The Generic Reaction SET (GRS) Model for Ozone Formation

Dr Merched Azzi

Air Quality Studies Group Leader

Commonwealth Scientific and Industrial Research Organisation (**CSIRO**) – Australia
Division of Energy Technology

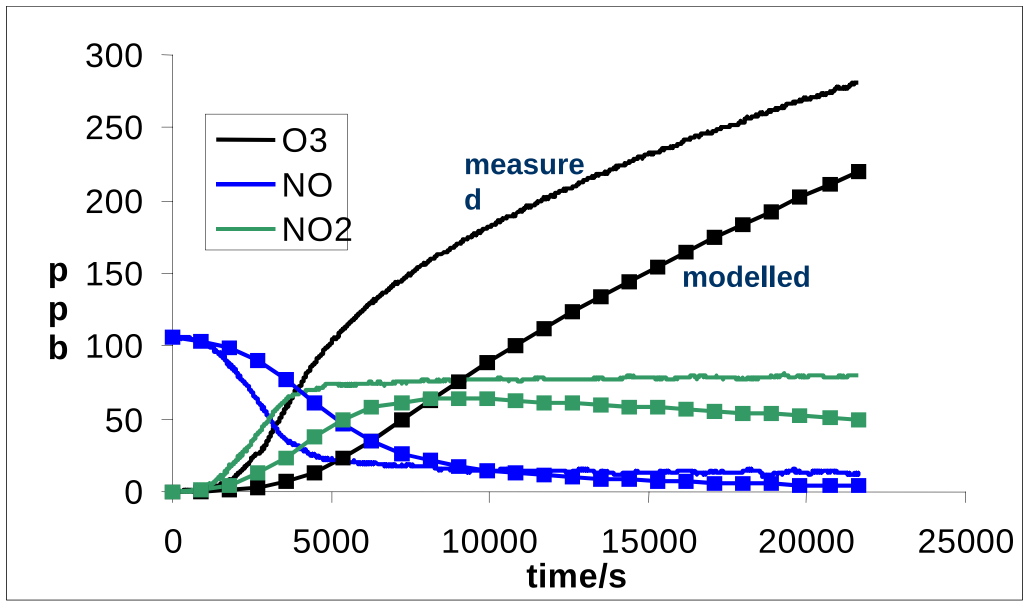
December 2006

www.csiro.au

Environmental Chamber Studies

Provide comprehensive data set to:
- Exhaust Emission Photochemistry.
- Evaporative Fuel Emissions Photochemistry.
- Air Quality Impacts of Fuel Blends.
- Ozone and Aerosol Formation Potential.
- Fate of Air Toxics (benzene, toluene etc.).

Photodecomposition of unleaded petrol-ethanol headspace vapour + NO



The Principles of The Tropospheric Photochemical Reactivity

It is know that:

- Radicals are responsible of the oxidation of gases in the troposphere (initiated by OH)
- OH will often add to double & triple bounds if the resulting bond is strong & the initial bonds are not strong

How the production of Radicals behave during Photochemical smog events?

Photochemical Smog Regimes

Three regimes of Photochemical smog production were identified

- Hydrocarbon Regime (SP proportional to VOC reactivities and the amount of sunlight exposure)
- Transition regime
- NO_x-limited regime (SP proportional to initial NO_x emissions)

When NO_x or VOC's are injected into a given air parcel the secondary oxidants production would depend on the Extent of smog formation

Integrated Empirical Rate (IER) Model

This is a screening model based on observations.

The rate of smog Produced increase is proportional to the photolytic rate coefficient defined as Rsmog , which is calculated by

$$[SP]^t = [R_{smog}]^{t} * \int JNO_2 * f(T)\, dt$$

$$R_{smog} = a_{ROC} [ROC] / [ROC]^{total}$$

The Generic Reaction Set (GRS) Model

$ROC + h\nu \rightarrow ROC + \mathbf{RP}$

$\mathbf{RP} + NO \rightarrow NO2$

$NO2 + h\nu \rightarrow NO + O3$

$NO + O3 \rightarrow NO2$

$RP + RP \rightarrow$

$RP + NO2 \rightarrow SGN$

$RP + NO2 \rightarrow SNGN$

The GRS Model Species

1. Reactive organic compounds **ROC**
2. nitric oxide **NO**,
3. radical pool **RP**
4. nitrogen dioxide **NO_2,**
5. ozone **O_3**,
6. stable gaseous nitrogen species **SGN**,
7. stable non-gaseous nitrogen species **SNGN**,

The GRS Model Verification

The model has been tested in three ways namely by:

- Comparison with outdoor smog chamber data
- Comparison with estimates from more detailed (lumped) photochemical mechanisms; and
- Incorporation into different urban airshed models and applications to different oxidant episodes from different locations

The model is being currently used for selecting control strategy scenarios

Outcomes from the GRS Model Validation

The GRS model has shown that in urban atmosphere

1. The model predictions compared well with those obtained from field
3. Under ambient conditions with ROC/NO_x ratios less than 5 the ozone predictions were overestimated by ~30%
4. The GRS can be used as screening tool for air quality assessment and for selecting scenarios for control strategies

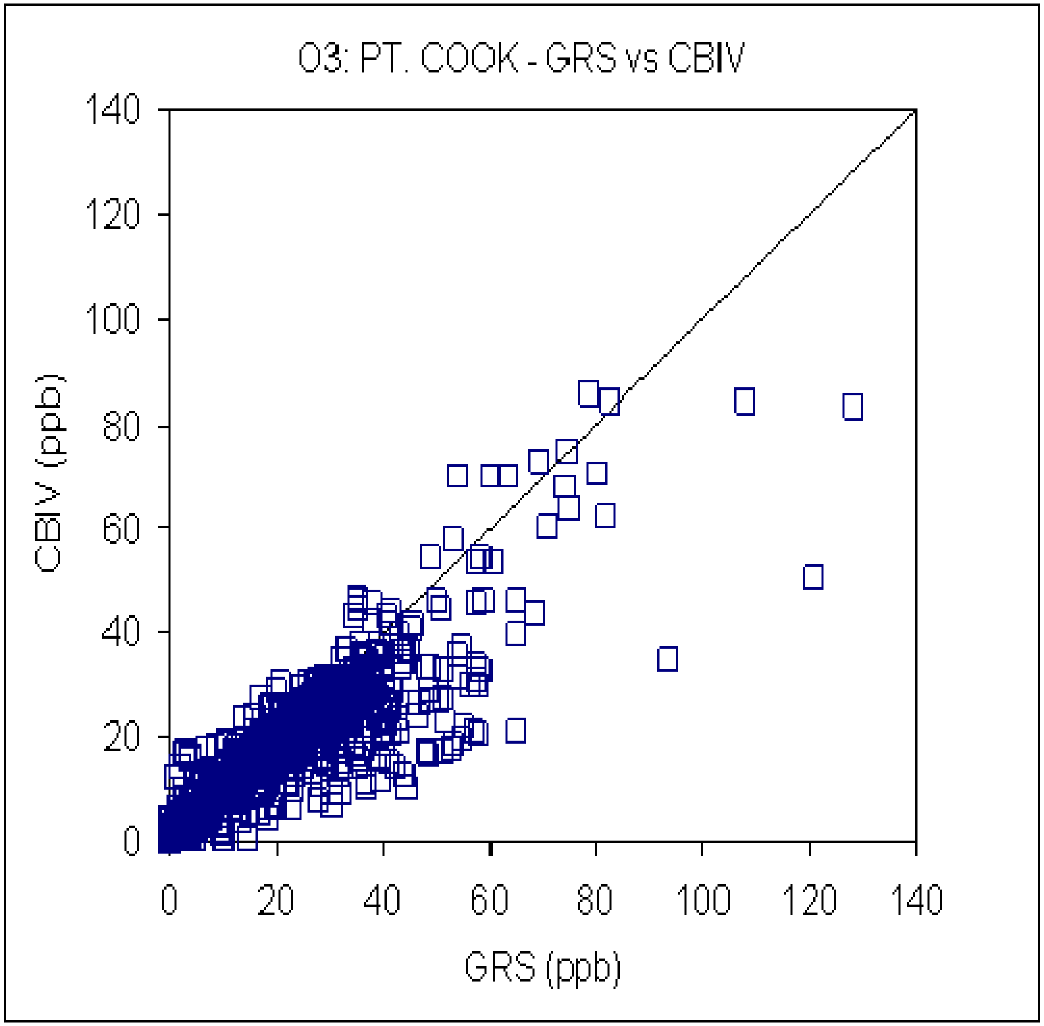
Outcomes from the GRS Model Validation

The GRS model has shown that in rural atmospheres

1. The model predictions do not compare well with predictions from more detailed models.

   WHY?

   1. Different composition and reactivity of typical rural ROC compared to urban ROC
   2. Lack of background radical production mechanism responsible for the initiation of smog production


O3: PT. COOK - GRS vs CBIV
CBIV (ppb)
GRS (ppb)
0
20
40
60
80
100
120
140

Limitations of the GRS Model

- In Urban atmospheres the main limitation of GRS is related to the description of radicals which are continuously produced as long as the light is available.

- At low ROC/NO_x ratios the model consume quickly the available NO_x and accelerate the production of ozone as has been observed in smog chamber data and field simulations

How can the GRS Model Be Improved ?

The model was modified to include:

- An extended treatment of key radical species
- A direct ozone photolysis

The Extended Generic Reaction Set (GRS) Model

$$ROC + h\nu \rightarrow HO_2 + RO_2 + ROC$$

Rate

$$RO_2 + NO \rightarrow NO_2 + 0.1HO_2 + 0.5RCHO$$

$$HO_2 + NO \rightarrow NO_2 + OH$$

$$ROC + OH \rightarrow RO_2$$

$$RCHO + OH \rightarrow C_2O_3$$

$$NO_2 + h\nu \rightarrow NO + O_3$$

$$NO + O_3 \rightarrow NO_2$$

$$O_3 + h\nu \rightarrow O(1D)$$

$$O(1D) + H_2O \rightarrow OH + OH$$

$$O_3 + HO_2 \rightarrow OH$$

The Extended Generic Reaction Set (GRS) Model – (Cntd.)

$$C_2O_3 + NO_2 \rightarrow PERNIT$$

$$PERNIT \rightarrow NO_2 + C_2O_3$$

$$OH + NO_2 \rightarrow HNO_3$$

$$HO_2 + HO_2 \rightarrow H_2O_2$$

$$O(1D) \rightarrow O$$

$$O \rightarrow O_3$$

$$H_2O_2 \rightarrow 2OH$$

$$OH + H_2O_2 \rightarrow HO_2$$

$$RO_2 + HO_2 \rightarrow ROOH$$

$$C_4H_6 + OH \rightarrow P1$$

$$C_4H_6 + O_3 \rightarrow P2$$

$$SO_2 + OH \rightarrow HOSO_2$$

The Extended Generic Reaction Set (GRS) Rate of Reactions

The GRS2 rate coefficients have largely been obtained from the literature.

- ***The rate for reaction (1) was deduced from the outdoor smog chamber experiments***
- ***Reaction (2) represents the oxidation of NO by RO_2 to produce NO_2, together with fractional amounts α and β respectively of the radical and reactive species HO_2 and RCHO***

GRSV2 Kinetic Parameters
(cm 3 molecule-1 s-1 units)

#	Reaction	A (units depend on order)	Ea/R	k_{298}		Comments
1	ROC + hv = HO2 + RO2 + ROC	k_6*FTT*tivity*2				Complex function derived from smog chamber experiments
2	RO2 + NO = NO2 + 0.1*HO2 + 0.5*RCHO	5.30E-12	-360	1.7739E-11		CB-IV_99; reaction rate for C2O3 + NO = NO2 + XO2 + HCHO + HO2; fitted values for HO2 and RCHO co-efficients
3	HO2 + NO = NO2 + OH	3.70E-12	-242	8.3346E-12		CBIV
4	ROC + OH = RO2	1.00E-11		1E-11		CBIV
5	RCHO + OH = C2O3	1.68E-11	559	2.5742E-12		Rate taken from Seinfeld (1986) for RH + OH + RO2 + H2O
6	NO2 + hv = NO + O3	radiation dependent				
7	NO + O3 = NO2	2.00E-12	1400	1.8227E-14		CB-IV_99
8	O3 + hv = O(1D)	radiation dependent				
9	O(1D)+ H2O = OH + OH	2.20E-10		2.20E-10		CB-IV
10	O3 + HO2 = OH	1.10E-14	580	1.5708E-15		CB-IV
11	C2O3 + NO2 = PERNIT	2.63E-12	-380	9.4136E-12		CB-IV; Rate for PERNIT=PAN
12	PERNIT = NO2 + C2O3	2.00E+16	13500	0.00042327		CB-IV; Rate for PERNIT=PAN
13	OH + NO2 = HNO3	1.00E-12	-713	1.0942E-11		CB-IV
14	HO2 + HO2 = H2O2	5.90E-14	-1150	2.7978E-12		CB-IV
15	O(1D) = O	1.92E-11	-126	2.93E-11		CB-IV
16	O=O3	6.0E-34 * $((1/T)^{-2.3})$				CBIV
17	H2O2=2OH	radiation dependent				
18	OH+H2O2=HO2	2.90E-12	160	1.70E-12		CBIV
19	RO2+HO2=ROOH	5.60E-12				Seinfeld
20	C4H6+OH=P1	1.48E-11	-448	6.66E-11		
21	C4H6+O3=P2	1.34E-14	2283	6.31E-18		
22	SO2+OH=HOSO2	9.00E-13		9.00E-13		DeMore et al 1997

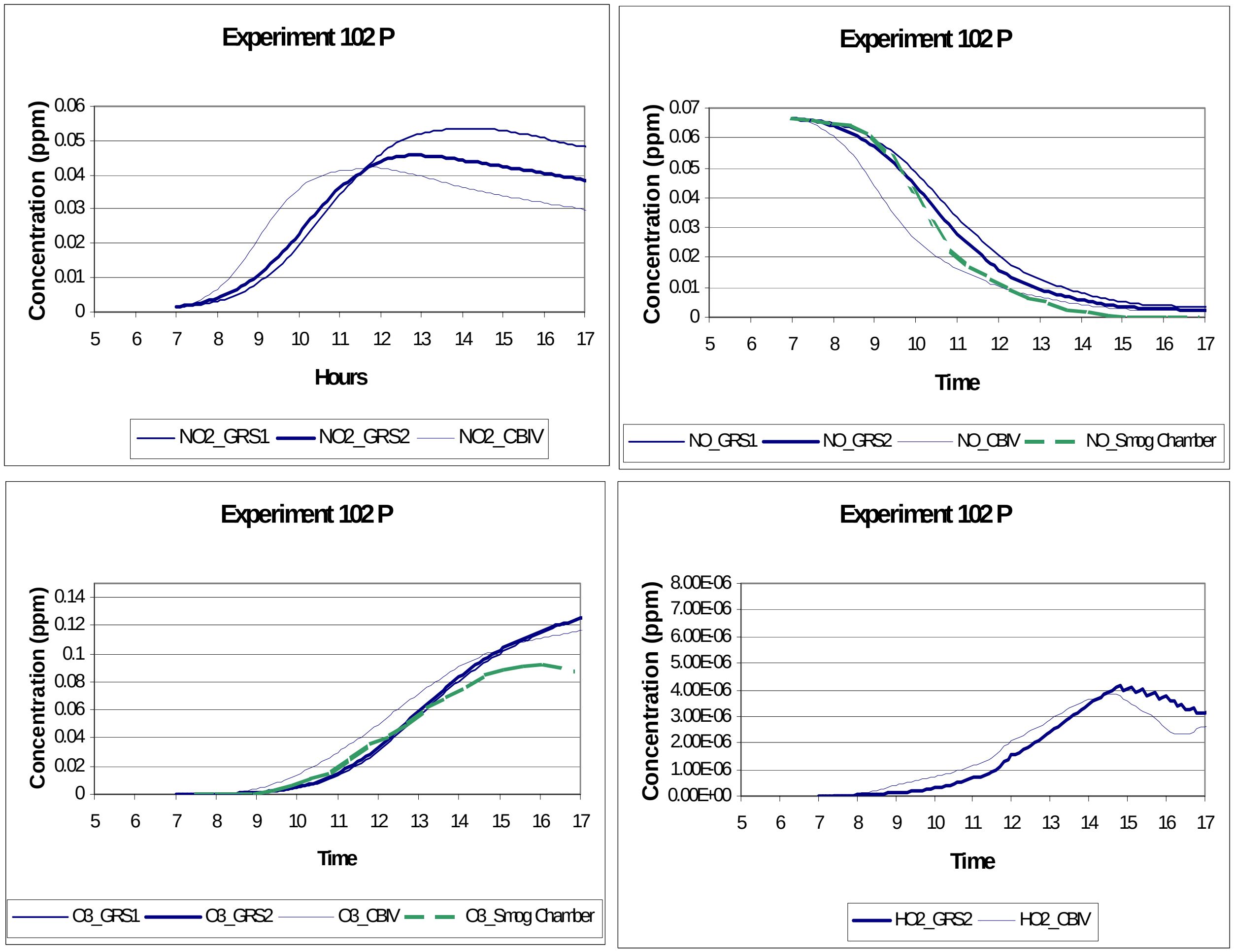
Smog Chamber Experiments

A mix of hydrocarbon species was used for these experiments including

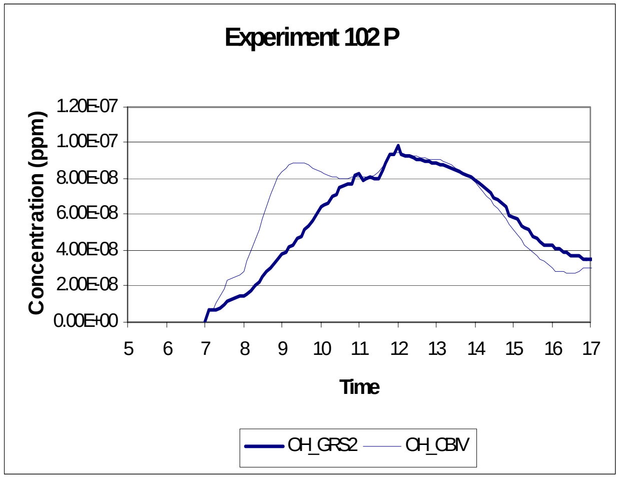
- ***Exhaust surrogate***
- ***Petrol and solvent components***

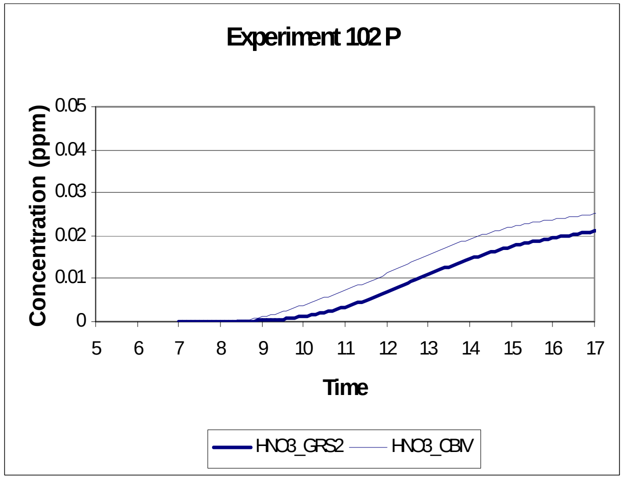
The ROC/NO_x ratios selected for these experiments varied between 15.6 and 3.6 to represent the wide variety of ambient conditions for most urban airsheds

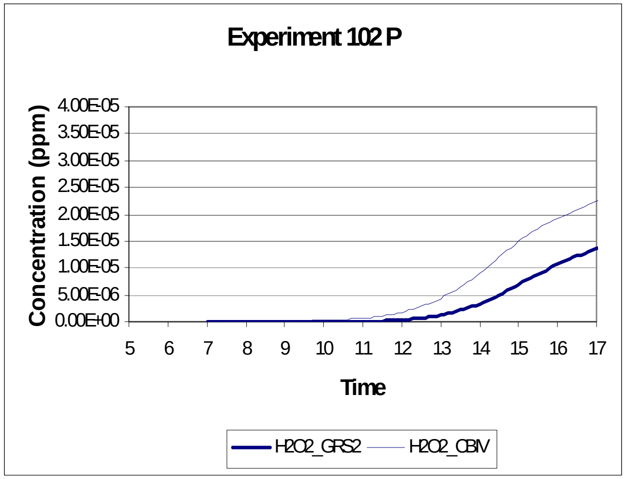
GRS1, GRS2, CBIV, Smog Chamber Model Predictions ROC/NOx=9.3



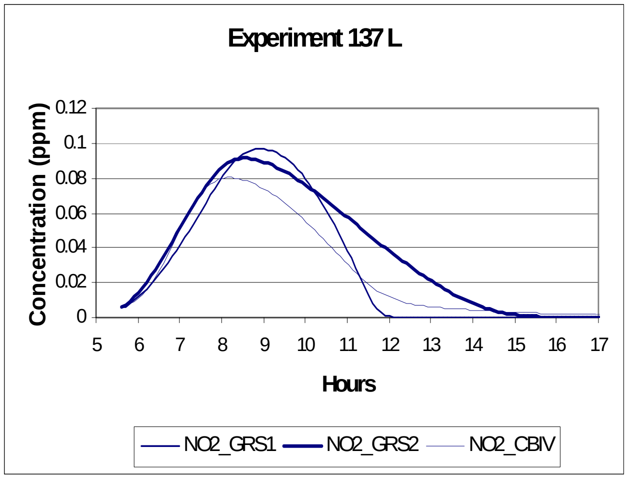
GRS1, GRS2, CBIV, Smog Chamber Model Predictions ROC/NOx=9.3

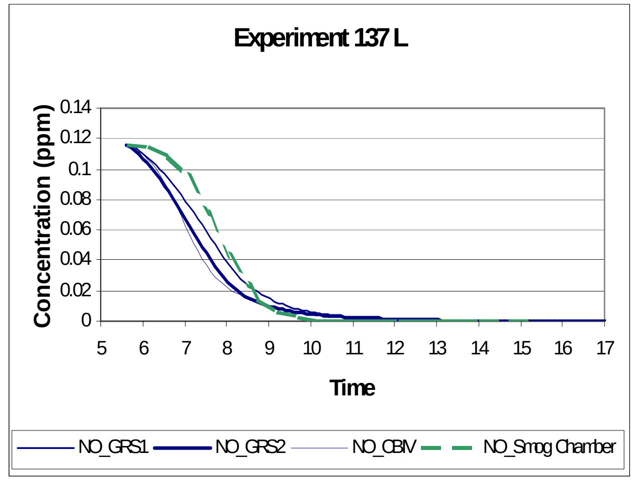


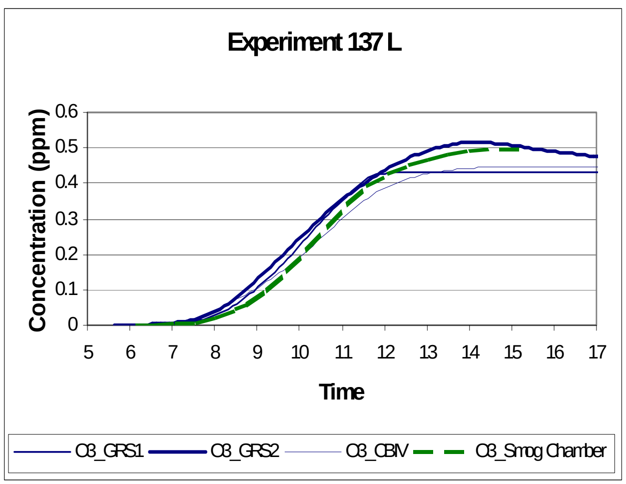


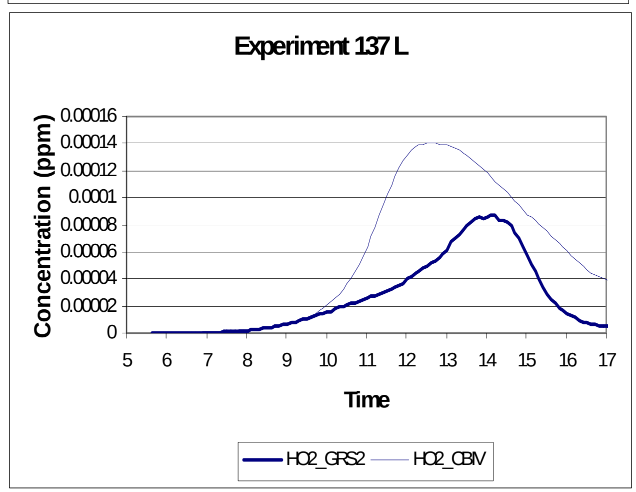


GRS1, GRS2, CBIV, Smog Chamber Model Predictions ROC/NOx=9.7

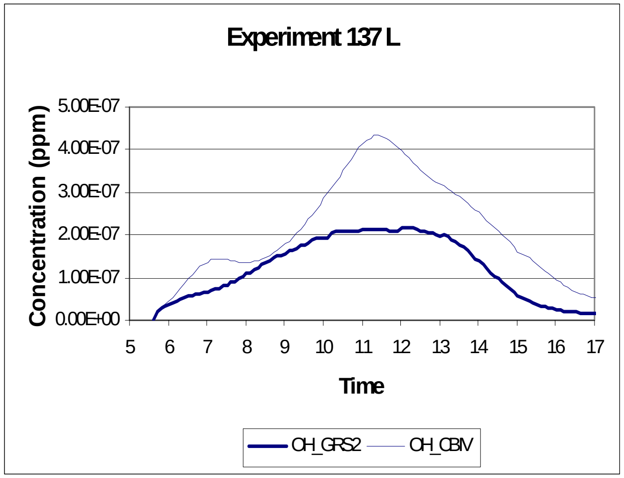


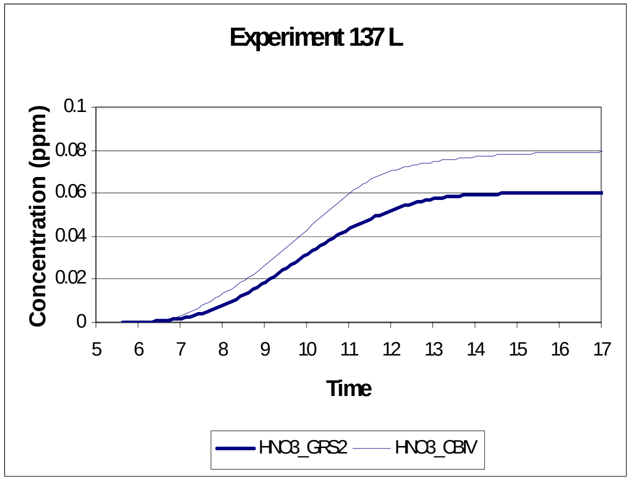


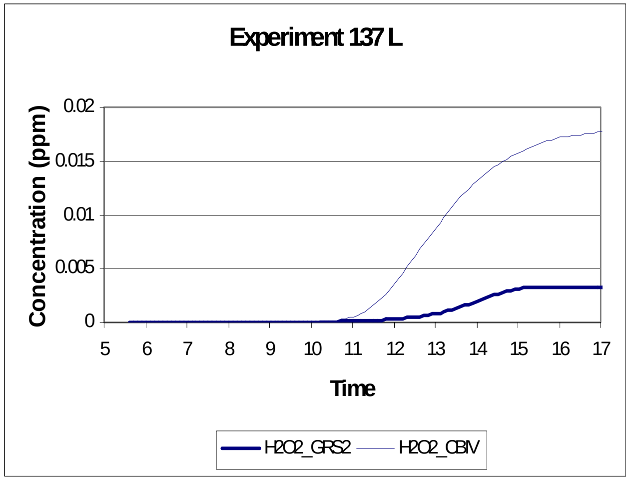




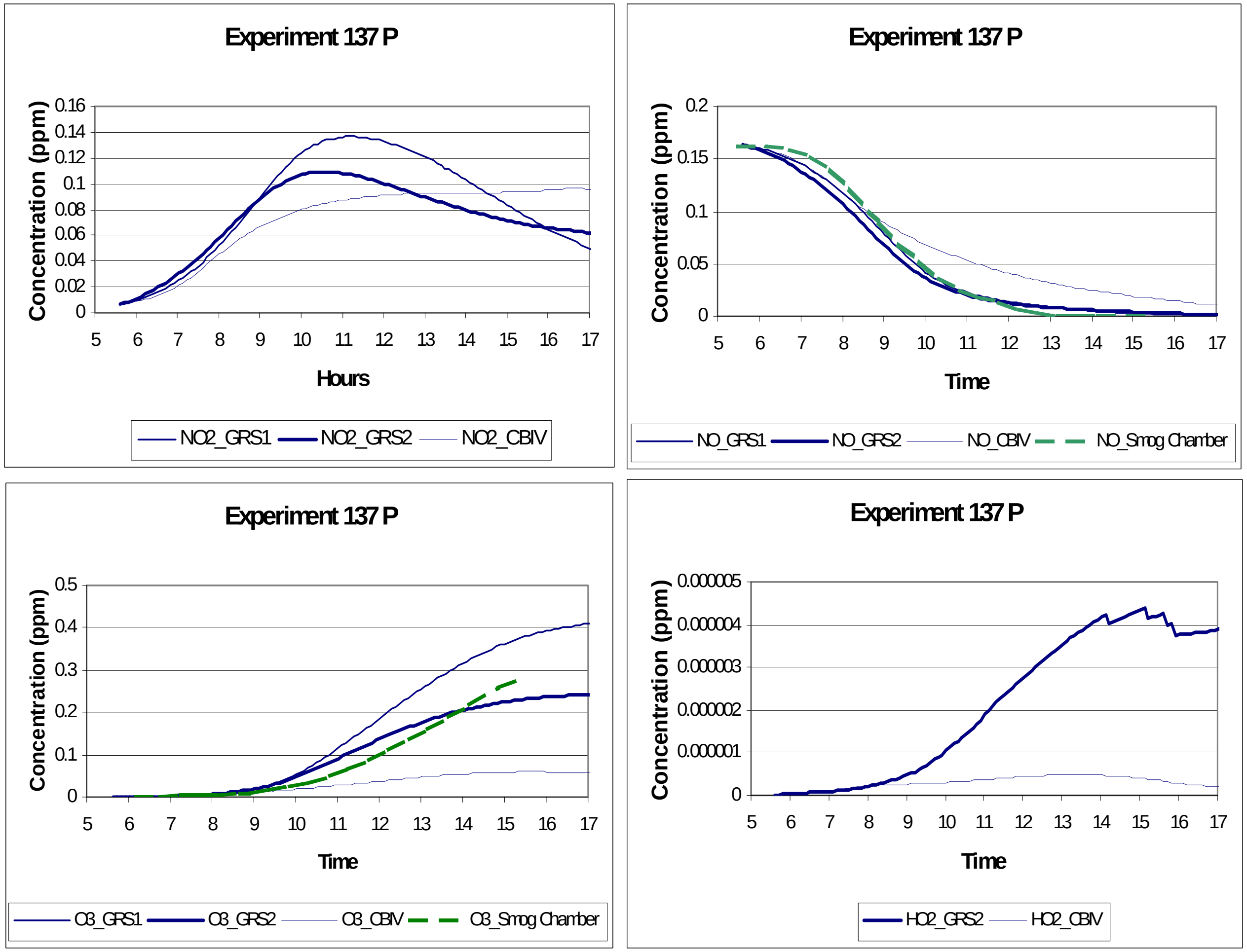
GRS1, GRS2, CBIV, Smog Chamber Model Predictions ROC/NOx=9.7



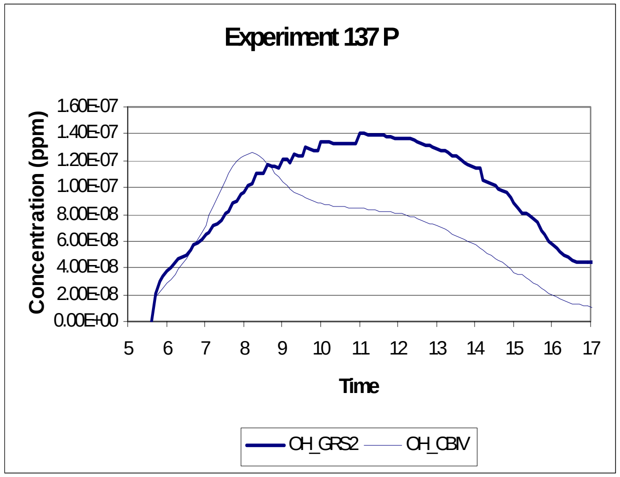


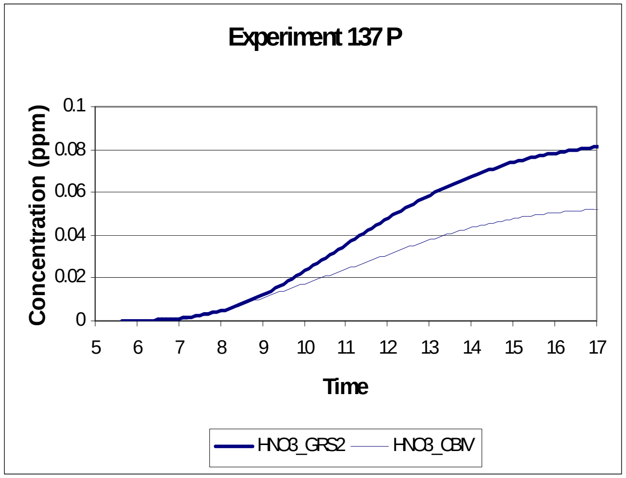


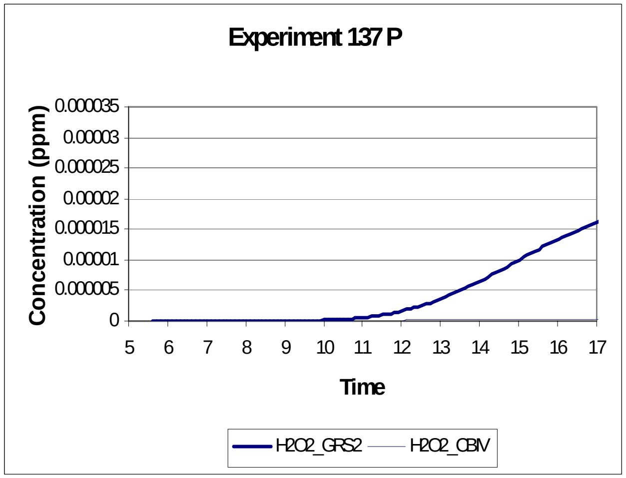
GRS1, GRS2, CBIV, Smog Chamber Model Predictions ROC/NOx=3.5



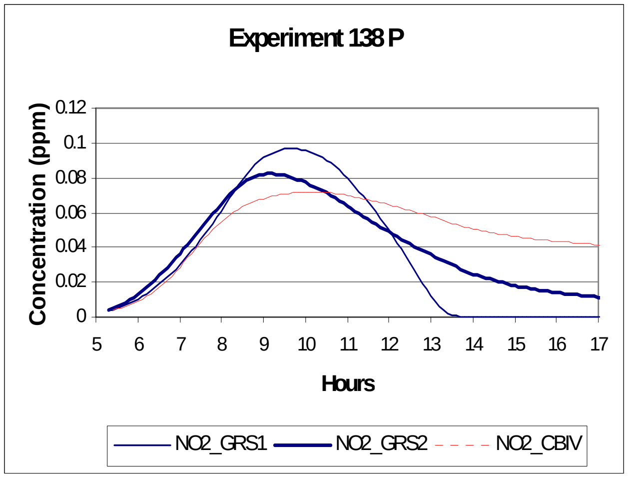
GRS1, GRS2, CBIV, Smog Chamber Model Predictions ROC/NOx=3.5

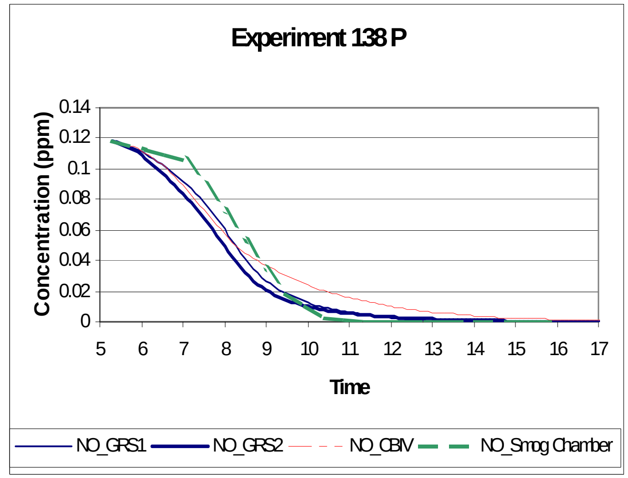


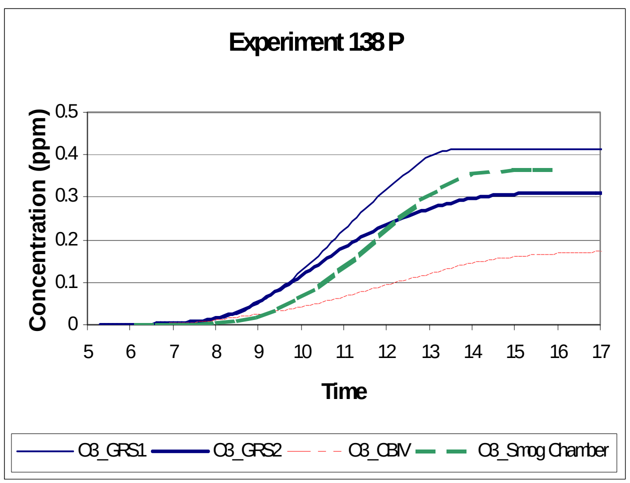


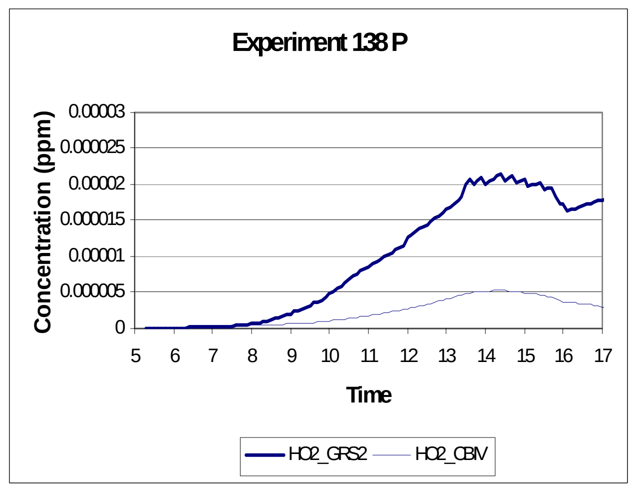


GRS1, GRS2, CBIV, Smog Chamber Model Predictions ROC/NOx=4.8

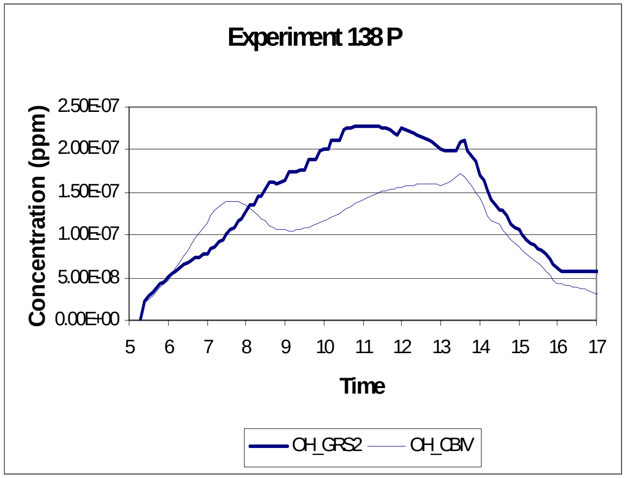


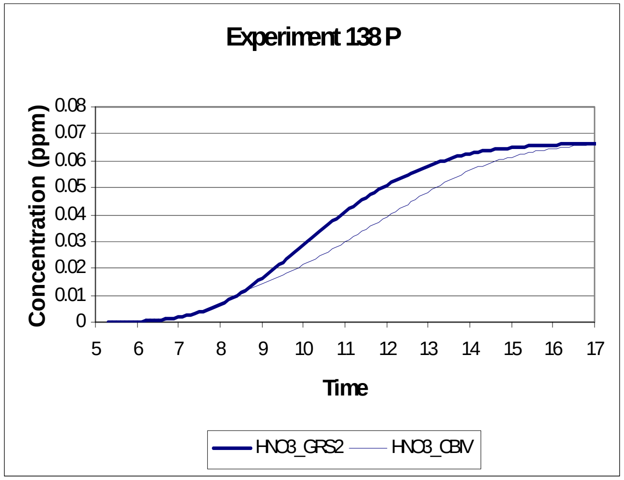


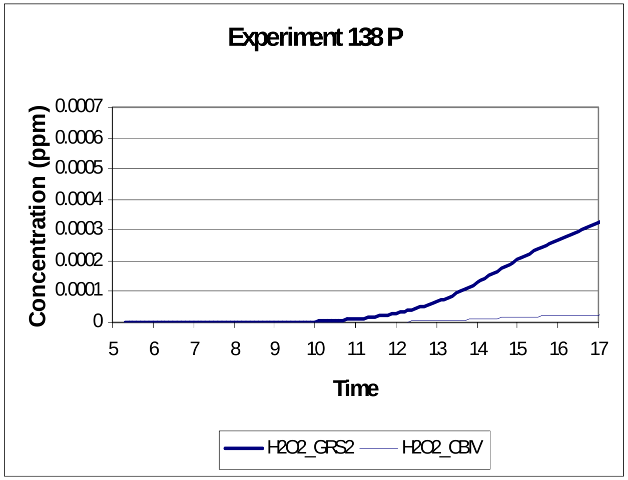




GRS1, GRS2, CBIV, Smog Chamber Model Predictions ROC/NOx=4.8







Outcomes

The modified model GRS2, extends the capability of the GRS1 by including reactions which explicitly account for the formation and destruction of key radical species OH and HO_2.

For ROC/NOx ratios varying between 3.5 – 15.6,

- ***ozone concentrations predicted by GRS2 were within ± 10-20% of measured concentrations.***
- ***OH, HO_2 , HNO_3 and H_2O_2 were not measured experimentally but were compared to CBIV predictions. However, this aspect can be subject to further investigations and refinements.***

Because of the short computer run time and chemical detail required by the GRS model, GRS can be successfully used as screening tool to select event days required to develop future control strategies.

CSIRO Energy Technology

Dr Merched Azzi

Principal Research Scientist

Phone 61 2 97106870)

Email merched.azzi@csiro.au

Web www.csiro.au/group

CSIRO

Thank You

Contact CSIRO

Phone 1300 363 400

+61 3 9545 2176

Email enquiries@csiro.au

Web www.csiro.au