Auxiliary Mechanism (Wall Model)

for

UNC Outdoor Chamber

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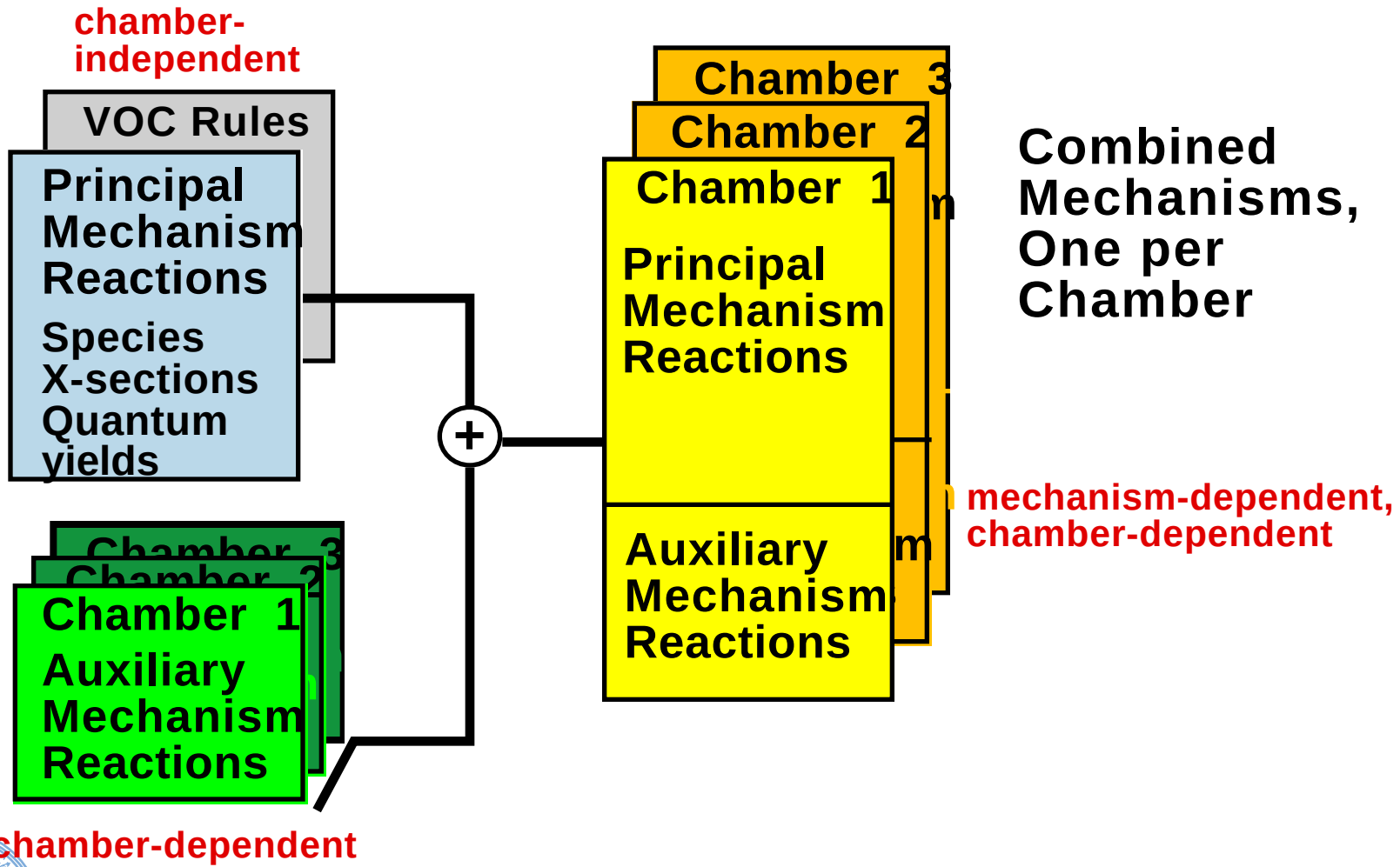
Principal & Aux Mechanisms



UNCAuxMech99_09.rxn

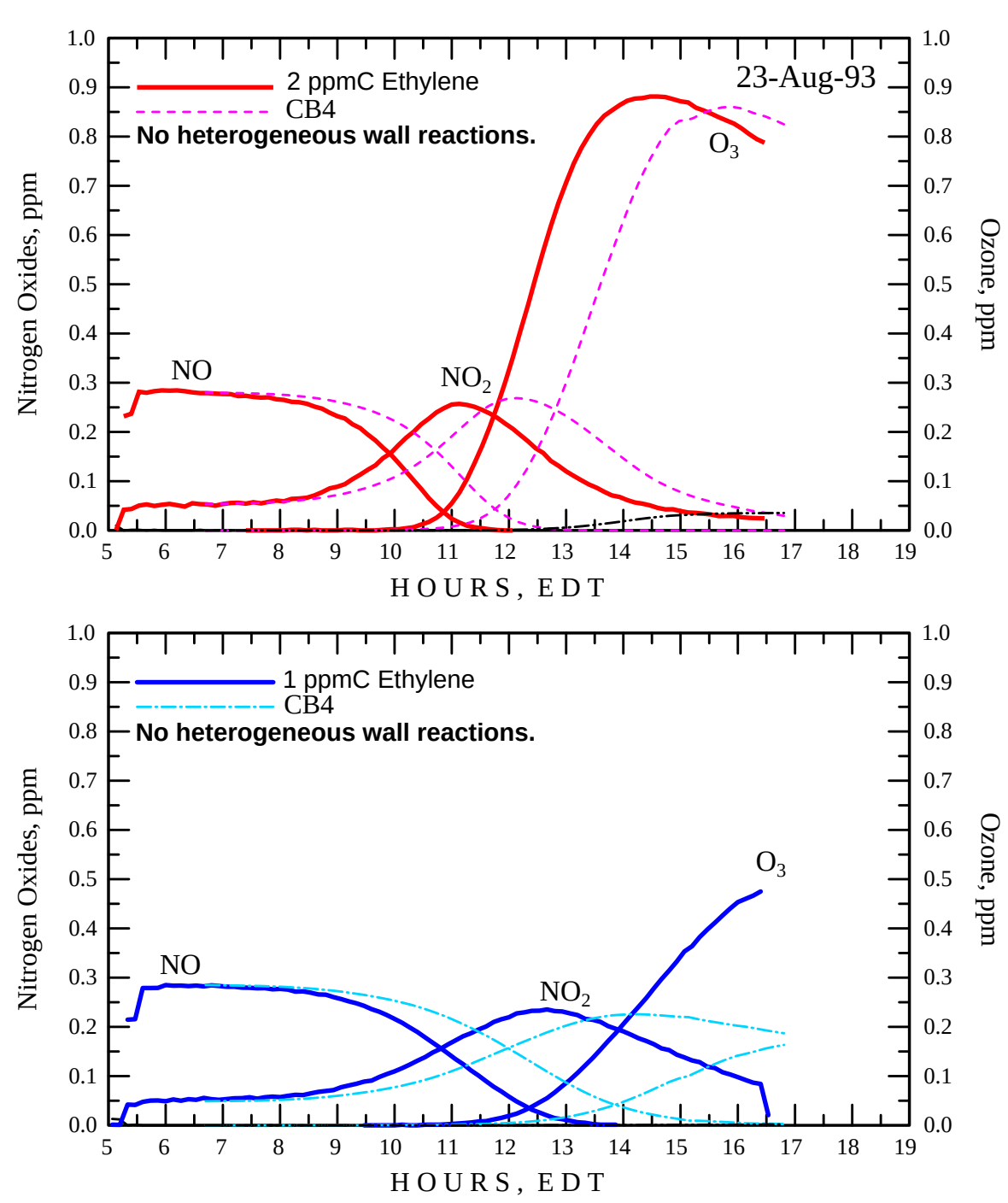
```
/*****************************************************************
 *  UNC Chamber Dependent Reactions  ( 9/30/99, HEJ )            *
 *  Units are molecules/cm^3/s and molecules/cm^2/s              *
 *****************************************************************/

// ============================================================================
//                                                    ambient air entrainment
//
// reactants added to chamber via dilution entrainment.
//   Stoichiometric factors are ambient concentrations
//   in ppm; change to mppc via total number density and factors.
SCALARS
 DL,
 mpcc_ppm,
 amb_CO , amb_O3 , amb_H2, amb_CH4, amb_HCHO, amb_BVOC, amb_CCl4 ;

start DL       = 1.0;              // used to adjust entrainment
withk mpcc_ppm = 1.0E-06 * b[M];
withk amb_CO   = 0.500 * mpcc_ppm; // i.e., 0.500 ppm CO in ambient air
withk amb_O3   = 0.085 * mpcc_ppm;
withk amb_H2   = 0.580 * mpcc_ppm;
withk amb_CH4  = 1.790 * mpcc_ppm;
withk amb_HCHO = 0.002 * mpcc_ppm;
withk amb_BVOC = 0.085 * mpcc_ppm;
withk amb_CCl4 = 0.000 * mpcc_ppm;

R[entrain] = ----> amb_CO   * CO   + amb_O3   * O3   + amb_H2   * H2   +
                   amb_CH4  * CH4  + amb_BVOC * BVOC + amb_CCl4 * CCl4 +
                   amb_HCHO *  HCHO
                                                    @ DL * p[k1st] ;



// ============================================================================
//                                                  background VOC oxidation
//
R[BVOC]   = OH + BVOC ---->  0.667*'CH3-OO.'   +
                             0.167*'CH3-CO-OO.'                 @ 3.0E-12;
```

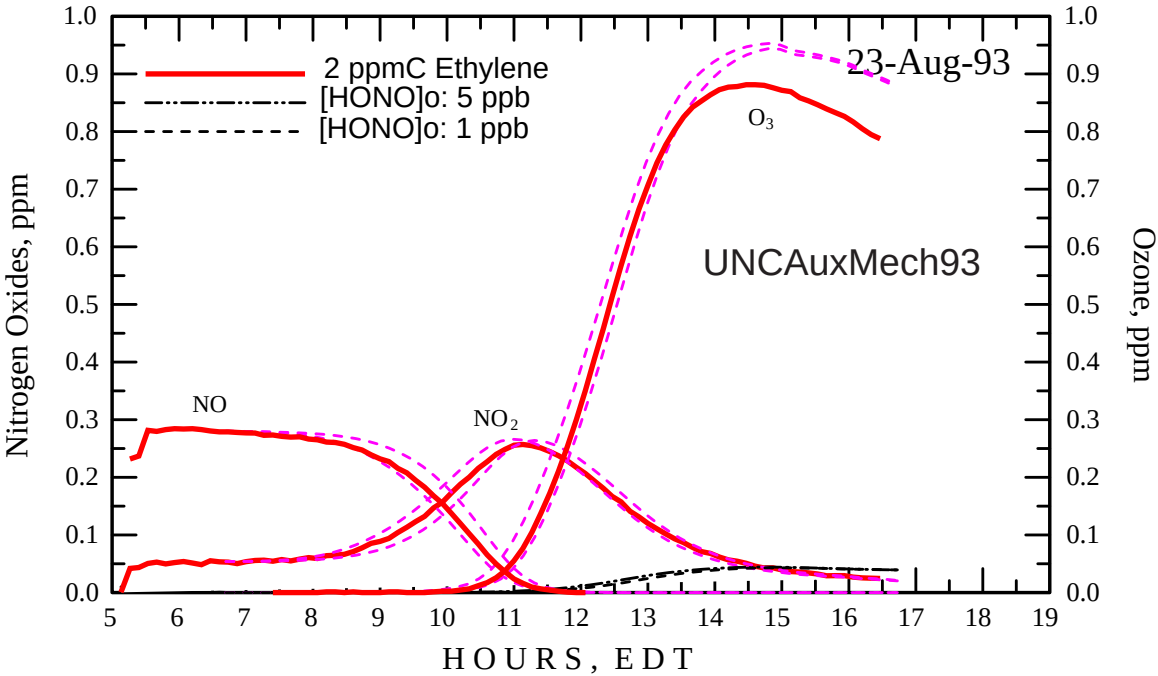
UNCAuxMech93.RXN

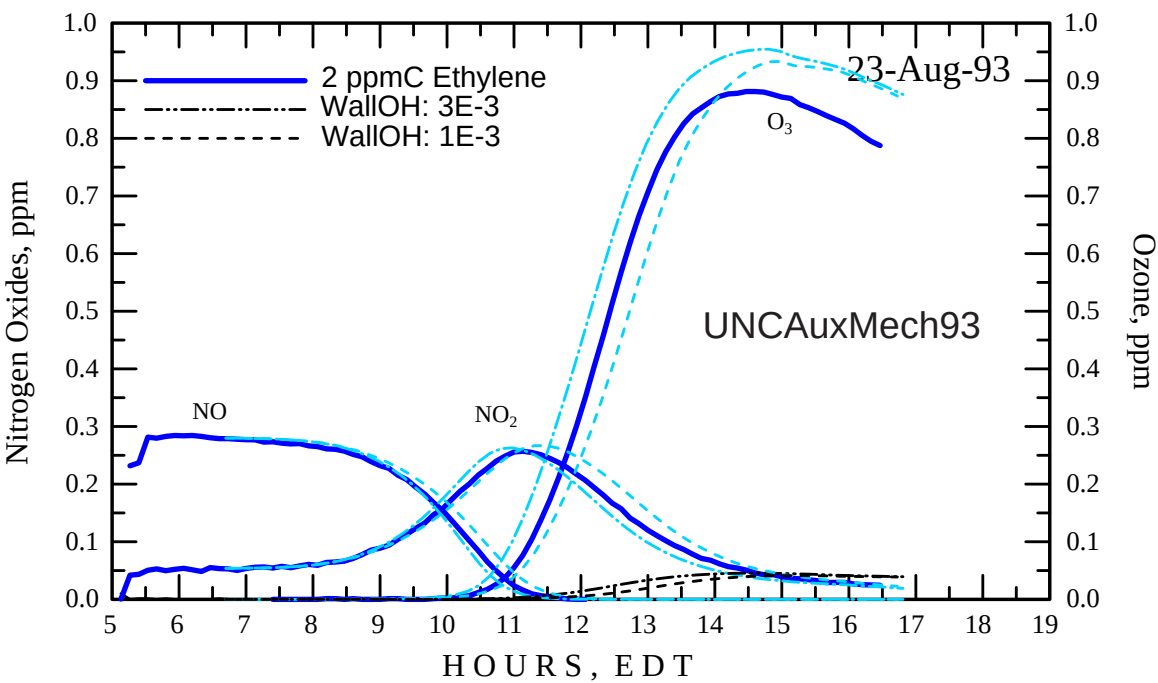
```
/*****************************************************************************
*   UNC Chamber Dependent Reactions                                          *
*   Units are molecules/cc/secs ( 6/15/93, HEJ )                             *
*****************************************************************************/

SCALARS
 WALLOH  =2.5E-3,  // scale factors, not rates
 WALLNO2 =2.0E-3;


 R[WallNO2a]=     NO2    -hv-> HONO                          @ j[NO2_to_O3P] * WALLOH ;
 R[WallNO2b]=     NO2    ----> 0.50*HONO + 0.50*WHNO3     @1.0E-19;
                                                             // 1.6E-4 /ppm-min

 R[WallNO2c]=     WHNO3  -hv-> NO2                        @ j[NO2_to_O3P] * WALLNO2;
```

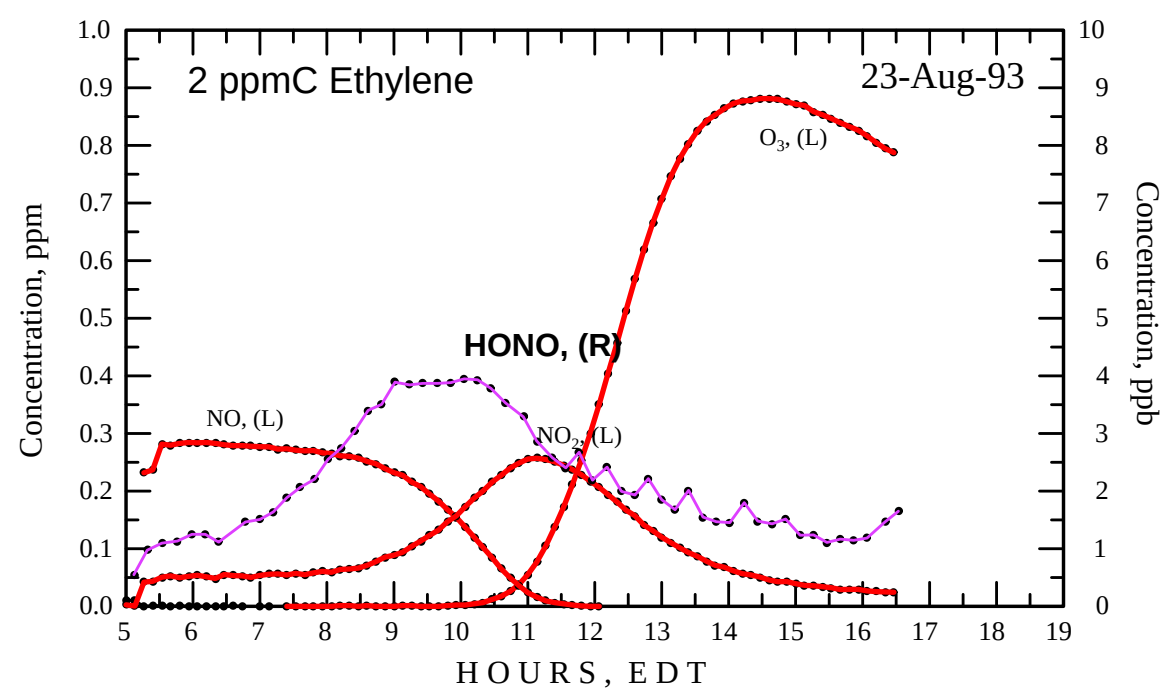
UNCAux93.react

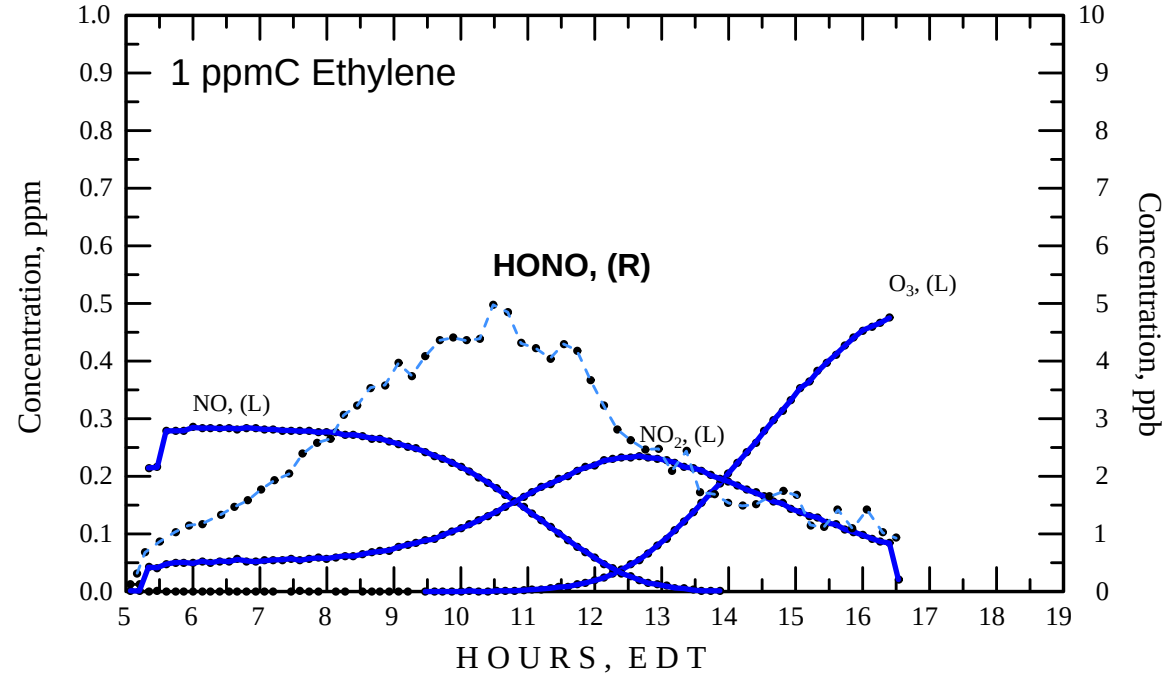
```
// Ambient Air background (all runs)
INJECT
{
  1790  PPB  CH4
   580  PPB  H2
}

// Seasonally variable Biogenic VOCs
INJECT
{
  0.140 PPM BVOC
}

// Provide initial HONO.
INJECT
{
  4.0 PPB HONO
}

// set the wall conditions
//  NO2 -hv--> HONO @ j[NO2_to_O3P] * sf_HONO_wall_src
VARIABLES
{
  sf_HONO_wall_src = 1.8E-3
}
```

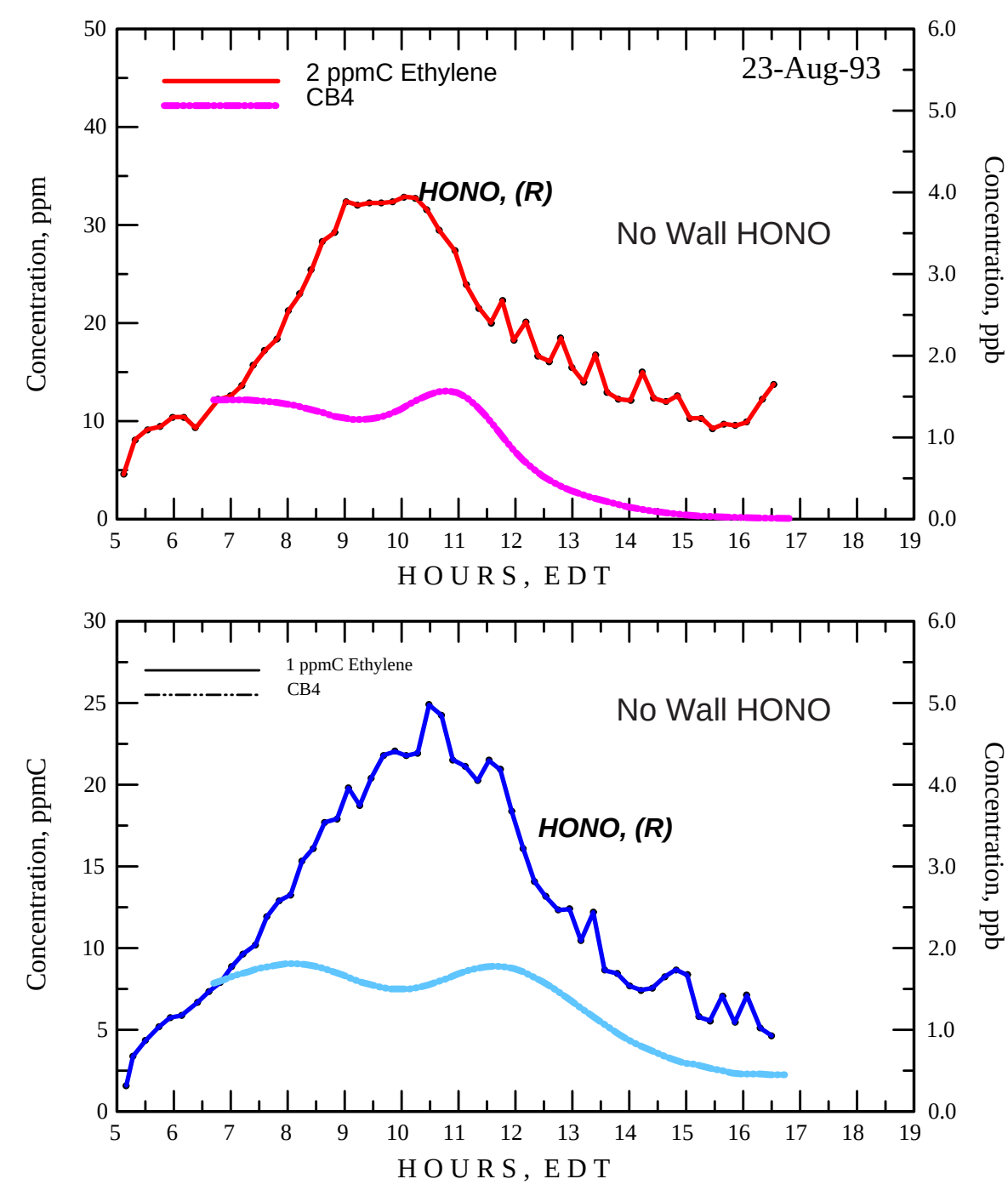

2 ppmC Ethylene
CB4
No heterogeneous wall reactions.
23-Aug-93
NO
NO2
O3
Nitrogen Oxides, ppm
Ozone, ppm
HOURS, EDT
1 ppmC Ethylene
CB4
No heterogeneous wall reactions.
NO
NO2
O3
Nitrogen Oxides, ppm
Ozone, ppm
HOURS, EDT

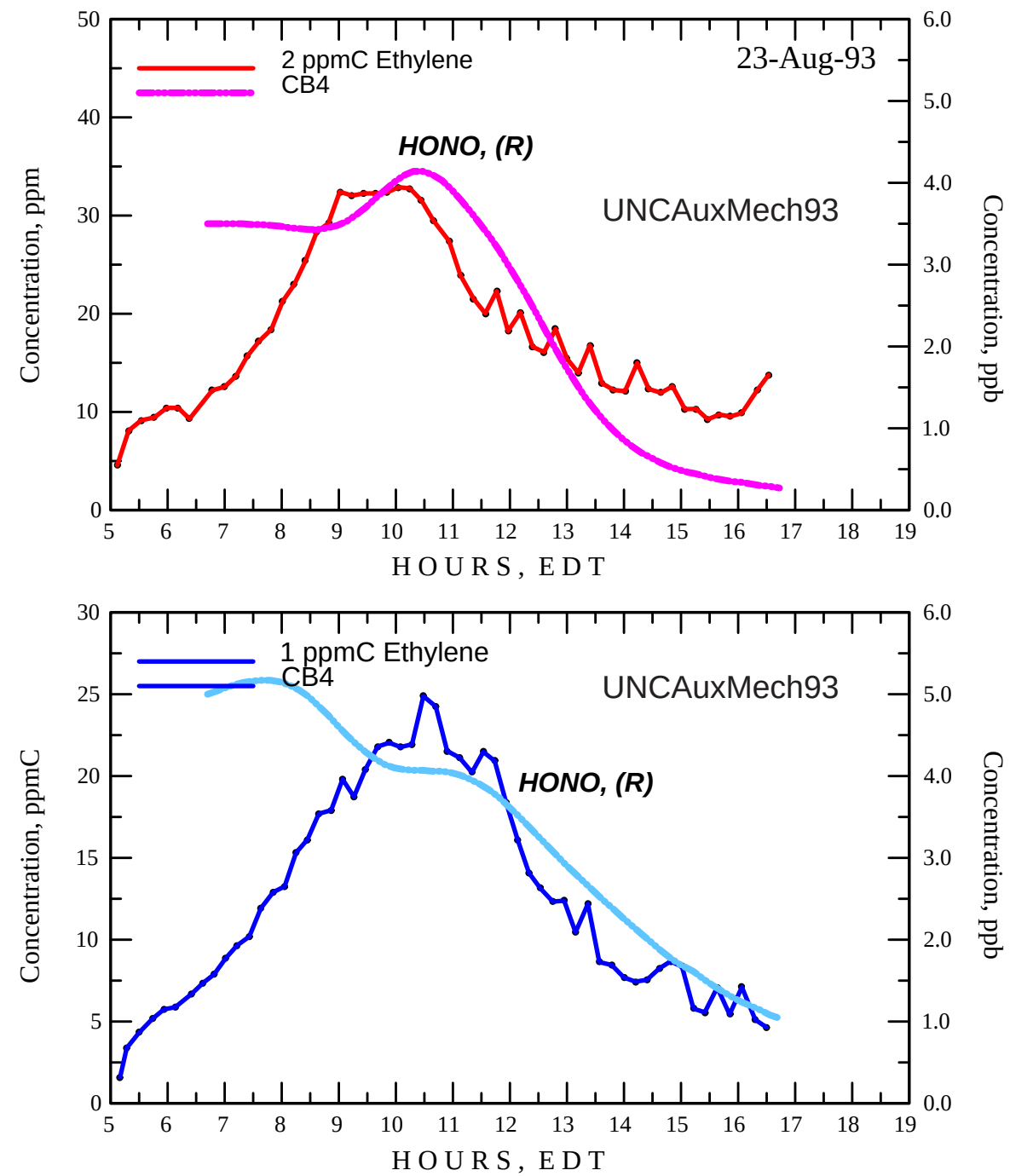

2 ppmC Ethylene
[HONO]o: 5 ppb
[HONO]o: 1 ppb
23-Aug-93
O3
UNCAuxMech93
NO
NO2
Nitrogen Oxides, ppm
Ozone, ppm
HOURS, EDT

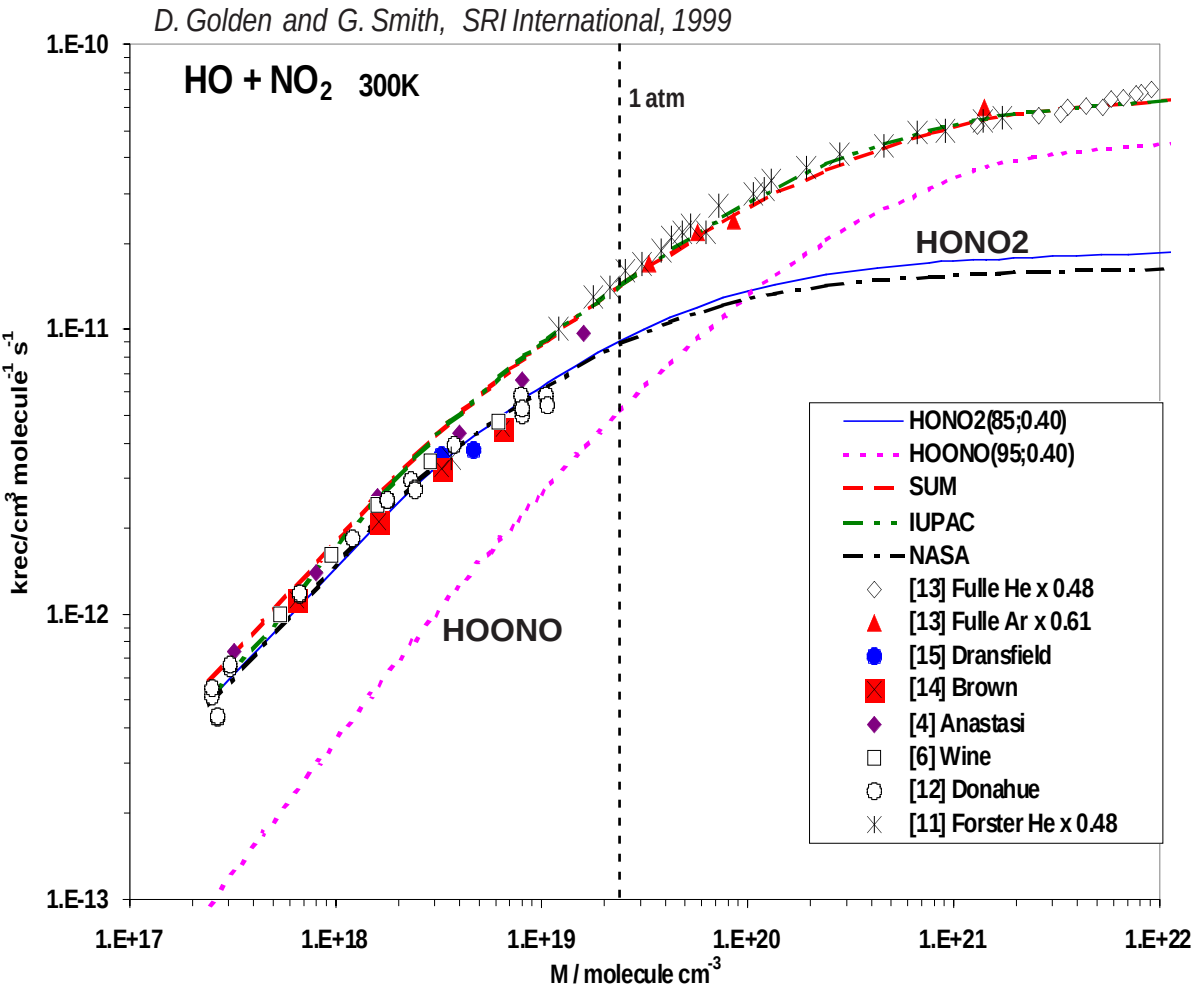

2 ppmC Ethylene
WallOH: 3E-3
WallOH: 1E-3
23-Aug-93
O3
UNCAuxMech93
NO
NO2
Nitrogen Oxides, ppm
Ozone, ppm
HOURS, EDT


2 ppmC Ethylene
23-Aug-93
O_3, (L)
HONO, (R)
NO, (L)
NO_2, (L)
Concentration, ppm
Concentration, ppb
HOURS, EDT


1 ppmC Ethylene
HONO, (R)
O_3, (L)
NO, (L)
NO_2, (L)
Concentration, ppm
Concentration, ppb
HOURS, EDT


2 ppmC Ethylene
CB4
23-Aug-93
HONO, (R)
No Wall HONO
Concentration, ppm
Concentration, ppb
HOURS, EDT
1 ppmC Ethylene
CB4
No Wall HONO
HONO, (R)
Concentration, ppmC
Concentration, ppb
HOURS, EDT

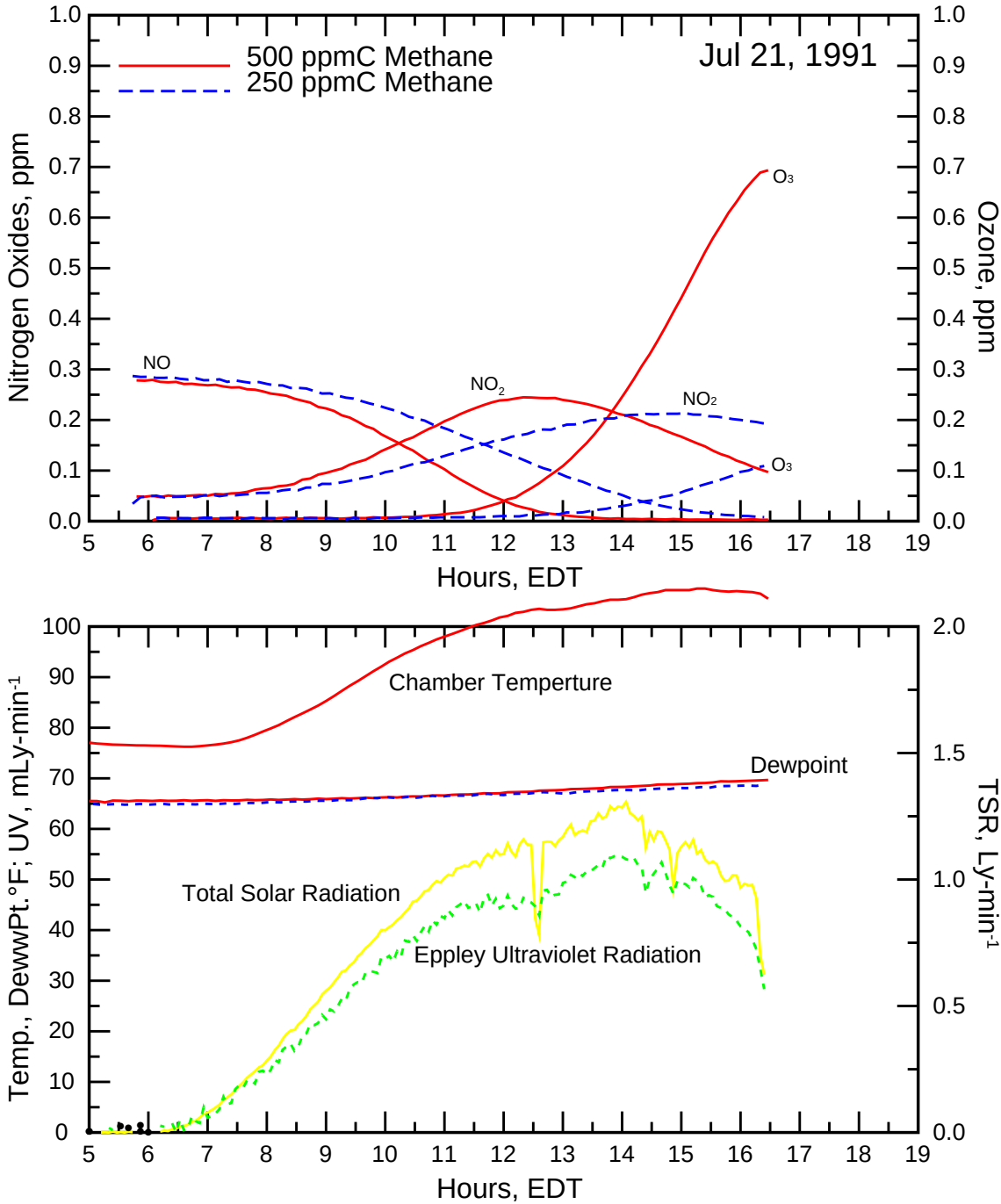

2 ppmC Ethylene
CB4
23-Aug-93
HONO, (R)
UNCAuxMech93
Concentration, ppm
Concentration, ppb
HOURS, EDT
1 ppmC Ethylene
CB4
UNCAuxMech93
HONO, (R)
Concentration, ppmC
Concentration, ppb
HOURS, EDT

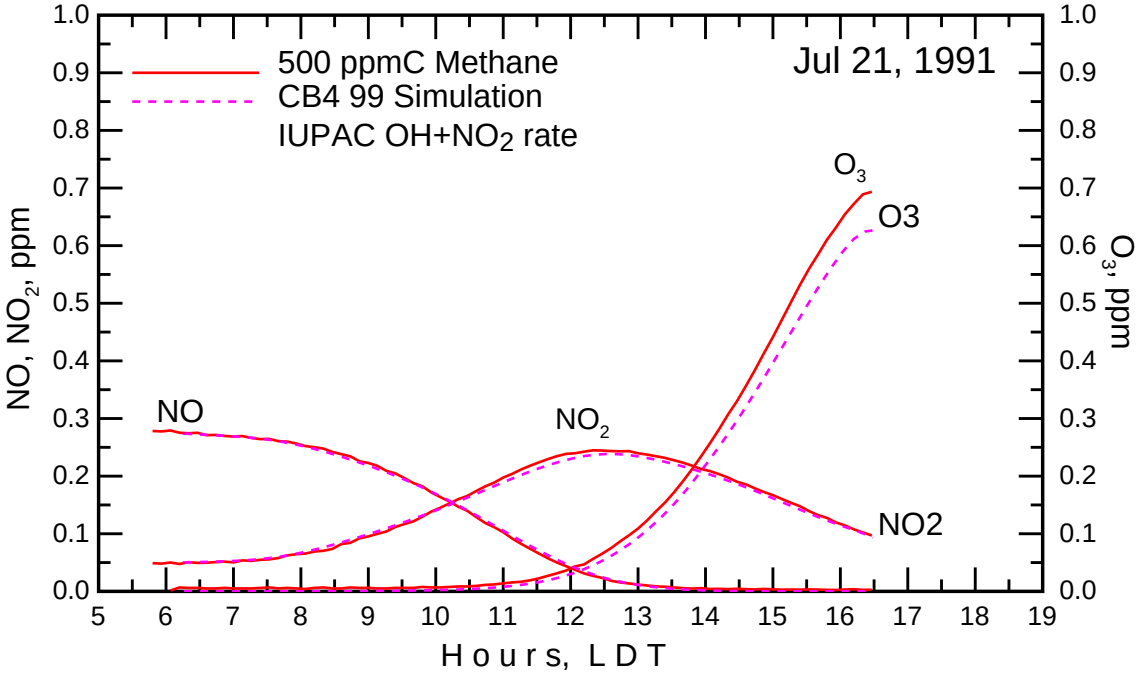

D. Golden and G. Smith, SRI International, 1999
HO + NO2 300K
1 atm
HONO2
HOONO
HONO2(85;0.40)
HOONO(95;0.40)
SUM
IUPAC
NASA
[13] Fulle He x 0.48
[13] Fulle Ar x 0.61
[15] Dransfield
[14] Brown
[4] Anastasi
[6] Wine
[12] Donahue
[11] Forster He x 0.48
krec/cm3 molecule-1 s-1
M / molecule cm-3
1.E-10
1.E-11
1.E-12
1.E-13
1.E+17
1.E+18
1.E+19
1.E+20
1.E+21
1.E+22

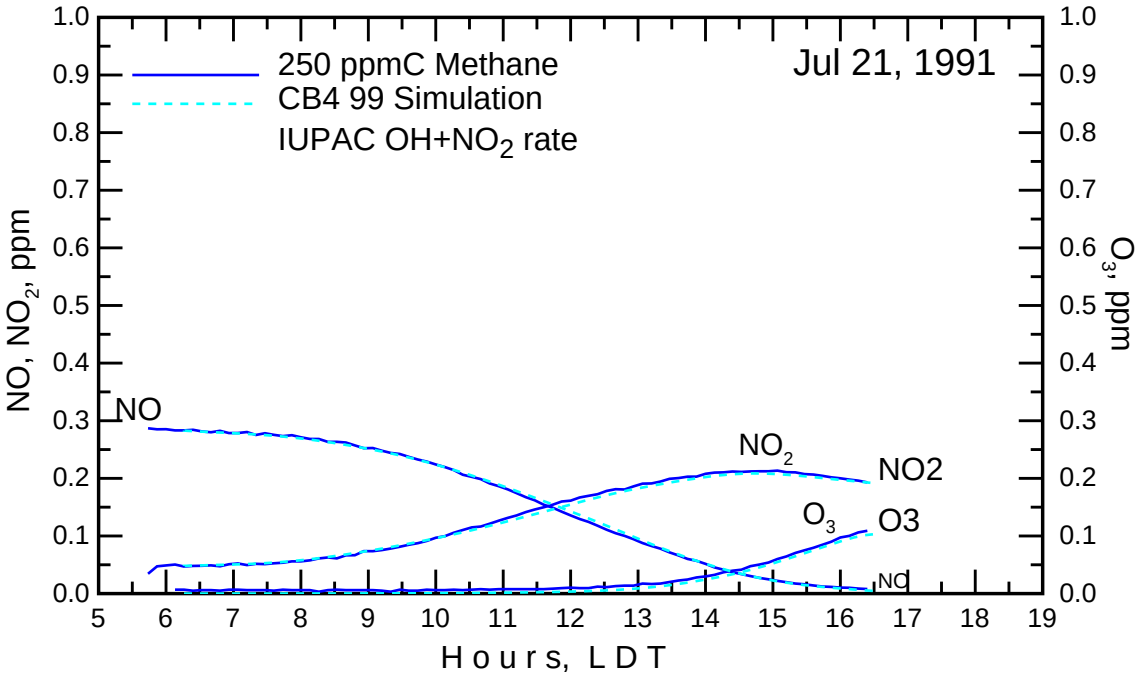
```
/*****************************************************************************
*   UNC Chamber Dependent Reactions                                          *
*   Units are molecules/cc/secs ( 3/10/99, HEJ )                             *
*****************************************************************************/



// ===========================================================================
//                                          H2O2 and O3 wall deposition
//
SCALAR
 k_depo_H2O2 = 6.7E-4, // measured  loss rate, 1/sec
 k_depo_O3   = 2.3E-6; // measured  loss rate, 1/sec (EUPHORE 3.0E-6 /sec)

 R[DepoH2O2] =       H2O2 ---->                          @ k_depo_H2O2 ;
 R[DepoO3  ] =       O3   ---->                          @ k_depo_O3   ;

// ===========================================================================
//                                      HNO3 wall deposition and emission
//
// EUPHORE first order dry rate was 8.2E-5 /sec
 R[DepoHNO3 ] =     HNO3  ---->     WHNO3                    @   1.5E-4 ;


// ===========================================================================
//                                    N2O5 wall deposition and hydrolysis
//
//    R[DepoN2O5a] is Tuazon 83 "dry" Rate;
//    R[DepoN2O5b] is 1.9E-4 ppm/min at 300K
 R[DepoN2O5a] =            N2O5  ----> 2.0*WHNO3   @4.2E-5;
 R[DepoN2O5b] =     N2O5 + WH2O  ----> 2.0*WHNO3   @1.67E-22*EXP(2000.0/TK);


/* -------------- ForUsewithIUPAC OH + NO2 rate   ------------------ */

// ===========================================================================
//                                                NOx wall water reactions
//
 R[WH2ONO   ] =     NO  + WH2O  ---->  WHNO3               @  6.77E-24 ;
 R[WH2ONO2  ] =     NO2 + WH2O  ---->  WHNO3               @  6.77E-24 ;


// ===========================================================================
//                                                  WNO2 acid reactions
//
 R[WHNO3NO ]  =     NO  + WHNO3 ----> 1.5*HONO + 0.5*NO2     @ 6.09E-17 ;
 R[WHNO3NO2]  =     NO2 + WHNO3 ----> 1.5*HONO + 0.5*NO2     @ 3.38E-18 ;


// ===========================================================================
//                                      light dependent HONO production
//
 SCALARS
  sf_HONO_wall_src = 1.0E-3;  // "scale factor", not rate

 R[WNO2_HONO]  =           NO2   -hv-> HONO          @ j[NO2_to_O3P] *
                                                       sf_HONO_wall_src ;
```

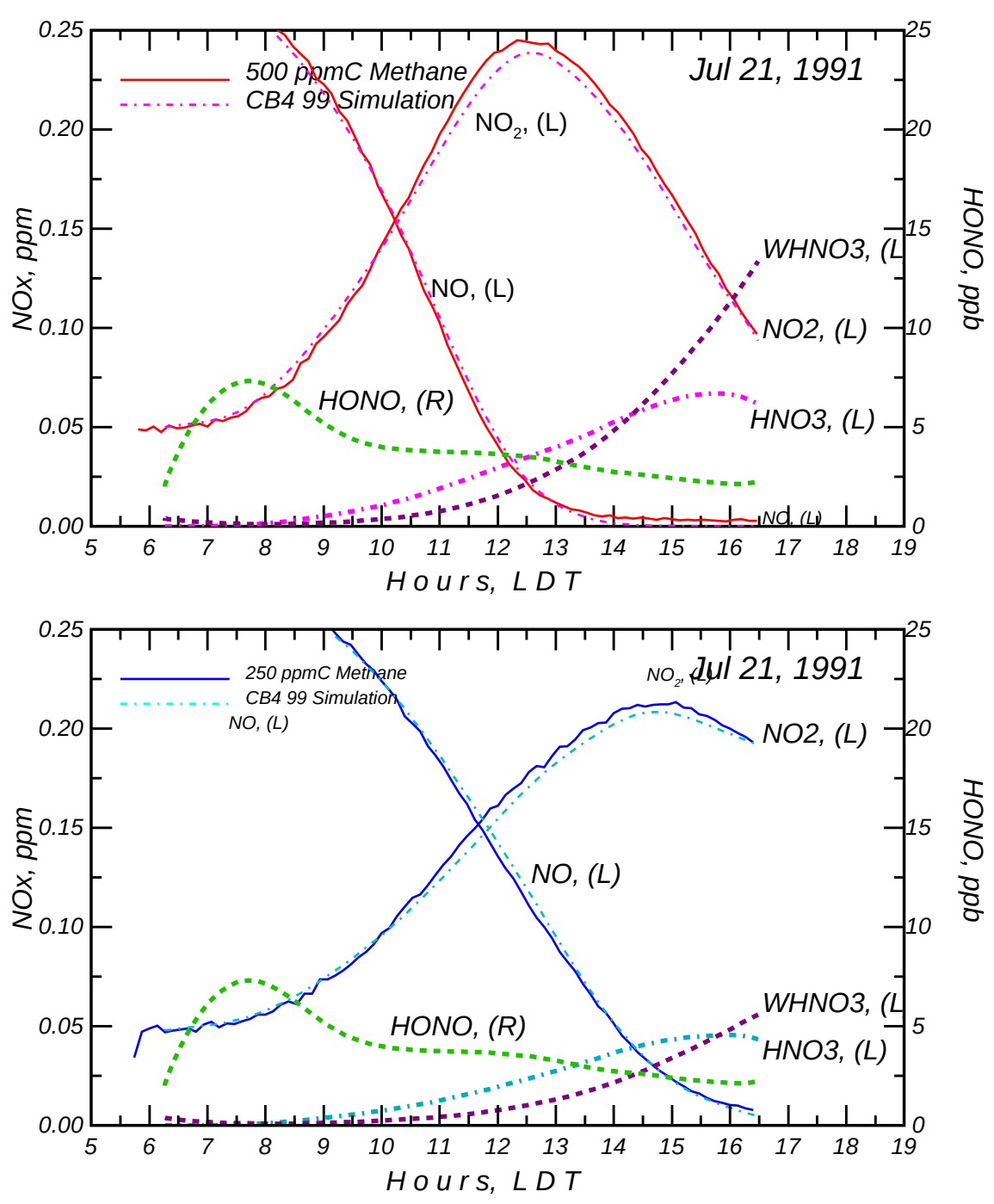
UNCAux99_03.react

```
// Ambient Air background (all runs)
INJECT
{
  1790  PPB  CH4
   580  PPB  H2
}

// Seasonally variable Biogenic VOCs
INJECT
{
  0.140 PPM  BVOC
}

// Initialize wall related species
INJECT
{
  0.5 PPB  HONO
  4.0 PPB  WHNO3
}

// set the wall conditions
//  NO2 -hv--> HONO @ j[NO2_to_O3P] * sf_HONO_wall_src
VARIABLES
{
  sf_HONO_wall_src = 0.8E-3
}
```


500 ppmC Methane
250 ppmC Methane
Jul 21, 1991
Nitrogen Oxides, ppm
Ozone, ppm
NO
NO2
NO2
O3
O3
Hours, EDT
Chamber Temperture
Dewpoint
Total Solar Radiation
Eppley Ultraviolet Radiation
Temp., DewwPt. °F; UV, mLy-min-1
TSR, Ly-min-1
Hours, EDT


500 ppmC Methane
CB4 99 Simulation
IUPAC OH+NO2 rate
Jul 21, 1991
O3
NO
NO2
NO2
O3, ppm
Hours, LDT

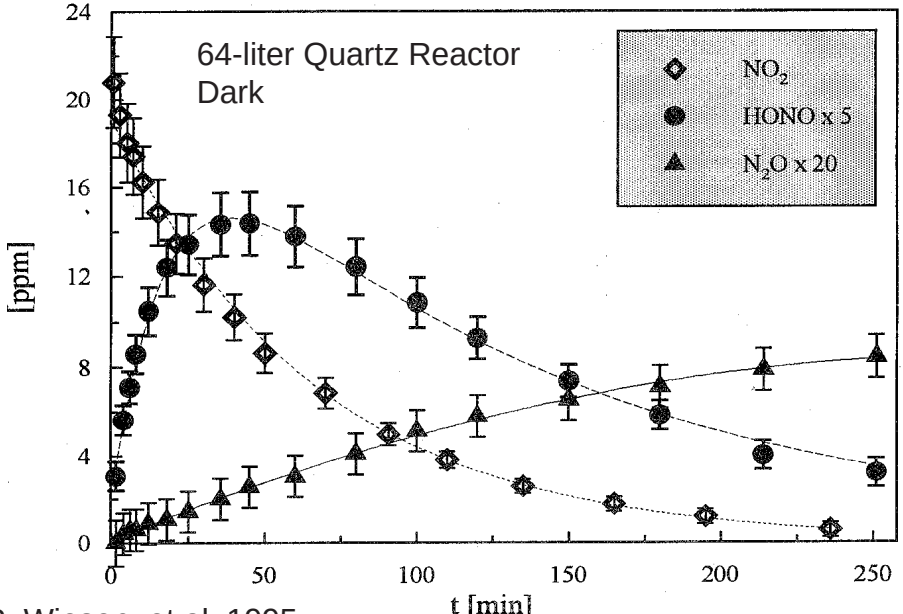

250 ppmC Methane
CB4 99 Simulation
IUPAC OH+NO2 rate
Jul 21, 1991
NO
NO2
NO2
O3
O3
NO
NO, NO2, ppm
O3, ppm
Hours, LDT


500 ppmC Methane
CB4 99 Simulation
Jul 21, 1991
NO2, (L)
NO, (L)
WHNO3, (L
NO2, (L)
HONO, (R)
HNO3, (L)
ND, (L)
NOx, ppm
HONO, ppb
Hours, LDT
250 ppmC Methane
CB4 99 Simulation
NO, (L)
NO2, (L)
NO, (L)
WHNO3, (L
HONO, (R)
HNO3, (L)
NOx, ppm
HONO, ppb
Hours, LDT

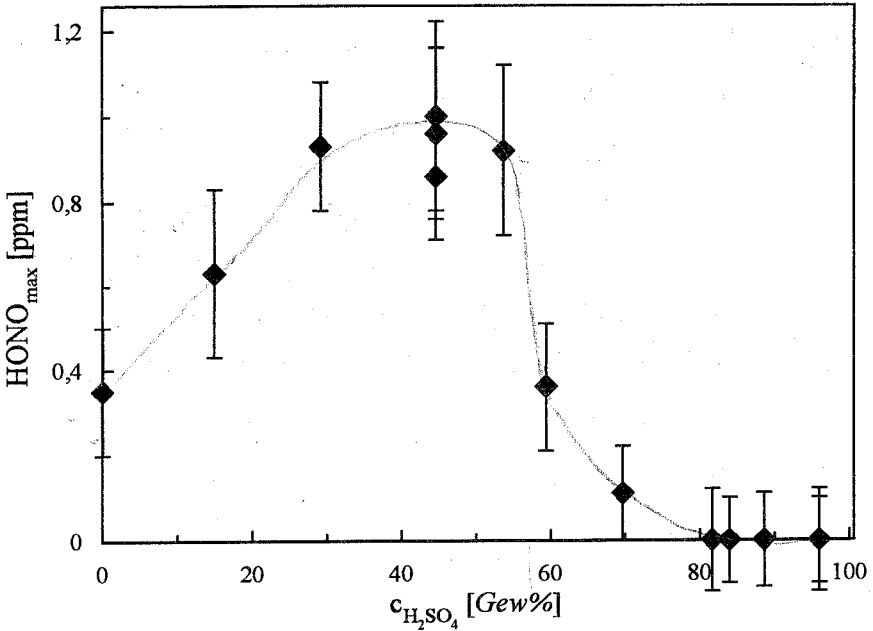
CB4_99 Mechanism with UNCAuxMech99_06 JL2191
IUPAC OH + NO2 Rate

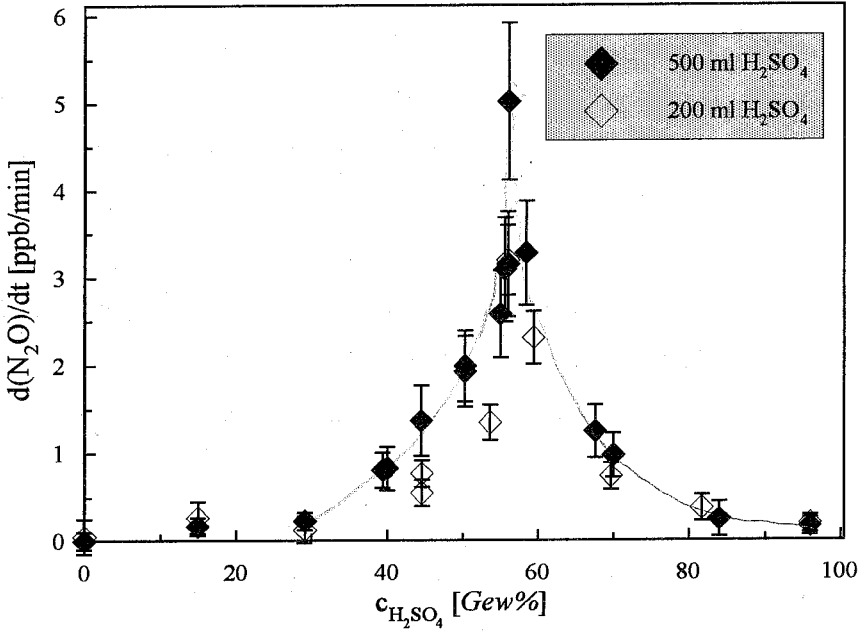
Initial CH4 500 ppm 250 ppm CH4

Reaction	ppb	ppb	in 613 MINS
Ib7	2.96	0.14	N2O5+H2O---->2.0*HNO3
Ic4	16.17	3.02	O1D+H2O---->2.0*OH
Id3	41.22	67.75	OH+NO---->HONO
Id4	137.82	170.32	HONO---->OH+NO
If1	216.69	154.08	OH+NO2---->HNO3
Ig2	417.51	158.39	OH+CH4---->XO2+HCHO+HO2
C1_4	108.67	35.16	OH+HCHO---->HO2+CO
BVOC	37.36	29.48	OH+BVOC---->0.667*(XO2+HCHO+HO2)+...
XO_1	443.78	182.71	XO2+NO---->NO2
Ie1	648.00	271.48	HO2+NO---->OH+NO2
C1_1	54.31	26.11	HCHO-hv->2.0*HO2+CO
DepoH2O2	2.67	0.00	H2O2---->
DepoO3	11.57	2.24	O3- ->
DepoN2O5a	0.15	0.01	N2O5---->2.0*WHNO3
DepoN2O5b	11.77	0.53	N2O5+WH2O---->2.0*WHNO3
DepoHNO3	154.46	106.04	HNO3---->WHNO3
WH2OpNO	2.19	2.50	NO+WH2O---->WHNO3
WH2OpNO2	1.51	1.26	NO2+WH2O---->WHNO3
WHNO3pNO	31.92	48.53	NO+WHNO3---->1.5*HONO+0.5*NO2
WHNO3pNO2	12.75	6.64	NO2+WHNO3---->1.5*HONO+0.5*NO2
WNO2hvHONO	32.67	25.77	NO2-hv->HONO



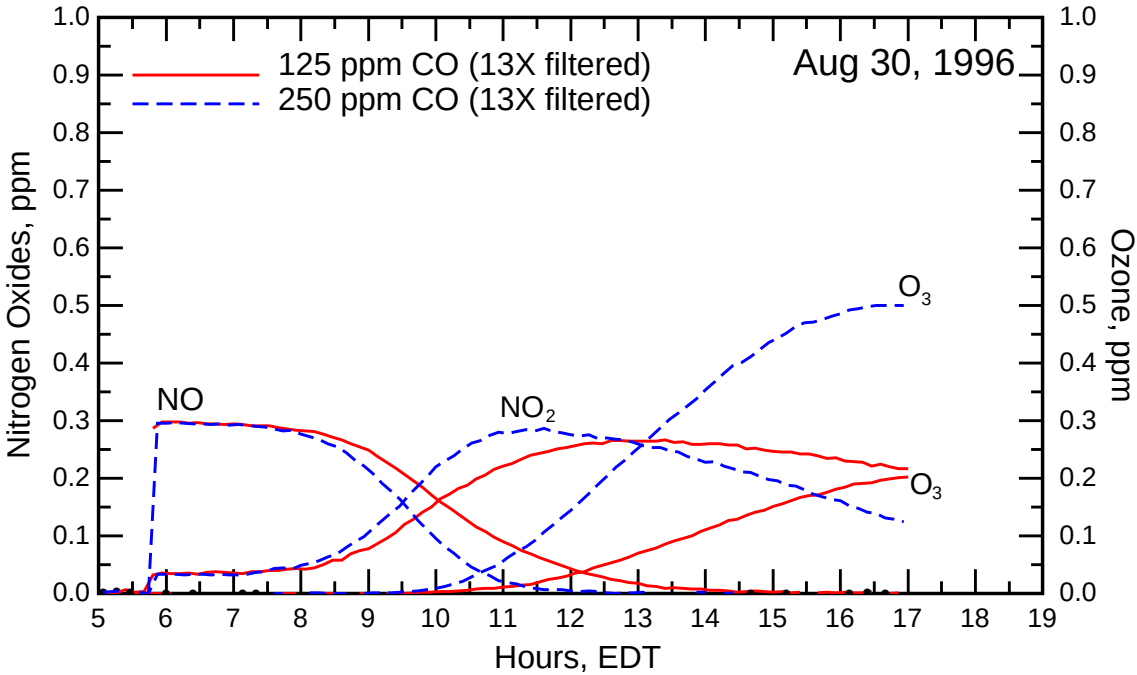
P. Wiesen, et al, 1995

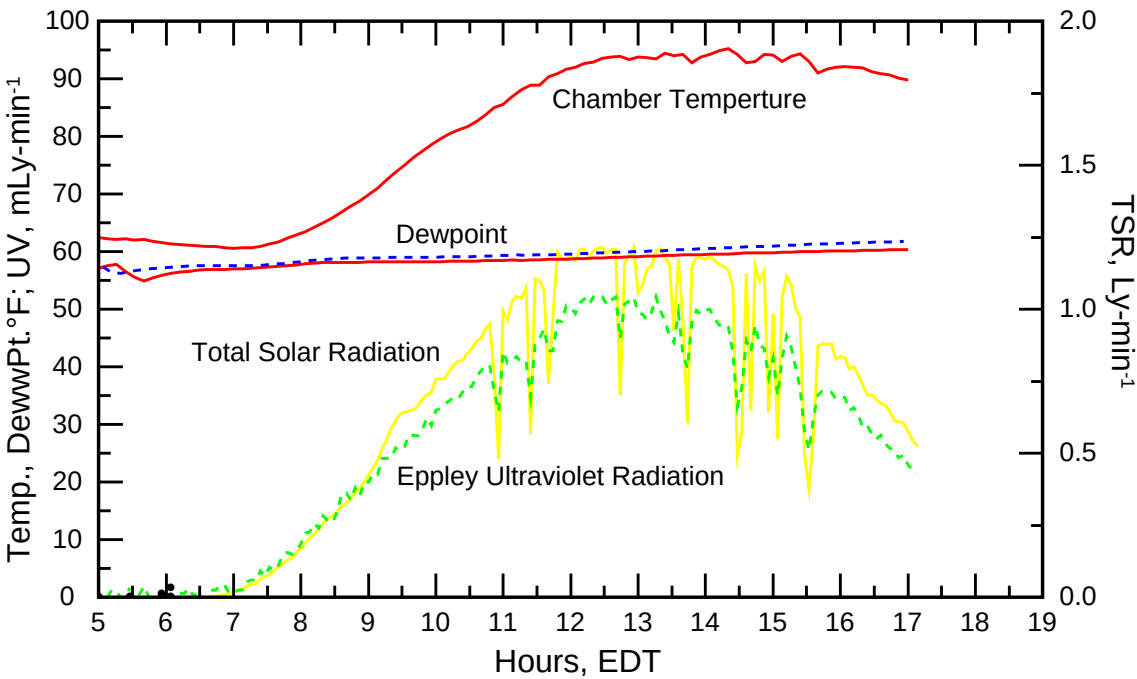

1,2
0,8
0,4
0
HONO$_{max}$ [ppm]
0
20
40
60
80
100
$c_{H_2SO_4}$ [*Gew%*]

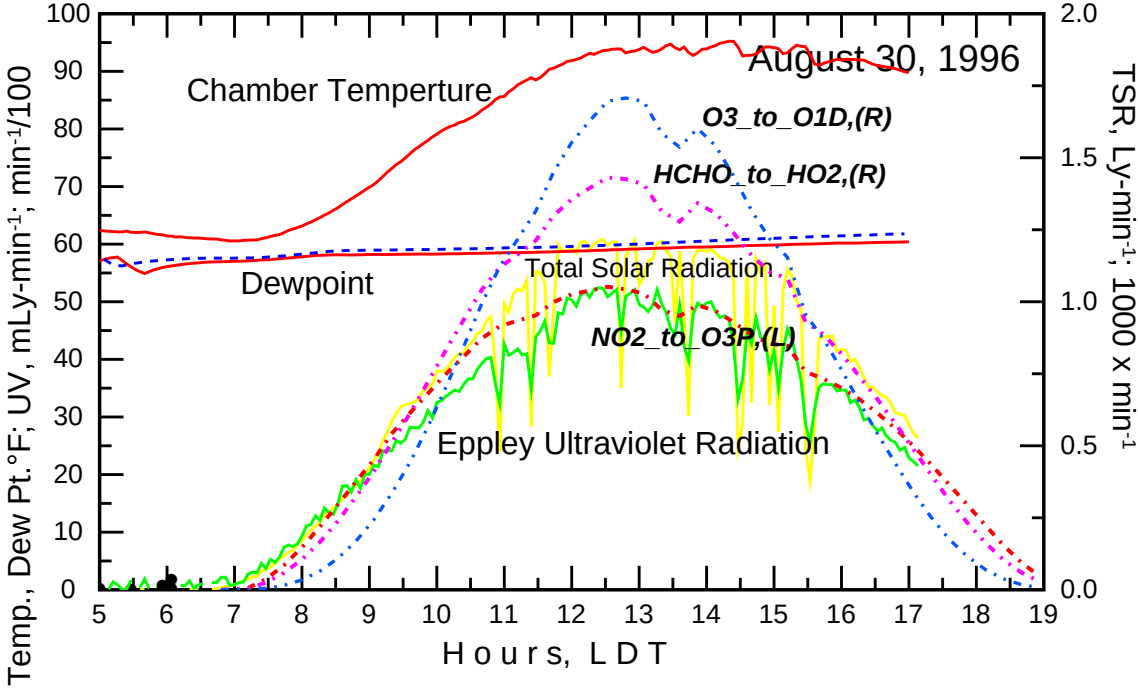

500 ml H_2SO_4
200 ml H_2SO_4
$d(N_2O)/dt$ [ppb/min]
$c_{H_2SO_4}$ [*Gew%*]
0
1
2
3
4
5
6
0
20
40
60
80
100

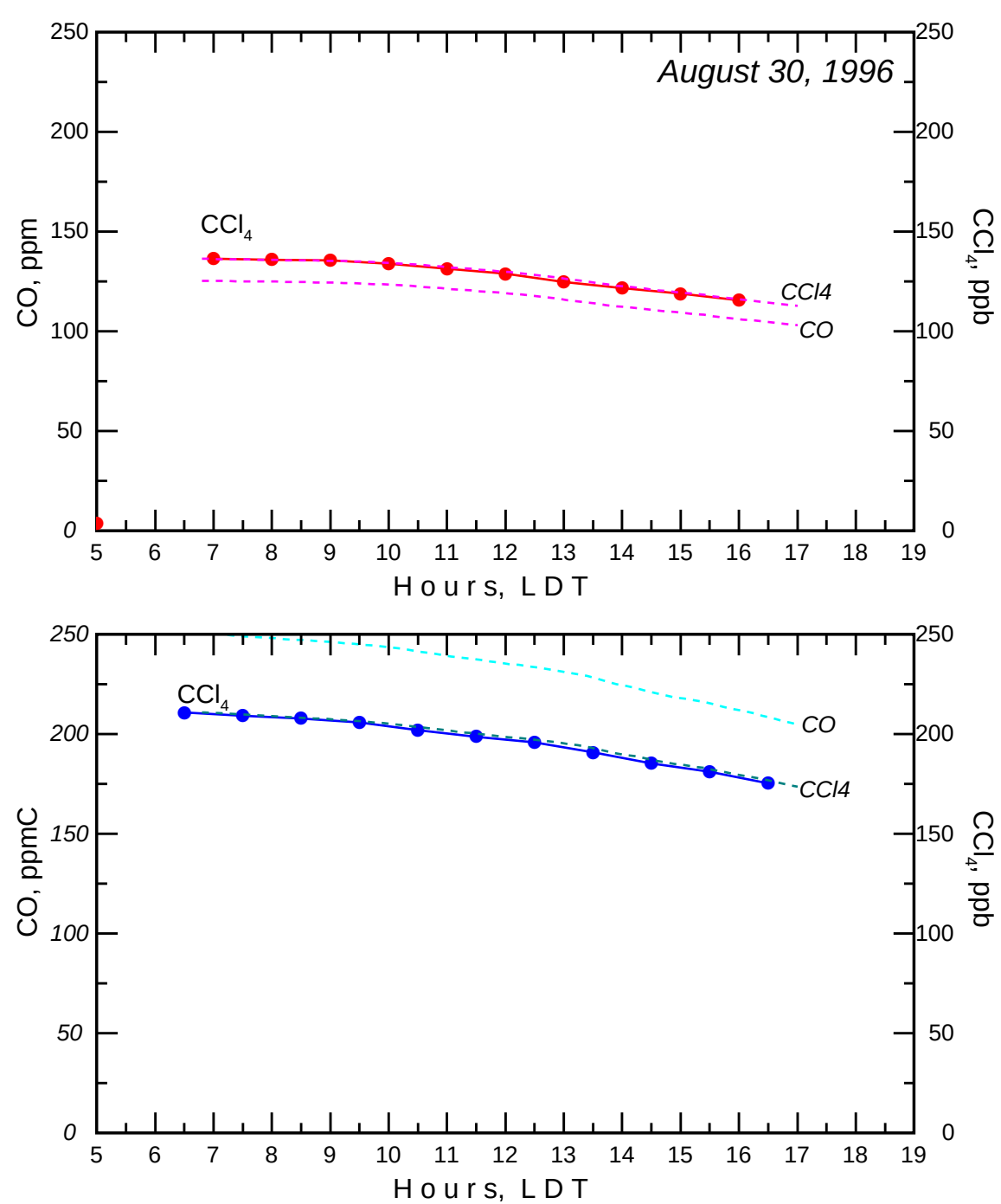
UNCAuxMech99_09.rxn

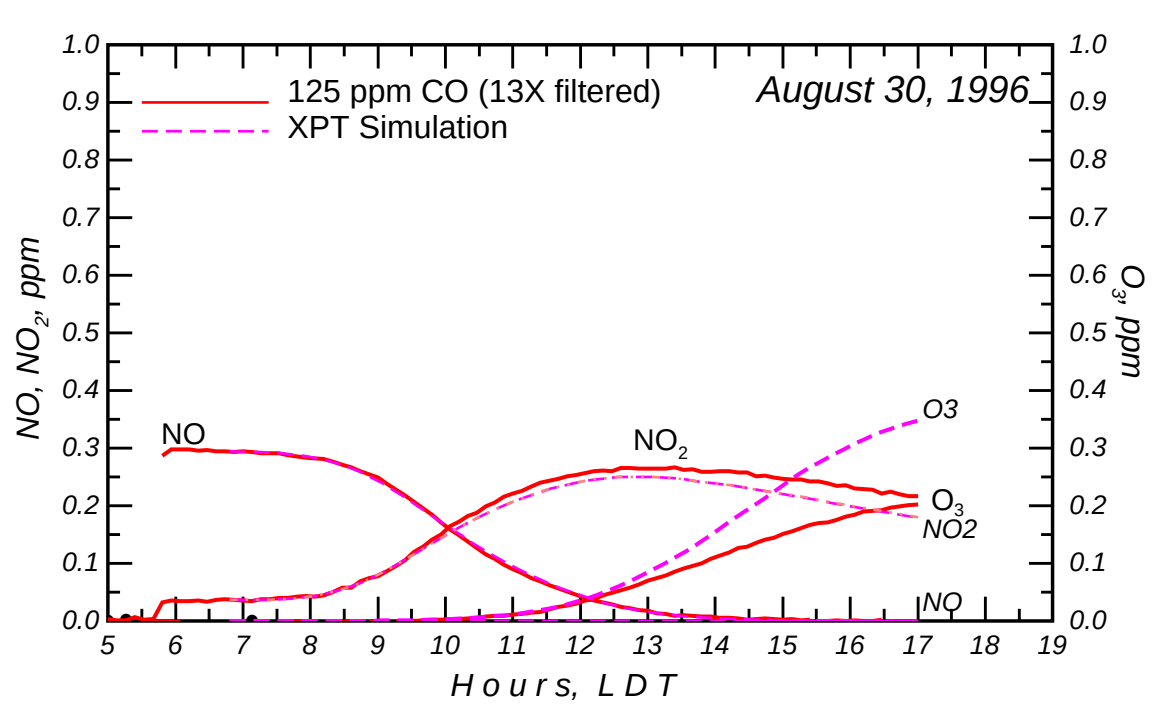
```
// ================================================================================
//                                                  H2O2 and O3 wall deposition
//
SCALAR
 k_depo_H2O2 = 6.7E-4, // measured  loss rate, 1/sec
 k_depo_O3   = 2.3E-6; // measured  loss rate, 1/sec (EUPHORE 3.0E-6 /sec)

 R[DepoH2O2] =       H2O2 ---->                @ k_depo_H2O2 ;
 R[DepoO3  ] =       O3   ---->                @ k_depo_O3   ;


// ================================================================================
//                                        N2O5 wall deposition and hydrolysis
// rate is based on Julich Chamber; here 5E-5 /s * WH2O

 R[DepoN2O5] =  N2O5 + WH2O  ----> 2.0 * WHNO3  @ 3.05E-21 ;

// ================================================================================
//                                          HNO3 wall deposition and emission
// EUPHORE first order dry rate was 8.2E-5 /sec

 R[DepoHNO3f] =    HNO3 + WH2O   ----> WHNO3   @ 2.6E-18  ;
 R[DepoHNO3r] =           WHNO3  ----> HNO3    @ 6.6E-7   ;
 R[DepoHNO3l] =           WHNO3  ---->         @ 3.0E-7   ;


// ================================================================================
//                                          HONO wall deposition and emission
//
 R[DepoHONOf] =    HONO  + WH2O  ----> WHONO   @ 8.9E-21 ;
 R[DepoHONOr] =           WHONO  ----> HONO    @ 6.6E-4  ;


// ================================================================================
//                                                  NO2 wall water reactions
//
 R[DepoNO2f ] =    NO2     +  H2O ---->  WNO2 @  2.5E-23 ;
 R[DepoNO2r ] =              WNO2 ---->  NO2  @  6.6E-7  ;

 R[WNO2pWNO2] =    WNO2    + WNO2 ---->  WN2O4         @ 1.0E-10 ;
 R[WH2OpWN2O4]=    WN2O4   + WH2O ---->  WHONO + WHNO3 @ 1.0E-14 ;


// ================================================================================
//                                                    WNO2 acid reactions
//
 R[WNO2pWHNO3 ]  =  WNO2    +  WHNO3       ----> 'W(NO2)NO3' + WH2O   @ 1.0E-12 ;
 R[WNO2pWHNO2P]  =  WNO2    + 'W(NO2)NO3'  ---->  WHONO      + WHNO3  @ 1.0E-9  ;
 R[WHNO2PpWHNO2P]= 'W(NO2)NO3'+'W(NO2)NO3' ---->  2.0*(WHONO + WHNO3) @ 1.0E-14 ;


// ================================================================================
//                                                    WHONO acid reactions
//
 R[WHONOpWHNO3a]=  WHONO   +  WHNO3   +  WHNO3  ----> N2O + WHNO3     @ 1.0E-26 ;
```

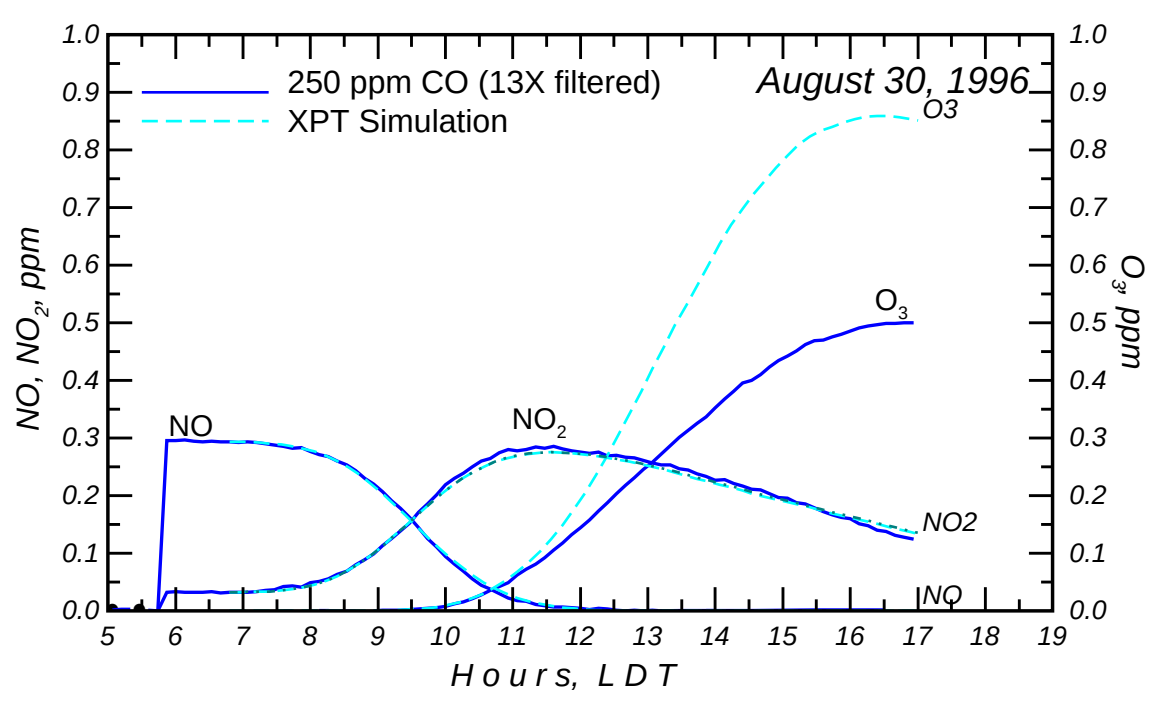

125 ppm CO (13X filtered)
250 ppm CO (13X filtered)
Aug 30, 1996
Nitrogen Oxides, ppm
Ozone, ppm
NO
NO2
O3
O3
Hours, EDT

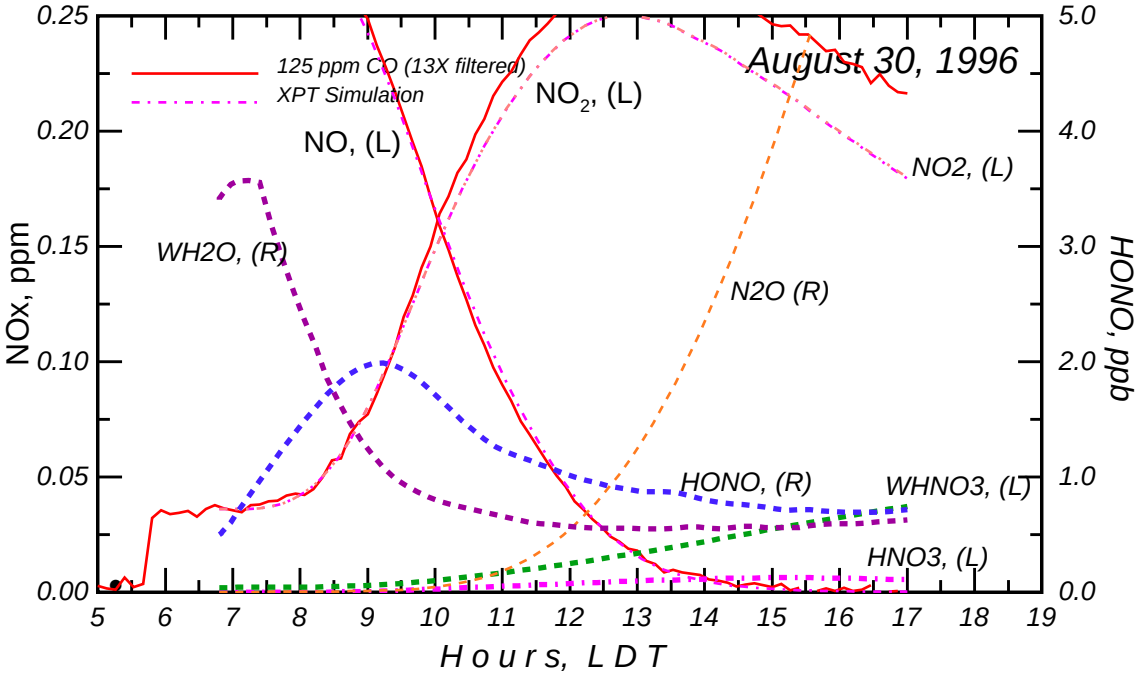

Chamber Temperture
Dewpoint
Total Solar Radiation
Eppley Ultraviolet Radiation
Temp., DewwPt. °F; UV, mLy-min-1
TSR, Ly-min-1
Hours, EDT

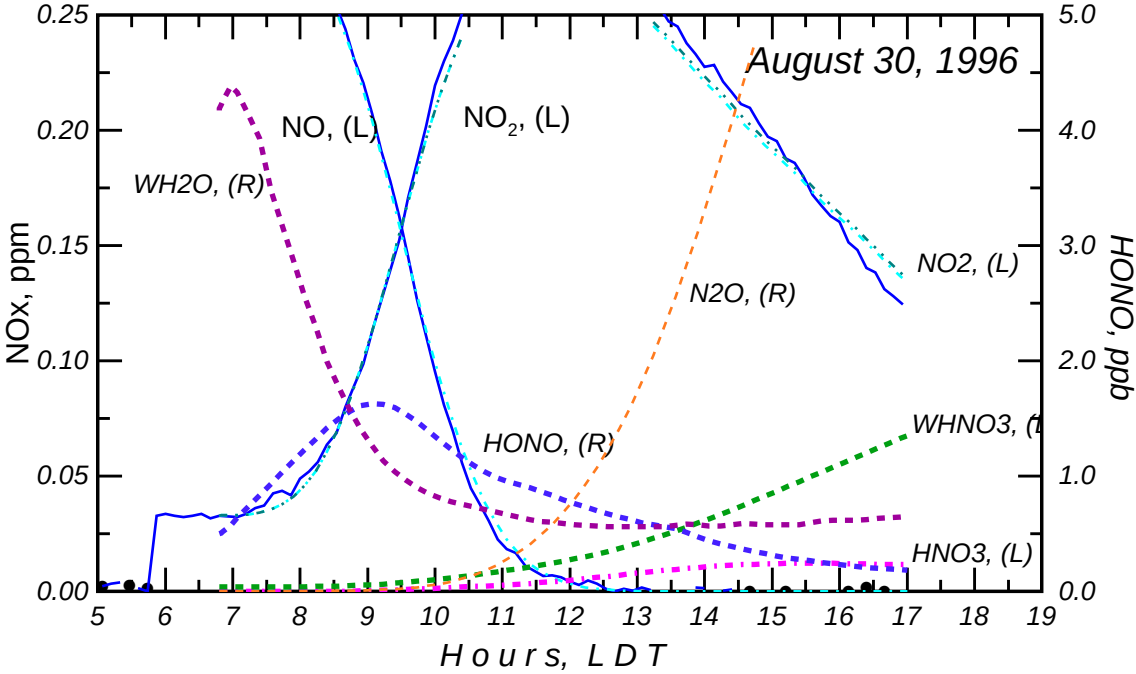

August 30, 1996
Chamber Temperture
O3_to_O1D,(R)
HCHO_to_HO2,(R)
Dewpoint
Total Solar Radiation
NO2_to_O3P,(L)
Eppley Ultraviolet Radiation
Temp., Dew Pt.°F; UV, mLy-min-1; min-1/100
TSR, Ly-min-1; 1000 x min-1
Hours, LDT
100
90
80
70
60
50
40
30
20
10
0
2.0
1.5
1.0
0.5
0.0
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

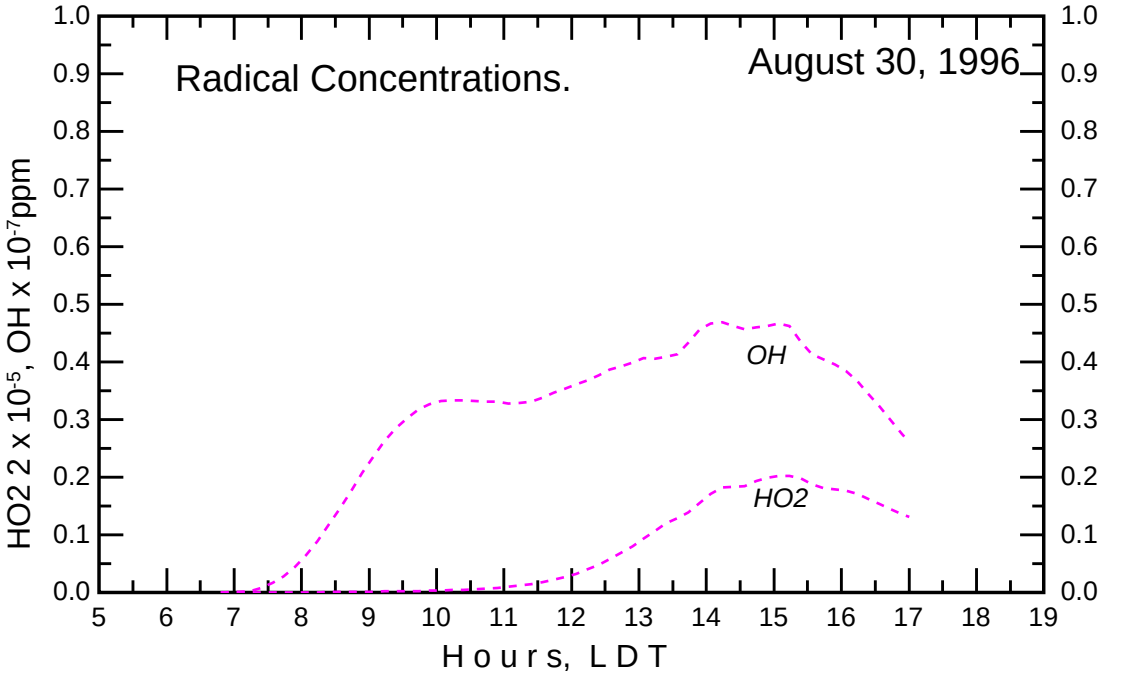

August 30, 1996
CCl4
CO
CCl4
CO, ppm
CCl4, ppb
Hours, LDT
CO
CCl4
CO, ppmC
CCl4, ppb
Hours, LDT

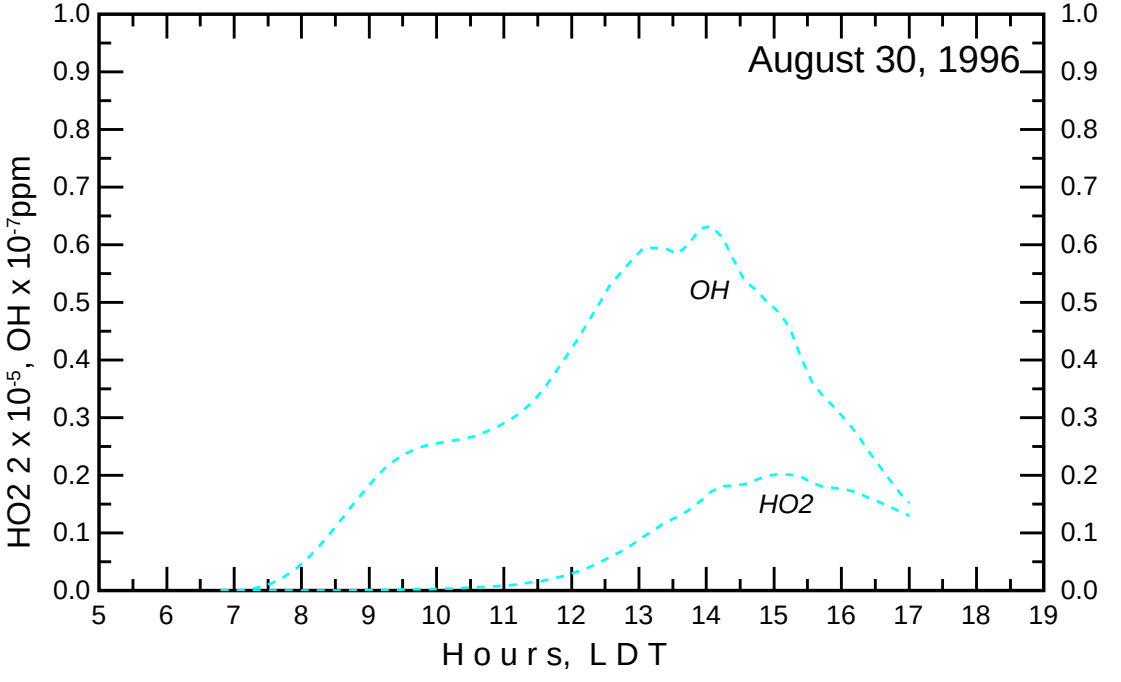

125 ppm CO (13X filtered)
XPT Simulation
August 30, 1996
NO
NO2
O3
NO
NO2
O3
NO, NO2, ppm
O3, ppm
Hours, LDT

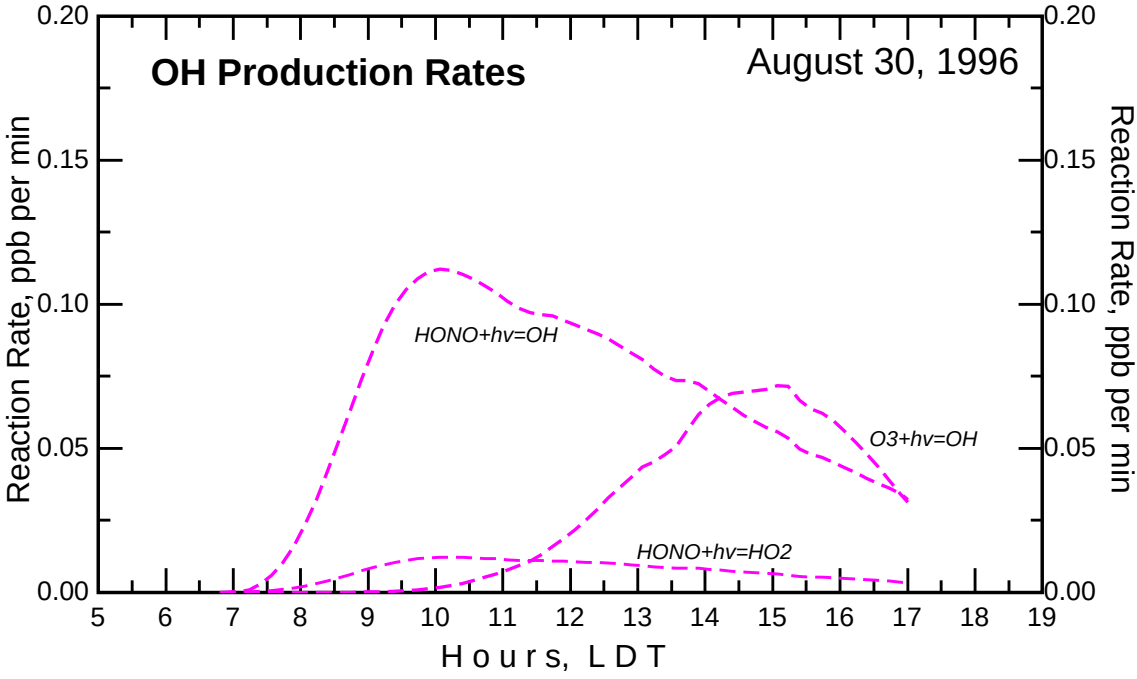

250 ppm CO (13X filtered)
XPT Simulation
August 30, 1996
O3
O3
NO
NO2
NO2
NO
NO, NO2, ppm
O3, ppm
Hours, LDT

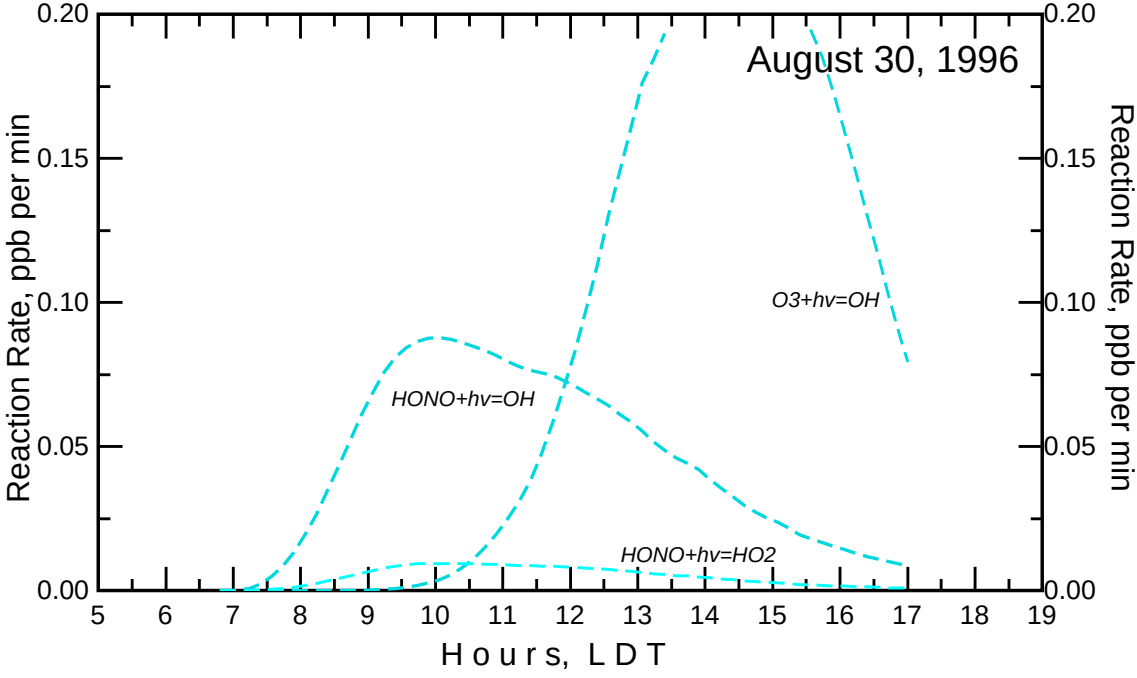

125 ppm CO (13X filtered)
XPT Simulation
August 30, 1996
NO, (L)
NO2, (L)
WH2O, (R)
N2O (R)
HONO, (R)
WHNO3, (L)
HNO3, (L)
NOx, ppm
HONO, ppb
Hours, LDT

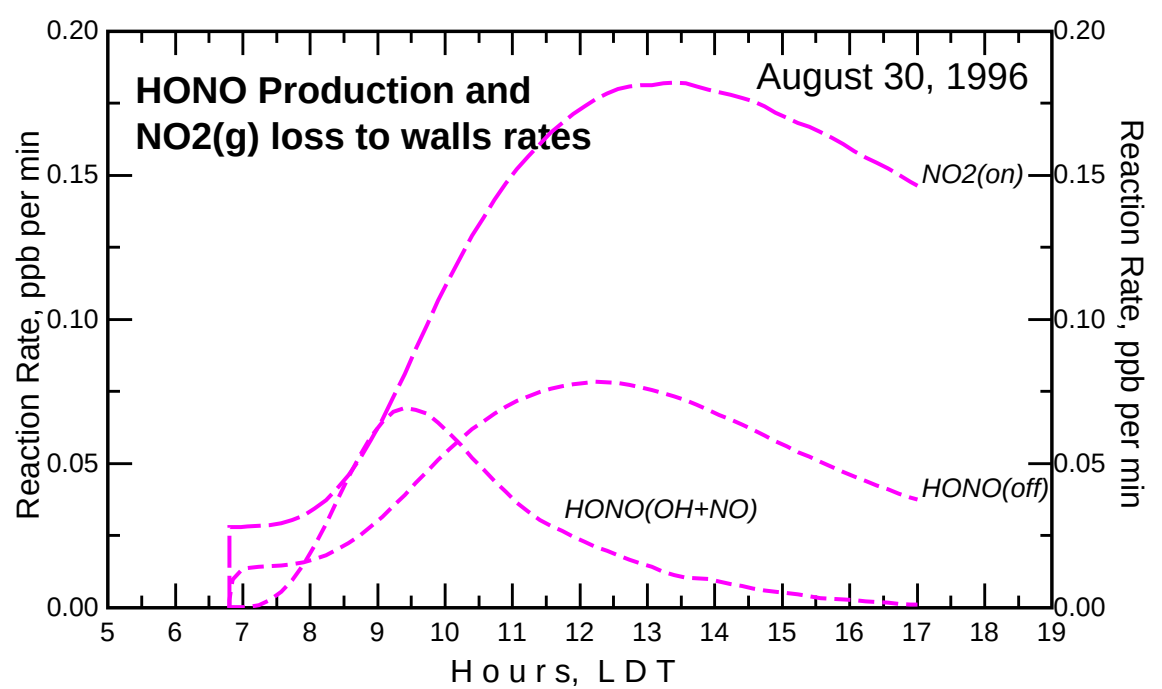

August 30, 1996
NO, (L)
NO2, (L)
WH2O, (R)
N2O, (R)
HONO, (R)
WHNO3, (L)
HNO3, (L)
NOx, ppm
HONO, ppb
Hours, LDT

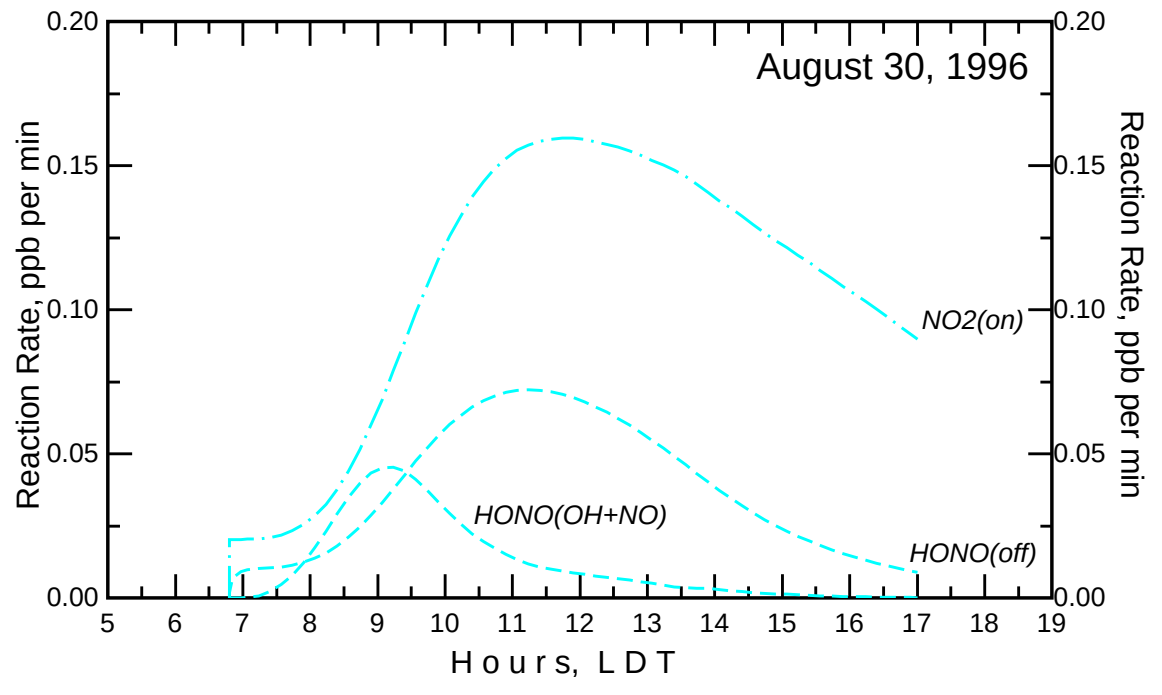

Radical Concentrations.
August 30, 1996
OH
HO2
HO2 2 x 10-5, OH x 10-7ppm
Hours, LDT
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

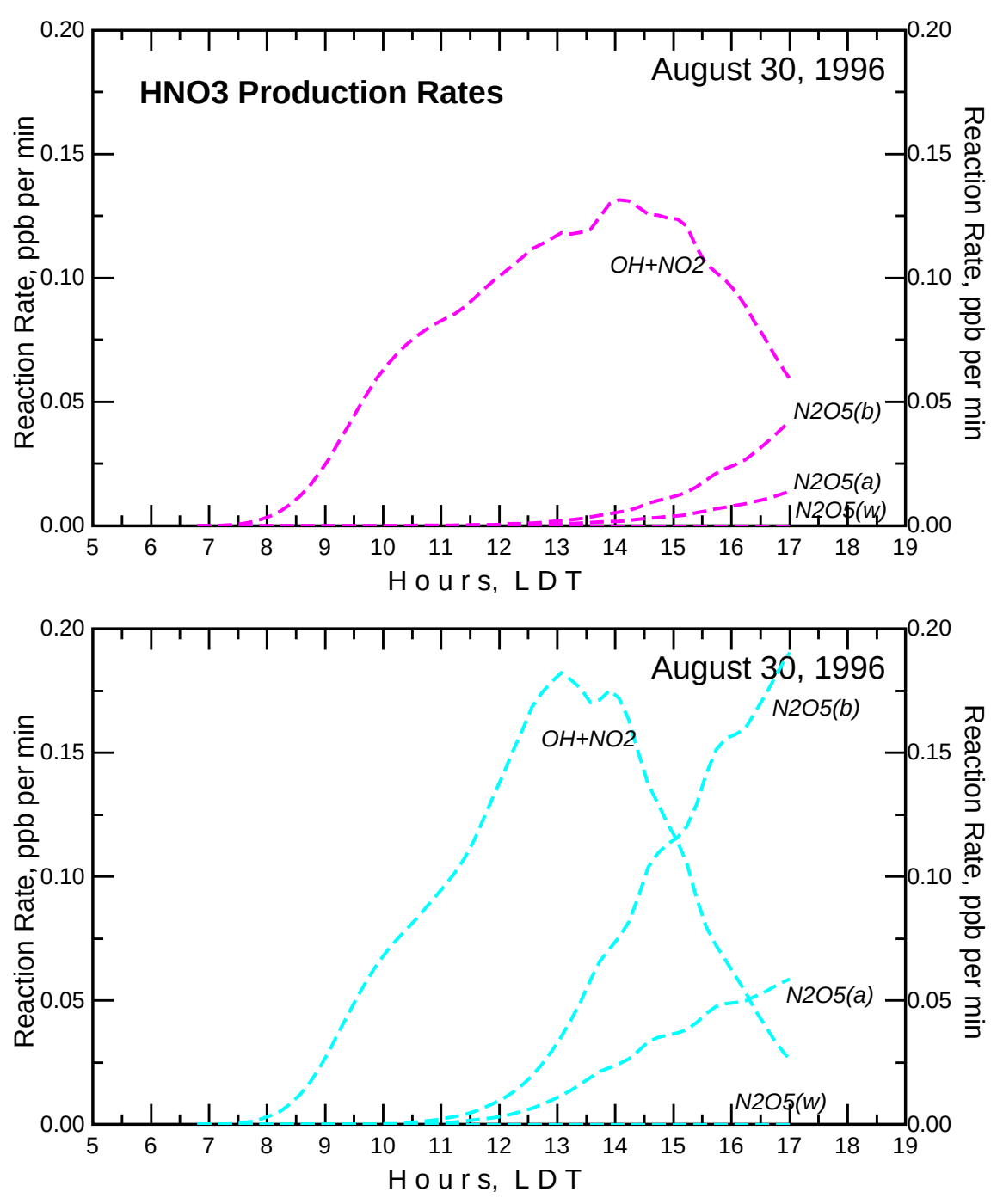

August 30, 1996
OH
HO2
HO2 2 x 10-5, OH x 10-7ppm
Hours, LDT
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

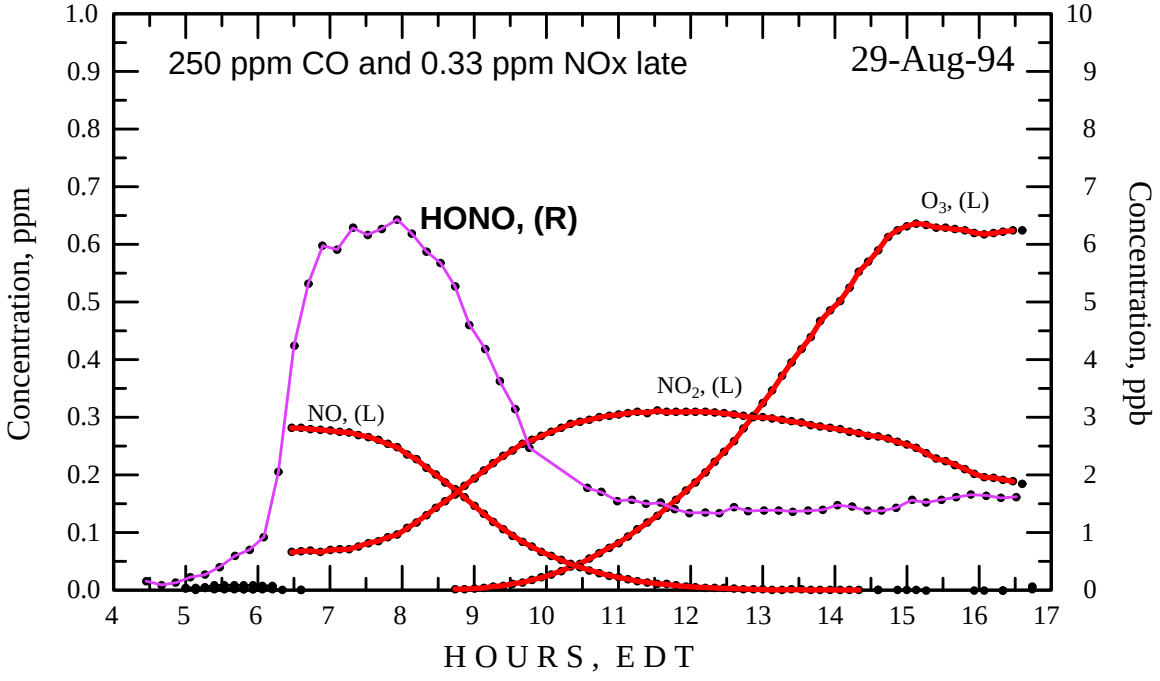

OH Production Rates
August 30, 1996
Reaction Rate, ppb per min
Hours, LDT
HONO+hv=OH
O3+hv=OH
HONO+hv=HO2
0.00
0.05
0.10
0.15
0.20
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

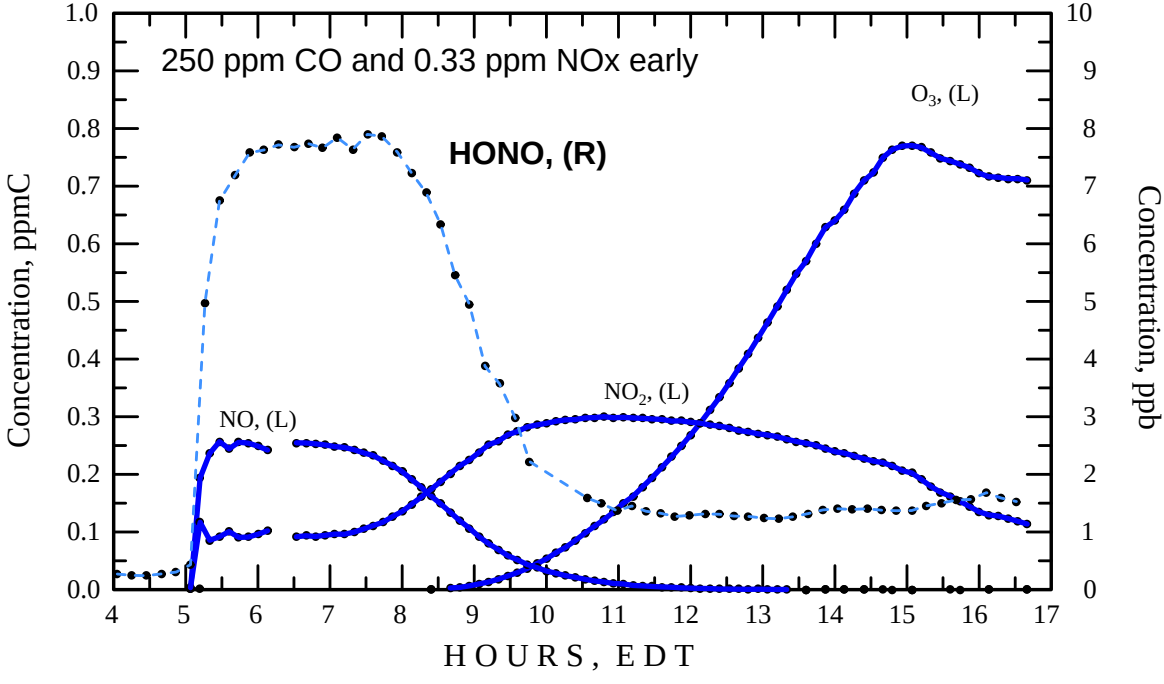

August 30, 1996
Reaction Rate, ppb per min
Hours, LDT
O3+hv=OH
HONO+hv=OH
HONO+hv=HO2
0.00
0.05
0.10
0.15
0.20
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

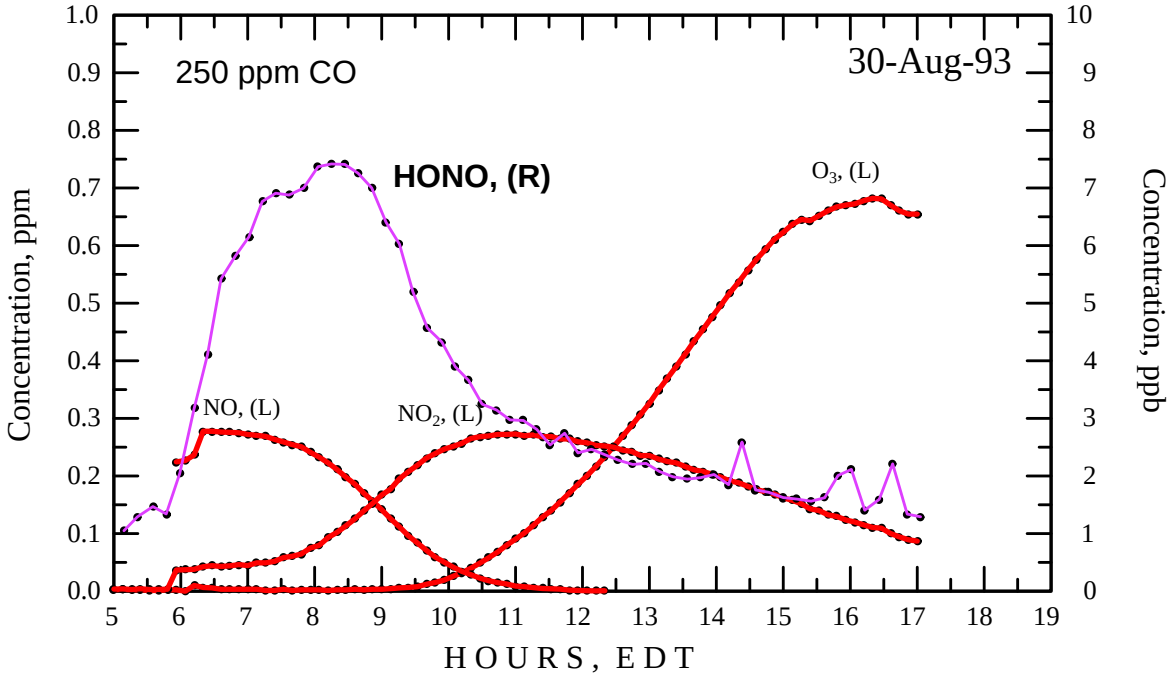

HONO Production and
NO2(g) loss to walls rates
August 30, 1996
NO2(on)
HONO(off)
HONO(OH+NO)
Reaction Rate, ppb per min
Hours, LDT
0.00
0.05
0.10
0.15
0.20
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

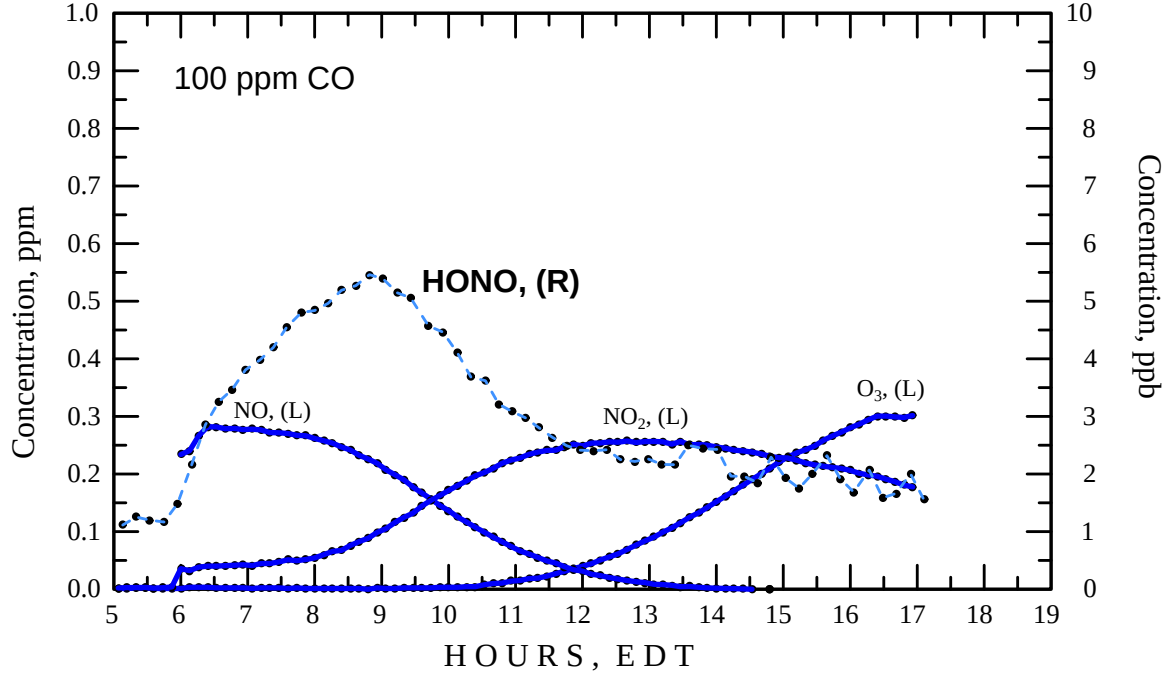

August 30, 1996
NO2(on)
HONO(OH+NO)
HONO(off)
Reaction Rate, ppb per min
Hours, LDT
0.00
0.05
0.10
0.15
0.20
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19


HNO3 Production Rates
August 30, 1996
OH+NO2
N2O5(b)
N2O5(a)
N2O5(w)
Reaction Rate, ppb per min
Hours, LDT
0.00
0.05
0.10
0.15
0.20
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19


250 ppm CO and 0.33 ppm NOx late
29-Aug-94
HONO, (R)
O3, (L)
NO2, (L)
NO, (L)
Concentration, ppm
Concentration, ppb
HOURS, EDT


250 ppm CO and 0.33 ppm NOx early
HONO, (R)
O3, (L)
NO2, (L)
NO, (L)
Concentration, ppmC
Concentration, ppb
HOURS, EDT


250 ppm CO
30-Aug-93
HONO, (R)
O3, (L)
NO, (L)
NO2, (L)
Concentration, ppm
Concentration, ppb
HOURS, EDT


100 ppm CO
HONO, (R)
NO, (L)
NO2, (L)
O3, (L)
Concentration, ppm
Concentration, ppb
HOURS, EDT

Explicit Mechanism with UNCAuxMech99_09 AU3096

NASA97* OH + NO2 Rate

	RED	BLUE	
Initial CO	125 ppm	250 ppm	
	ppb	ppb	in 612 MINS
Ic6a	0.62	4.57	N2O5+H2O---->2.0*HNO3
Ic6b	1.87	14.41	N2O5+H2O+H2O---->2.0*HNO3+H2O
Ib4	8.32	28.49	O1D+H2O---->2.0*OH
Id3	14.49	7.62	OH+NO---->HONO
Id5a	40.86	28.00	HONO---->OH+NO
Id5b	4.52	3.09	HONO---->HO2+NO2
If1a	46.12	52.11	OH+NO2---->HNO3
If1b	27.68	31.25	OH+NO2---->HOONO
If1c	27.67	31.25	HOONO---->OH+NO2
If2	0.00	0.00	OH+HOONO- ->NO+H2O+O2
Ih1	754.29	1552.75	OH+CO---->HO2+CO2
Ie1	756.38	1486.59	HO2+NO---->OH+NO2
DepoN2O5	0.00	0.02	N2O5+WH2O---->2.0*WHNO3
DepoHNO3f	45.07	79.10	HNO3+WH2O---->WHNO3
DepoHONOr	31.54	23.46	WHONO---->HONO
DepoNO2f	79.10	66.87	NO2+H2O---->WNO2
WNO2pWNO2	1.72	1.49	WNO2+WNO2---->WN2O4
WH2OpWN2O4	1.72	1.49	WN2O4+WH2O---->WHONO+WHNO3
WNO2pWHNO3	37.86	31.98	WNO2+WHNO3---->W(NO2)NO3+WH2O
WNO2pWHNO2P	37.82	31.90	WNO2+W(NO2)NO3---->WHONO+WHNO3
WHNO2PpWHNO2P	0.00	0.01	W(NO2)NO3+W(NO2)NO3---->2.0*(WHONO+WHNO3)
WHONOpWHNO3a	7.85	9.89	WHONO+WHNO3+WHNO3---->N2O+WHNO3