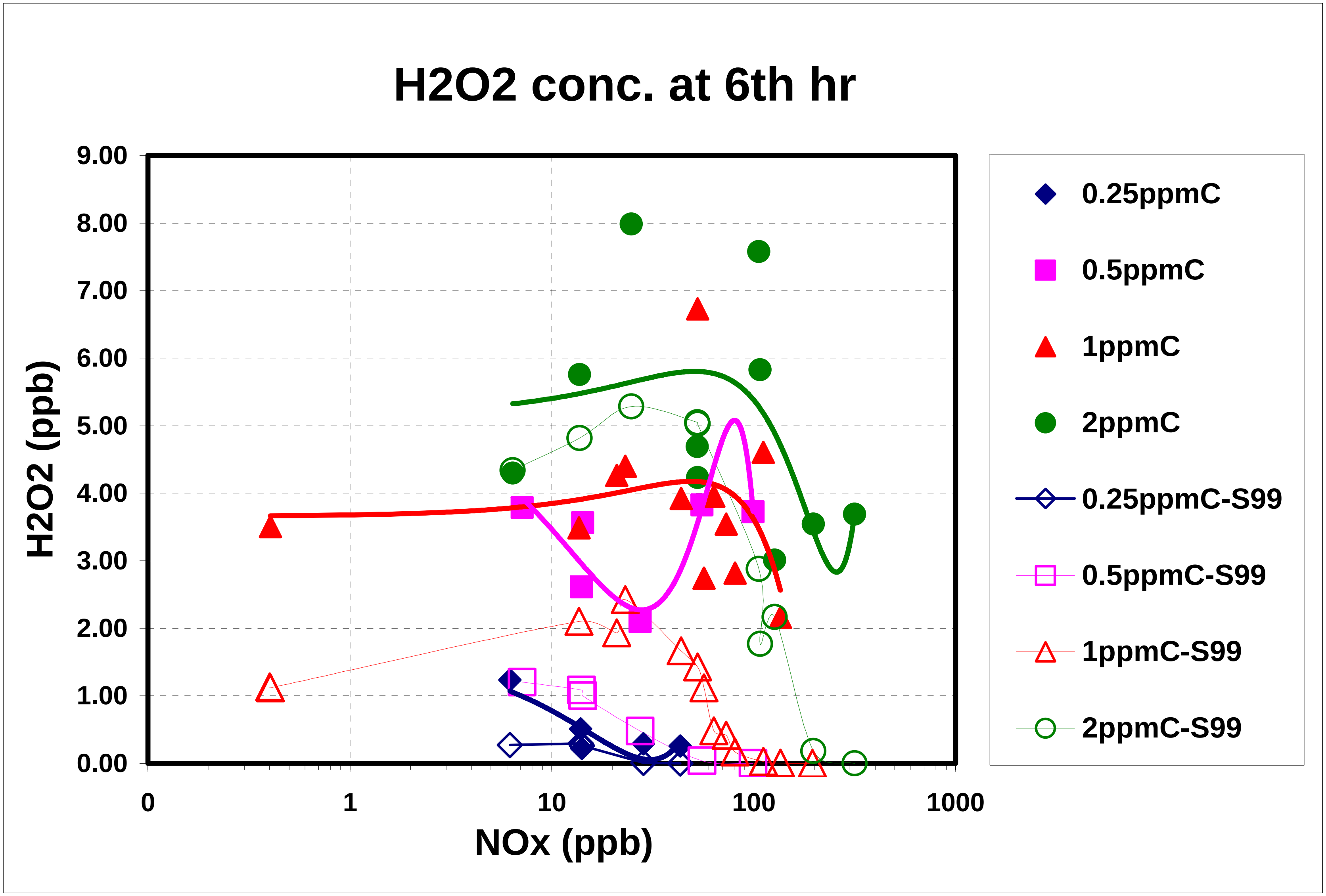


Note: these are not time-series, each data point is the measurement at 360 min for a single chamber experiment.

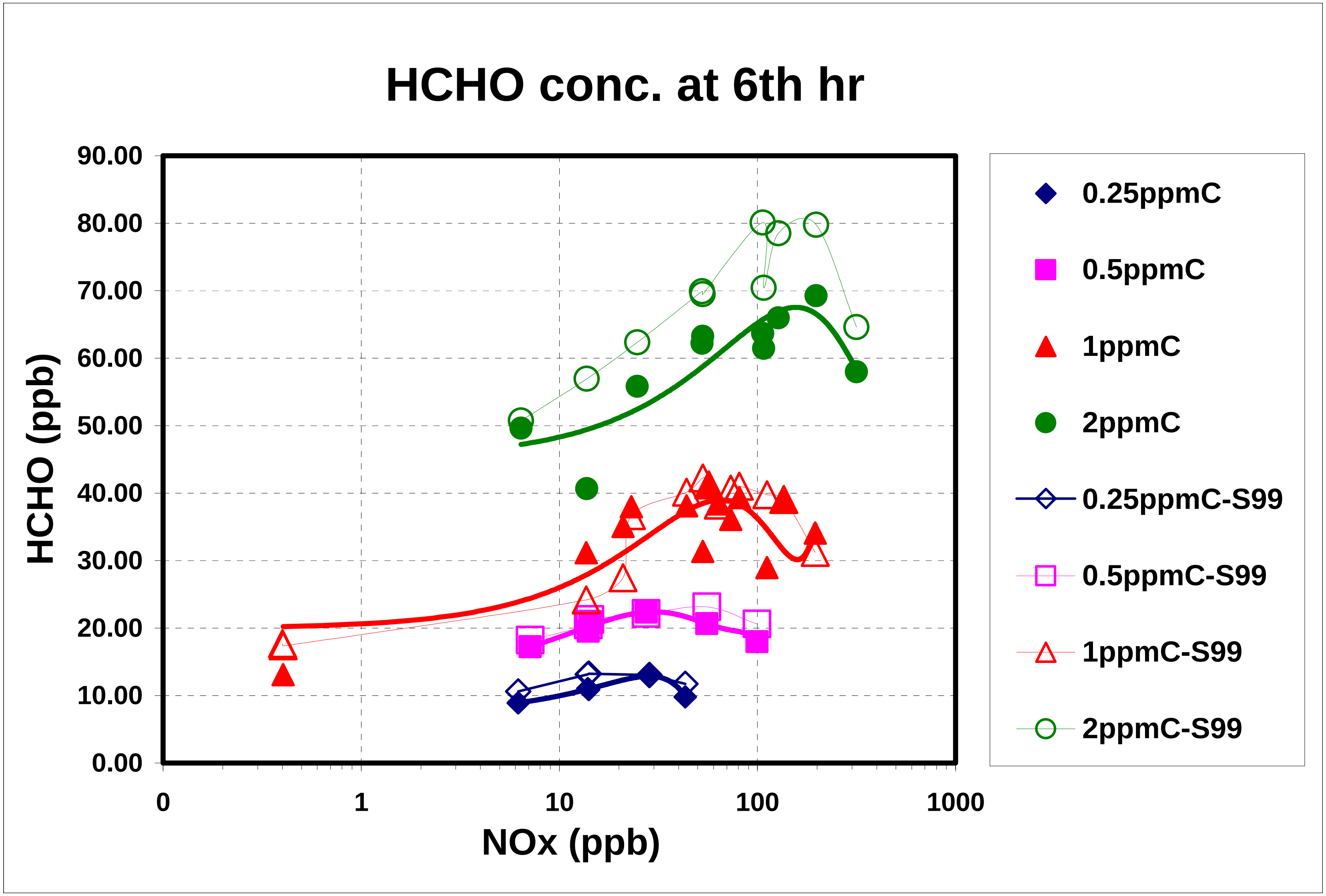
HNO3 Chamber vs. SAPRC99 Modeled



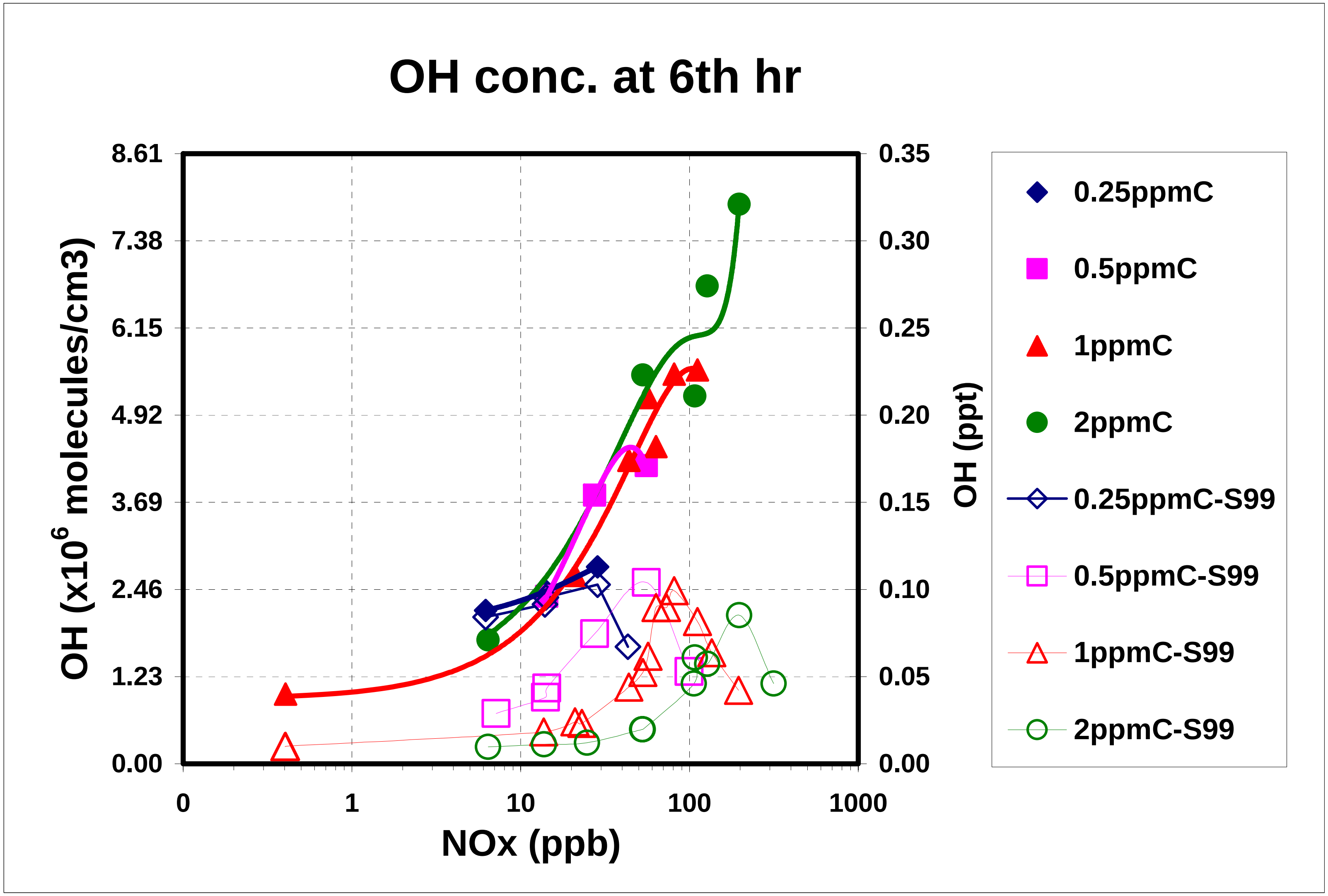
H2O2 Chamber vs. SAPRC99 Modeled



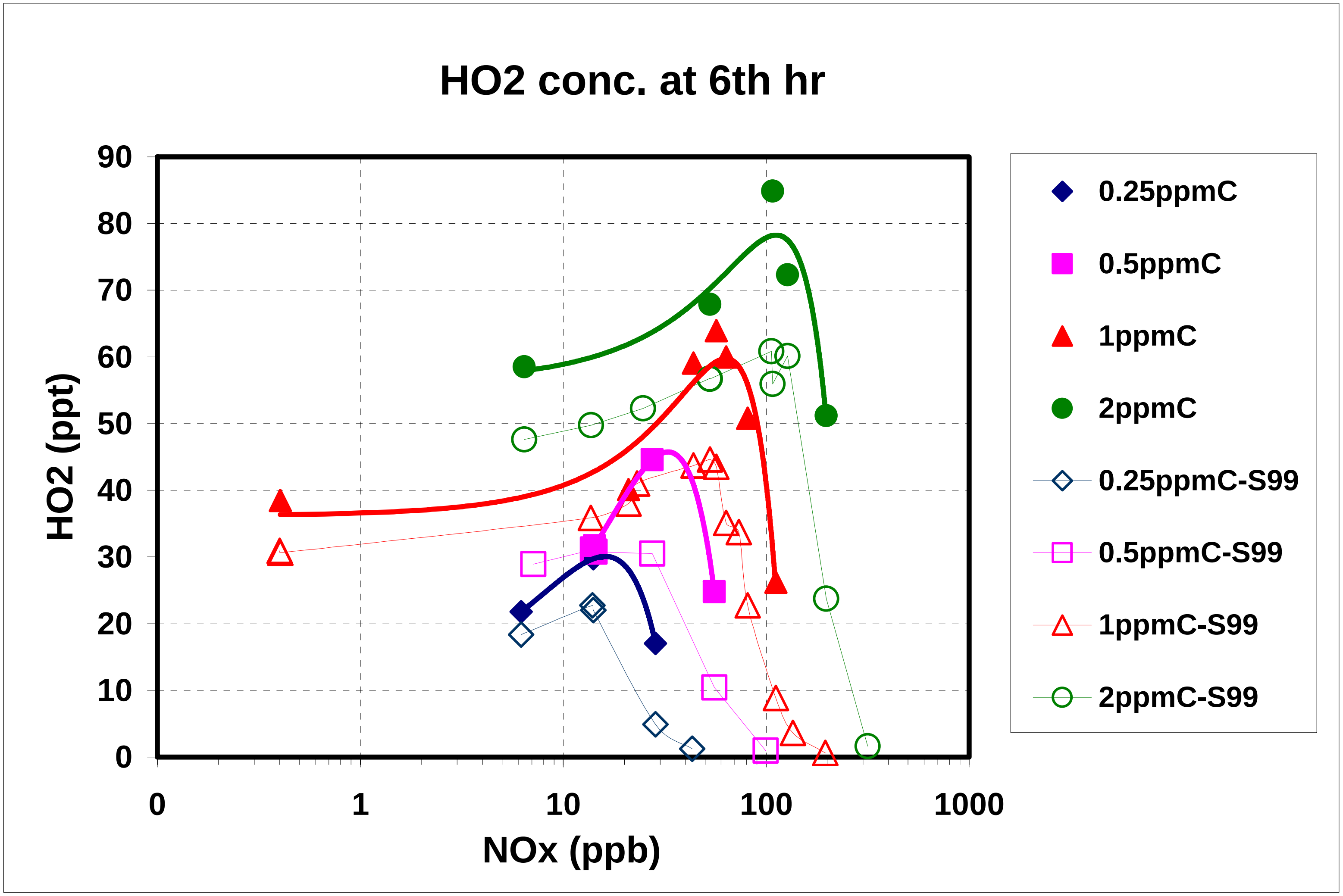
HCHO Chamber vs. SAPRC99 Modeled



OH Chamber vs. SAPRC99 Modeled



HO2 Chamber vs. SAPRC99 Modeled

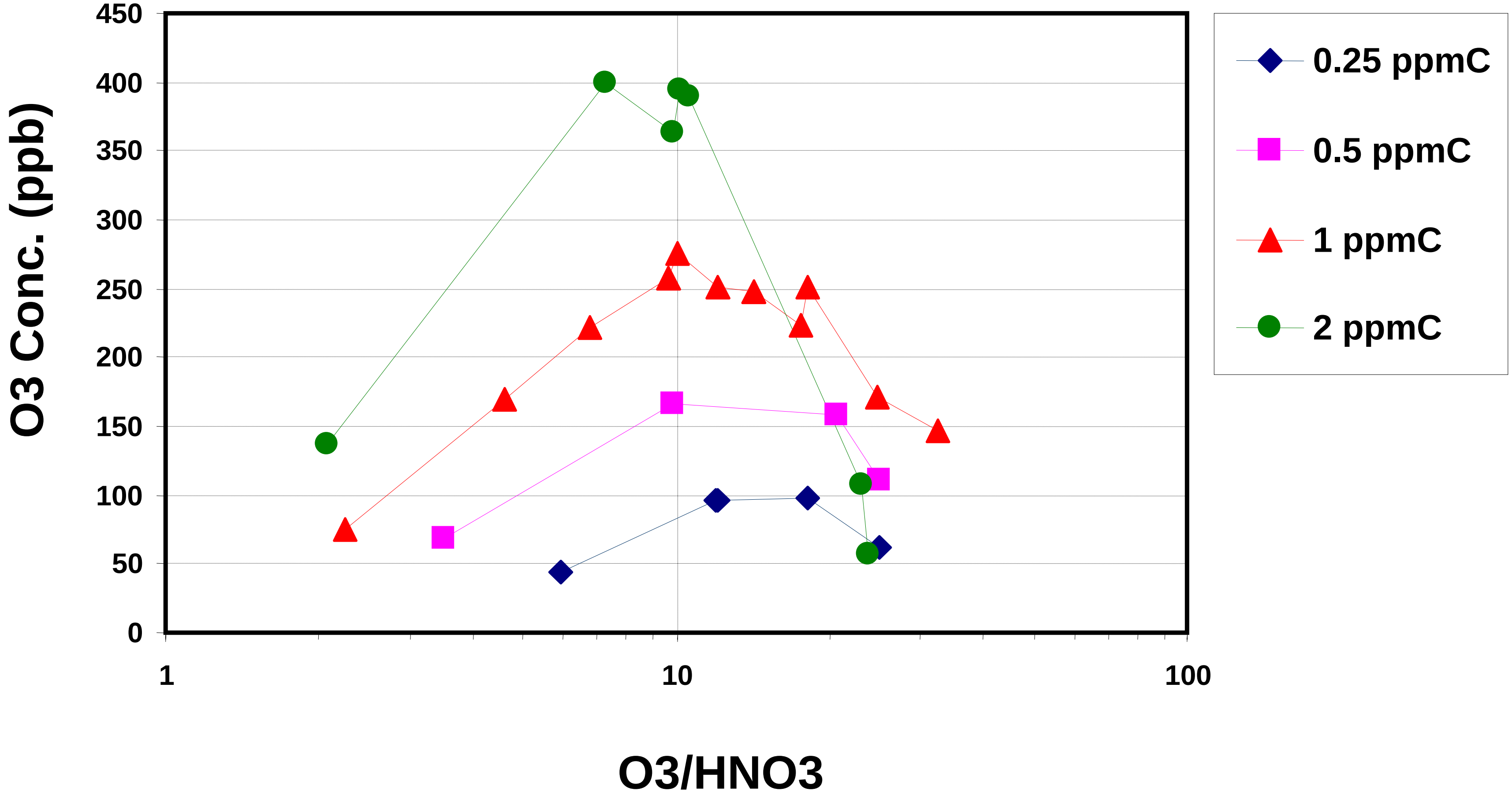


Summary of Model vs. Data

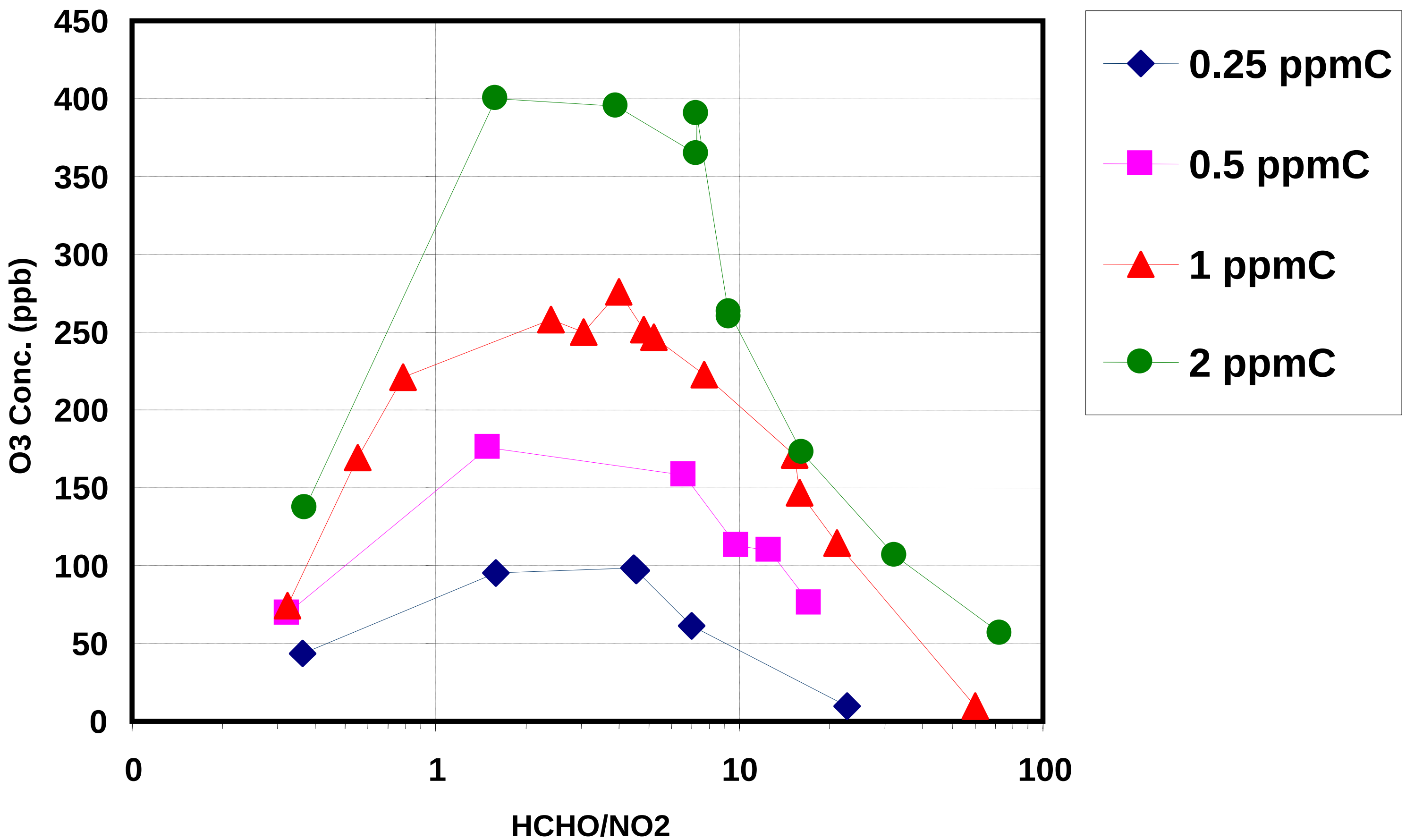
- SAPRC99 has negative O_3 bias at low VOC/NOx.
- SAPRC99 predicts lower OH and HO_2 vs. LIF.
  - LIF data does not show expected drop in OH at low VOC/NOx.
- SAPRC99 has large negative bias vs. H_2O_2 data but the H_2O_2 data have large noise.
- SAPRC99 agrees well with data for HNO_3 and HCHO.

O3 vs. O3/HNO3

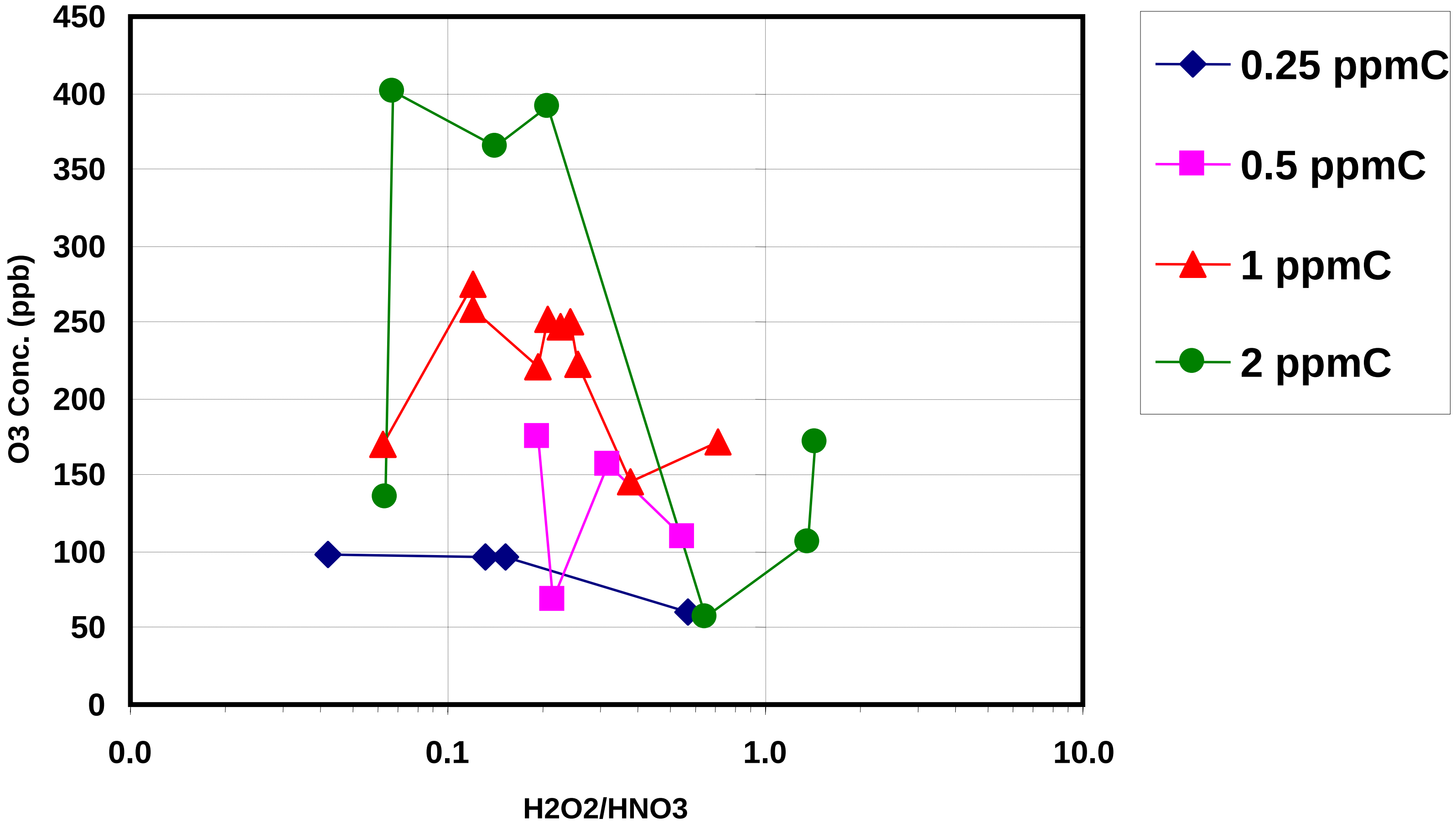
Notes: background O_3 =0, and no aerosol nitrate formed in chamber.



O3 vs. HCHO/NO2



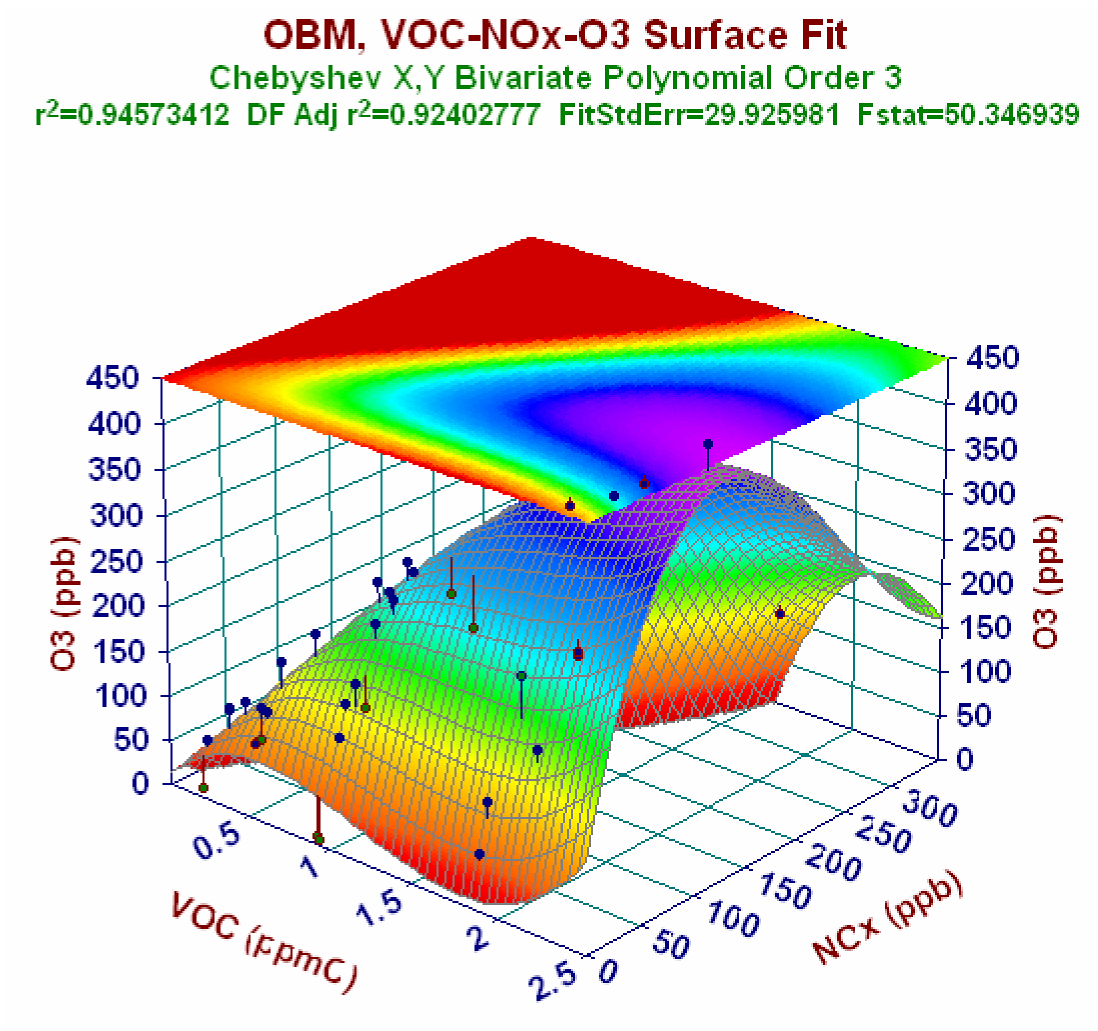
O3 vs. H2O2/HNO3



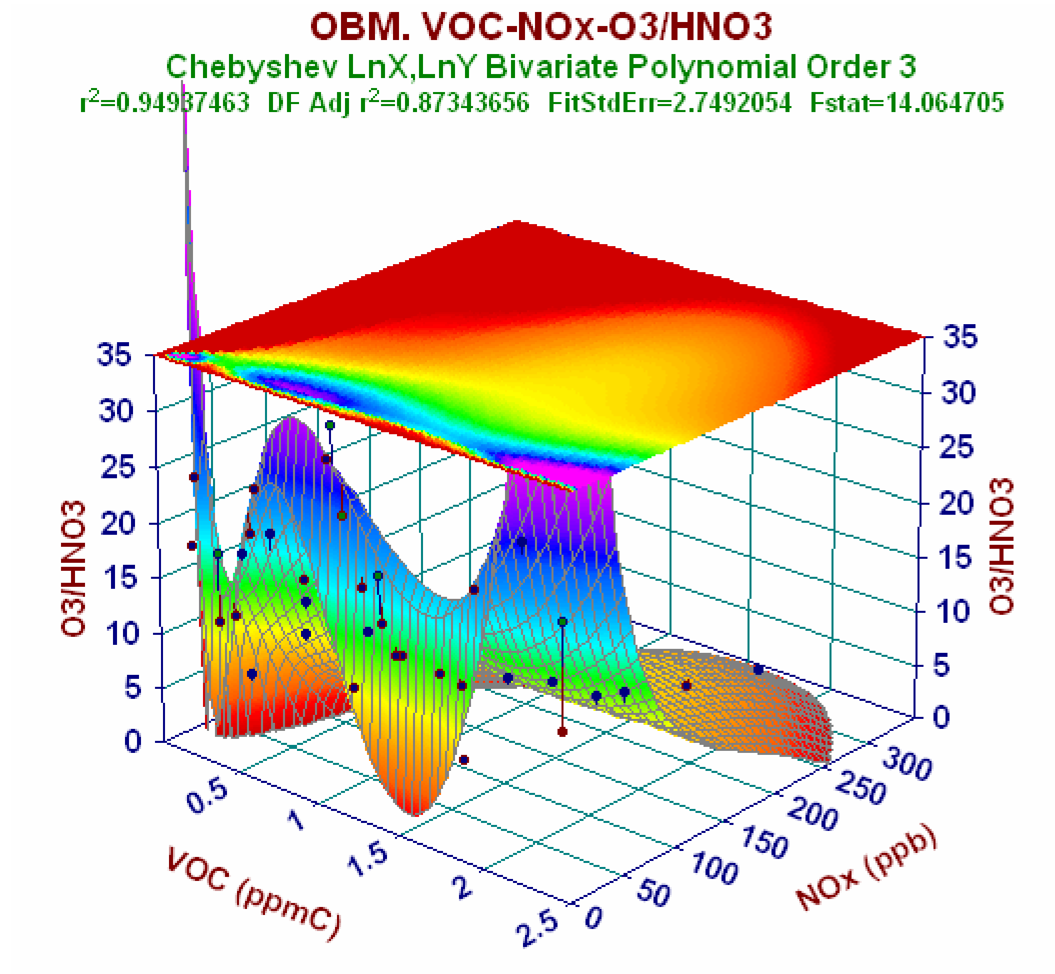
Surface Fitting Approach

- Initial VOC loading in chamber is not precise:
  - the 1 ppmC experiments had 0.95 to 1.05 ppmC VOC.
  - this shifts the location of experiments on the response surface.
  - makes it difficult to identify ridgeline for level of VOC.
- Solution: Try surface fitting algorithms using all data points to generate a more accurate response surface:
  - TableCurve 3D (Systat Software Inc.) using Chebyshev Bivariate Polynomial equations gave the best fit.

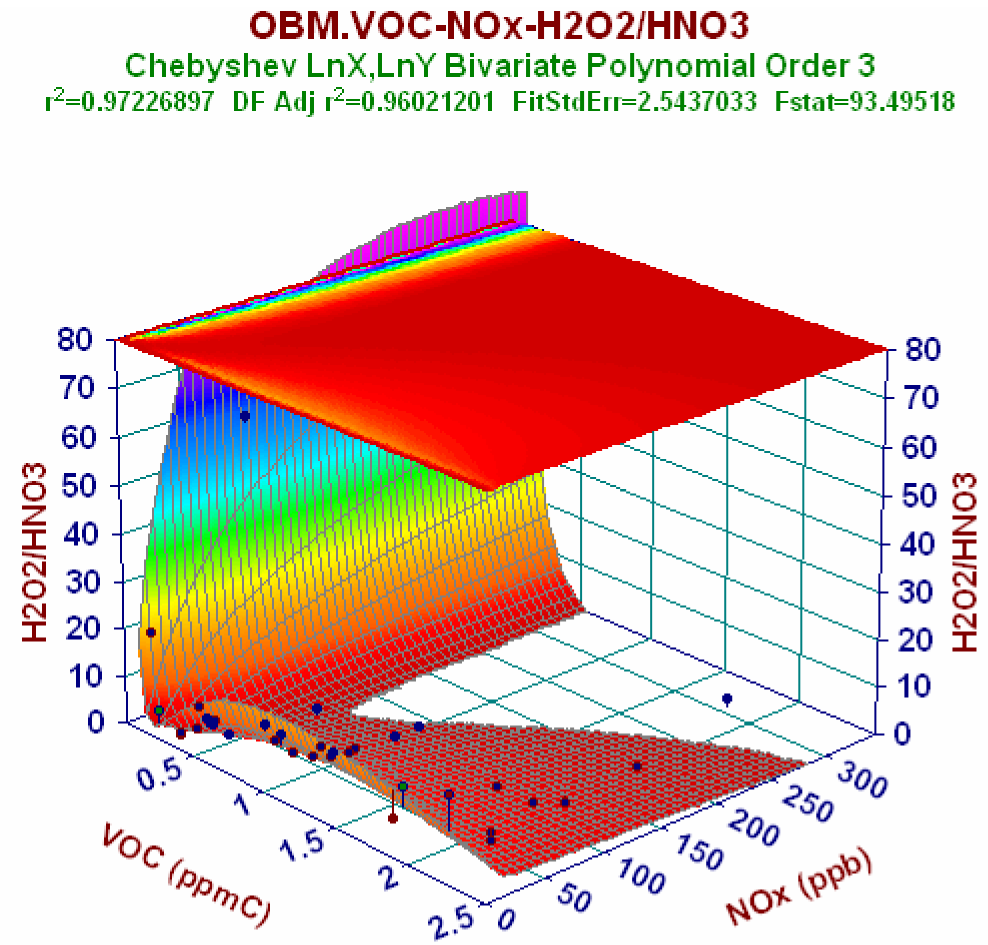
O3 Response Surface



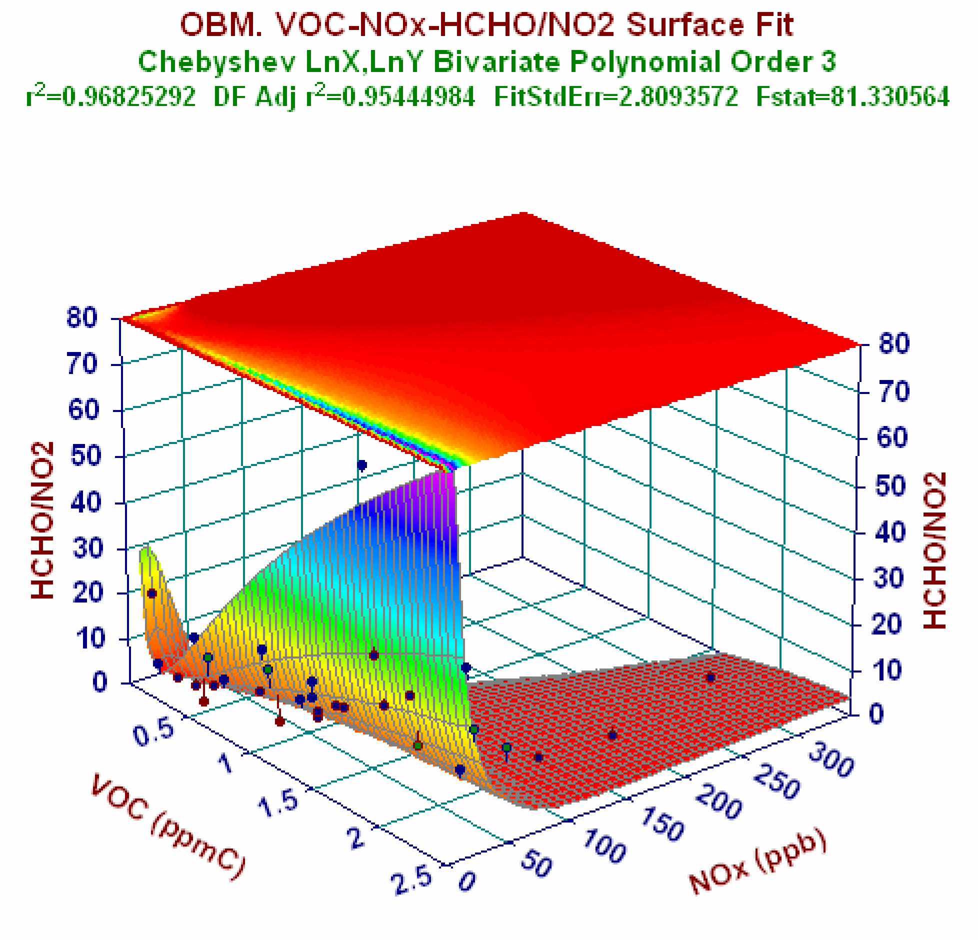
O3/HNO3 Response Surface



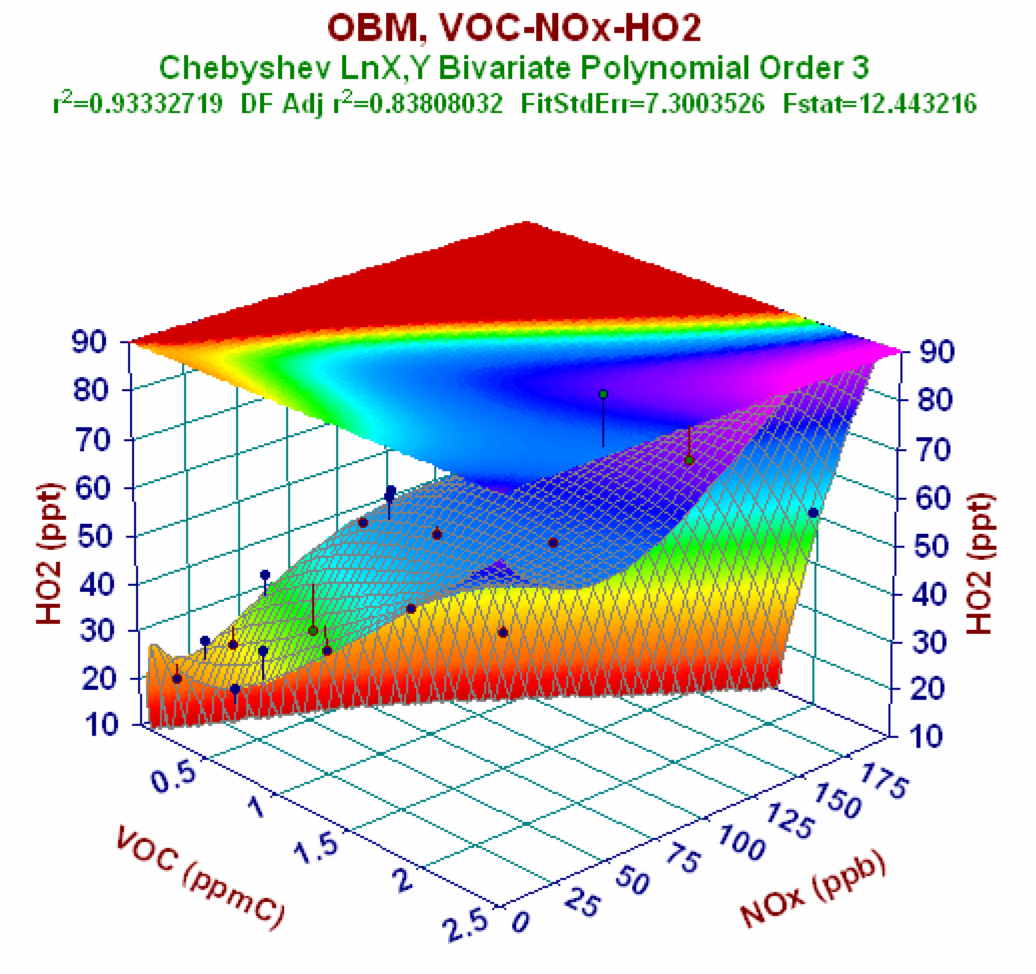
H2O2/HNO3 Response Surface



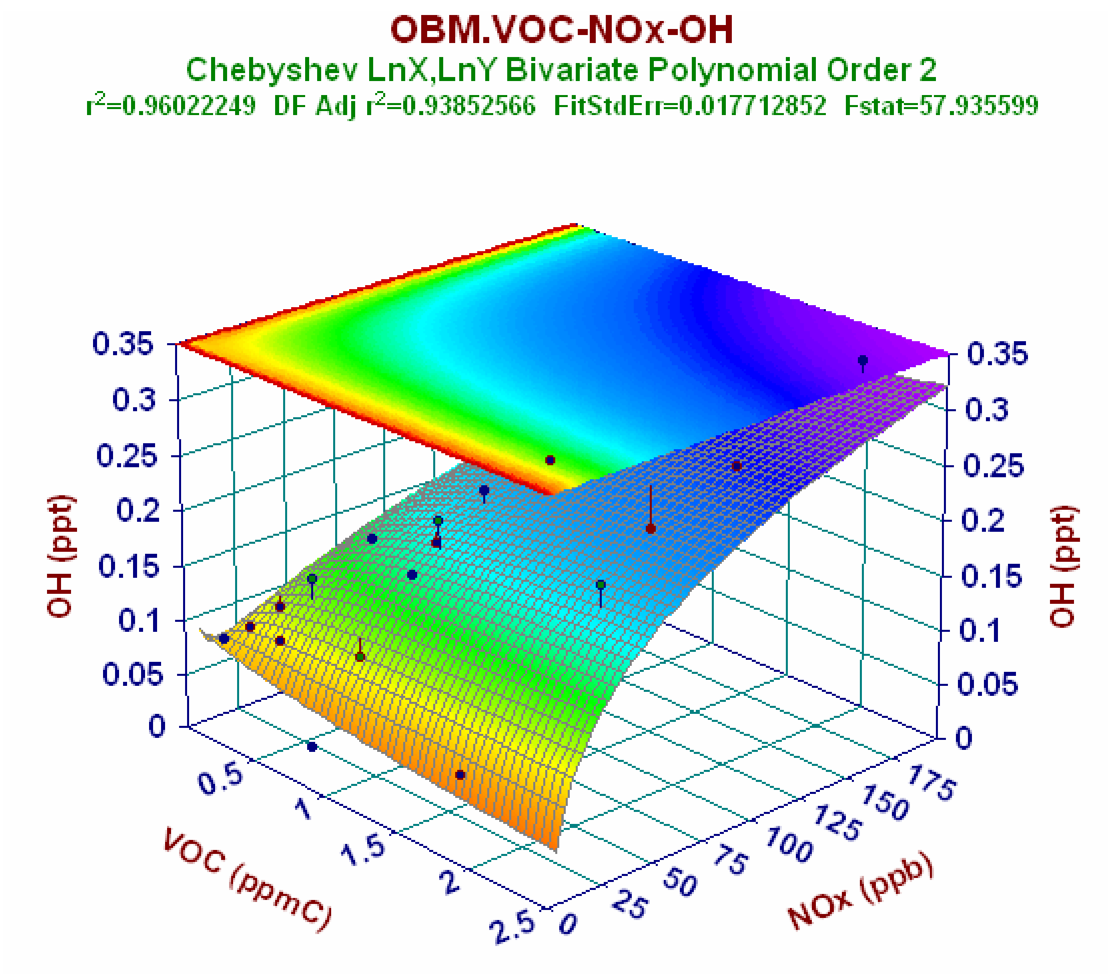
HCHO/NO2 Response Surface



HO2 Response Surface



OH Response Surface



Transition value of Indicator Ratios

Chamber Data vs. Curve Fitting

VOC (ppmC)	O3max (ppb)		O3/NOx		O3/HNO3		H2O2/HNO3		HCHO/NO2		HO2 (ppt)	
	Obs	*fit*	*Obs*	*fit*	*Obs*	*fit*	*Obs*	*fit*	*Obs*	*fit*	*Obs*	*fit*
0.25	104	75	5.4	-	11	12.7	0.15	0.15	2.5	3.3	30	7.6
0.5	178	140	4.6	-	15	10.3	0.2	0.09	3	2.2	32	27.5
1	260	264	3.9	-	13	8.3	0.12	0.15	4	3.2	63	45.3
2	420	407	2.9	-	9	9.1	0.10	0.20	4	3.9	90	77.2

Transition value of Indicator Ratios

Chamber Data vs. SAPC99 Model

VOC (ppmC)	O3max (ppb)		O3/NOx		O3/HNO3		H2O2/HNO3		HCHO/NO2		HO2 (ppt)	
	Obs	*S99*	*Obs*	*S99*	*Obs*	*S99*	*Obs*	*S99*	*Obs*	*S99*	*Obs*	*S99*
0.25	**104**	94	**5.4**	7.5	**11**	18	**0.15**	0.06	**2.5**	3.8	**30**	22
0.5	**178**	154	**4.6**	6.8	**15**	16	**0.20**	0.10	**3**	5	**32**	25
1	**260**	230	**3.9**	4.1	**13**	11	**0.12**	0.03	**4**	4	**63**	38
2	**420**	380	**2.9**	4.0	**9**	9	**0.10**	0.05	**4**	7	**90**	68

Summary of [O_3] 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 0.15

- Small variation in transition 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 can vary by +/-10%
- Problem with high noise in TDL H_2O_2 measurements.
- No background O_3 or H_2O in chamber, this might bias results relative to ambient air.

Conclusions

- O_3/HNO_3, O_3/NOx and $HCHO/NO_2$ seem useful
  - O_3/NOx data is most widely available but “NOx box” measurements are too uncertain.
  - in ambient air we need to measure the sum $HNO_3+NO_3^-$
- H_2O_2 is too difficult to measure.
- Indicators are not robust in chamber nor in model.
  - value of indicator associated with O_3 ridgeline varies depending on VOC level.

Use of Indicators

- If they work indicators predict whether O_3 is more sensitive to VOC or NOx at a particular set of conditions
  - Indicators do not predict how much emissions control is needed to attain air quality goals.
  - Indicators do not determine if attainment of NAAQS is feasible with a VOC or NOx control strategy.
- Indicators should be used to gain more confidence in the model simulations that are used to develop emissions controls.

Caveat for Application in ambient air

- Chamber has low water vapor therefore low OH production from H_2O + O^1D therefore it is possible that performance of indicators differs in chamber versus ambient air.
- To account for effect of O^1D on indicators, we need to develop improved chemical mechanism and use model simulations of ambient air with improved mechanism to further evaluate OBMs.