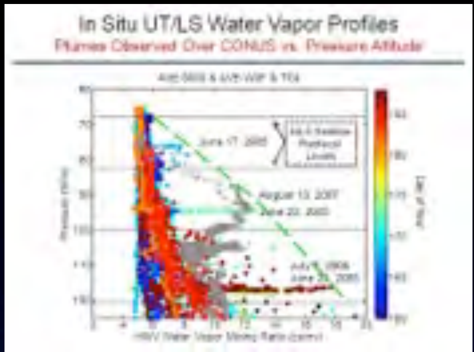
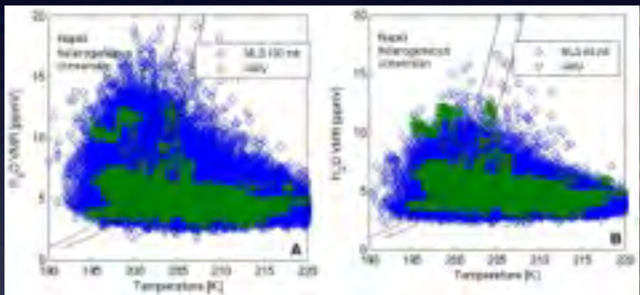
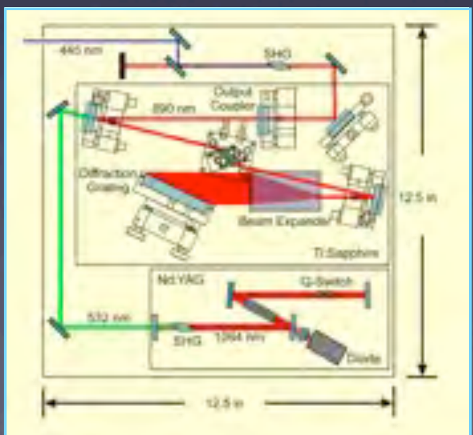
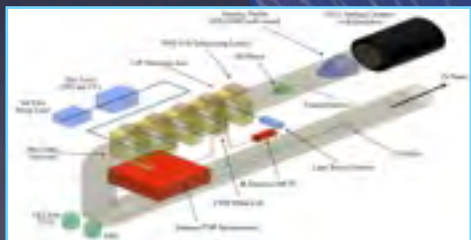
Climate Forcing and Free Radical Response: Convective Injection of Water Vapor Into the Summertime Stratosphere at Mid-Latitudes

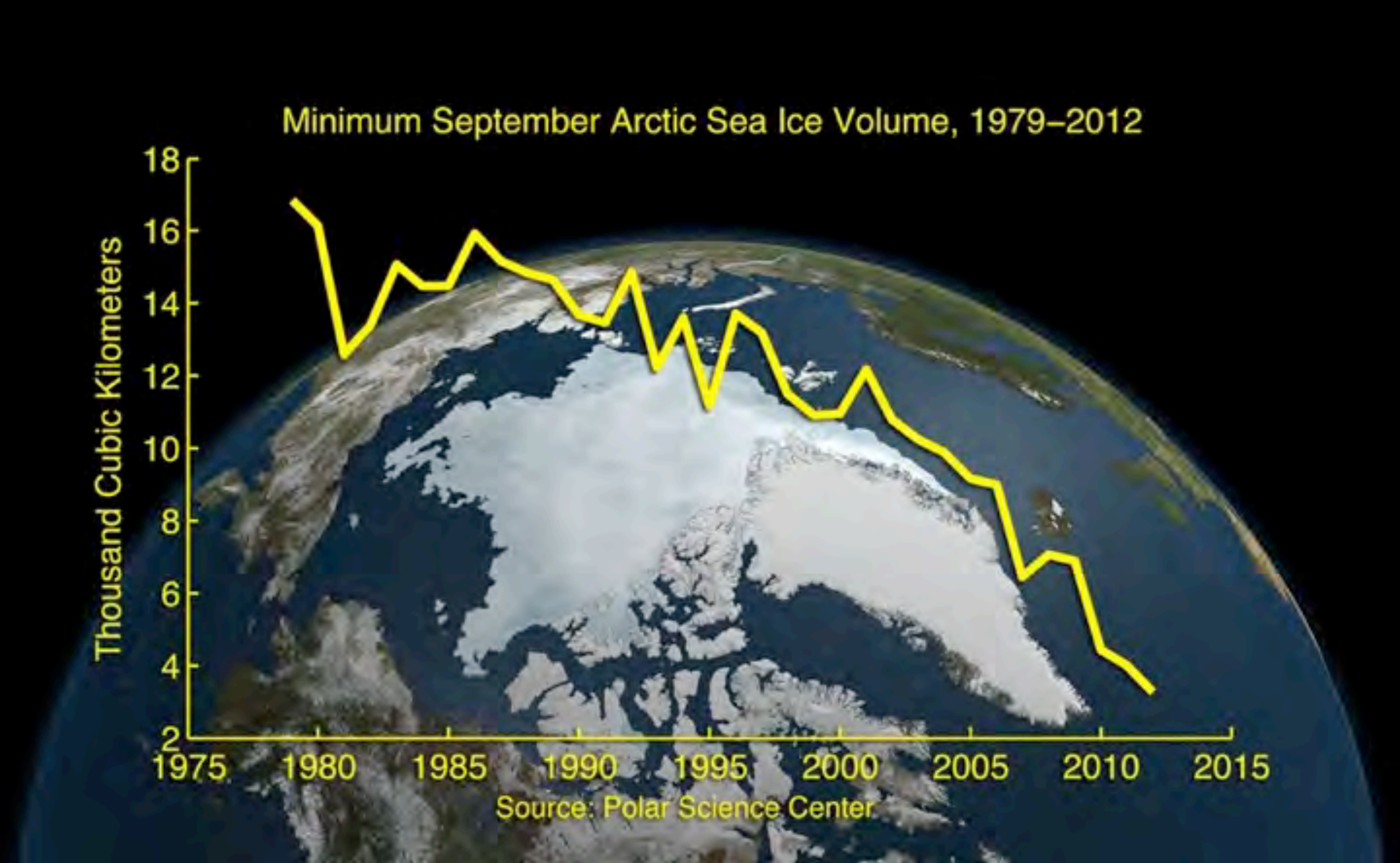


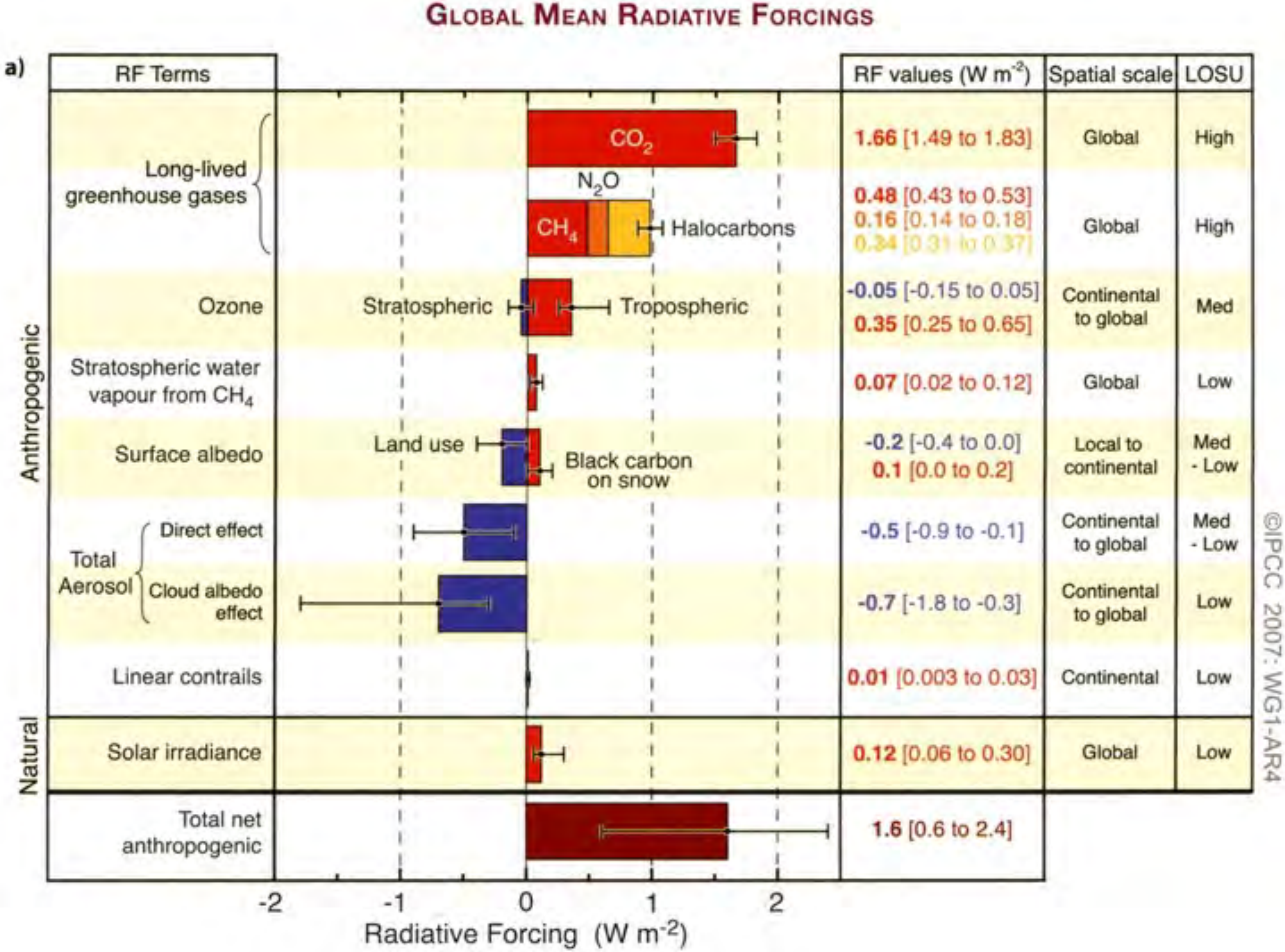
Jim Anderson, Dave Wilmouth, Jessica Smith and John Dykema
Harvard University
Cambridge, MA 02138



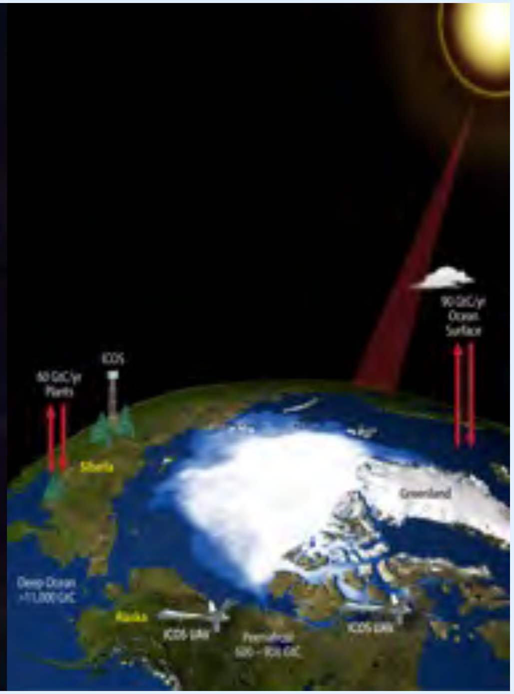


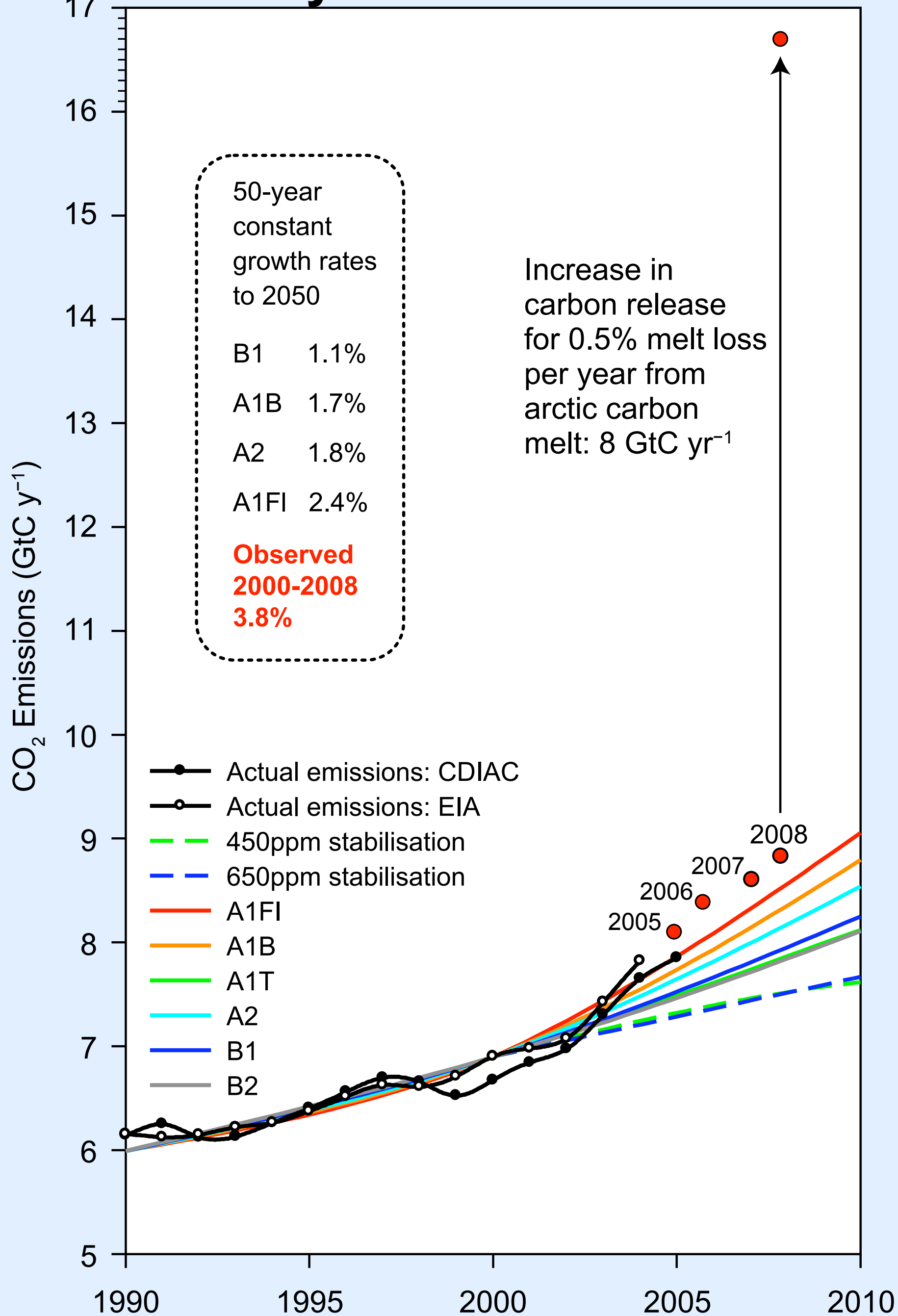


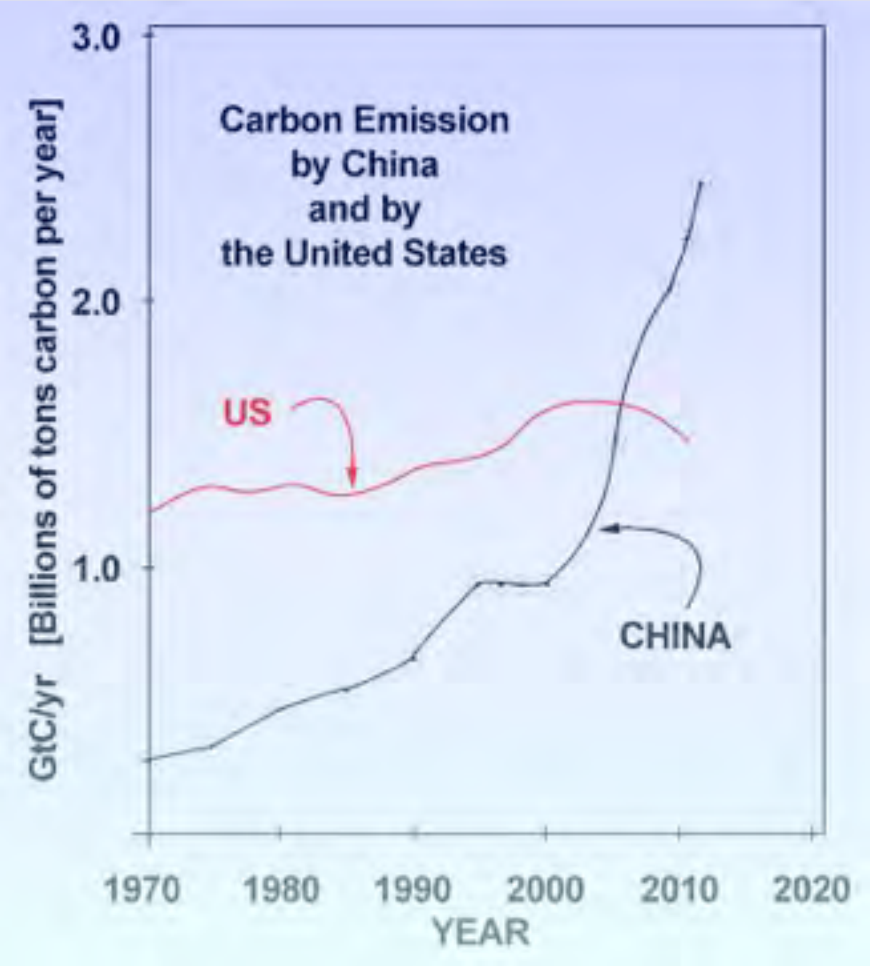

Minimum September Arctic Sea Ice Volume, 1979–2012
Thousand Cubic Kilometers
18
16
14
12
10
8
6
4
2
1975
1980
1985
1990
1995
2000
2005
2010
2015
Source: Polar Science Center


GLOBAL MEAN RADIATIVE FORCINGS
a)
RF Terms
RF values (W m-2)
Spatial scale
LOSU
Anthropogenic
Long-lived greenhouse gases
CO2
1.66 [1.49 to 1.83]
Global
High
N2O
CH4
Halocarbons
0.48 [0.43 to 0.53]
0.16 [0.14 to 0.18]
0.34 [0.31 to 0.37]
Global
High
Ozone
Stratospheric
Tropospheric
-0.05 [-0.15 to 0.05]
0.35 [0.25 to 0.65]
Continental to global
Med
Stratospheric water vapour from CH4
0.07 [0.02 to 0.12]
Global
Low
Surface albedo
Land use
Black carbon on snow
-0.2 [-0.4 to 0.0]
0.1 [0.0 to 0.2]
Local to continental
Med - Low
Total Aerosol
Direct effect
-0.5 [-0.9 to -0.1]
Continental to global
Med - Low
Cloud albedo effect
-0.7 [-1.8 to -0.3]
Continental to global
Low
Linear contrails
0.01 [0.003 to 0.03]
Continental
Low
Natural
Solar irradiance
0.12 [0.06 to 0.30]
Global
Low
Total net anthropogenic
1.6 [0.6 to 2.4]
-2
-1
0
1
2
Radiative Forcing (W m-2)
©IPCC 2007: WG1-AR4

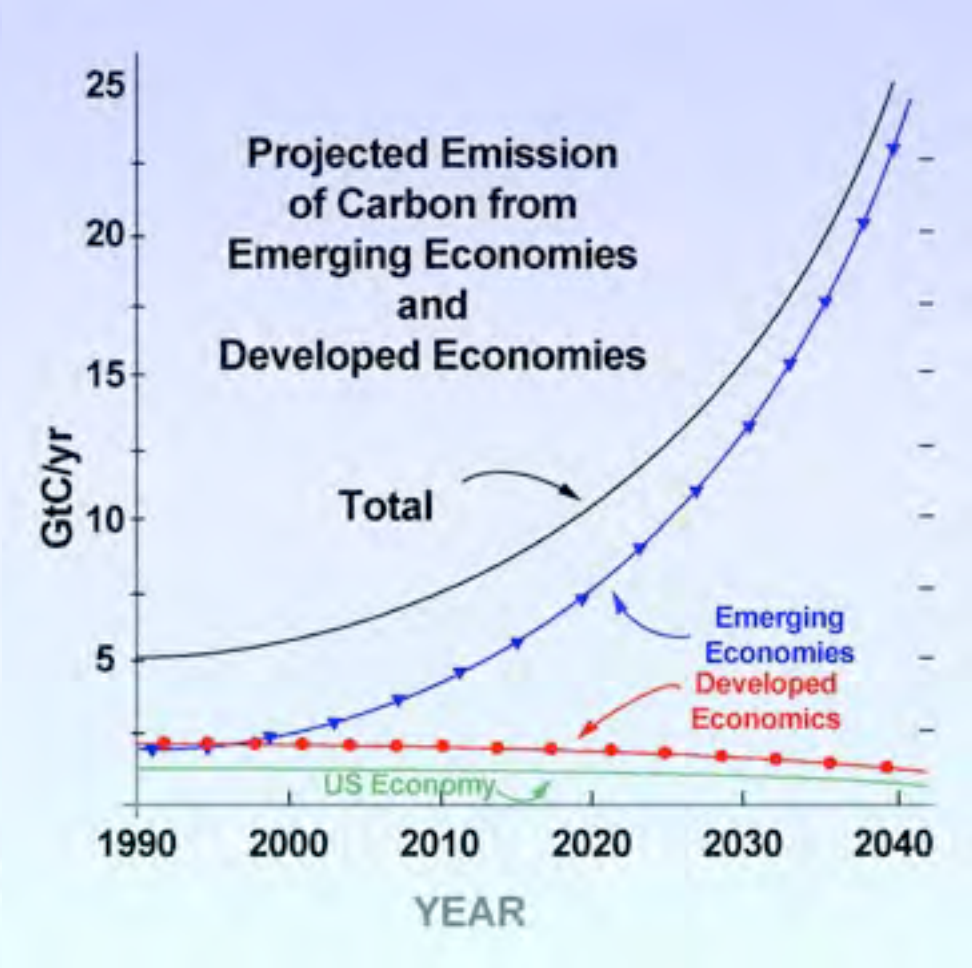
Key Feedbacks in the Climate System







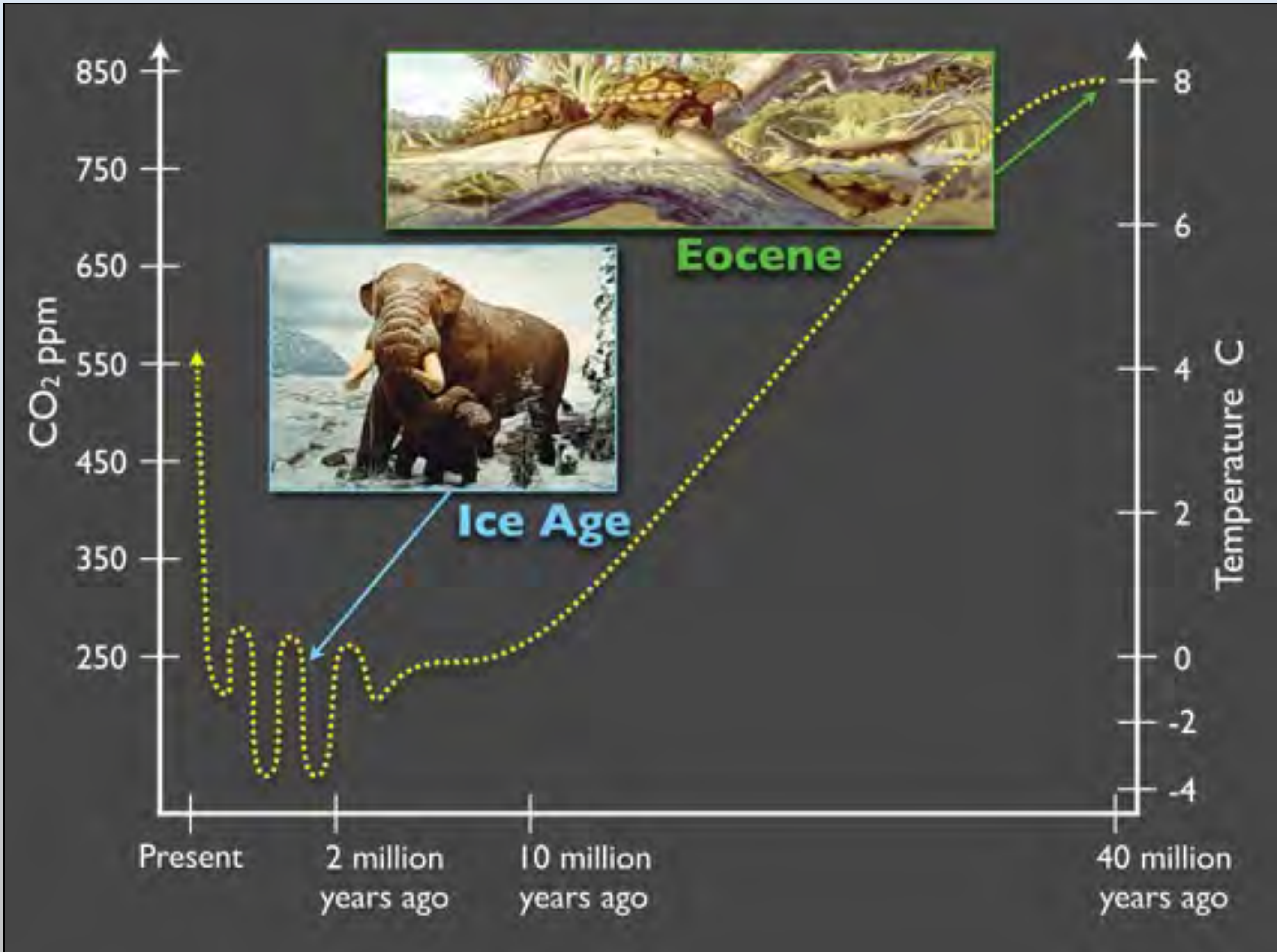
Carbon Emission
by China
and by
the United States
3.0
2.0
1.0
GtC/yr [Billions of tons carbon per year]
US
CHINA
1970
1980
1990
2000
2010
2020
YEAR



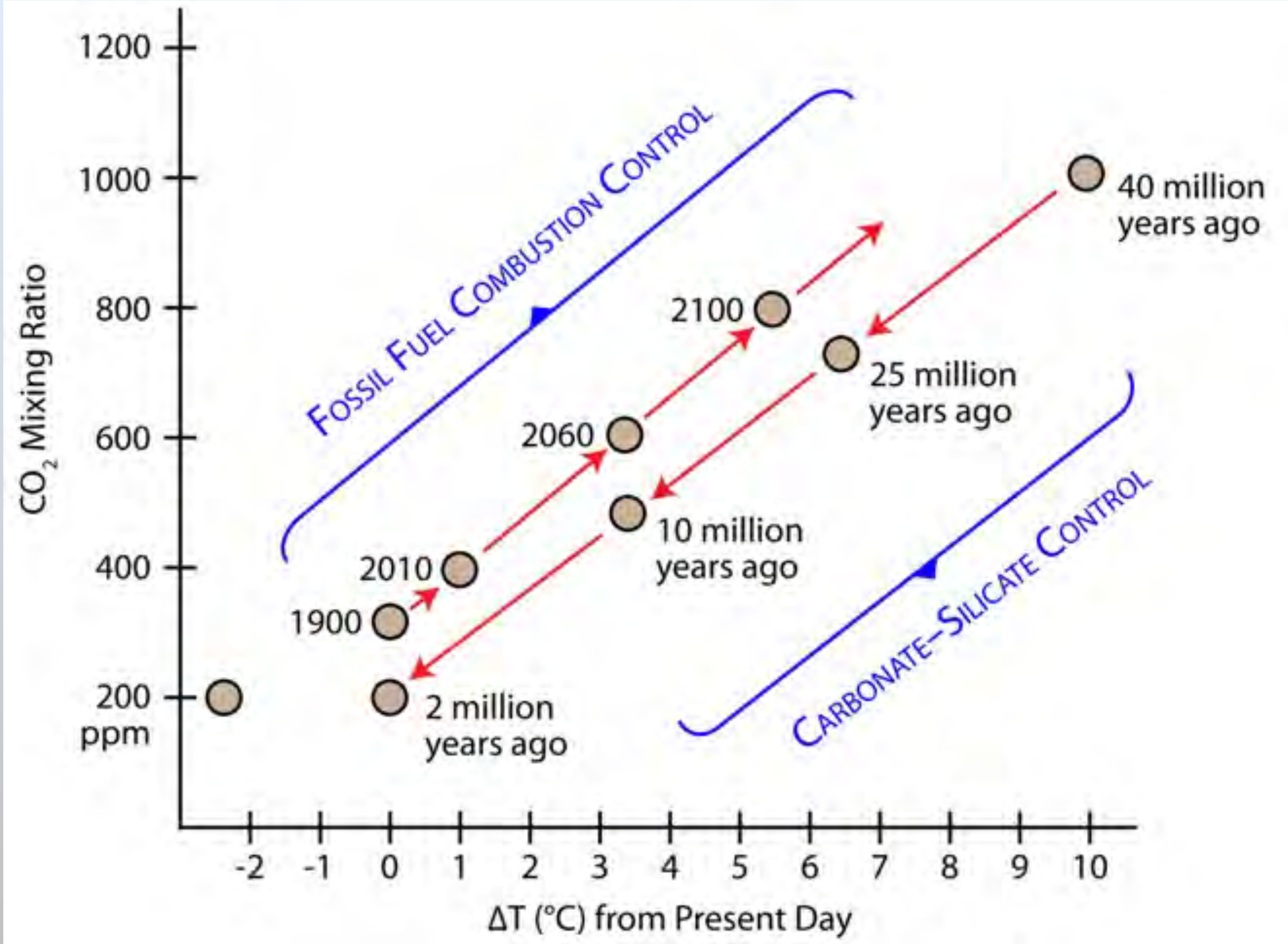
Projected Emission
of Carbon from
Emerging Economies
and
Developed Economies
25
20
15
10
5
GtC/yr
Total
Emerging
Economies
Developed
Economics
US Economy
1990
2000
2010
2020
2030
2040
YEAR

An artist's picture of the Arctic coast during the Eocene epoch, about 40 million years ago.

What do we know from past climate stages?



Measured in CO_2 Years



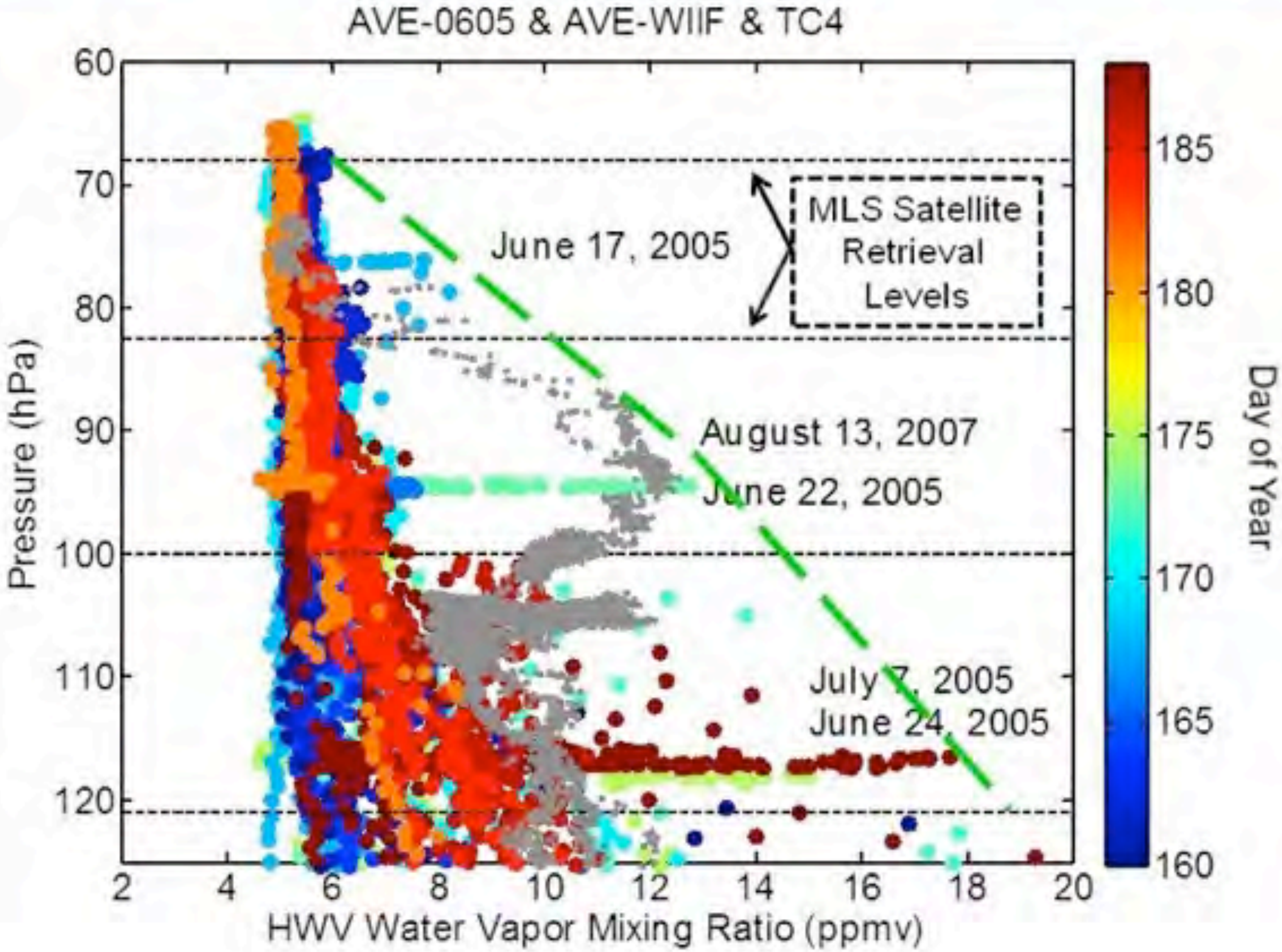
Climate Forcing

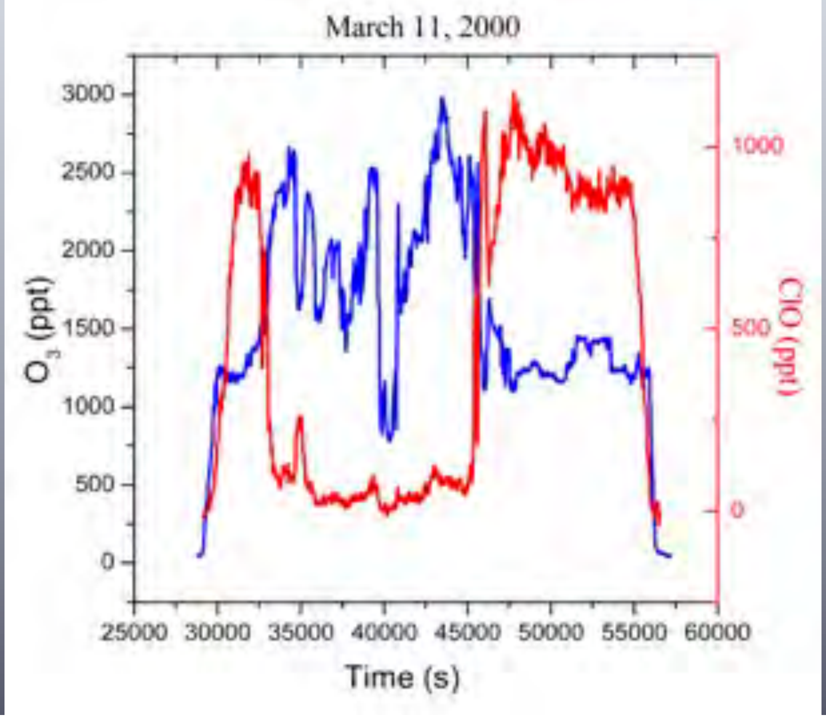
- Feedbacks within the Climate Structure Set the Timescale for Irreversibility
- The Rate of Increase in Forcing is Both Unprecedented and On Track to Transition the Climate System to a Pre-Pleistocene Structure.
- Remarkably Little Thermal Energy (Heat) is Required to Eliminate the Arctic Floating Ice. That Loss of Arctic Floating Ice is Irreversible Given the Strength of the Feedbacks.
- The Loss of Arctic Ice Triggers a Cascade of Coupled Feedbacks.
- During the High CO_2 Period Characterized by a Moist Stratosphere, Ozone Was Sustained Because There Was Insufficient Halogen Loading to Titrate NOx From the Lower Stratosphere.
- With the Coming Reduction in Shortwave Forcing, the IR Forcing Will Increase at a Far Faster Rate. Alternatively Stated, We Owe a Great Deal to the Emerging Economies of Asia!

That’s Forcing, What About Response?

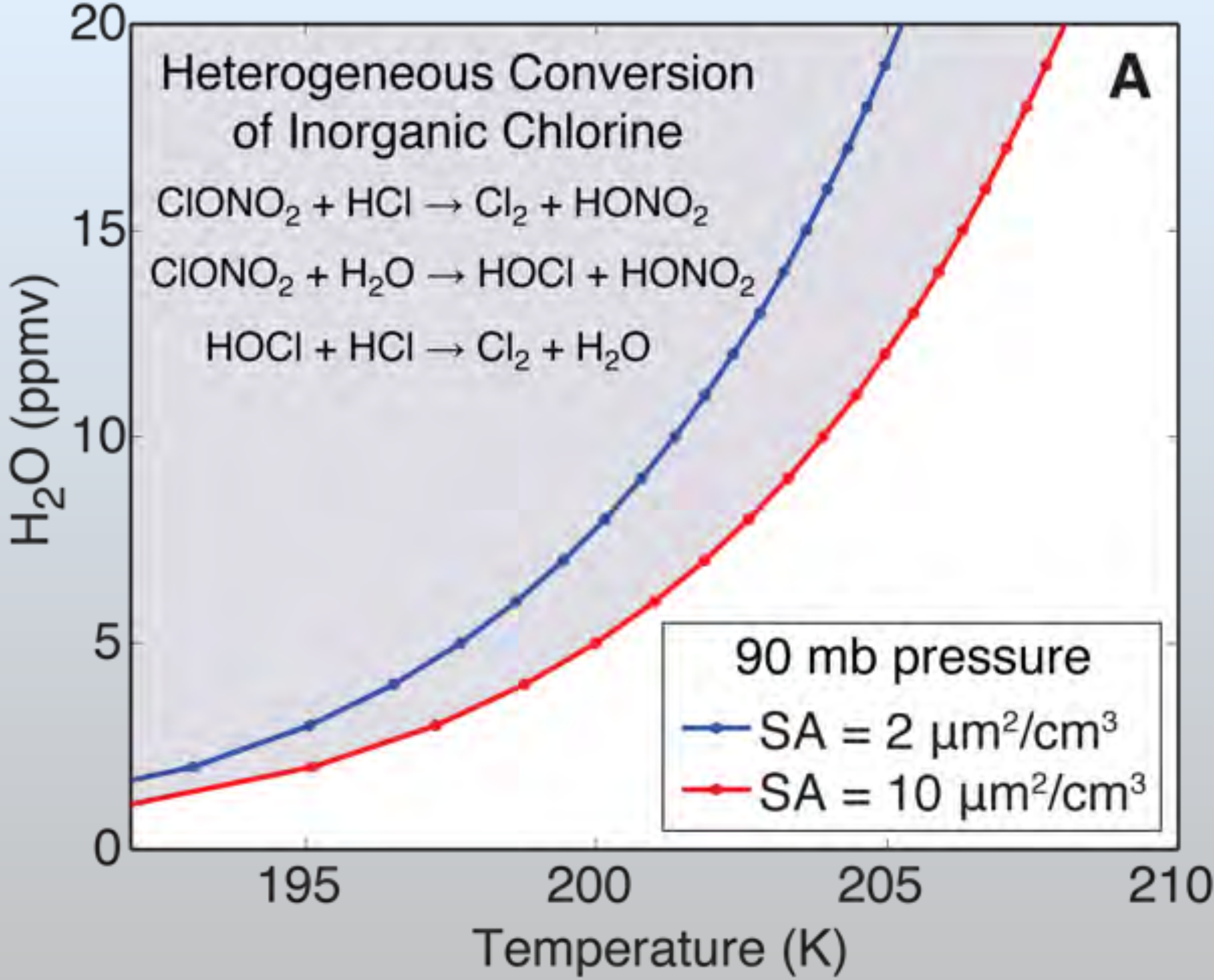
In Situ UT/LS Water Vapor Profiles

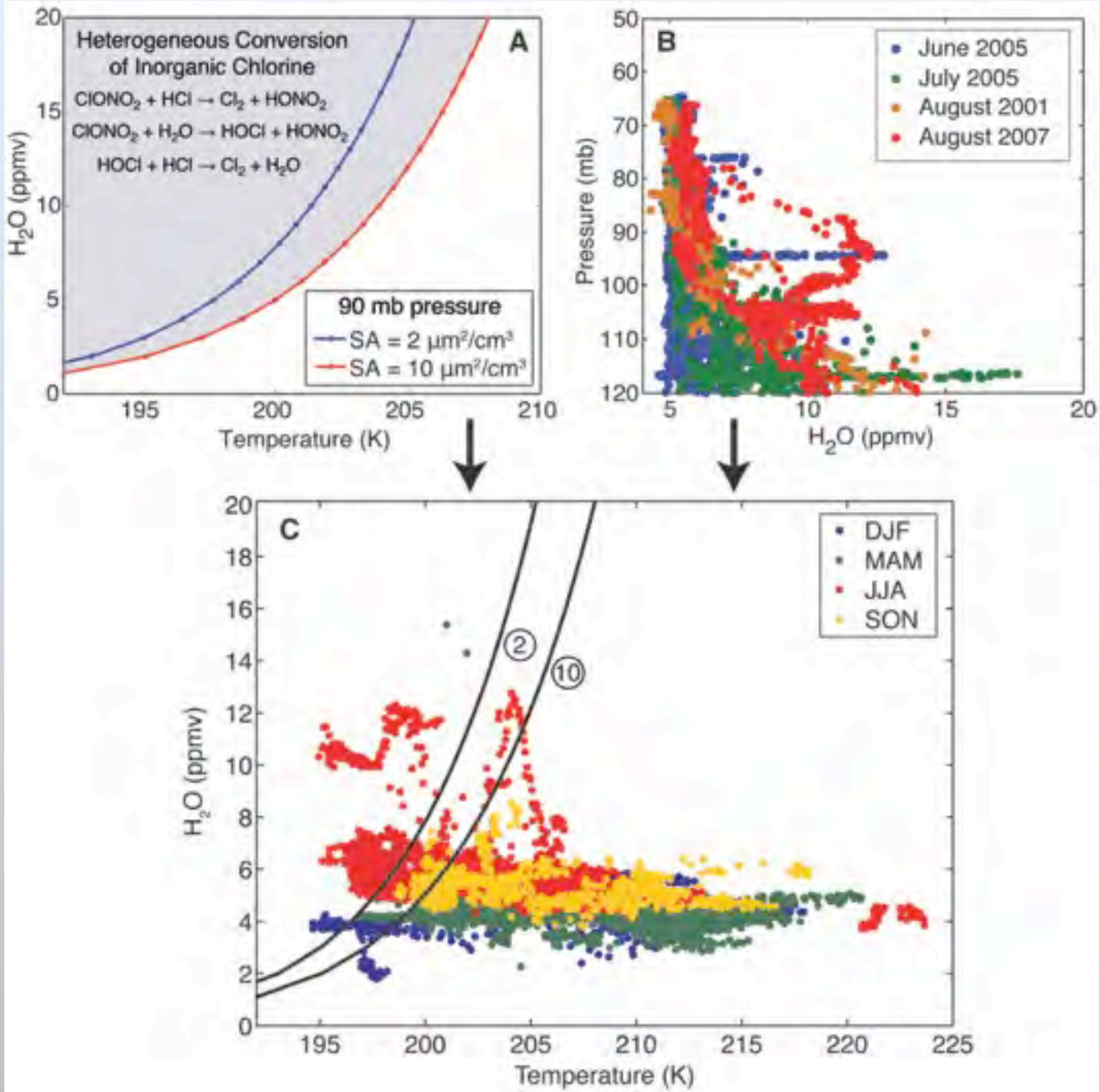
Plumes Observed Over CONUS vs. Pressure Altitude





March 11, 2000
3000
2500
2000
1500
1000
500
0
O_3 (ppt)
1000
500
0
ClO (ppt)
25000 30000 35000 40000 45000 50000 55000 60000
Time (s)

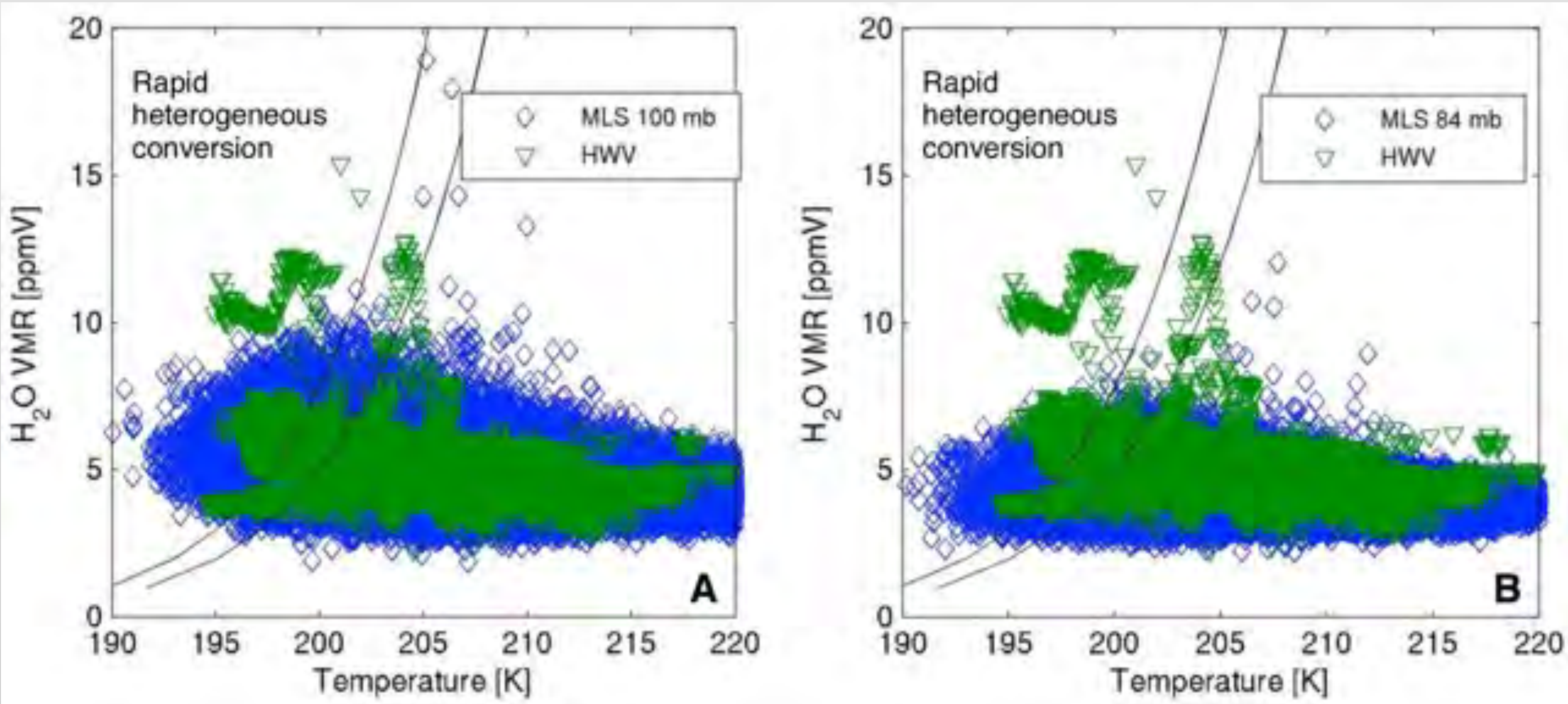

Heterogeneous Conversion of Inorganic Chlorine
$ClONO_2 + HCl \rightarrow Cl_2 + HONO_2$
$ClONO_2 + H_2O \rightarrow HOCl + HONO_2$
$HOCl + HCl \rightarrow Cl_2 + H_2O$
A
90 mb pressure
SA = 2 μm²/cm³
SA = 10 μm²/cm³
H_2O (ppmv)
Temperature (K)
0
5
10
15
20
195
200
205
210



Heterogeneous Conversion of Inorganic Chlorine
$ClONO_2 + HCl \rightarrow Cl_2 + HONO_2$
$ClONO_2 + H_2O \rightarrow HOCl + HONO_2$
$HOCl + HCl \rightarrow Cl_2 + H_2O$
A
90 mb pressure
SA = 2 µm²/cm³
SA = 10 µm²/cm³
H_2O (ppmv)
Temperature (K)
B
June 2005
July 2005
August 2001
August 2007
Pressure (mb)
H_2O (ppmv)
C
DJF
MAM
JJA
SON
2
10
H_2O (ppmv)
Temperature (K)

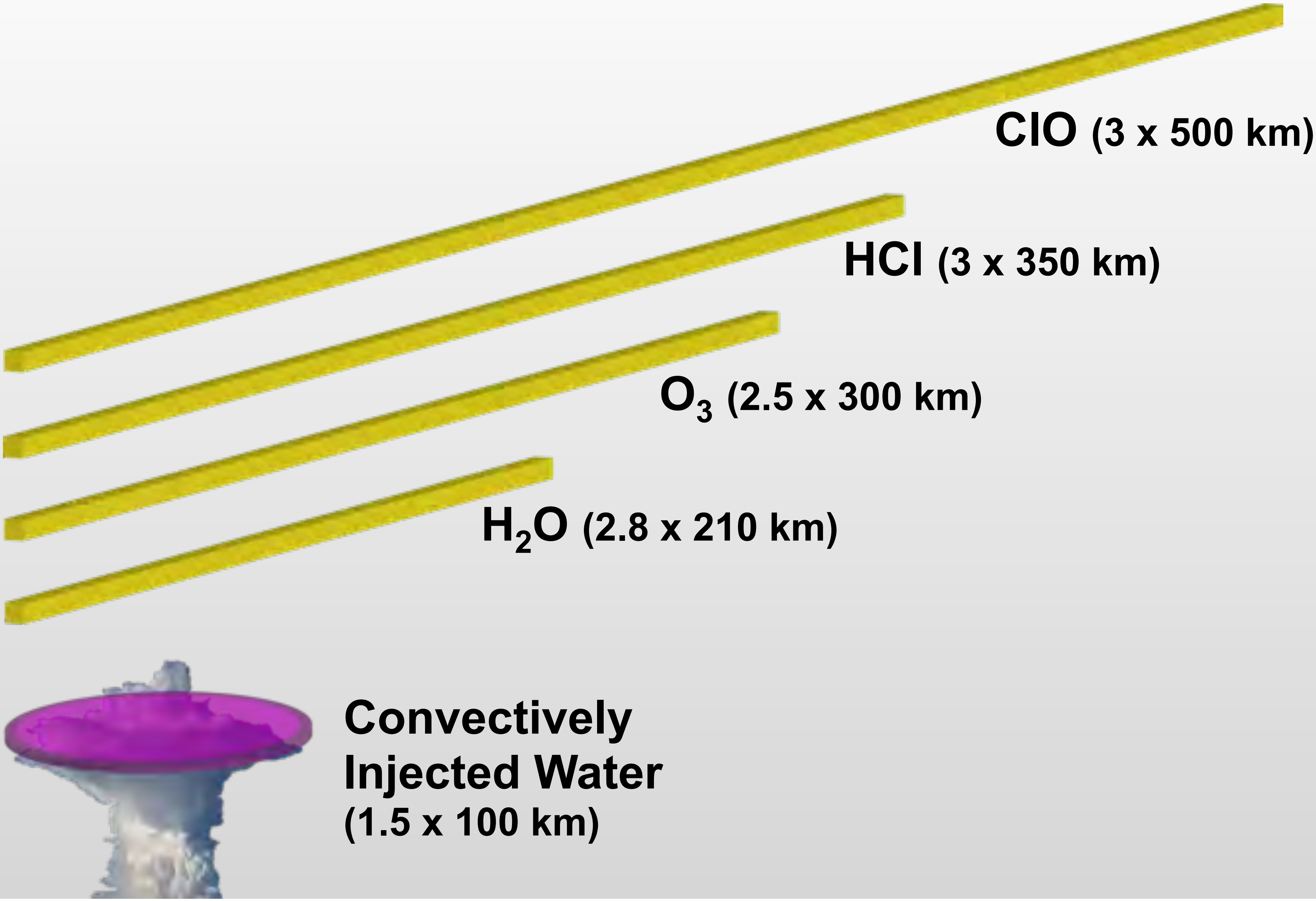
Placed in the Proper Coordinate System:

- What Do the Satellite Data Tell Us?
- MLS Provides the Foundation of the Satellite Data Set



Rapid heterogeneous conversion
MLS 100 mb
HWV
A
MLS 84 mb
B
H_2O VMR [ppmV]
Temperature [K]

Importance of Satellite Spatial Resolution: MLS Case Study at 100 mb

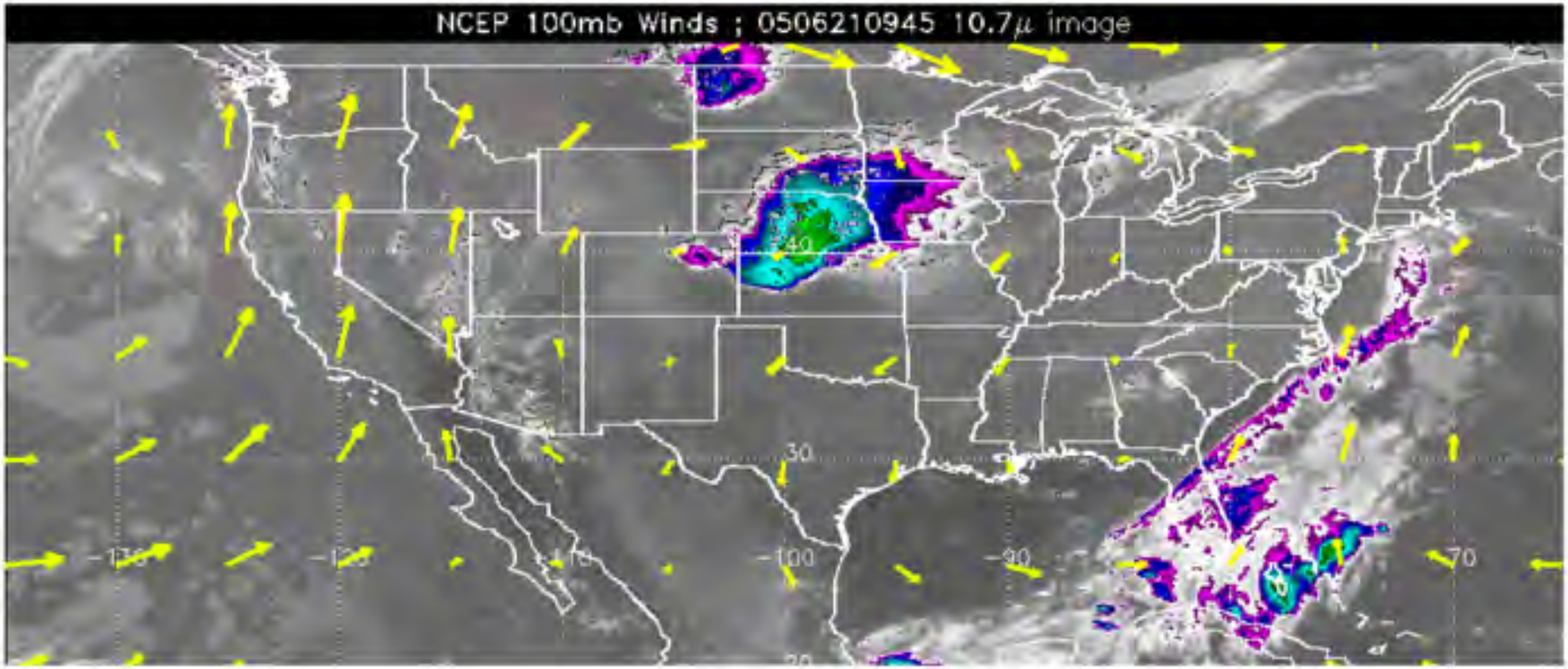


Single Profile Limits of Detection for MLS in a High Water Event 1.5 km x 100 km at 100 mb

Storm Size Relative to MLS Sampling Resolution			Precision	Minimum Δ required for MLS detection
ClO	F = 0.10	(3 x 500km)	100 ppt	1000 ppt
HCl	F = 0.14	(3 x 350km)	300 ppt	2100 ppt
O_3	F = 0.20	(2.5 x 300km)	40 ppb	200 ppb
H_2O	F = 0.26	(2.8 x 210km)	0.7 ppm	2.7 ppm

GOES Storm Image from June 21, 2005

1 – 2 days Prior to Plume Encounter

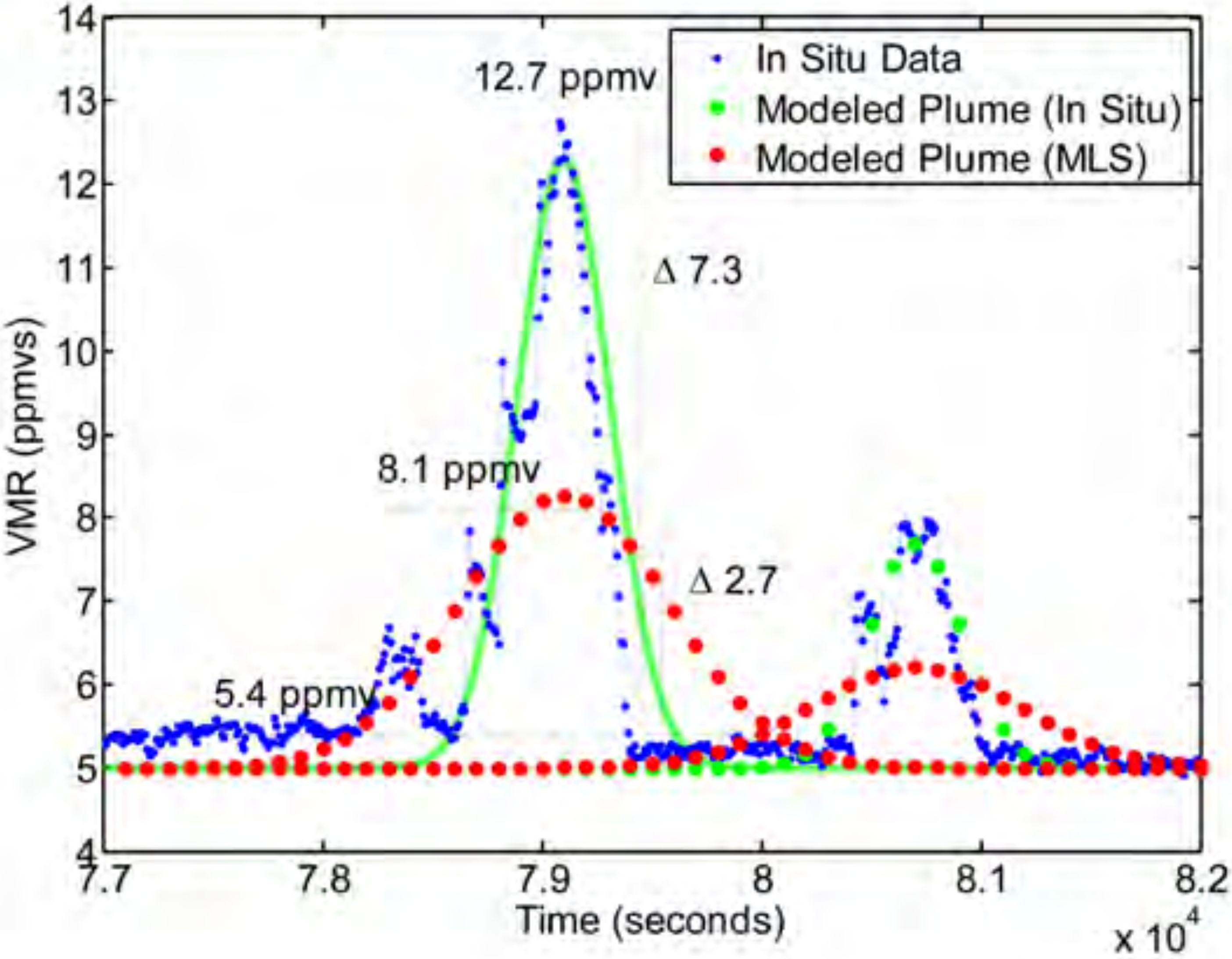


- Storm over region evident in GOES data on **June 21, 2005** at 09:45 GMT = 04:45 CDT
- ~24 hours prior to the first MLS pass and ~36 hours prior to the HWV flight encounter

Screen capture of movie by Lenny Pfister and Marion Legg

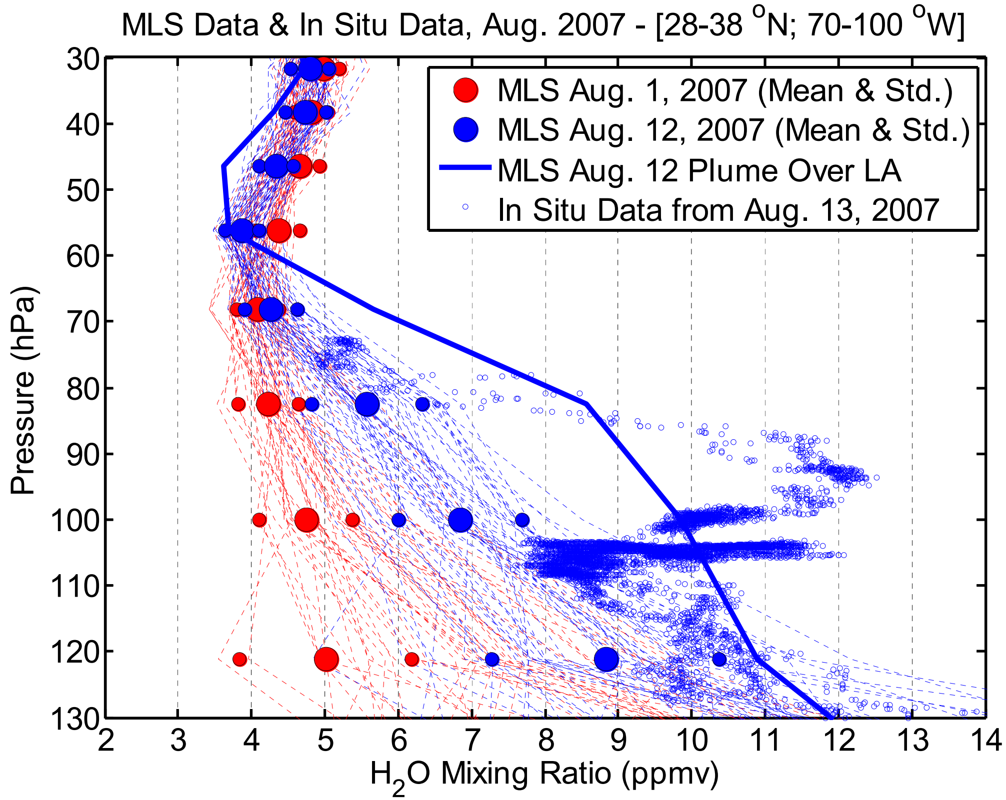
Plume Sampled on June 22, 2005

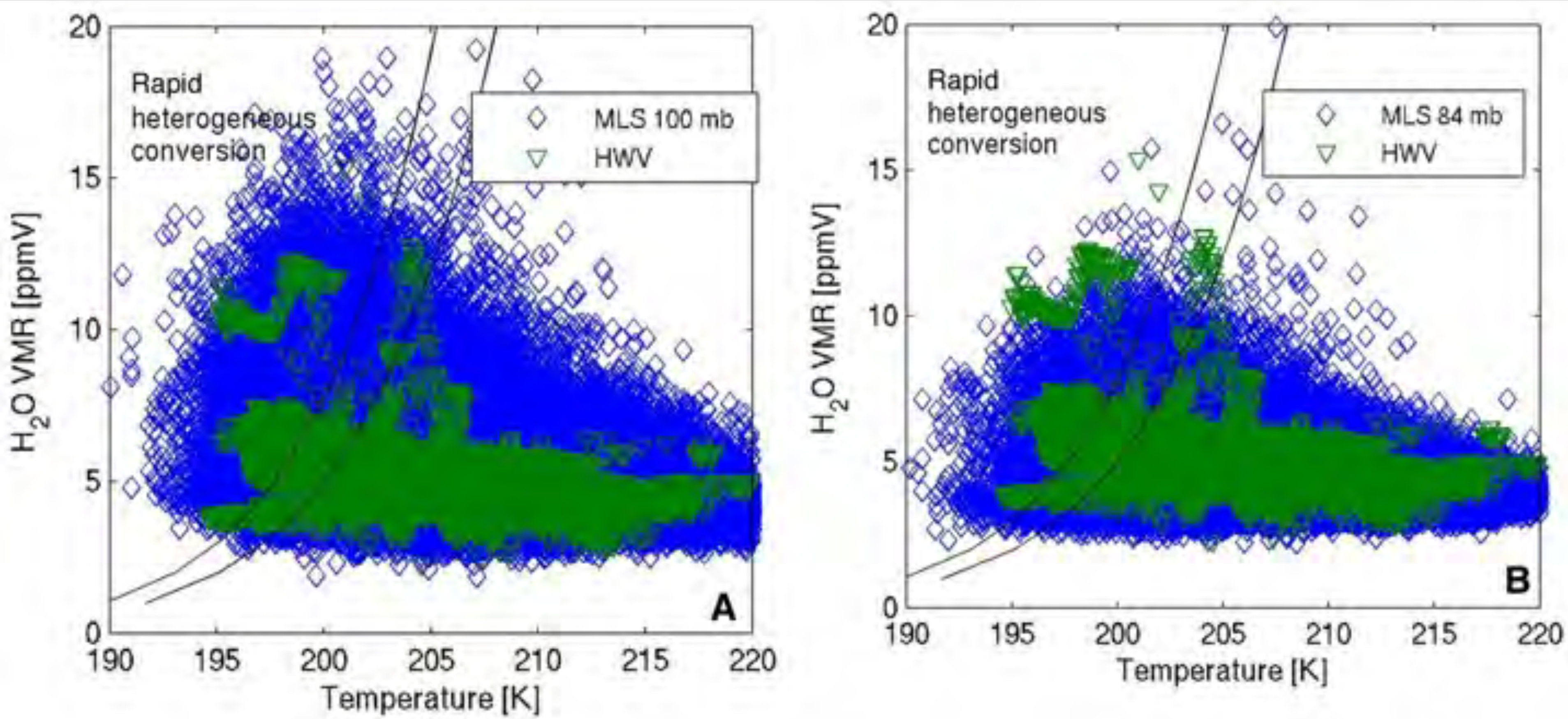
Aircraft Data and Modeled MLS Measurement (200 km Horiz. Res.)



MLS & In Situ Water Vapor Profiles, Aug. 2007

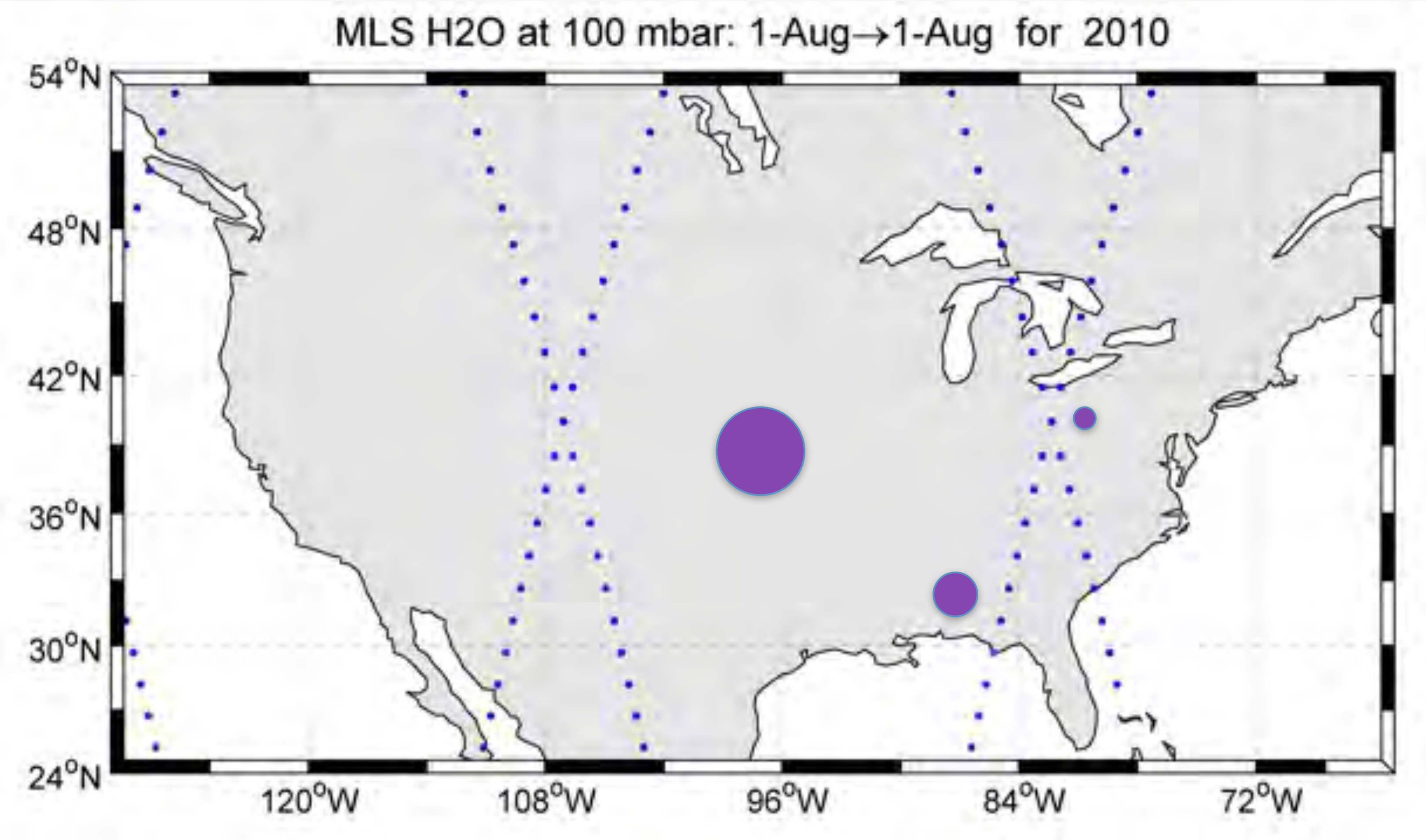
Moistening in Lower Strat., Plume Evident in Both Datasets



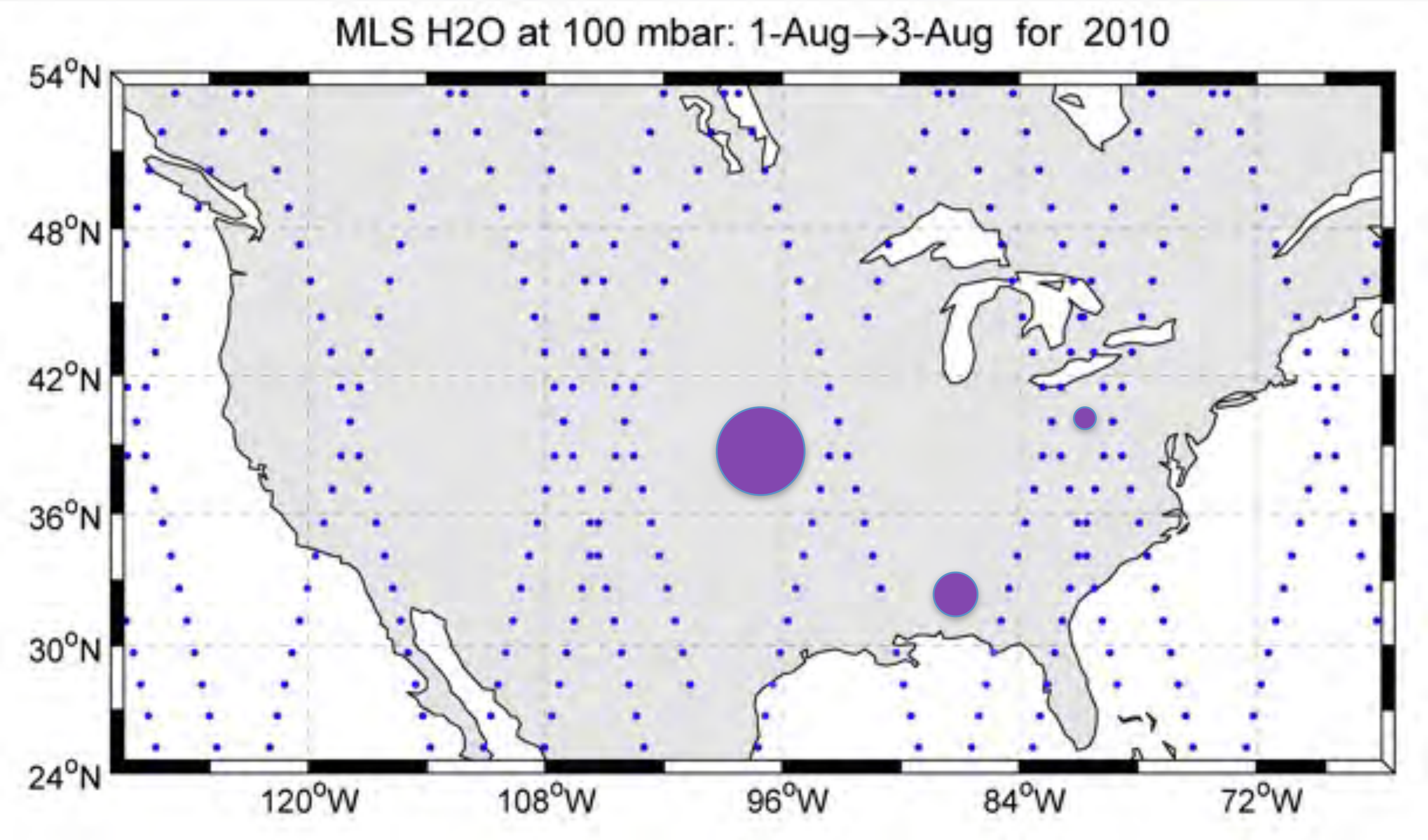


Rapid heterogeneous conversion
MLS 100 mb
HWV
H_2O VMR [ppmV]
Temperature [K]
A
Rapid heterogeneous conversion
MLS 84 mb
HWV
H_2O VMR [ppmV]
Temperature [K]
B

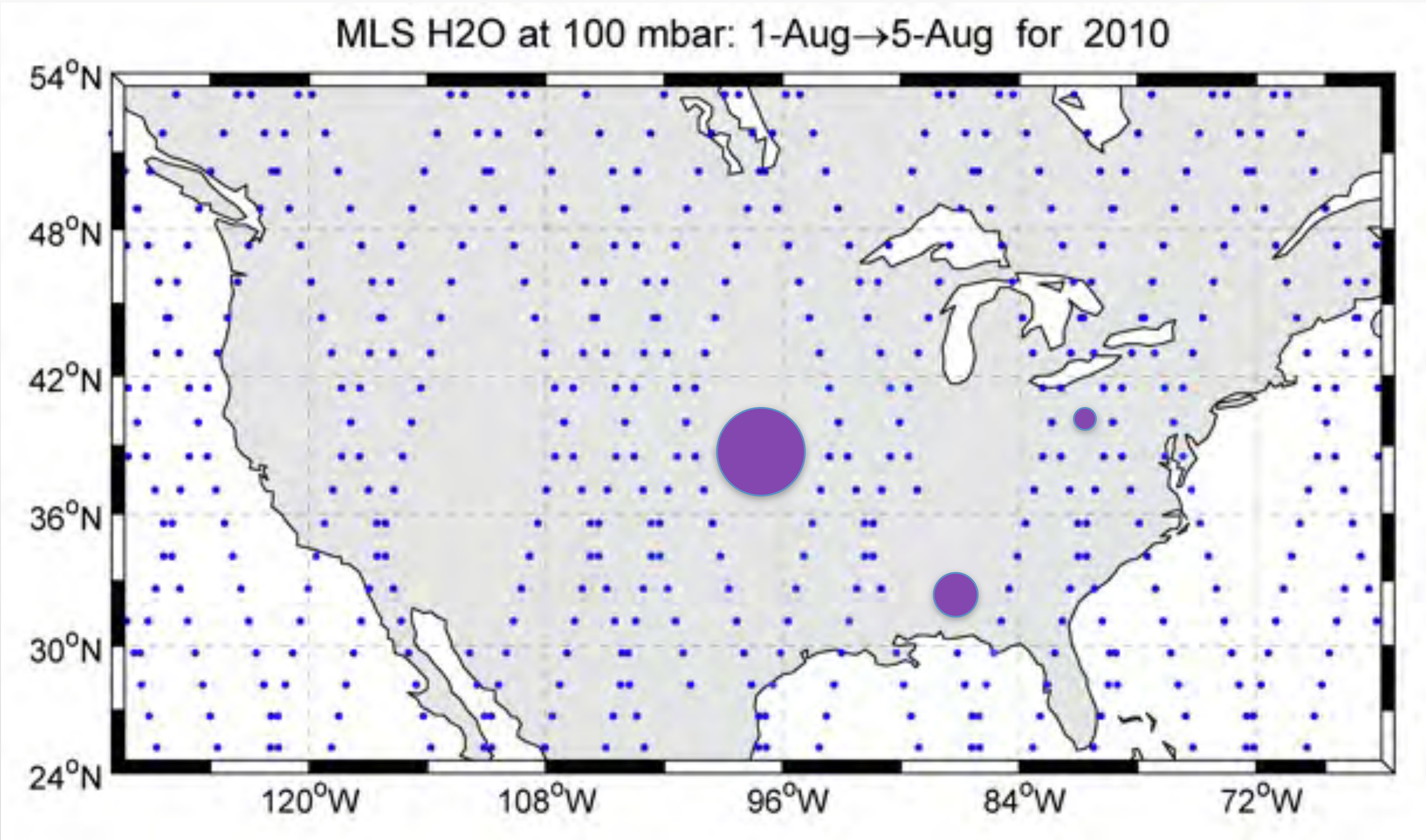
MLS Sampling over the US at 100 mb with Localized High Water Events of 100, 200, & 400 km diameter : 1 day

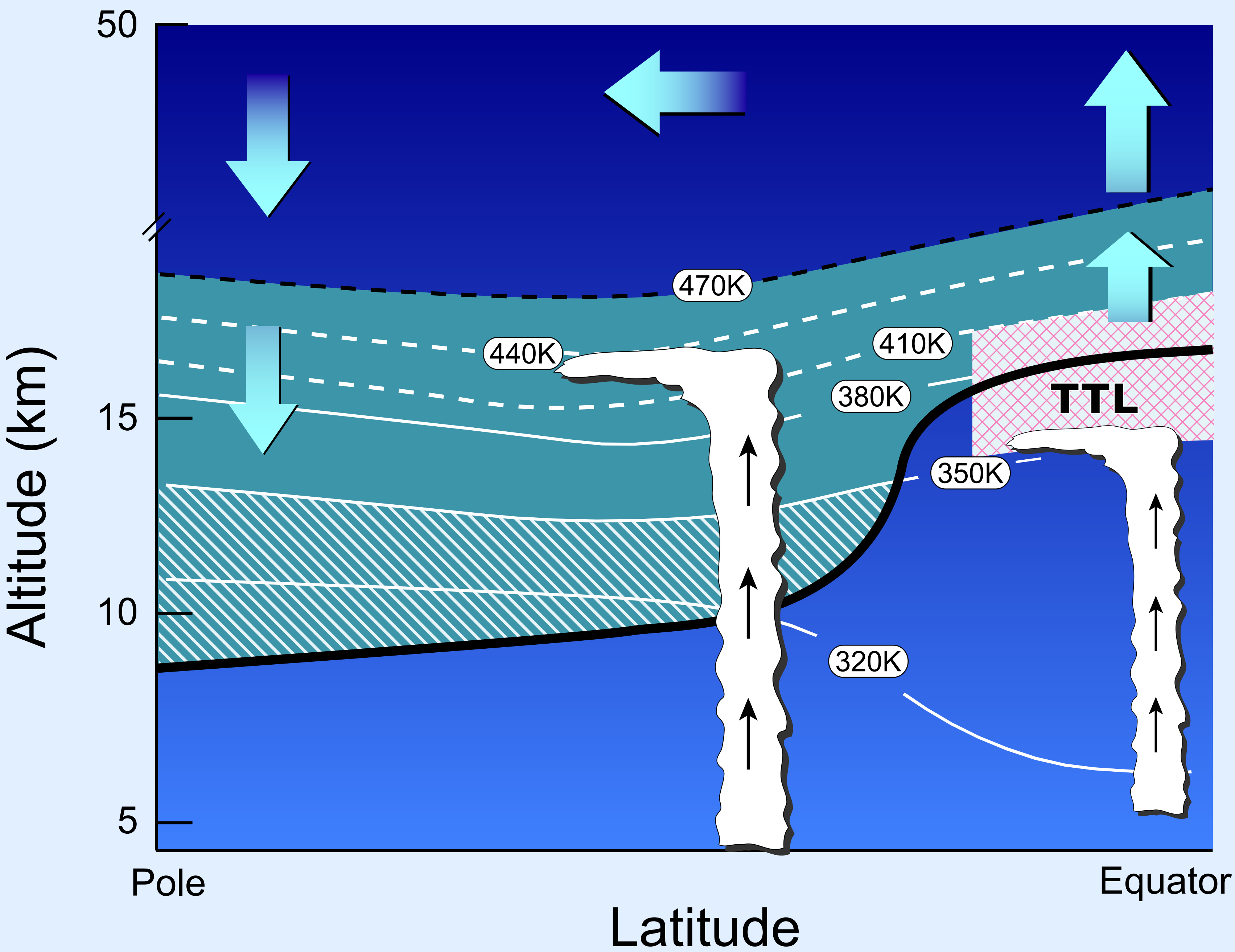


MLS Sampling over the US at 100 mb with Localized High Water Events of 100, 200, & 400 km diameter : 3 day



MLS Sampling over the US at 100 mb with Localized High Water Events of 100, 200, & 400 km diameter : 5 day




50
15
10
5
Altitude (km)
470K
440K
410K
380K
350K
320K
TTL
Pole
Equator
Latitude

Questions:

1. What is the convective physics that can deliver this depth and frequency of injection of water vapor? How will the frequency and intensity of that deep convective injection respond to increased forcing of the climate by CO_2 and CH_4?

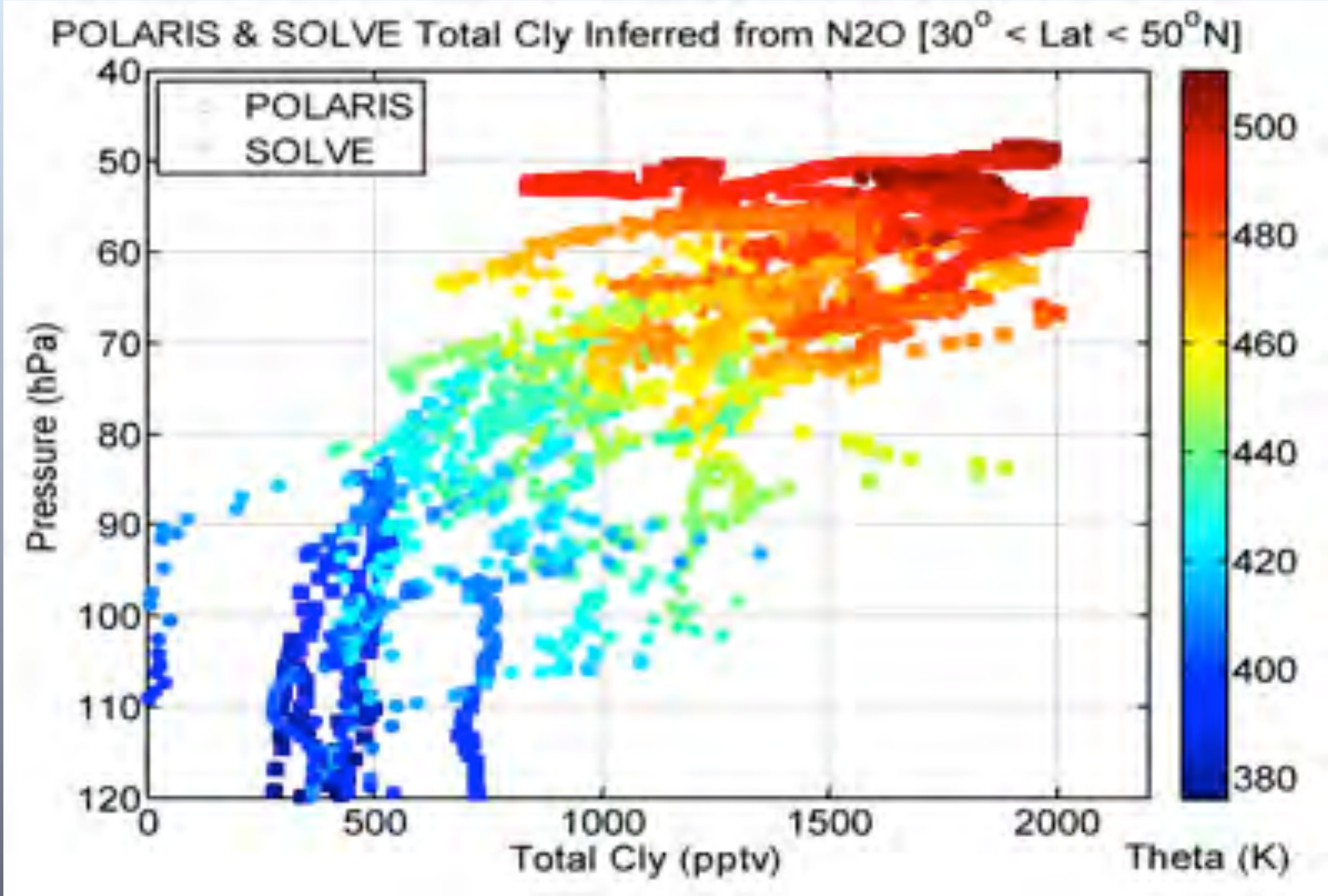
2. How did the stratosphere transition from a climate structure characterized by a very dry stratosphere to that of a moist stratosphere? Mid-latitude convective injection? Methane release?

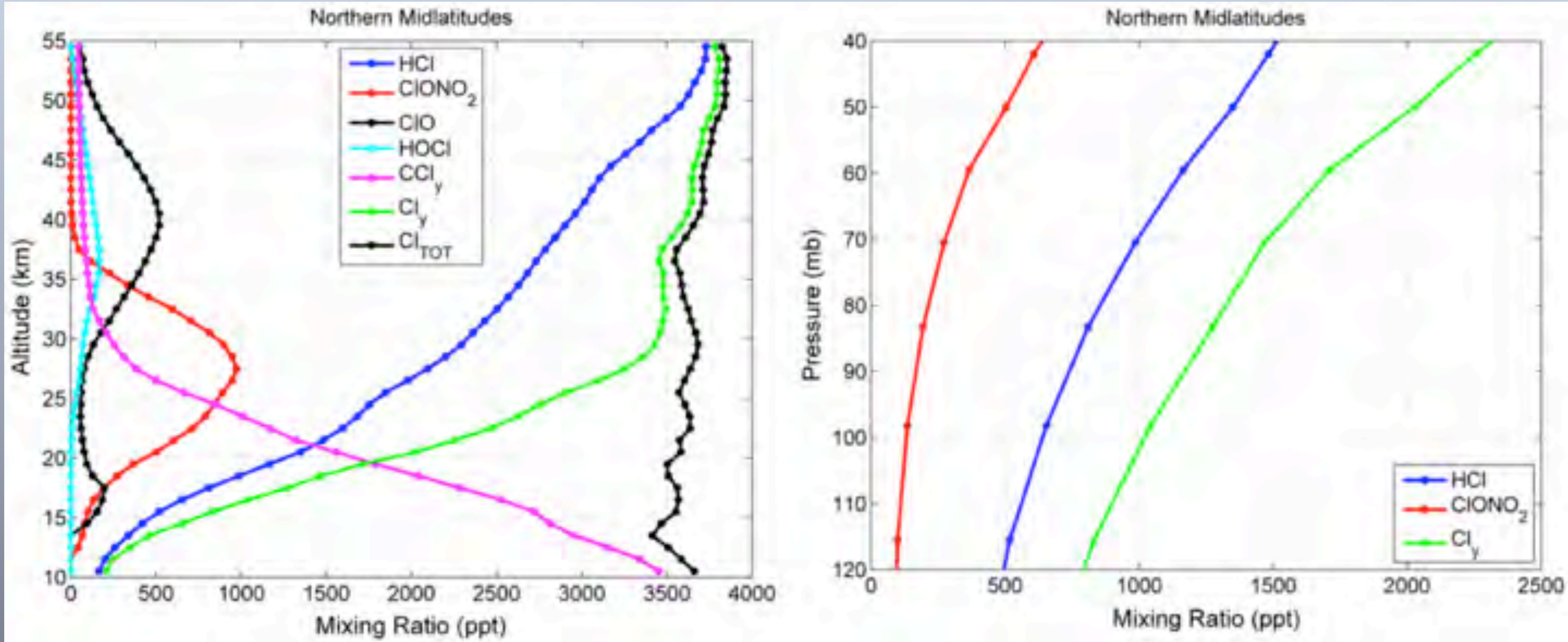
3. Within the domain of convectively injected water vapor, what other source molecules (organic bromines, chlorines, hydrocarbons, heavy metals, etc.) are present in the injected air-mass capable of carrying radical precursors into the stratosphere that could significantly accelerate the catalytic destruction of ozone?

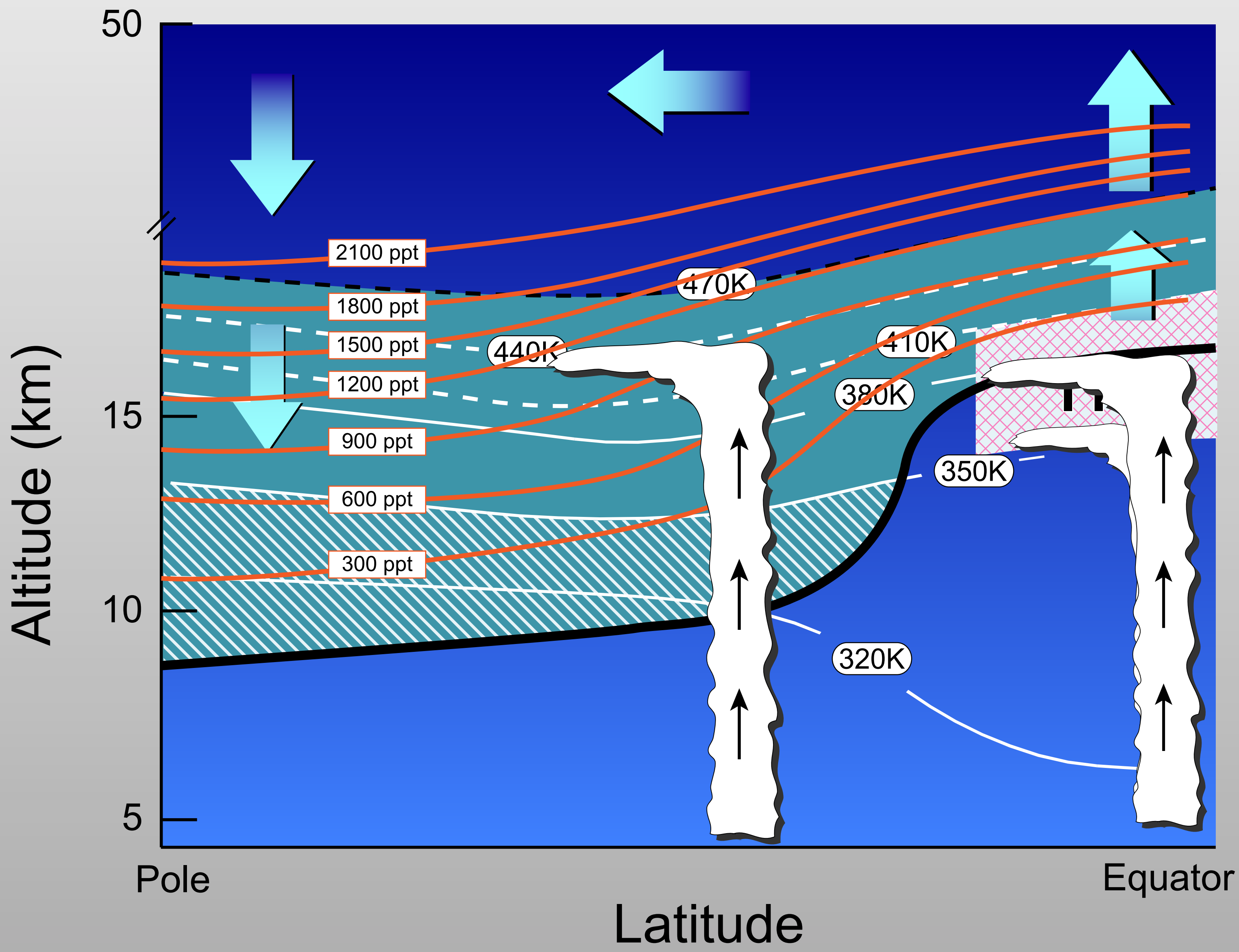
How Does the Catalytic Chemistry of the Summer Lower Stratosphere Respond to Convective Injection of Water Vapor?

29

What is the Distribution of Inorganic Chlorine?

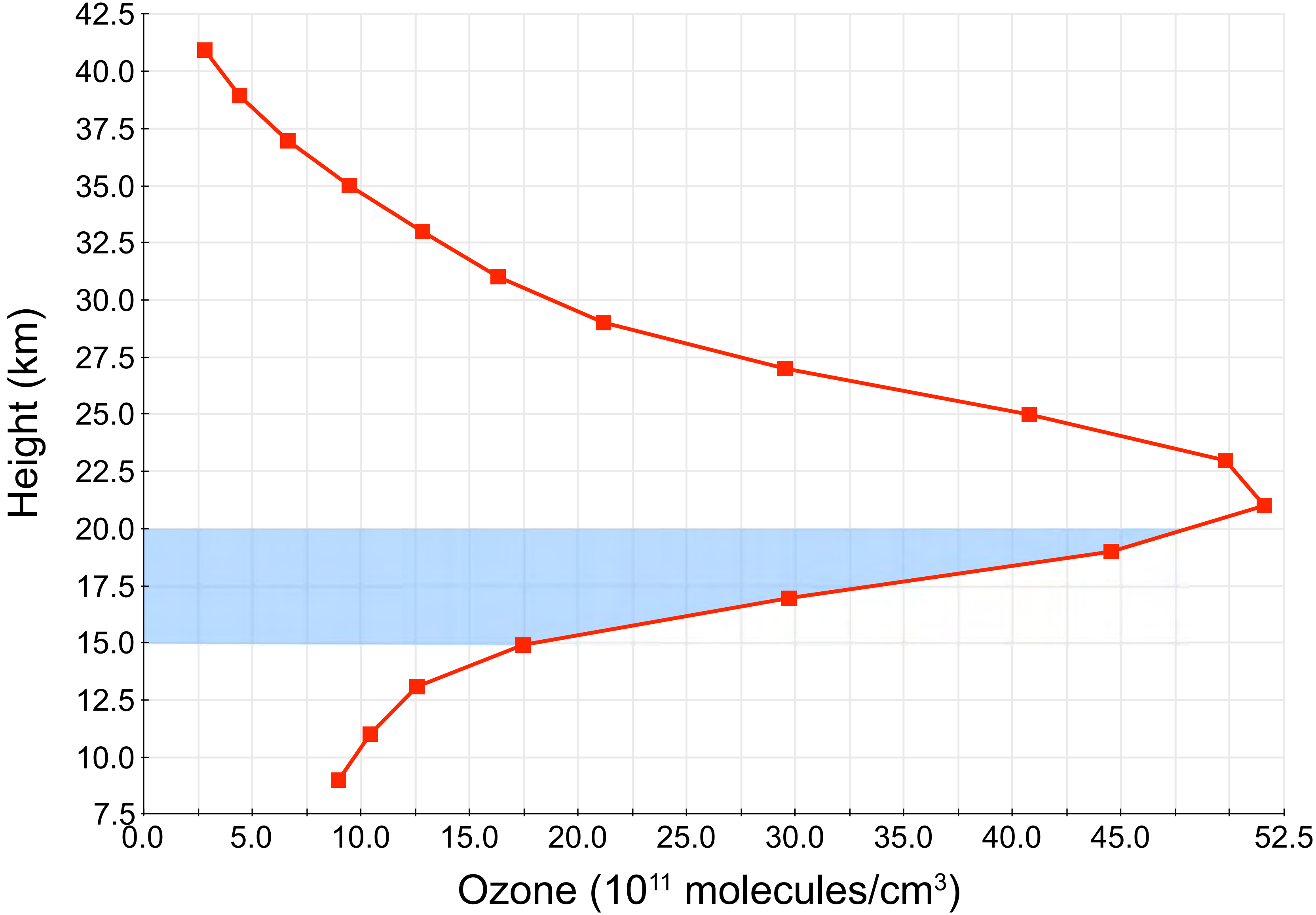

POLARIS & SOLVE Total Cly Inferred from N2O [30° < Lat < 50°N]
POLARIS
SOLVE
Pressure (hPa)
40
50
60
70
80
90
100
110
120
0
500
1000
1500
2000
Total Cly (pptv)
500
480
460
440
420
400
380
Theta (K)

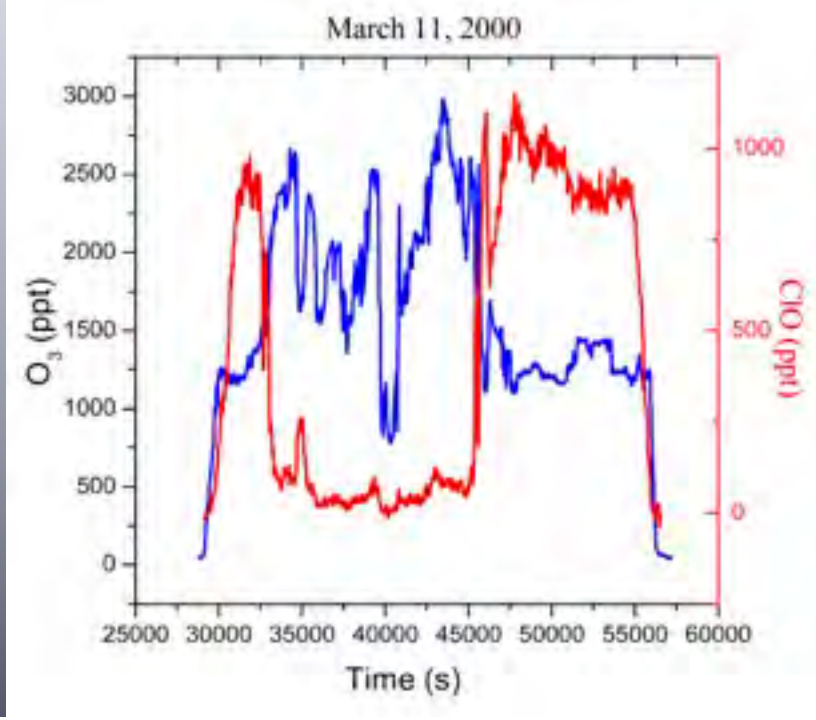

Northern Midlatitudes
HCl
ClONO2
ClO
HOCl
CCly
Cly
ClTOT
Altitude (km)
Mixing Ratio (ppt)
Northern Midlatitudes
Pressure (mb)
Mixing Ratio (ppt)
HCl
ClONO2
Cly

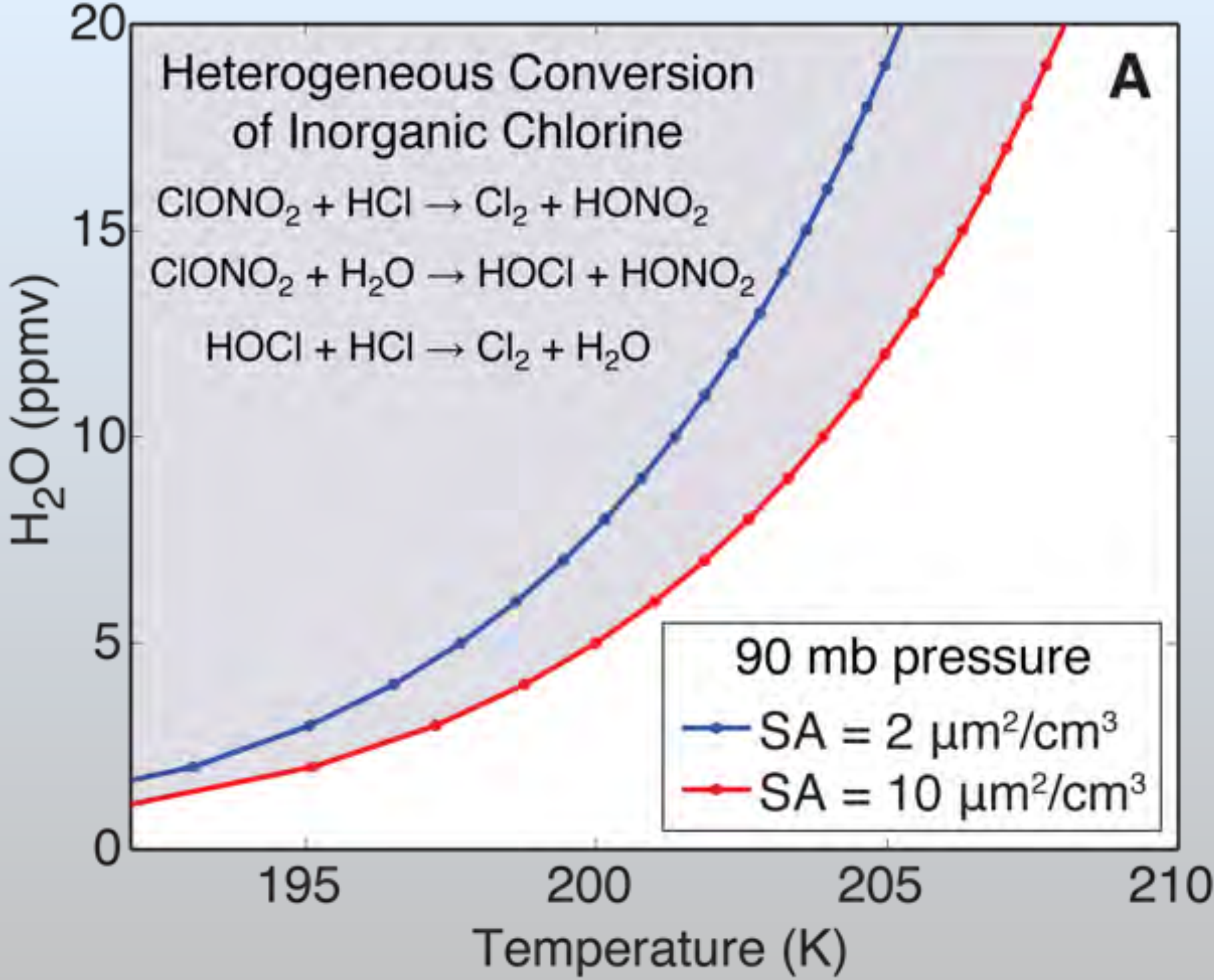


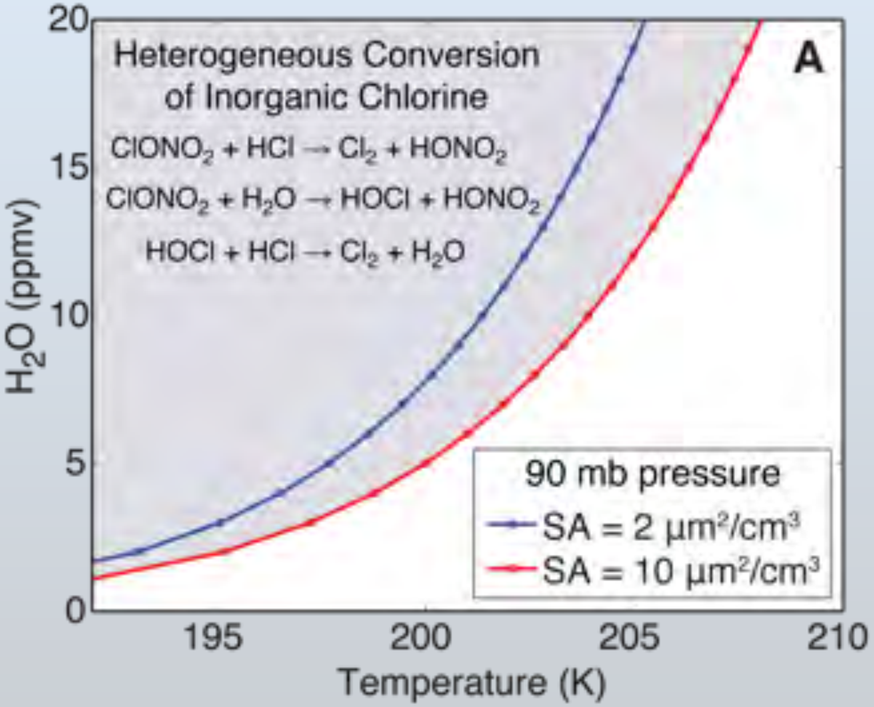
Altitude (km)
50
15
10
5
2100 ppt
1800 ppt
1500 ppt
1200 ppt
900 ppt
600 ppt
300 ppt
470K
440K
410K
380K
350K
320K
Pole
Equator
Latitude

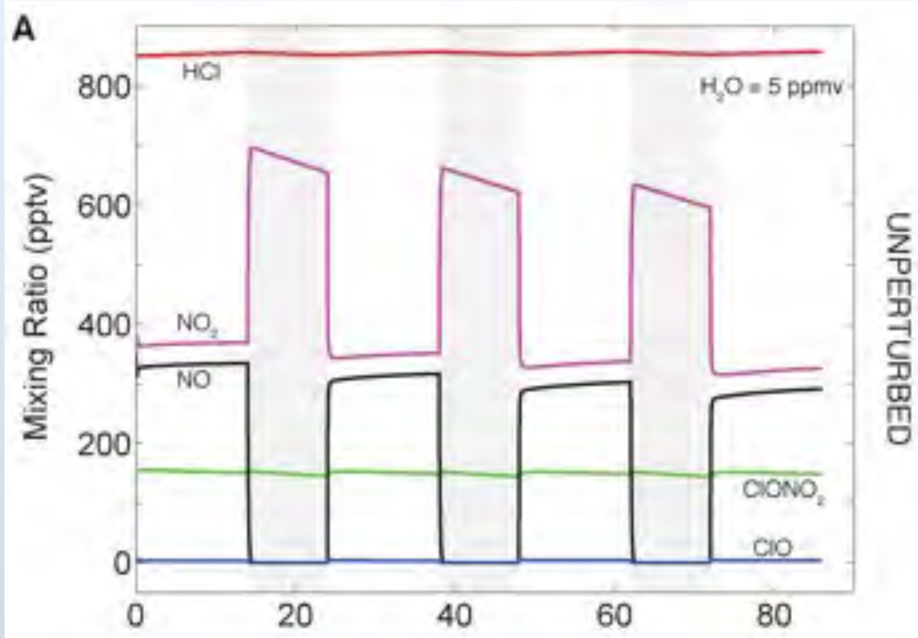
Ozone Profile at Raleigh, NC on 2012-07-04

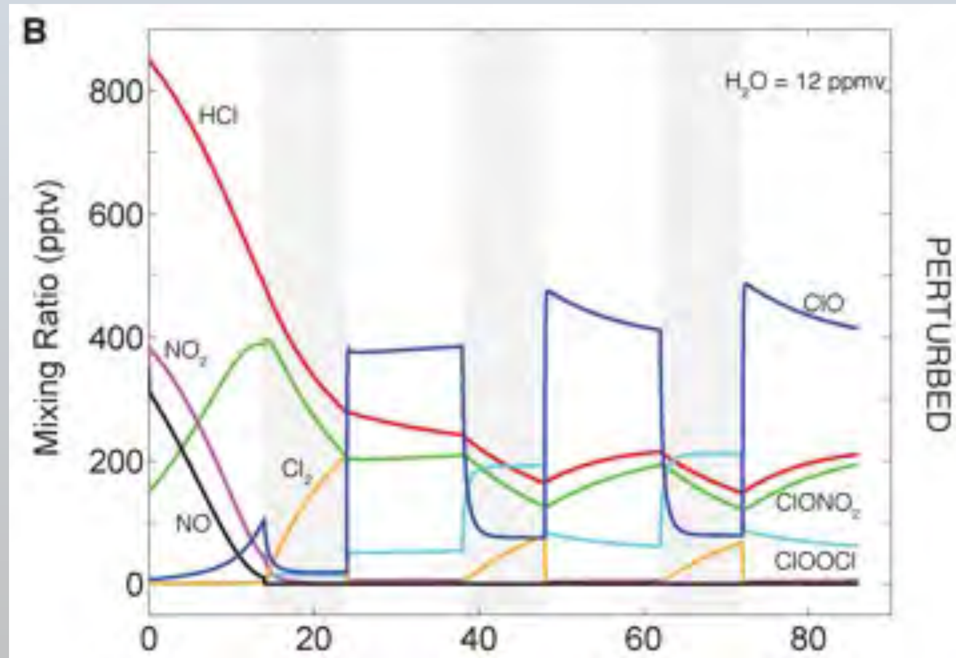


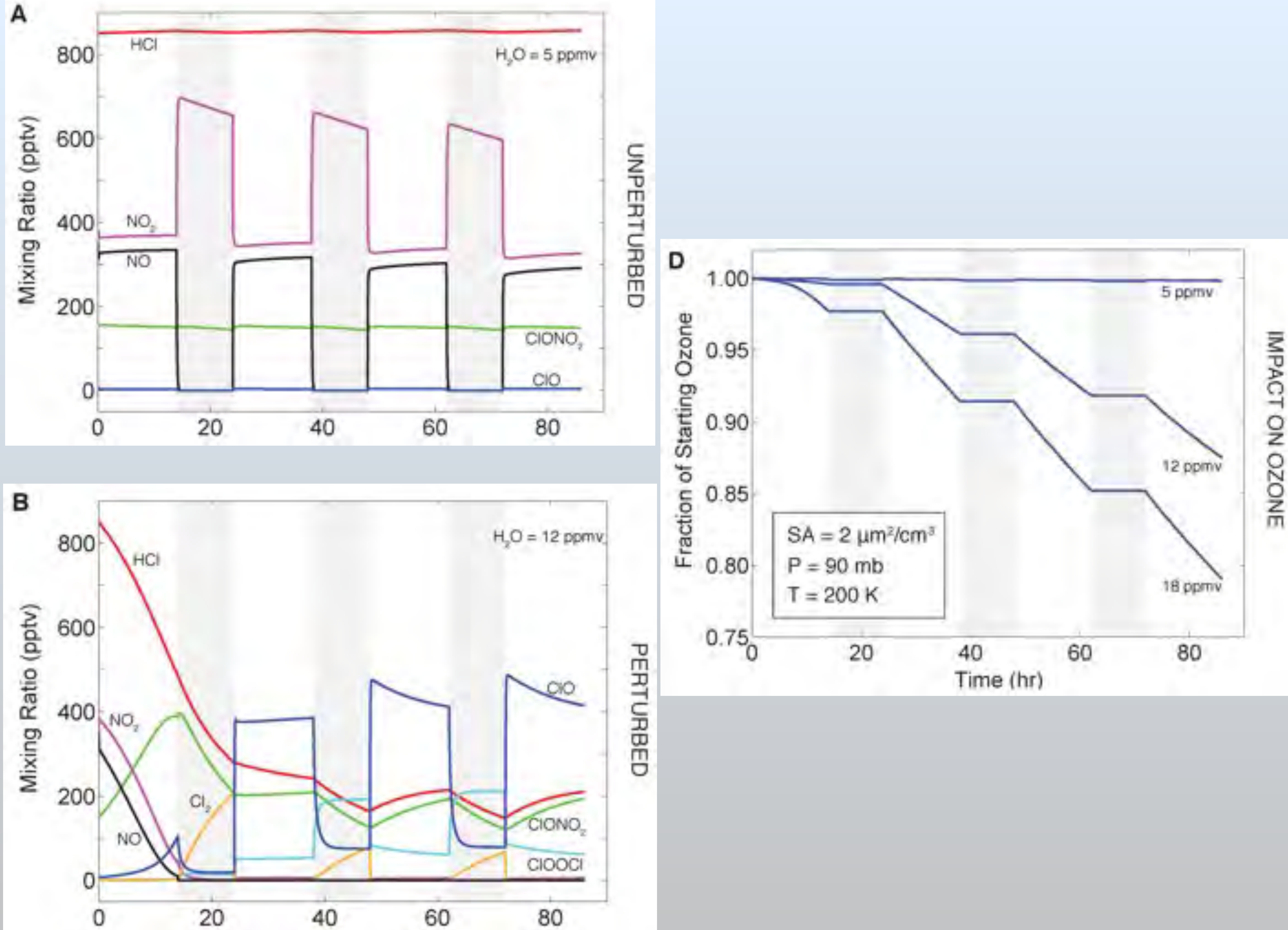

March 11, 2000
O_3 (ppt)
ClO (ppt)
Time (s)
3000
2500
2000
1500
1000
500
0
1000
500
0
25000 30000 35000 40000 45000 50000 55000 60000

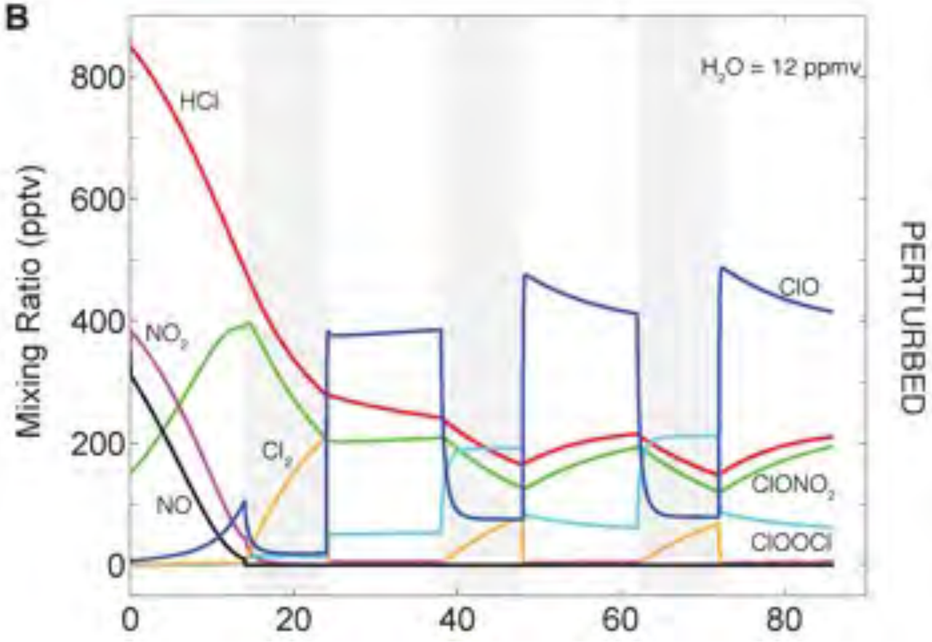

Heterogeneous Conversion
of Inorganic Chlorine
$ClONO_2 + HCl \rightarrow Cl_2 + HONO_2$
$ClONO_2 + H_2O \rightarrow HOCl + HONO_2$
$HOCl + HCl \rightarrow Cl_2 + H_2O$
A
90 mb pressure
SA = 2 μm²/cm³
SA = 10 μm²/cm³
H_2O (ppmv)
0
5
10
15
20
195
200
205
210
Temperature (K)

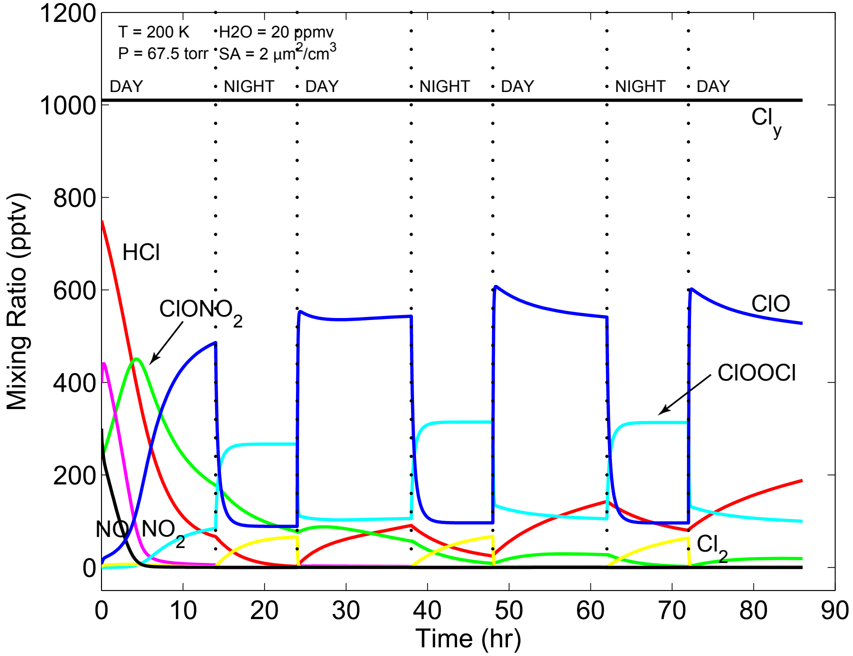

Heterogeneous Conversion of Inorganic Chlorine
$ClONO_2 + HCl \rightarrow Cl_2 + HONO_2$
$ClONO_2 + H_2O \rightarrow HOCl + HONO_2$
$HOCl + HCl \rightarrow Cl_2 + H_2O$
A
90 mb pressure
SA = 2 μm²/cm³
SA = 10 μm²/cm³
H_2O (ppmv)
Temperature (K)
0
5
10
15
20
195
200
205
210

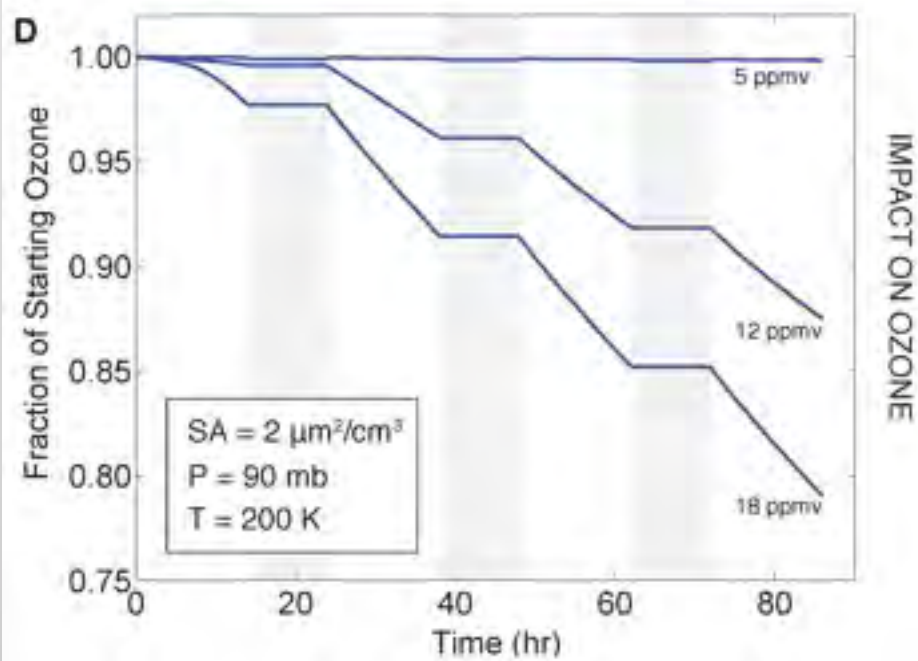

A
HCl
H_2O = 5 ppmv
NO_2
NO
$ClONO_2$
ClO
UNPERTURBED
Mixing Ratio (pptv)
0
200
400
600
800
0
20
40
60
80

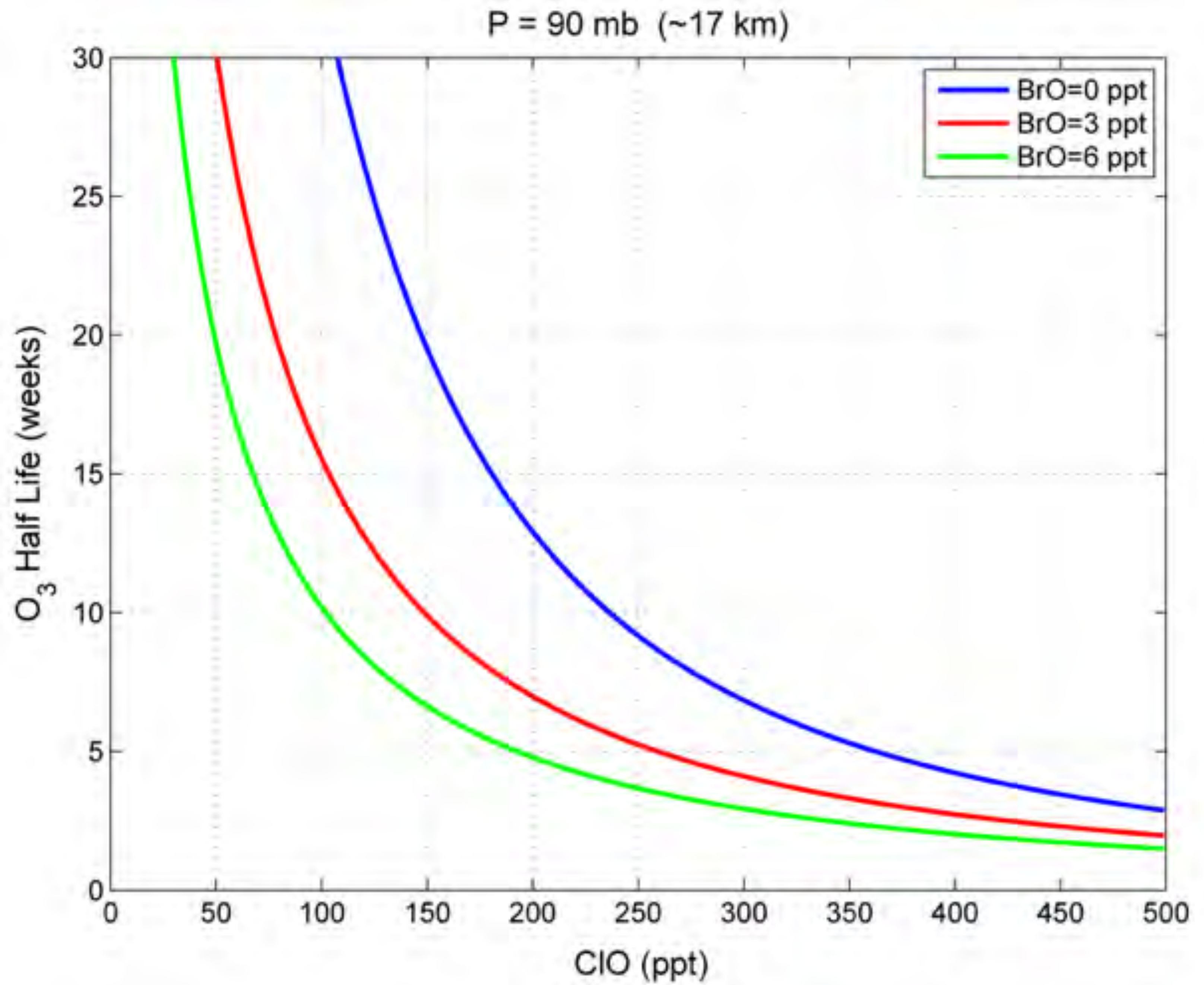

B
H_2O = 12 ppmv
HCl
NO_2
NO
Cl_2
ClO
$ClONO_2$
ClOOCl
PERTURBED
Mixing Ratio (pptv)
0
200
400
600
800
0
20
40
60
80


A
HCl
H2O = 5 ppmv
NO2
NO
ClONO2
ClO
Mixing Ratio (pptv)
UNPERTURBED
B
H2O = 12 ppmv
HCl
NO2
NO
Cl2
ClO
ClONO2
ClOOCl
Mixing Ratio (pptv)
PERTURBED
D
5 ppmv
12 ppmv
18 ppmv
SA = 2 μm²/cm³
P = 90 mb
T = 200 K
Fraction of Starting Ozone
Time (hr)
IMPACT ON OZONE


B
H$_2$O = 12 ppmv
PERTURBED
Mixing Ratio (pptv)
HCl
NO$_2$
NO
Cl$_2$
ClO
ClONO$_2$
ClOOCl
0
200
400
600
800
0
20
40
60
80

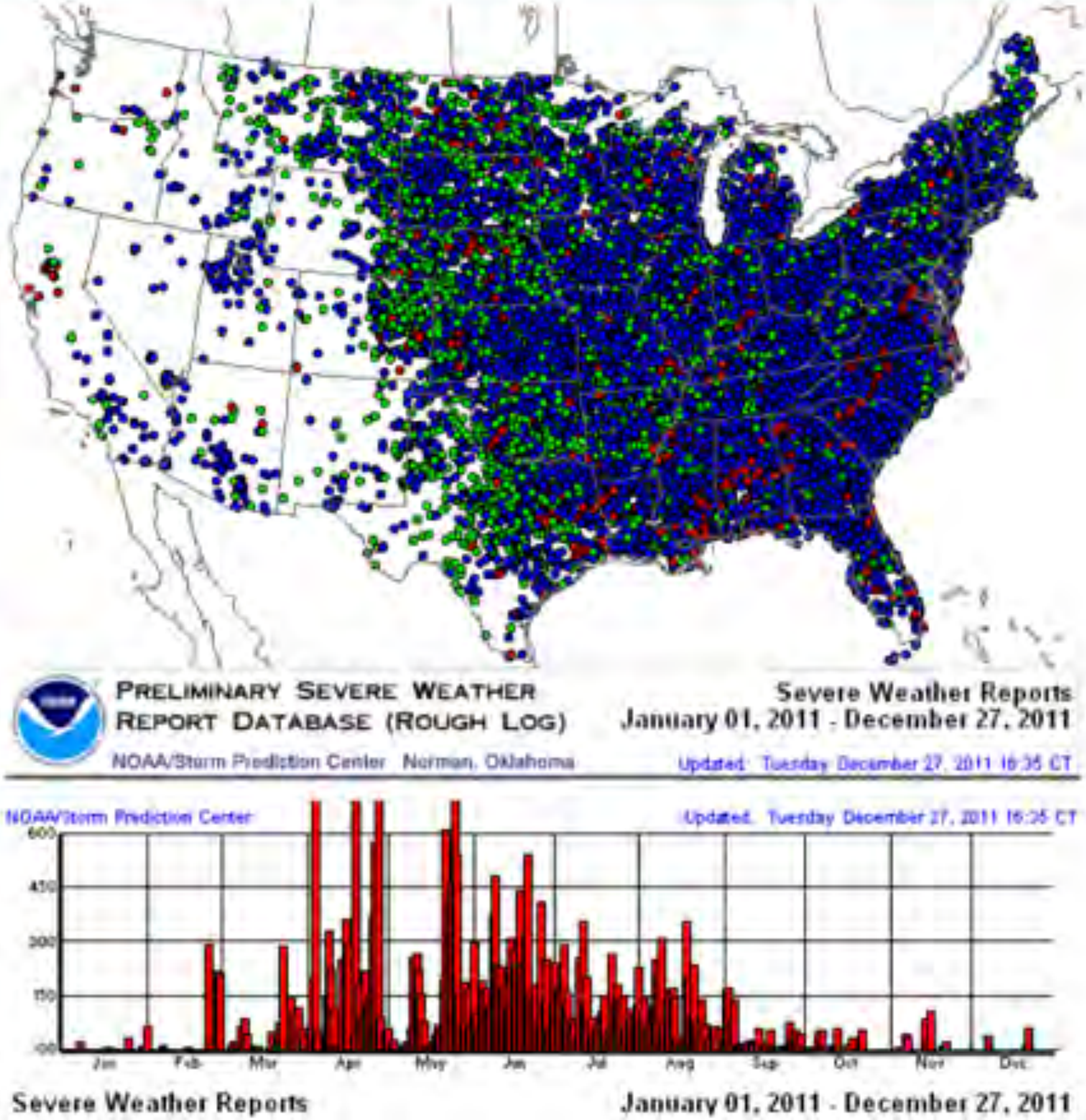

T = 200 K
P = 67.5 torr
H2O = 20 ppmv
SA = 2 μm^2/cm^3
DAY
NIGHT
DAY
NIGHT
DAY
NIGHT
DAY
Cl$_y$
HCl
ClONO$_2$
ClO
ClOOCl
NO
NO$_2$
Cl$_2$
Mixing Ratio (pptv)
Time (hr)
0
200
400
600
800
1000
1200
0
10
20
30
40
50
60
70
80
90


D
IMPACT ON OZONE
Fraction of Starting Ozone
5 ppmv
12 ppmv
18 ppmv
SA = 2 μm^2/cm^3
P = 90 mb
T = 200 K
Time (hr)
0.75
0.80
0.85
0.90
0.95
1.00
0
20
40
60
80


P = 90 mb (~17 km)
BrO=0 ppt
BrO=3 ppt
BrO=6 ppt
O3 Half Life (weeks)
ClO (ppt)
0
5
10
15
20
25
30
0
50
100
150
200
250
300
350
400
450
500

NOAA Severe Weather Report – Summary 2011

Green – Hail; Blue – Wind; Red – Tornados



Conclusions

- Conversion of inorganic chlorine to free radical form is extraordinarily sensitive to convective injection of H_2O over NH mid-latitudes in summer.
- There is clear evidence from both *in situ* and satellite observations for frequent injection of H_2O at temperatures required for rapid catalytic conversion of inorganic chlorine to free radical form over the US in summer.
- Given the steep gradient in inorganic chlorine (Cly) with respect to altitude and latitude in the domain of convective injection, increases in convective intensity have significant consequences.

Conclusions (cont.)

- Given the steep gradient in Cly with respect to latitude, any poleward shift in convective injection has significant consequences.
- Incomplete quantitative analysis of the catalytic chemistry and dynamics of the NH mid-latitude lower stratosphere has come back to haunt us.
- The fundamental elements of this link between climate forcing and ozone loss establishes the irreversible nature of this problem.
- Because ozone is transport controlled in the lower stratosphere, and because of the resulting large natural variability in ozone, the only way to separate catalytic loss of ozone from transport is by the simultaneous *in situ* observation of the covariance between the rate limiting radicals and ozone.

Linking Issues

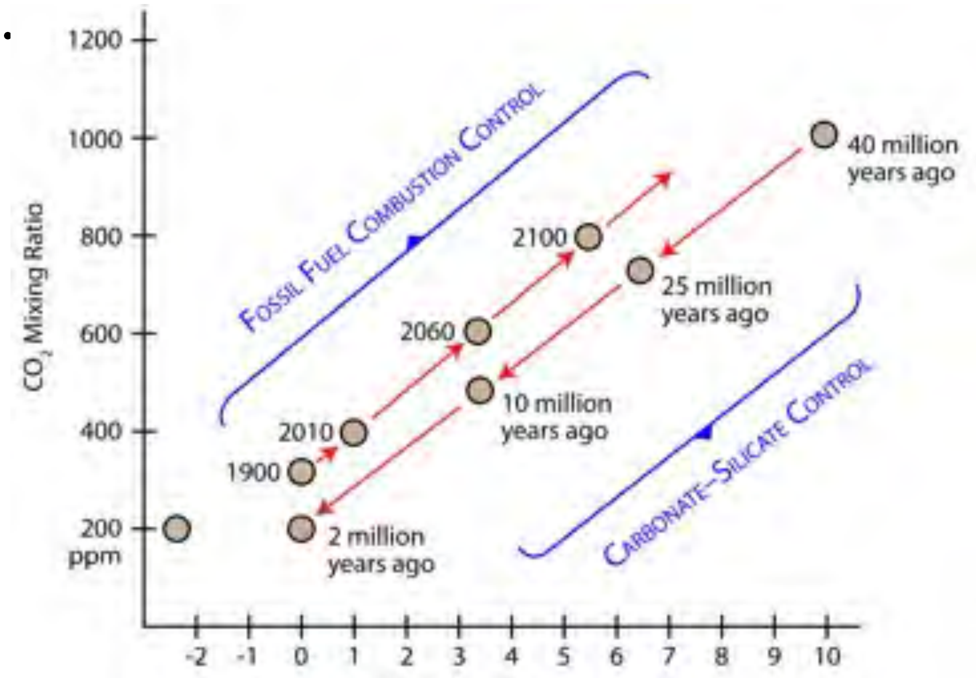
- The relationship between ozone column loss and skin cancer incidence involves both an optical amplification factor and a biological amplification factor: result is x 2-3 fractional increase in skin cancer.

- The idea that because we have controlled the rate of release of CFCs and halons we can assume ozone “recovery” will occur ignores the potential climate coupling through enhanced convective injection, radiative cooling of the lower stratosphere from water and CO_2, and the crucial role of bromine catalysis.

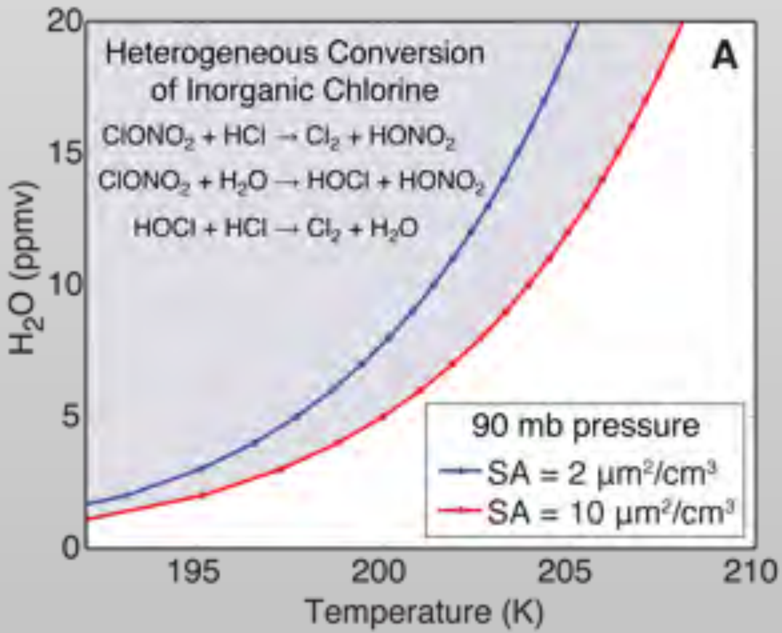
- With the loss of Arctic Floating Ice, the widening melt zones of the Arctic basin will release carbon from both clathrates and permafrost: 0.5%/yr release rate equals the 8GtC/yr carbon release rate from all

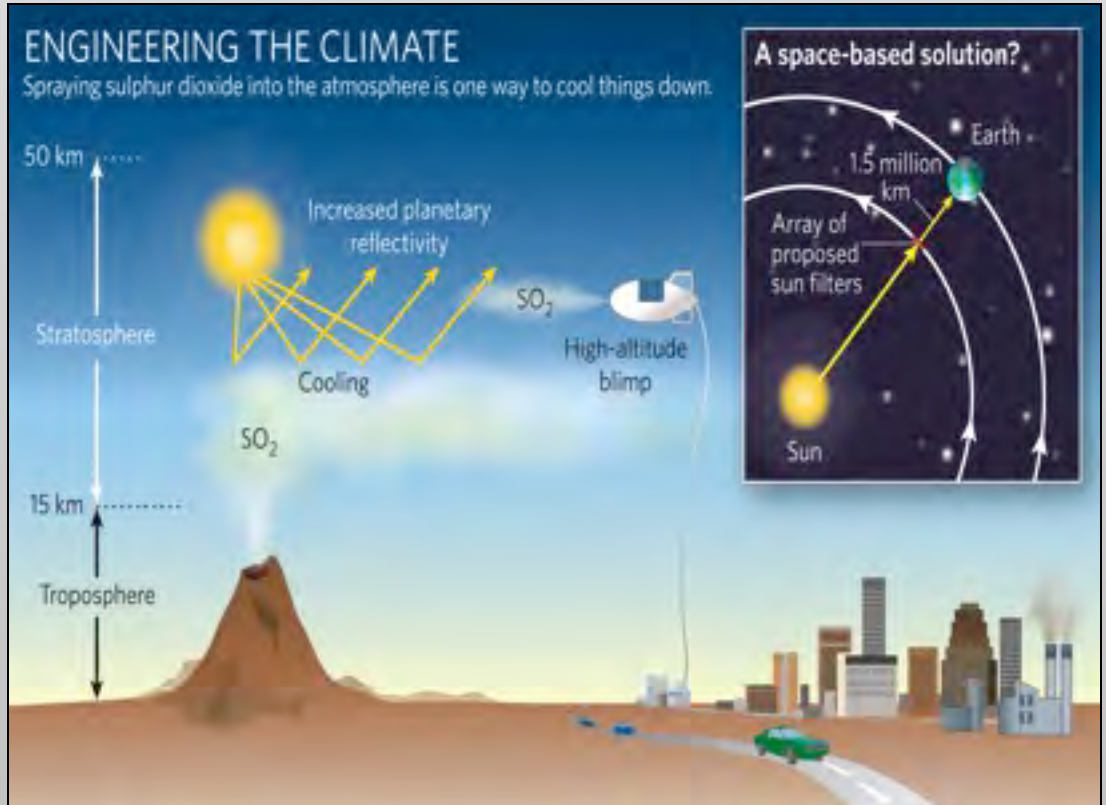
Linking Issues (cont.)

- Paleo-record: The very dry stratosphere of today is a climate state that may well not have been the case in the Eocene. It may well be that the only quantitatively viable way of flattening the equator-to-pole temperature gradient is through downwelling thermal radiation from PSCs/aerosols from a stratosphere with elevated water vapor concentrations.



- Finally, the current formulation of climate engineering (aka SRM) involves the direct injection of sulfuric acid vapor; this will significantly increase the reactive surface area of the cold binary aerosols and accelerate the heterogeneous processing.





Questions:

1. How rapidly is ClO converted back to HCl and $ClONO_2$ in the summertime lower stratosphere at mid-latitudes?
2. What is the quantitative role of BrO in the time integrated removal of ozone?
3. How rapidly does NO_x recover?
4. How rapidly does the lower stratosphere cool in the presence of elevated water vapor concentrations?
5. What are the implications of increasing convective injection of water vapor into a stratosphere with elevated sulfate concentration from, for example, volcanoes?
6. What are the implications for Solar Radiation Management (SRM) strategies using sulfate injection for decreasing the shortwave forcing of the Earth's climate system?

END