Observations of Nitryl Chloride, $ClNO_2$, a Significant Chlorine Atom Source in the Houston-Galveston Region

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NOAA Ship
RONALD H. BROWN

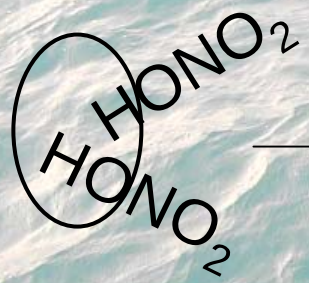
What is $ClNO_2$?

The Anhydride of HCl and HNO_3

$$\longrightarrow \quad \mathbf{H_2O + ClNO_2}$$

What is N_2O_5 ?

The Anhydride of Two HNO_3



$$\longrightarrow \quad \mathbf{H_2O + N_2O_5}$$

Just because you can draw it doesn't mean the reaction goes. Gas phase anhydride formation from two acids is not thermodynamically favorable

How do these things get made in the atmosphere?

N_2O_5; Gas Phase Radical Chemistry

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$

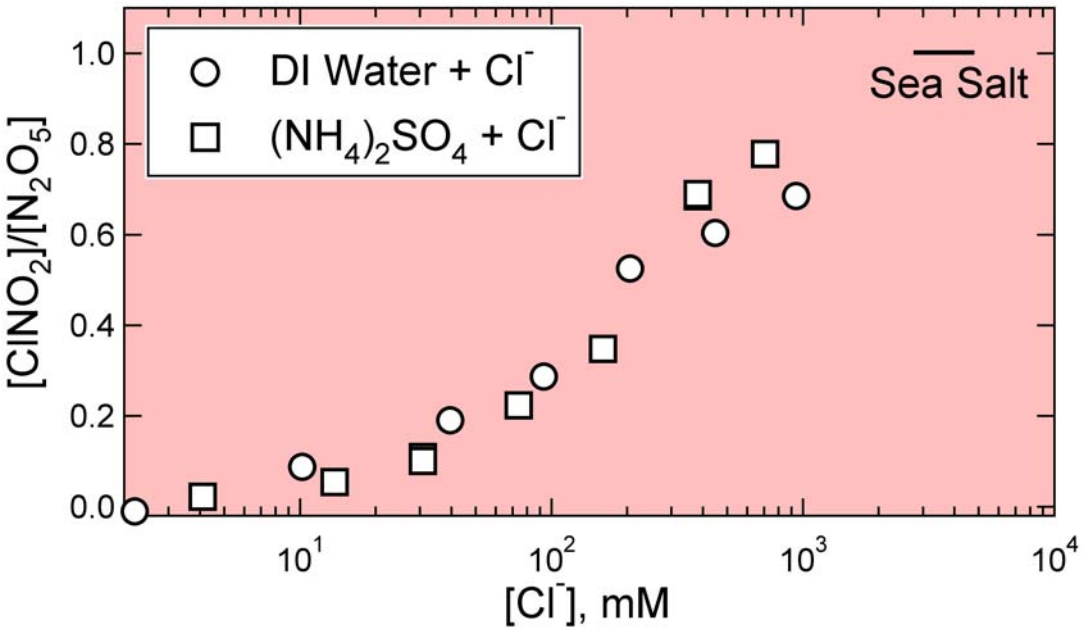
$$NO_3 + NO_2 \longleftrightarrow N_2O_5$$

$ClNO_2$; N_2O_5 Solution Chemistry

$N_2O_5 + H_2O_{(g)}$ too slow to be important

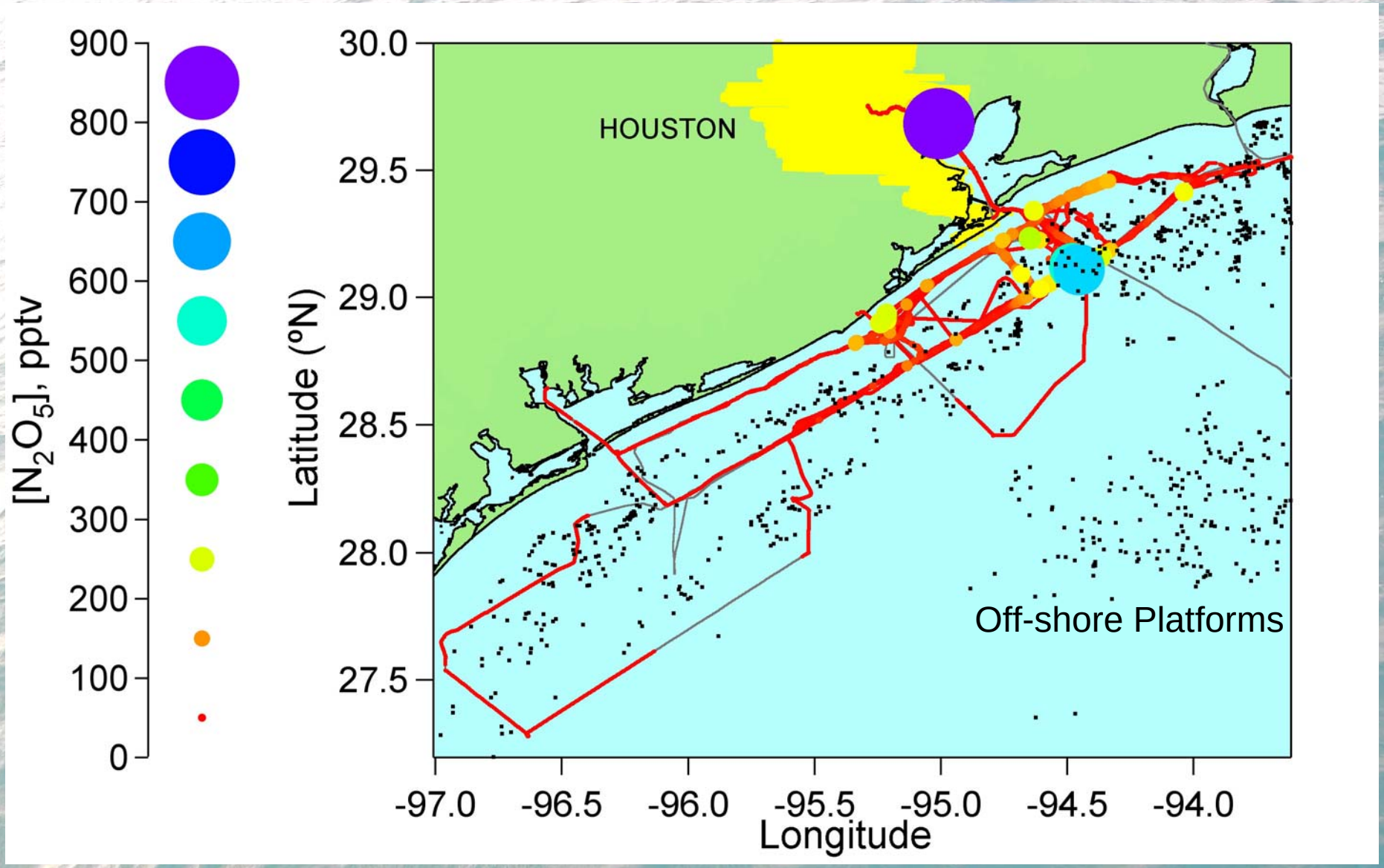
$N_2O_5 + H_2O_{(aq)} \longrightarrow NO_2^+NO_3^- + H_2O \longrightarrow 2\ HNO_3$, $\gamma = 0.03$ major loss for NO_x

$N_2O_5 + Cl^-_{(aq)} \longrightarrow NO_2^+ + Cl^- \longrightarrow ClNO_2 + NO_3^-$

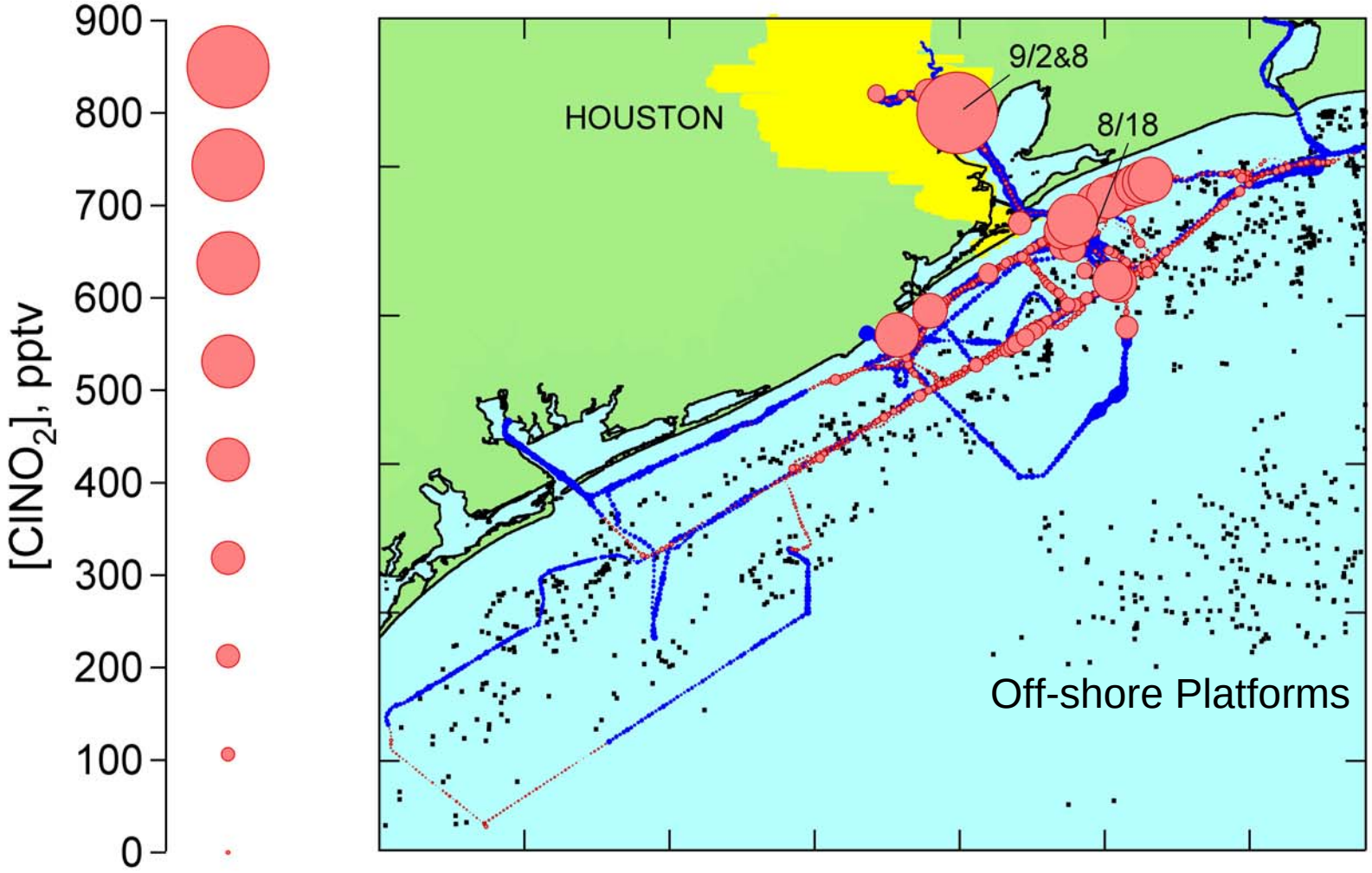


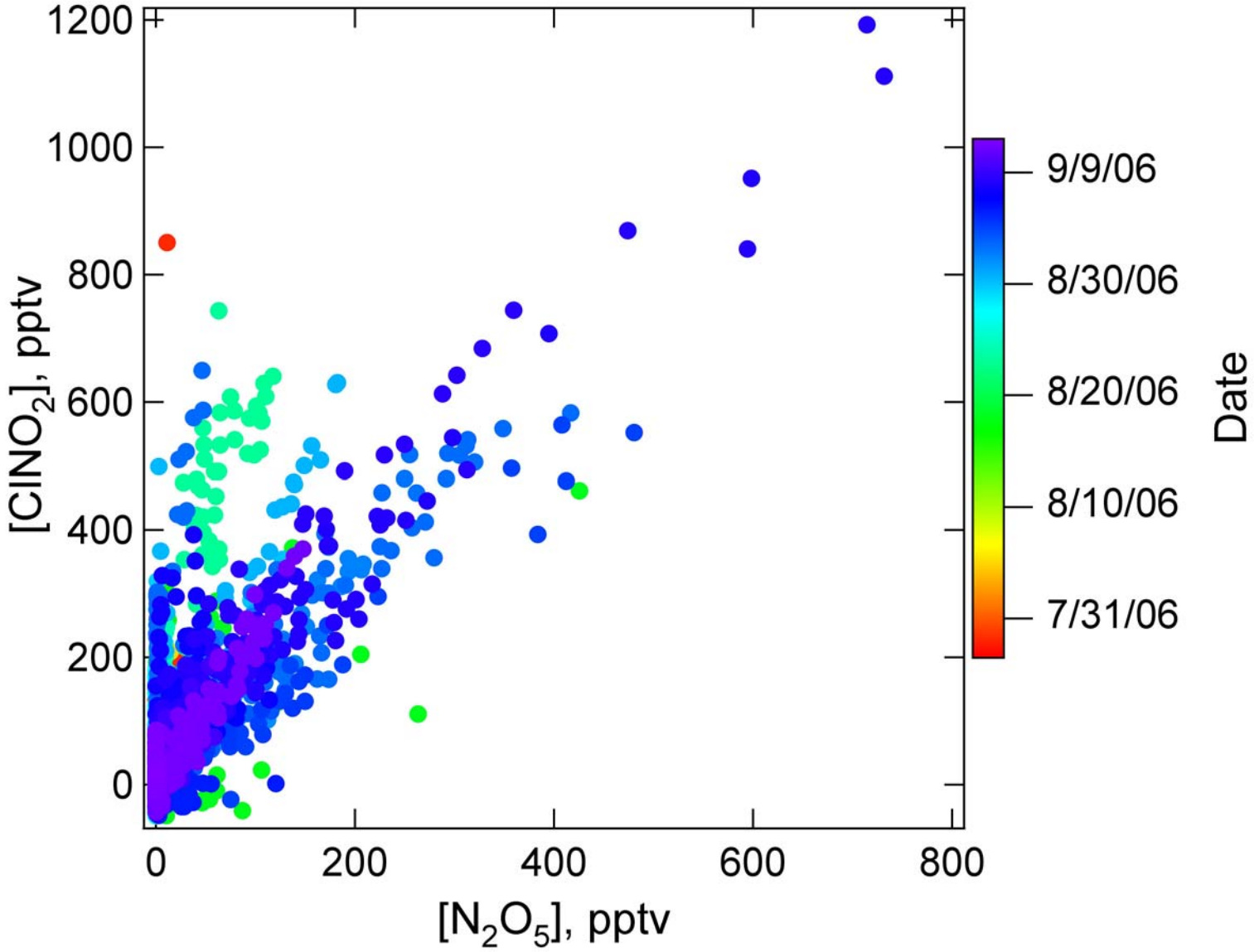
This happens at $[Cl^-]$ from Sea Salt down to 0.02 M, so almost all aerosol surface area is available for reaction.

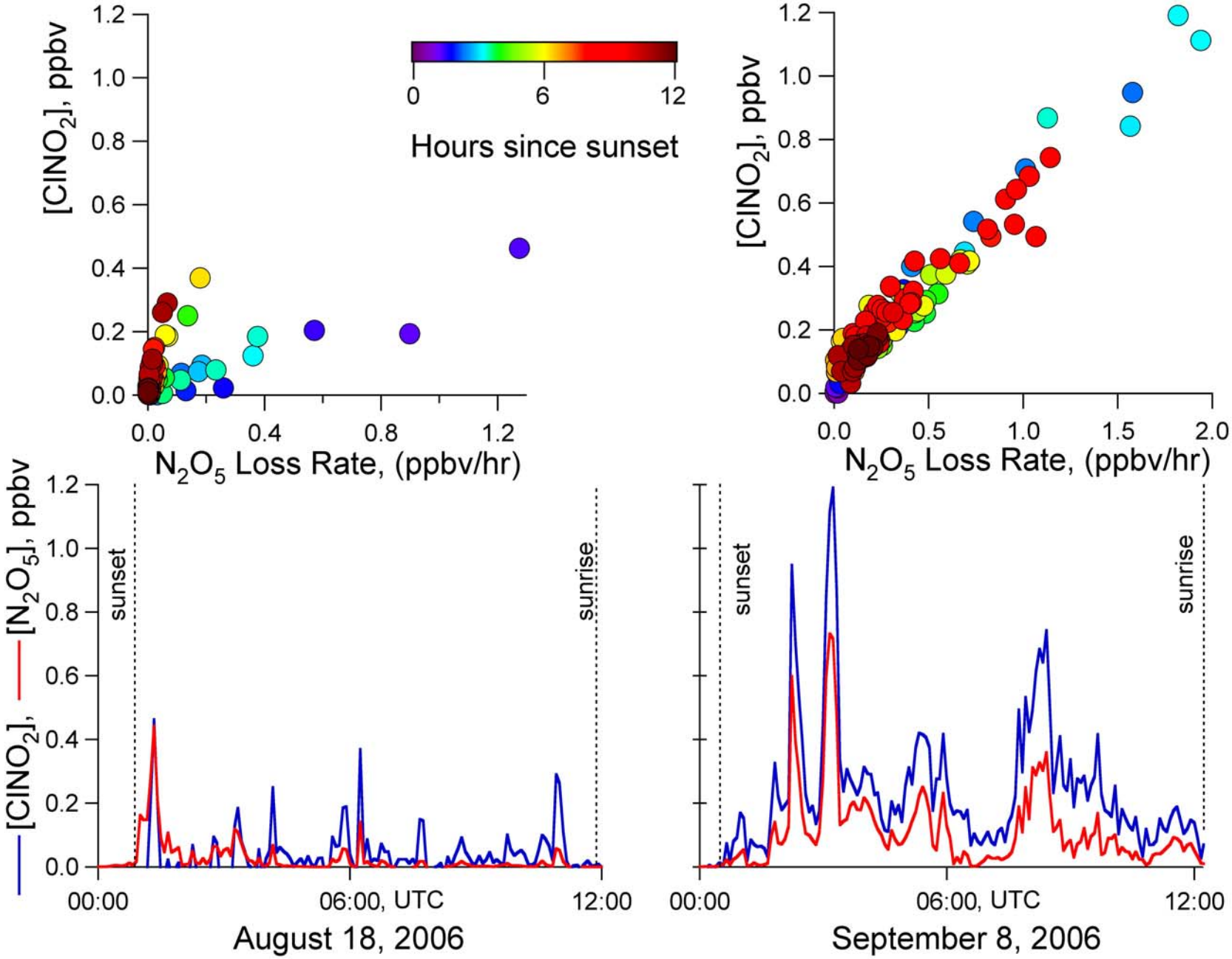
N_2O_5 Map


900
800
700
600
500
400
300
200
100
0
[N2O5], pptv
30.0
29.5
29.0
28.5
28.0
27.5
Latitude (ºN)
HOUSTON
Off-shore Platforms
-97.0
-96.5
-96.0
-95.5
-95.0
-94.5
-94.0
Longitude

$ClNO_2$ Map


900
800
700
600
500
400
300
200
100
0
[ClNO2], pptv
HOUSTON
9/2&8
8/18
Off-shore Platforms


1200
1000
800
600
400
200
0
[ClNO2], pptv
0
200
400
600
800
[N2O5], pptv
9/9/06
8/30/06
8/20/06
8/10/06
7/31/06
Date


[ClNO2], ppbv
N2O5 Loss Rate, (ppbv/hr)
Hours since sunset
0
6
12
[ClNO2], ppbv
N2O5 Loss Rate, (ppbv/hr)
[ClNO2], [N2O5], ppbv
sunset
sunrise
00:00
06:00, UTC
12:00
August 18, 2006
September 8, 2006

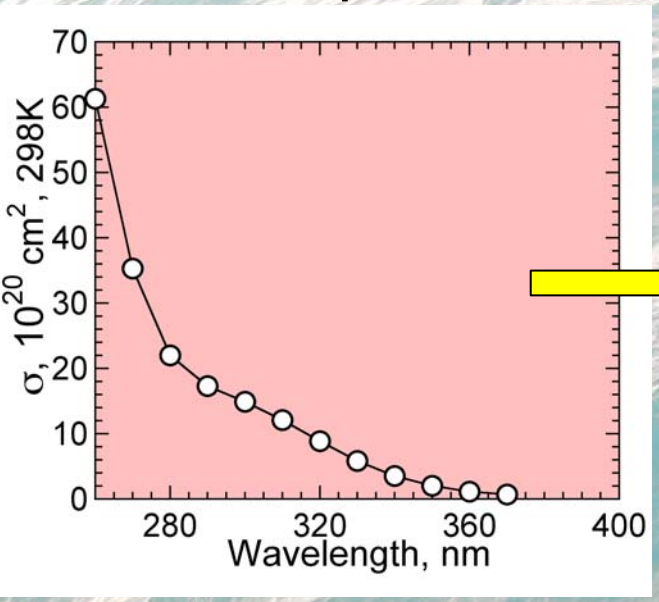
What does $ClNO_2$ do in the Lower Troposphere?

Thermal stability: $ClNO_2 \longrightarrow Cl + NO_2$, ΔH=32.8 kcal/mole STABLE

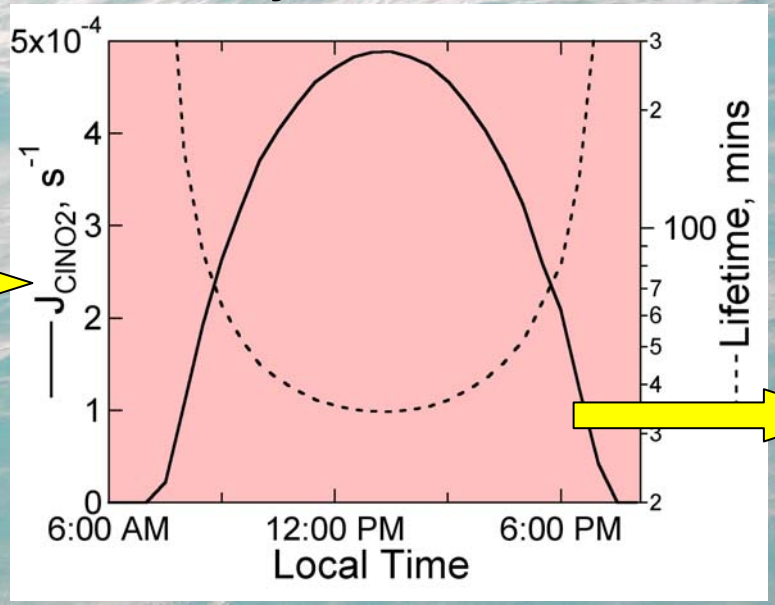
Solubility in Liquid Water: $\mathcal{H}$ = 3.5 x10^{-2} M/atm INSOLUBLE

Photolysis: $ClNO_2 \longrightarrow Cl + NO_2$

UV-Vis spectrum



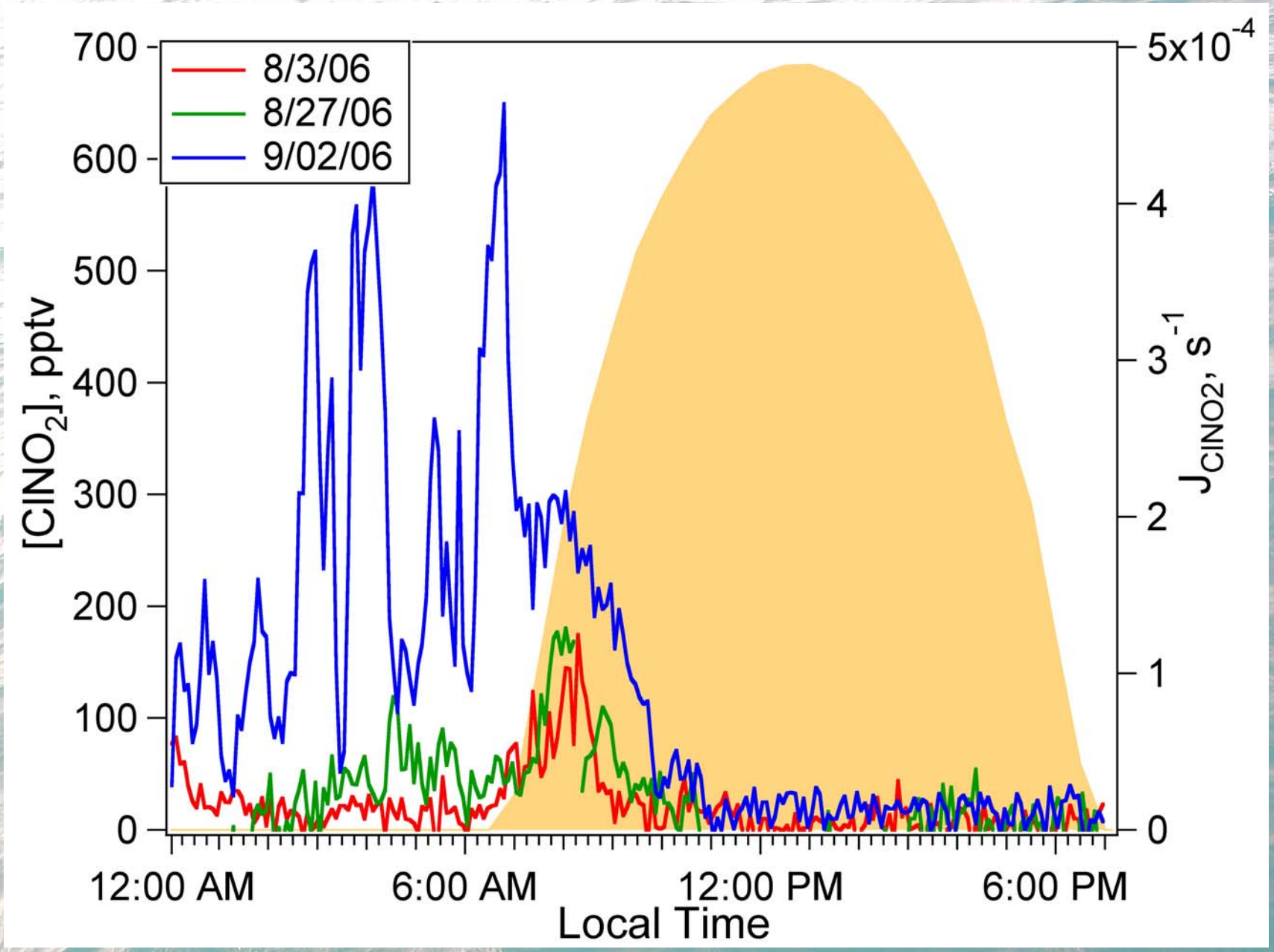
Photolysis Rate

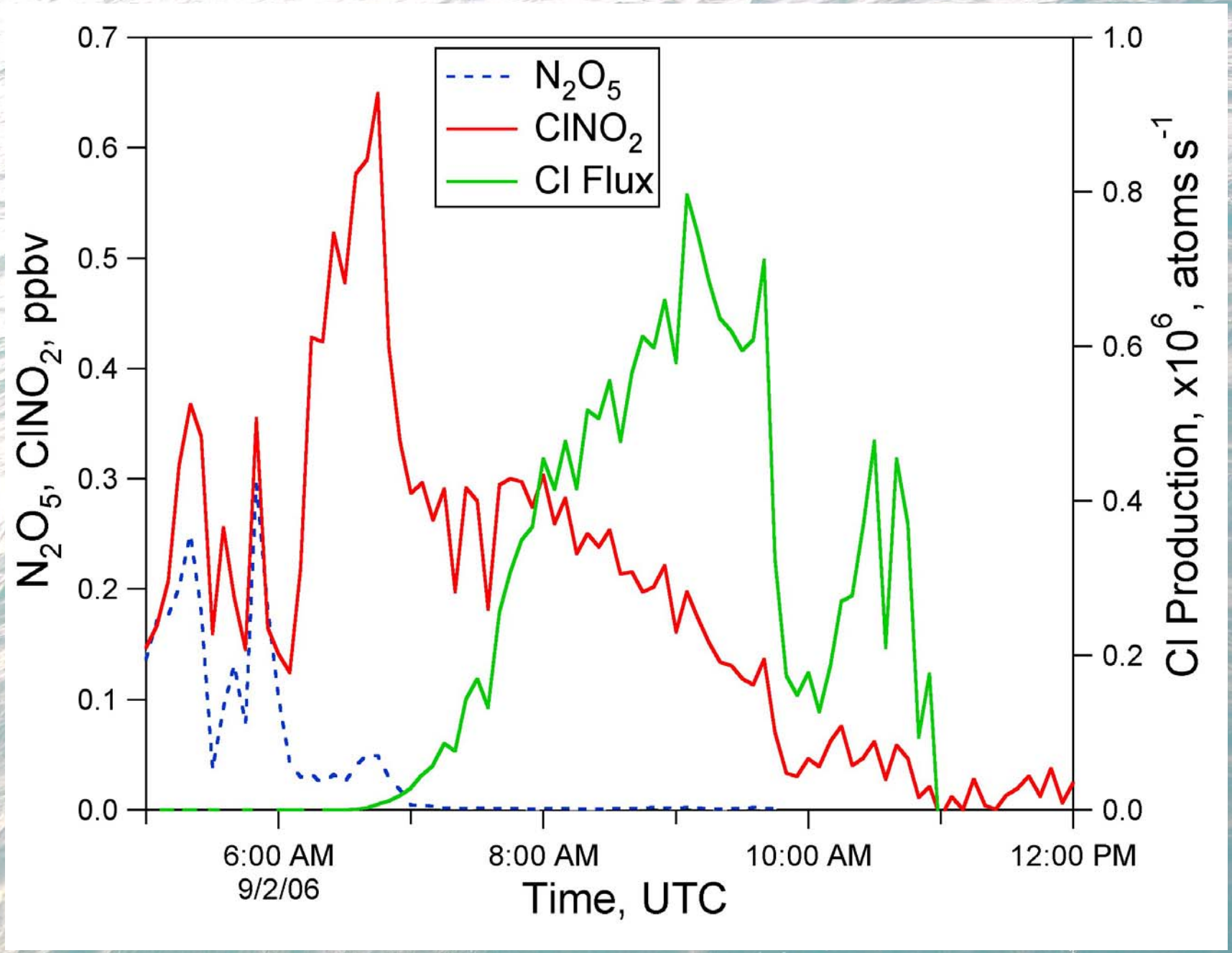


Lifetime

35 min

We would expect $ClNO_2$ to survive into the morning hours and produce Cl atoms.


8/3/06
8/27/06
9/02/06
[ClNO2], pptv
700
600
500
400
300
200
100
0
5x10-4
4
3
2
1
0
JClNO2, s-1
12:00 AM
6:00 AM
12:00 PM
6:00 PM
Local Time

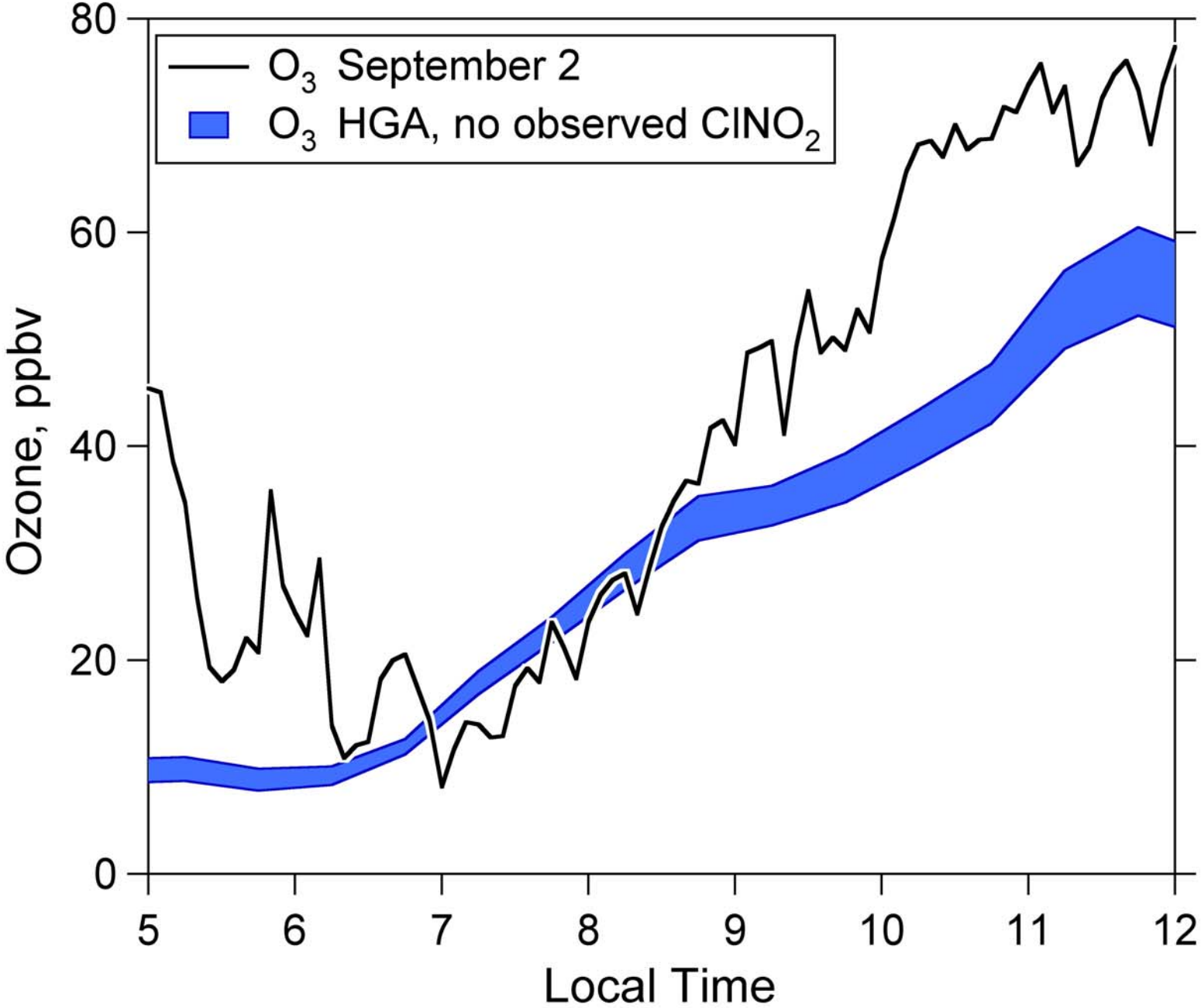

N_2O_5
$ClNO_2$
Cl Flux
N_2O_5, $ClNO_2$, ppbv
Cl Production, x10^6, atoms s^{-1}
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.0
0.2
0.4
0.6
0.8
1.0
6:00 AM
9/2/06
8:00 AM
10:00 AM
12:00 PM
Time, UTC

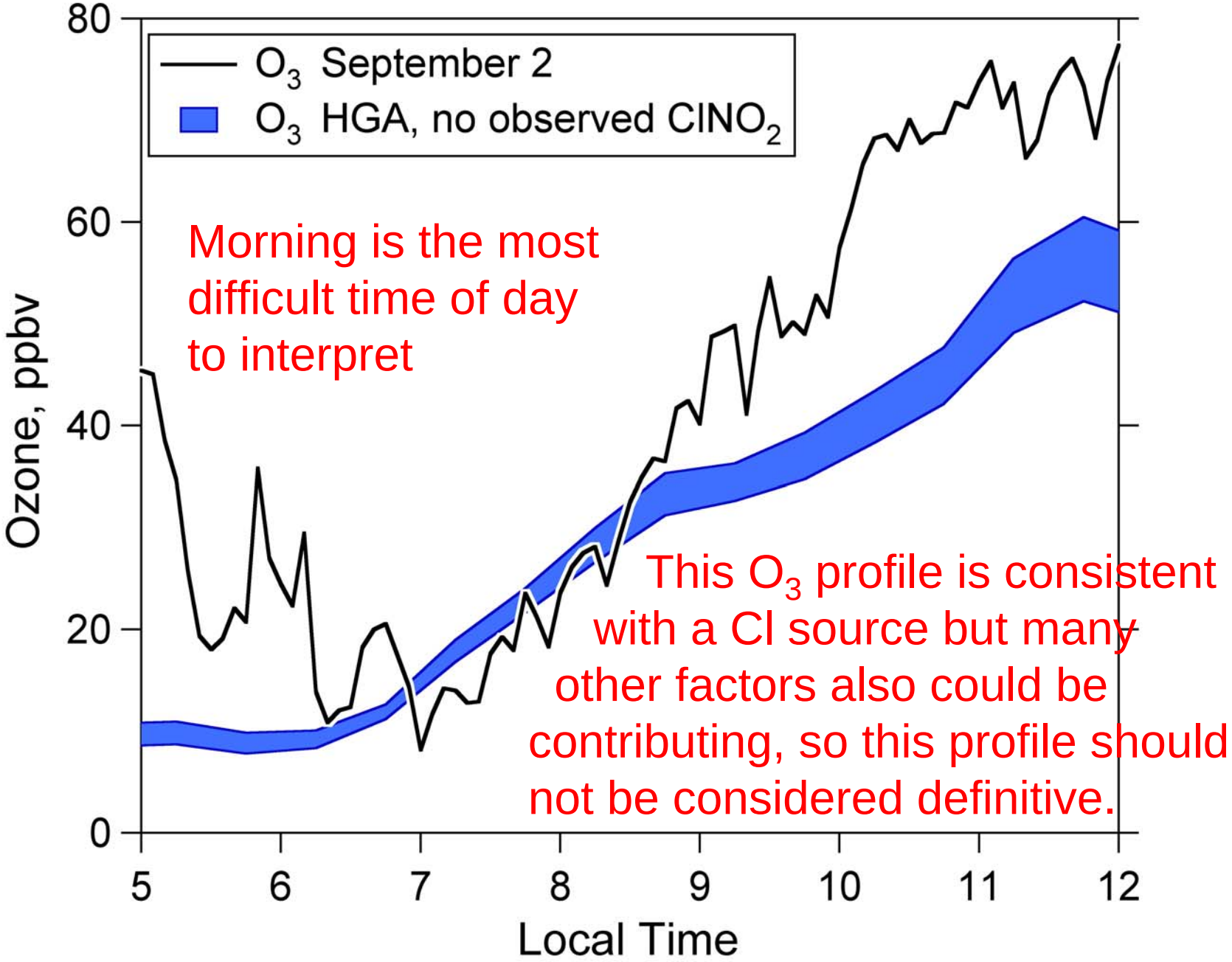
What does this Cl atom source do?

Cl atoms react up to 100 times faster with VOC relative to OH, so that some VOCs (alkanes) become highly reactive.

This Cl atom source occurs in the early to mid morning, at time when NO_3 and OH radical sources are scarce.

These factors can “kickstart” the VOC-NO_x photochemistry, resulting in a faster morning start and a longer photochemical day.


O_3 September 2
O_3 HGA, no observed $ClNO_2$
Ozone, ppbv
Local Time
0
20
40
60
80
5
6
7
8
9
10
11
12


O_3 September 2
O_3 HGA, no observed $ClNO_2$
Morning is the most difficult time of day to interpret
This O_3 profile is consistent with a Cl source but many other factors also could be contributing, so this profile should not be considered definitive.
Ozone, ppbv
Local Time
0
20
40
60
80
5
6
7
8
9
10
11
12

Master Chemical Mechanism

- Explicit VOC Chemistry
- N_2O_5 + Aerosol, $ClNO_2$, and Cl atom Chemistry added
- VOC mixture and NO_x “typical” Urban plume in MBL

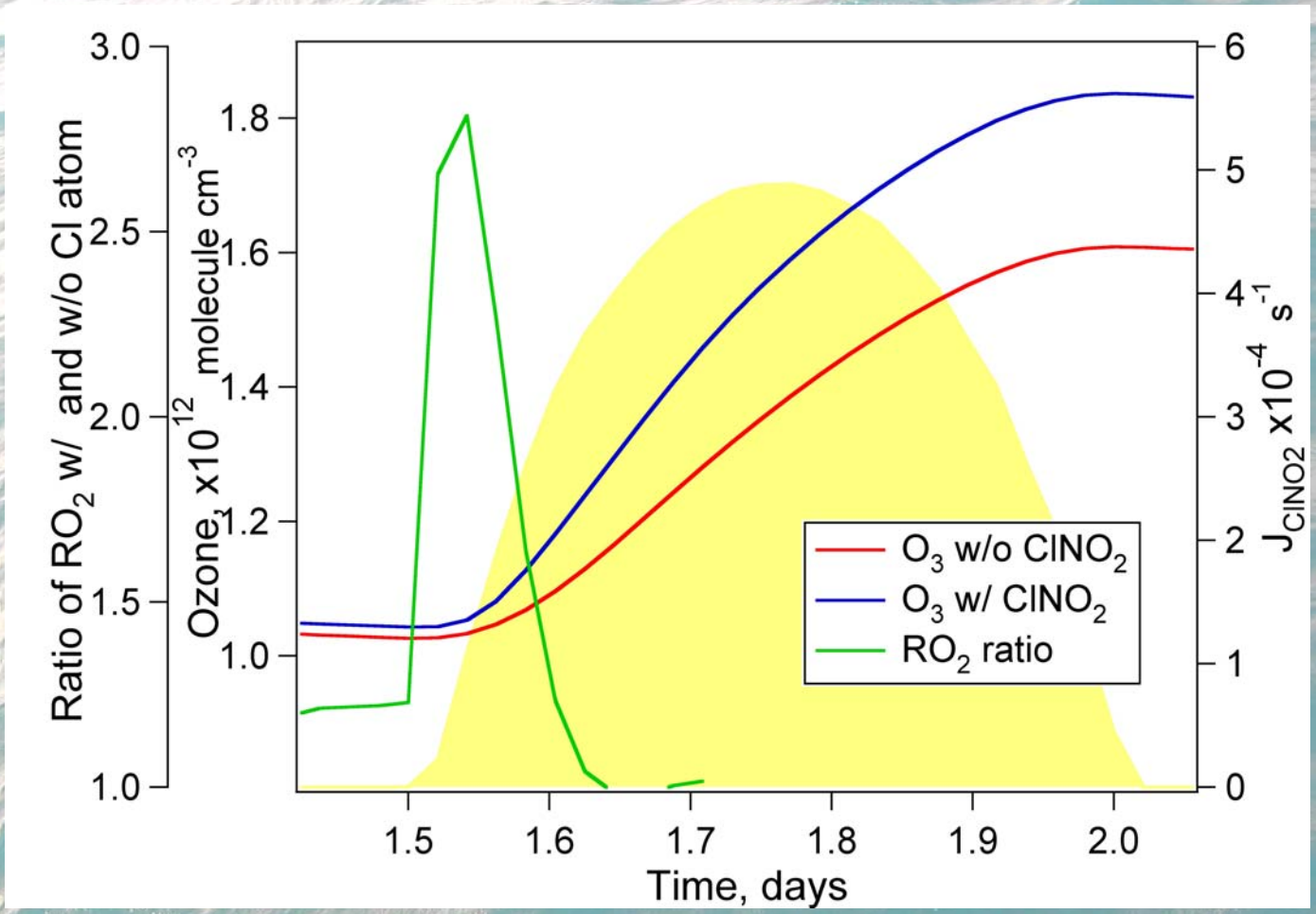
References; http://mcm.leeds.ac.uk/

Master Chemical Mechanism

Explicit VOC Chemistry

N_2O_5 + Aerosol, $ClNO_2$, and Cl atom Chemistry added

VOC mixture and NO_x "typical" Urban plume in MBL



References; http://mcm.leeds.ac.uk/

Summary

N_2O_5 uptake on Cl^- containing aerosols is producing potentially important quantities of $ClNO_2$.

$ClNO_2$ survives into the morning hours, releasing Cl atoms through photolysis.

Those Cl atoms cause earlier and more intense O_3 production.

This N_2O_5 - aerosol chemistry should be added to regional models.

How should we look into this further ?

Regional modeling with N_2O_5, aerosol uptake, $ClNO_2$, and Cl^- VOC photochemistry

SAPRC-99 Mechanism - It's got good Isoprene chemistry to which Cl - Isoprene reactions can be added, so Reimer measurements from TexAQS2000 can be used as a metric.

Warning: it lumps 1,3-butadiene chemistry with Isoprene.

Things to look for:

Sensitivity of the Cl atom source to NO_x

Land-Sea breeze modulation of the $ClNO_2$ source

Control of this source of reactive Cl may require strategies different from control of industrial or domestic HOCl or Cl_2.