Airborne Observations of Oxidation During NOMADSS

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Atmospheric oxidation is a key phenomenon that connects atmospheric chemistry with globally challenging environmental issues such as climate change, stratospheric ozone loss, acidification of soils and water, and health effects of air quality.

The Nitrogen, Oxidants, Mercury and Aerosol Distributions, Sources and Sinks (NOMADSS) project integrates three proposed studies: the Southern Oxidant and Aerosol Study (SOAS), the North American Airborne Mercury Experiment (NAAMEX), and the TROPospheric HONO (TROPHONO)

SUOMI – SUlfuric OH and MSA Instrument

Hydroxyl (OH) – Primary oxidant in the Earth's atmosphere
Sulfuric Acid (H_2SO_4) – Oxidation product of SO_2. Important in aerosol formation and growth
Methane Sulfonic Acid (MSA) – Oxidation product of dimethyl sulfide (DMS)

Utilizes Nitrate Chemical Ionization – Mass Spectrometry

OH is measured by first converting it to $H_2{}^{34}SO_4$ via:

$$OH + {}^{34}SO_2 \rightarrow H^{34}SO_3$$

$$H^{34}SO_3 + O_2 \rightarrow {}^{34}SO_3 + HO_2$$

$$^{34}SO_3 + 2H_2O \rightarrow H_2{}^{34}SO_4 + H_2O$$

^{34}S is used to discriminate between H_2SO_4 produced from OH above and ambient H_2SO_4 – which is also measured

Then detecting via : Nitrate Ion Chemical Ionization Mass Spectrometry

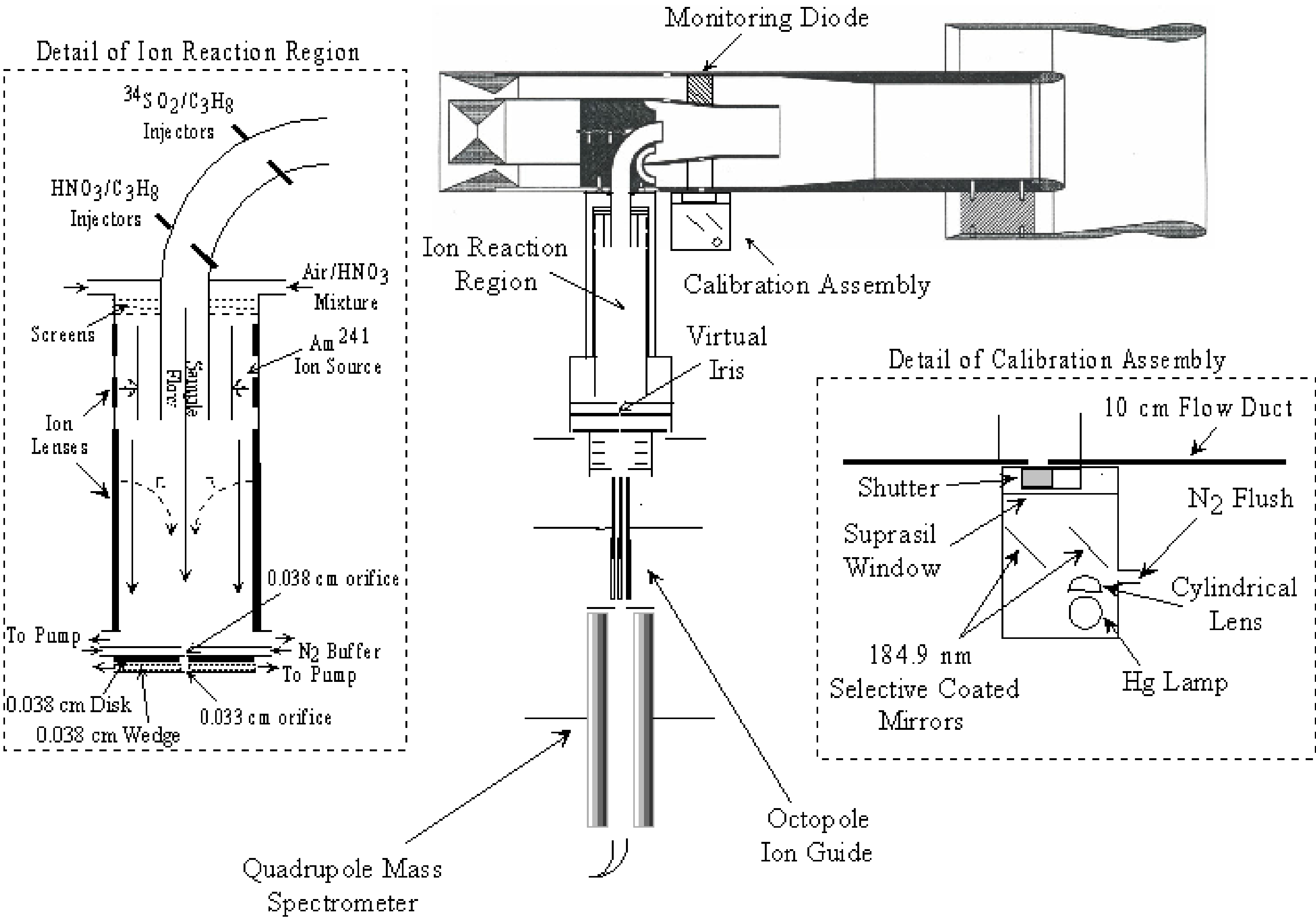
$$HNO_3 \xrightarrow{\text{Ionized}} NO_3^-$$ ← Mass 62

$$NO_3^- + H_2SO_4 \rightarrow HNO_3 + HSO_4^-$$ ← Mass 99 for $H^{34}SO_4^-$ (OH); ← Mass 97 for HSO_4^-

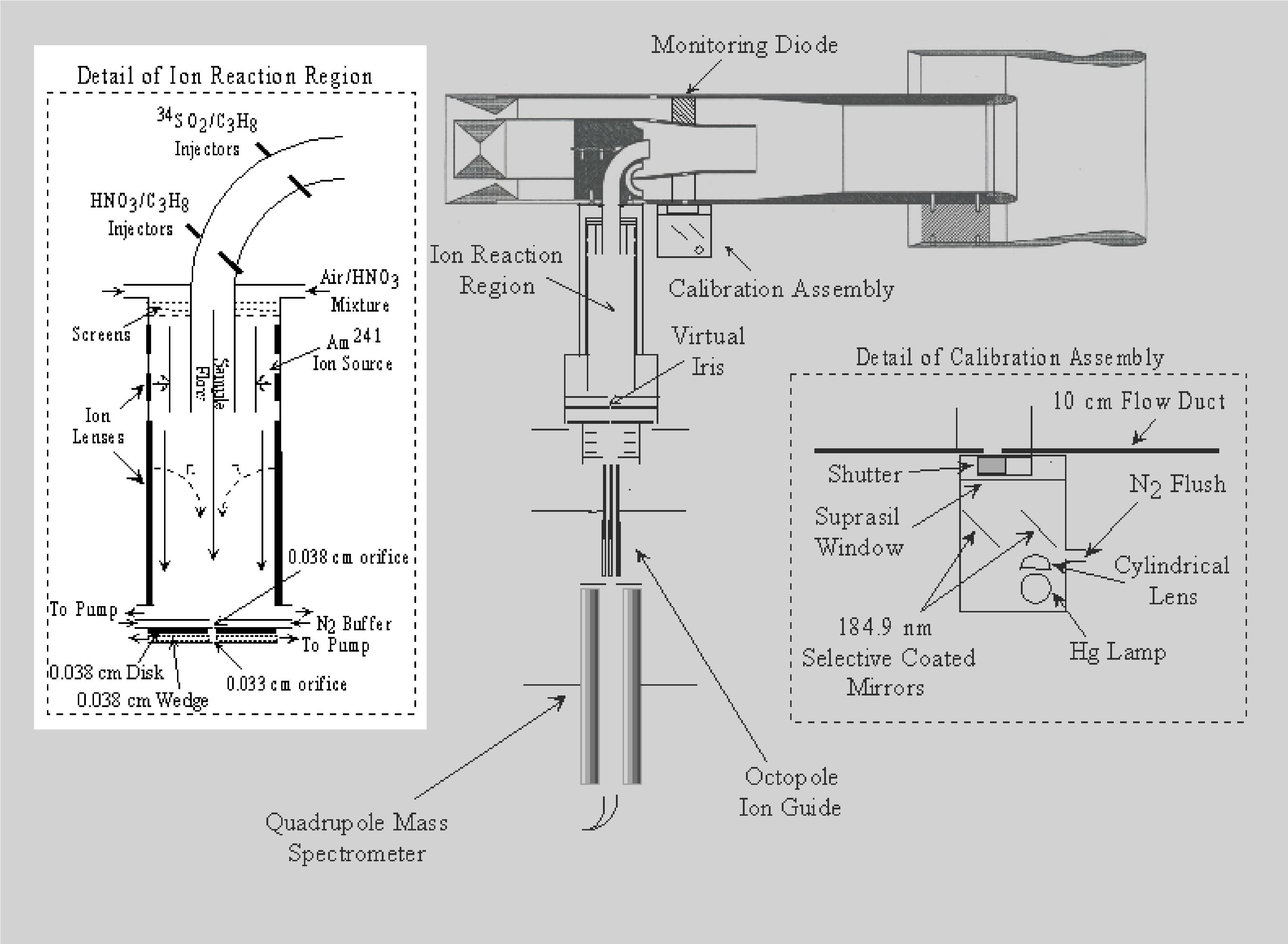
$$NO_3^- + (CH_3)SO_3H \rightarrow (CH_3)SO_3^-$$ ← Mass 95

$$[OH] = C \frac{H^{34}SO_4^-}{NO_3^-} \qquad [H_2SO_4] = C \frac{HSO_4^-}{NO_3^-} \qquad [MSA] = C \frac{(CH_3)SO_3^-}{NO_3^-}$$

Where C is a directly measured calibration coefficient

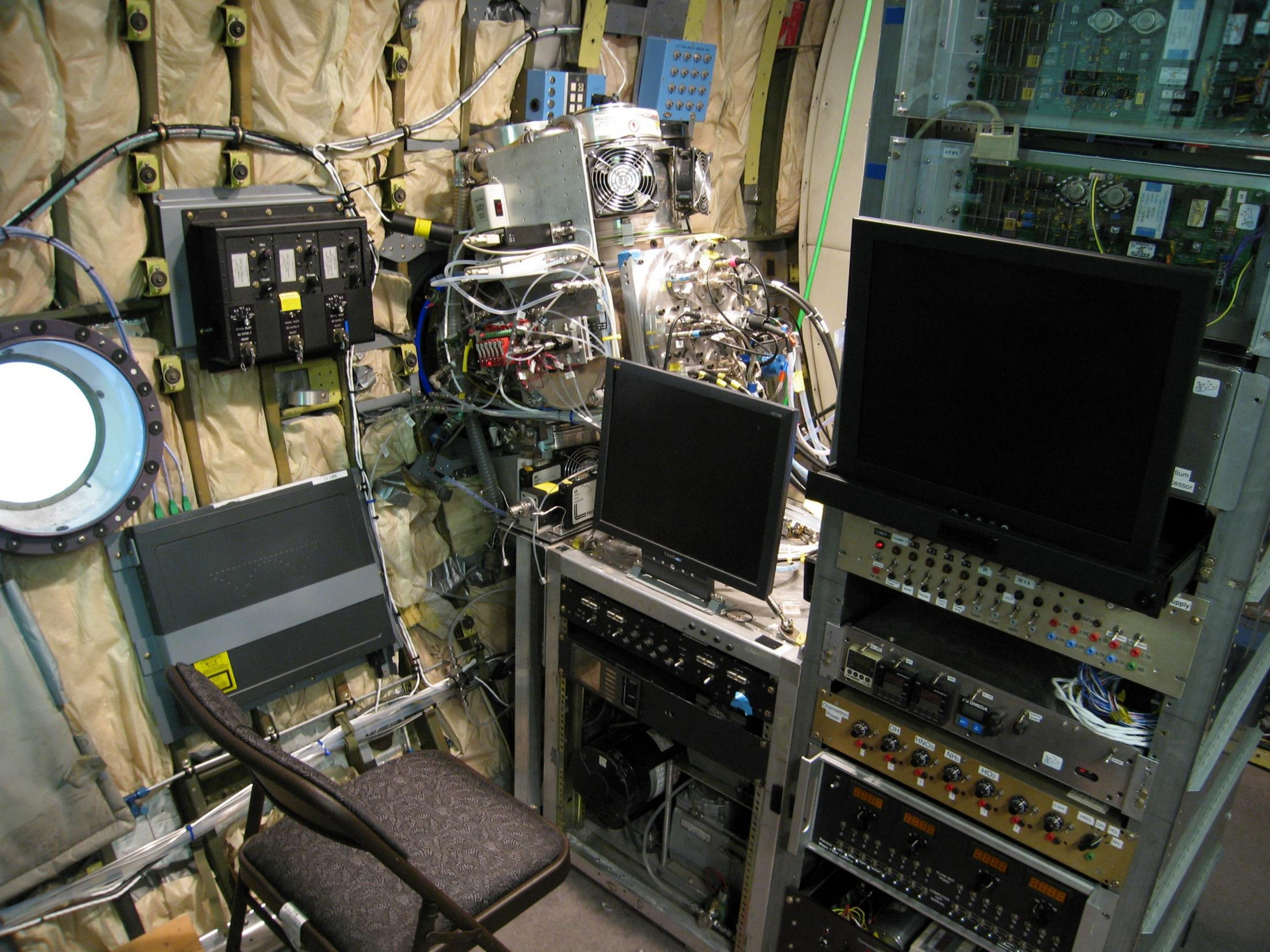


Detail of Ion Reaction Region
34SO2/C3H8
Injectors
HNO3/C3H8
Injectors
Air/HNO3
Mixture
Screens
Am 241
Ion Source
Sample
Flow
Ion
Lenses
0.038 cm orifice
To Pump
N2 Buffer
To Pump
0.038 cm Disk
0.038 cm Wedge
0.033 cm orifice
Monitoring Diode
Ion Reaction
Region
Calibration Assembly
Virtual
Iris
Detail of Calibration Assembly
10 cm Flow Duct
Shutter
N2 Flush
Suprasil
Window
Cylindrical
Lens
184.9 nm
Selective Coated
Mirrors
Hg Lamp
Quadrupole Mass
Spectrometer
Octopole
Ion Guide



Detail of Ion Reaction Region
$^{34}SO_2/C_3H_8$
Injectors
HNO_3/C_3H_8
Injectors
Air/HNO_3
Mixture
Screens
Am 241
Ion Source
Sample
Flow
Ion
Lenses
0.038 cm orifice
To Pump
N_2 Buffer
To Pump
0.038 cm Disk
0.038 cm Wedge
0.033 cm orifice
Monitoring Diode
Ion Reaction
Region
Calibration Assembly
Virtual
Iris
Detail of Calibration Assembly
10 cm Flow Duct
Shutter
N_2 Flush
Suprasil
Window
Cylindrical
Lens
184.9 nm
Selective Coated
Mirrors
Hg Lamp
Quadrupole Mass
Spectrometer
Octopole
Ion Guide


NSF
National
Science
Foundation
Where Discoveries Begin
RAF
N130AR
Research Aviation Facility


OH
HNO3
NH3
HO2
OMEGA

OH Measurement Chemistry

Eisele et al., 1991

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$$H^{34}SO_3 + O_2 \rightarrow {}^{34}SO_3 + HO_2$$

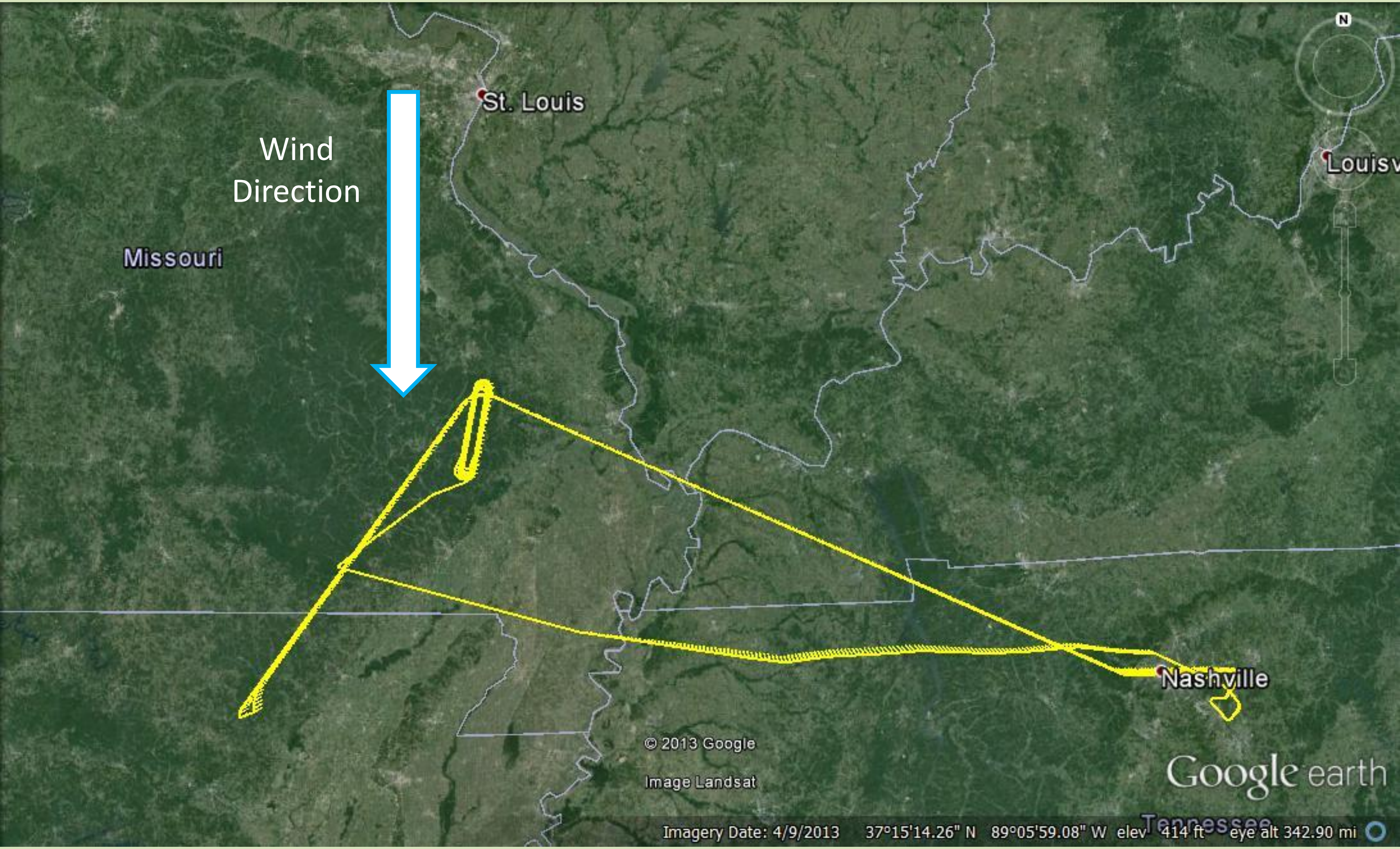
$${}^{34}SO_3 + 2H_2O \rightarrow H_2{}^{34}SO_4 + H_2O$$

and then measuring $H_2{}^{34}SO_4$

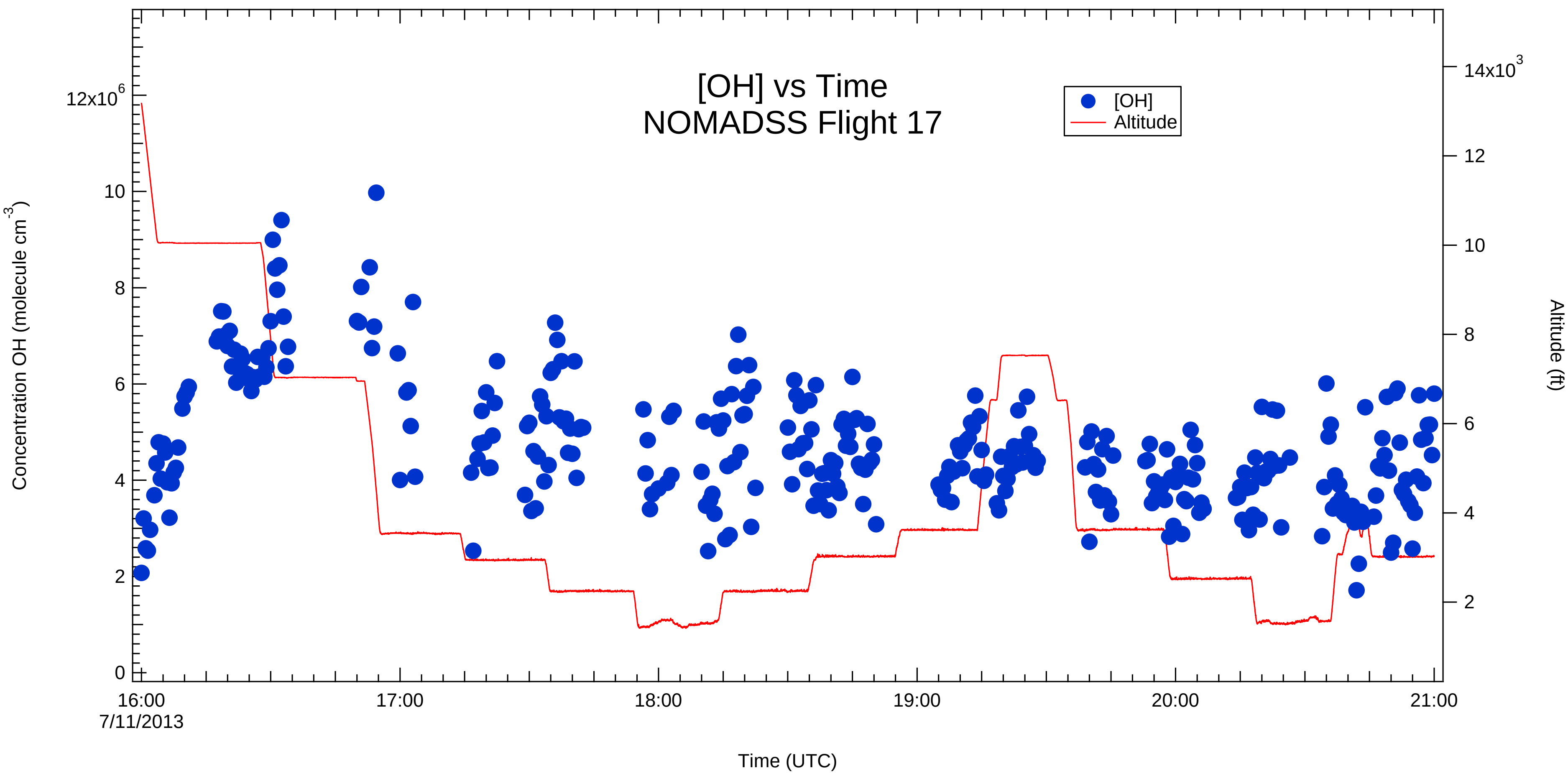
^{34}S is used to discriminate between H_2SO_4 produced from OH above and ambient H_2SO_4 – which is also measured

Additionally other unknown oxidants can also convert SO_2 into H_2SO_4. To account for these processes a background is measured by adding a small amount of OH scavenger, propane, to the front injectors. Thus, the background represents other oxidants that can oxidize SO_2 to produce H_2SO_4 but do not react with propane.

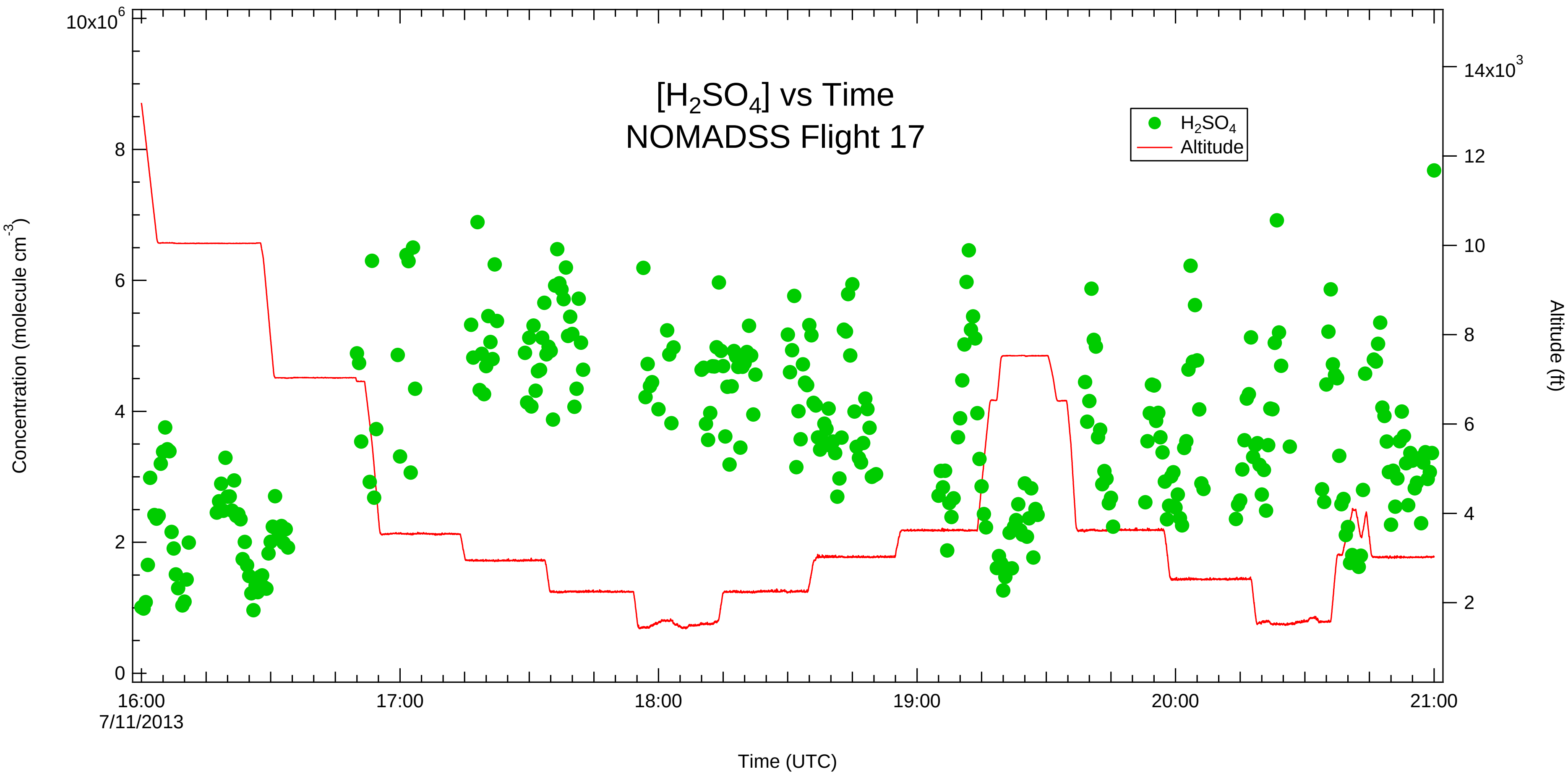
The difference in the $H_2{}^{34}SO_4$ without and with propane added is attributable to $H_2{}^{34}SO_4$ produced OH chemistry.

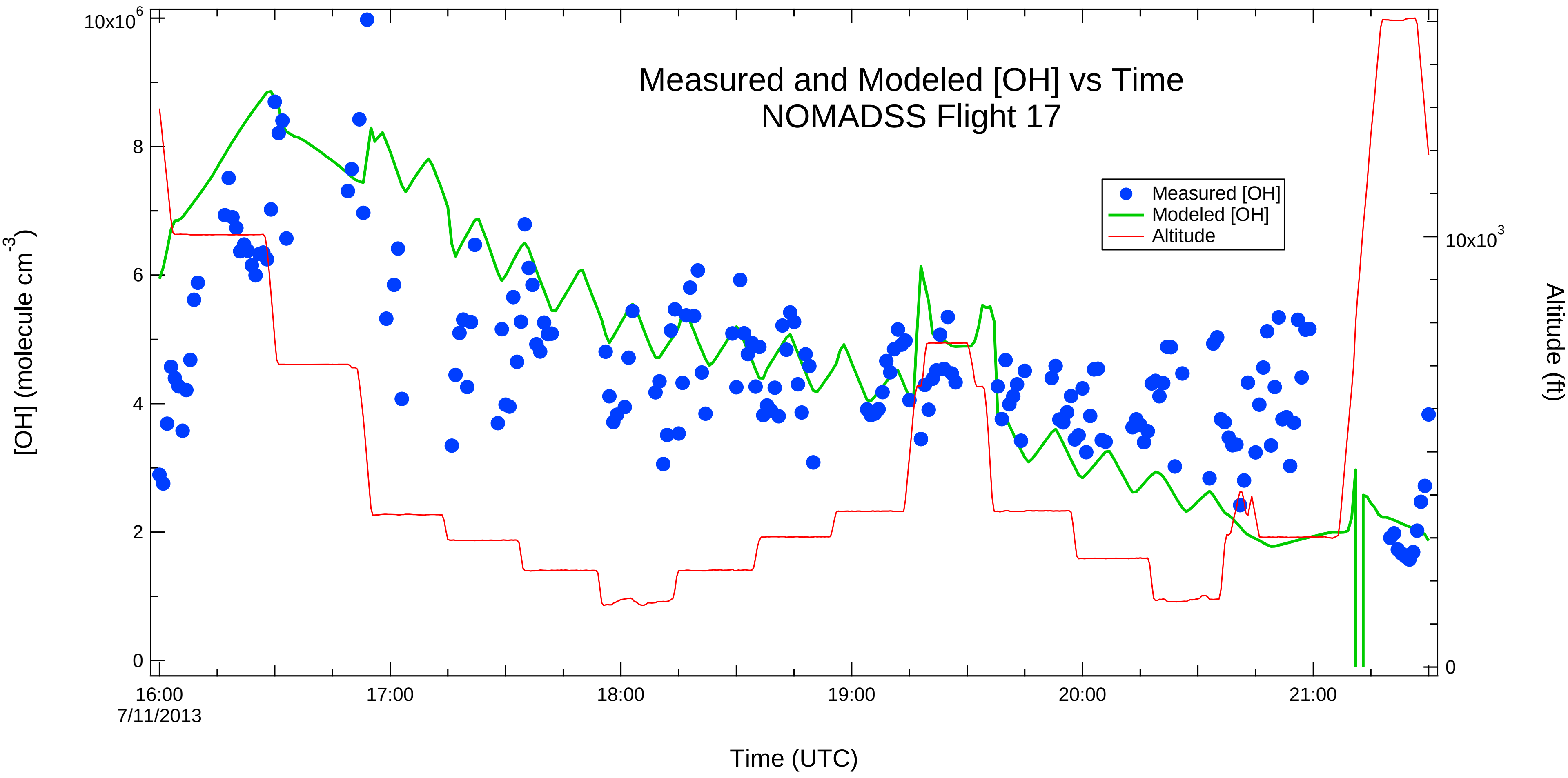


Wind
Direction
St. Louis
Missouri
Louisv
Nashville
Tennessee
© 2013 Google
Image Landsat
Google earth
Imagery Date: 4/9/2013 37°15'14.26" N 89°05'59.08" W elev 414 ft eye alt 342.90 mi

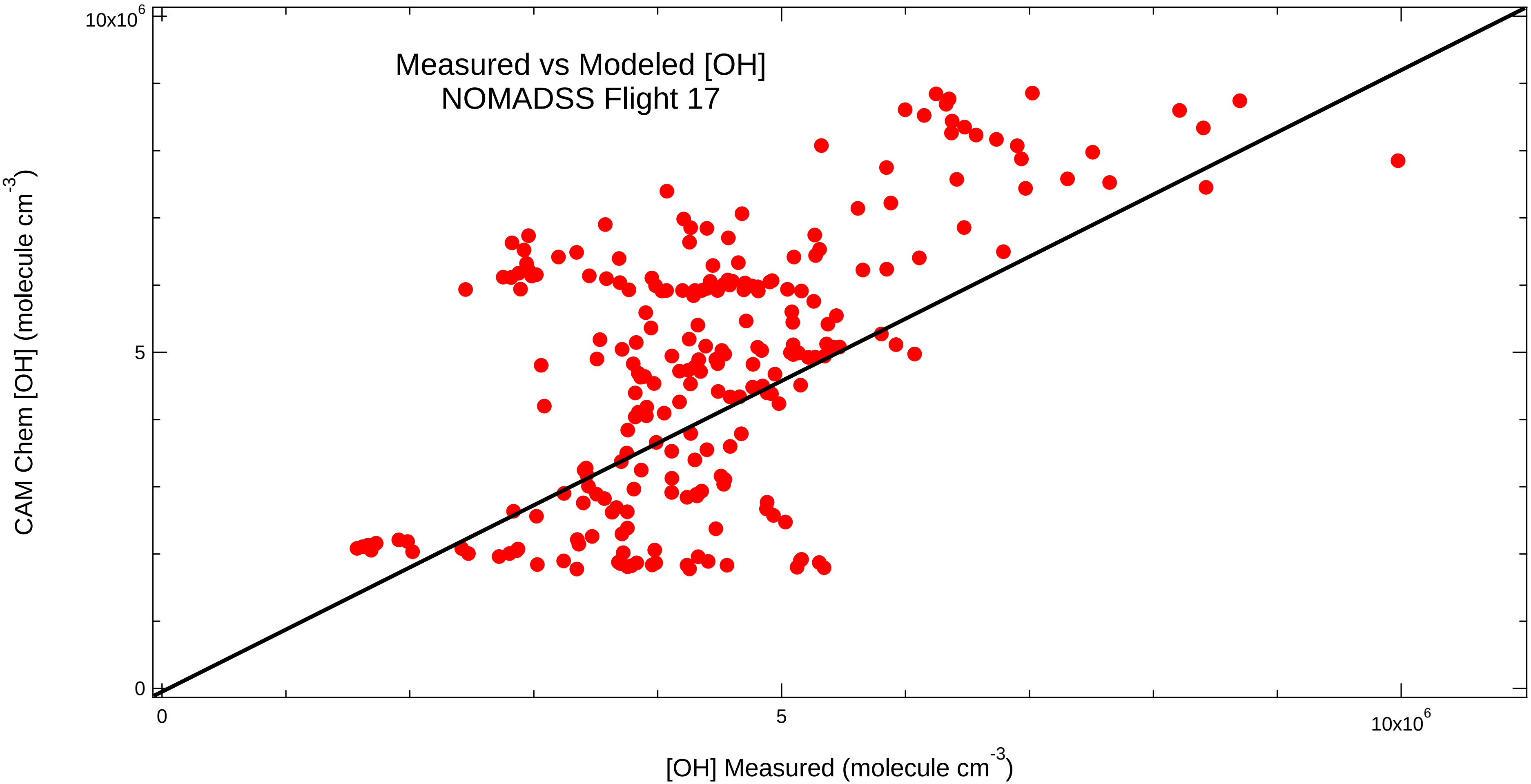


[OH] vs Time
NOMADSS Flight 17
[OH]
Altitude
Concentration OH (molecule cm^{-3})
12x10^{6}
10
8
6
4
2
0
Altitude (ft)
14x10^{3}
12
10
8
6
4
2
16:00
7/11/2013
17:00
18:00
19:00
20:00
21:00
Time (UTC)


[H2SO4] vs Time
NOMADSS Flight 17
H2SO4
Altitude
Concentration (molecule cm-3)
10x10^6
8
6
4
2
0
Altitude (ft)
14x10^3
12
10
8
6
4
2
16:00
7/11/2013
17:00
18:00
19:00
20:00
21:00
Time (UTC)



Measured and Modeled [OH] vs Time
NOMADSS Flight 17
Measured [OH]
Modeled [OH]
Altitude
[OH] (molecule cm^{-3})
10x10^{6}
8
6
4
2
0
Altitude (ft)
10x10^{3}
0
16:00
7/11/2013
17:00
18:00
19:00
20:00
21:00
Time (UTC)



Measured vs Modeled [OH]
NOMADSS Flight 17
10x10^6
5
0
0
5
10x10^6
CAM Chem [OH] (molecule cm^-3)
[OH] Measured (molecule cm^-3)

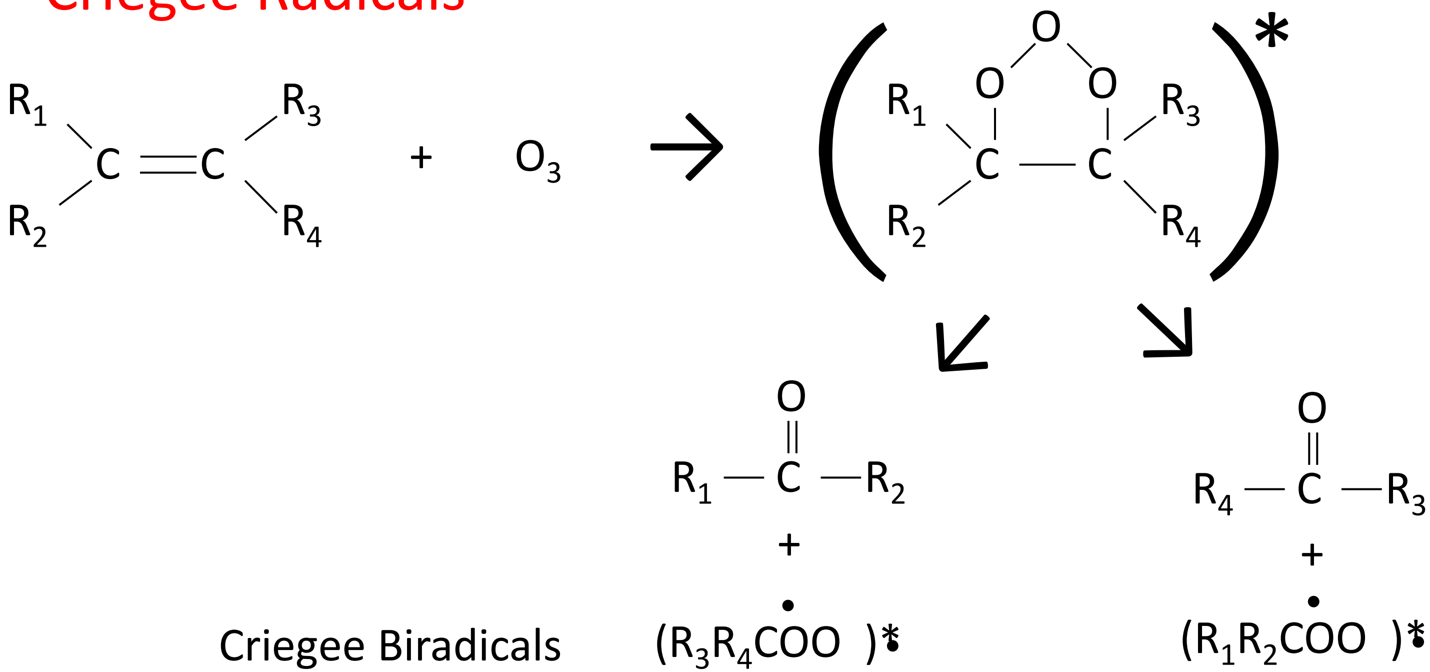
General consensus considers ozone, OH and NO_3 to be the dominating, or even the only important, oxidants in atmosphere initiating removal processes.

But there are other oxidants – produced from the ozonolysis of alkenes.
Stabilized Criegee Radicals (sCI)

Welz et al., *Science,* 2012
Mauldin et al., *Nature,* 2012
Boy et al., *Atmos. Chem. Phys.,* 2013
Percival et al., *Faraday Discuss.,* 2013

sCIs effectively oxidize SO_2
oxidize DMS

Criegee Radicals



Criegee Biradicals

$(R_1CH_2C(\dot{R}_2)OO)^{*}\bullet \rightarrow R_1CH_2C(\dot{R}_2)OO\bullet$ (Stabilization)

$\rightarrow R_1CH_2C(O)R_2 + O$

$\rightarrow (R_1CH_2C(O)OR_2)^{*} \rightarrow$ Decomposition

$\rightarrow R_1CH{=}C(OOH)R_2 \rightarrow R_1CHC(\dot{O})R_2 + OH$

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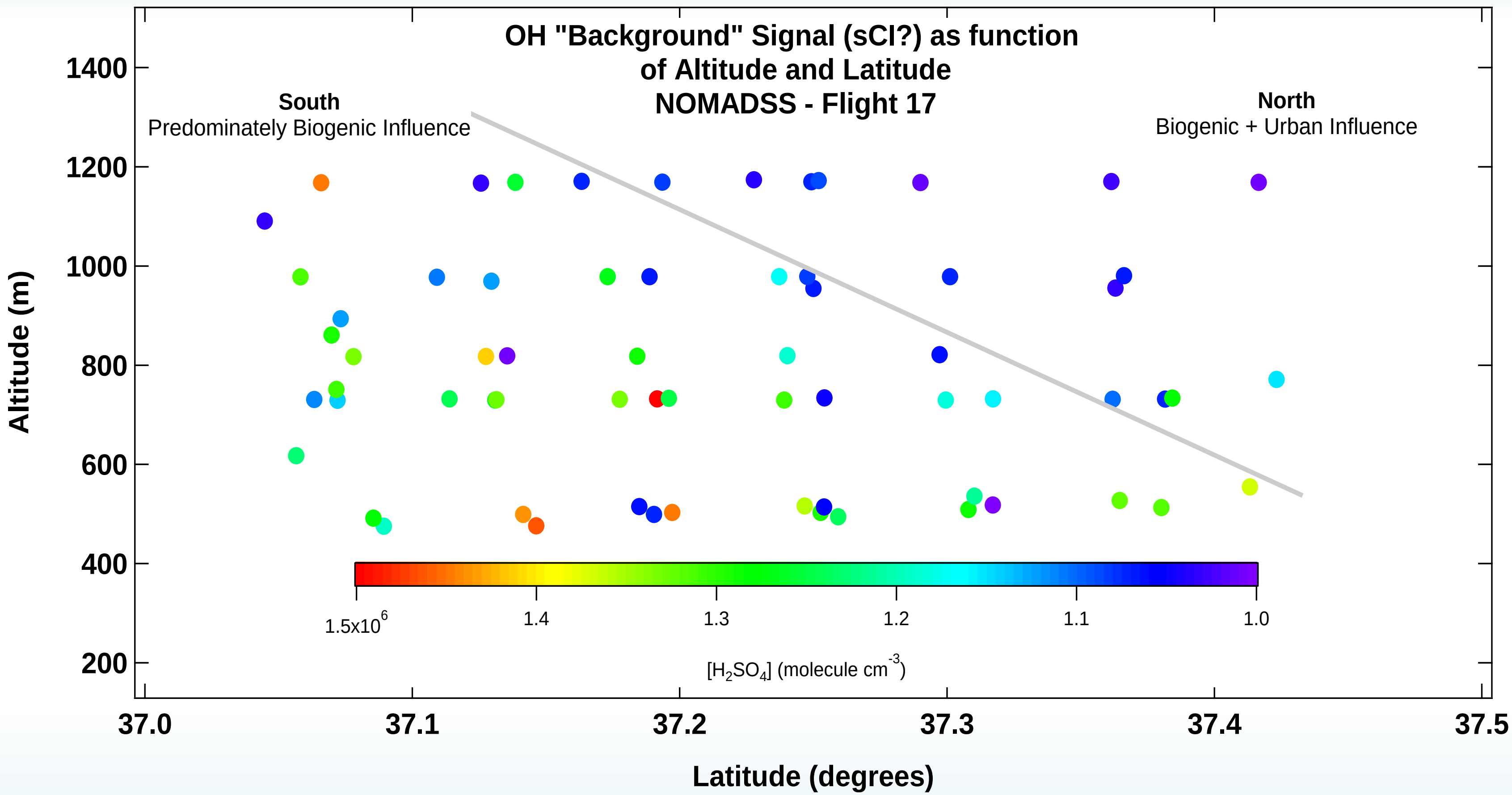
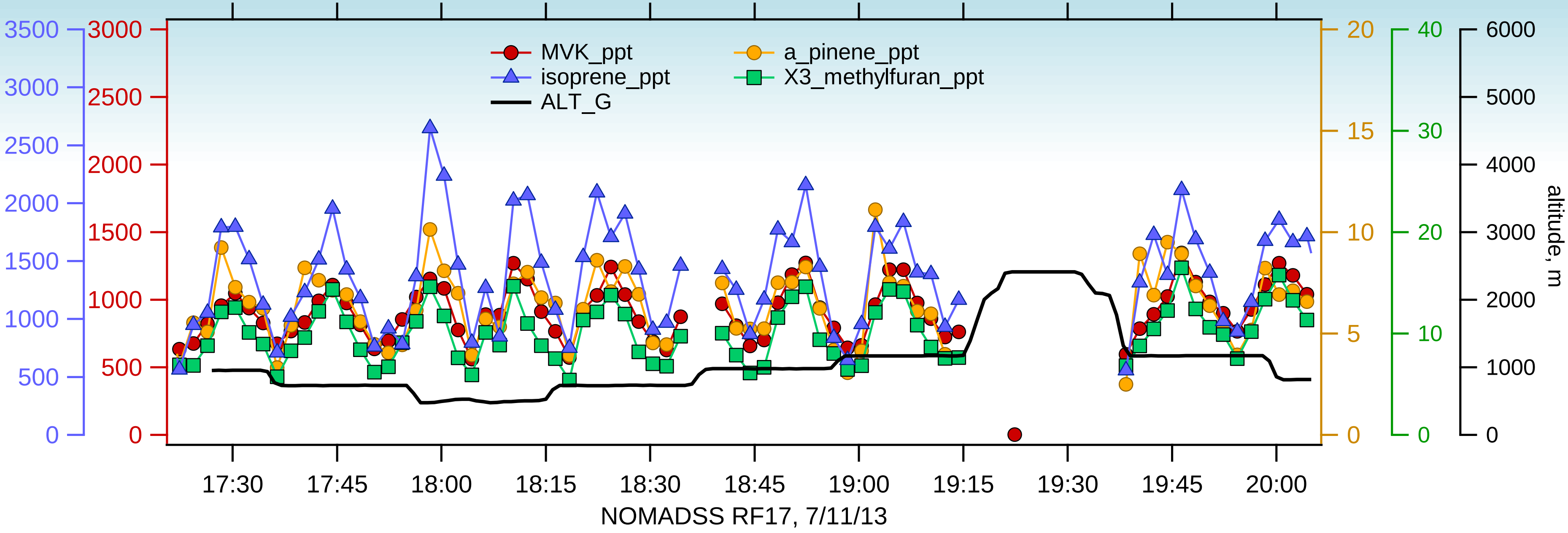
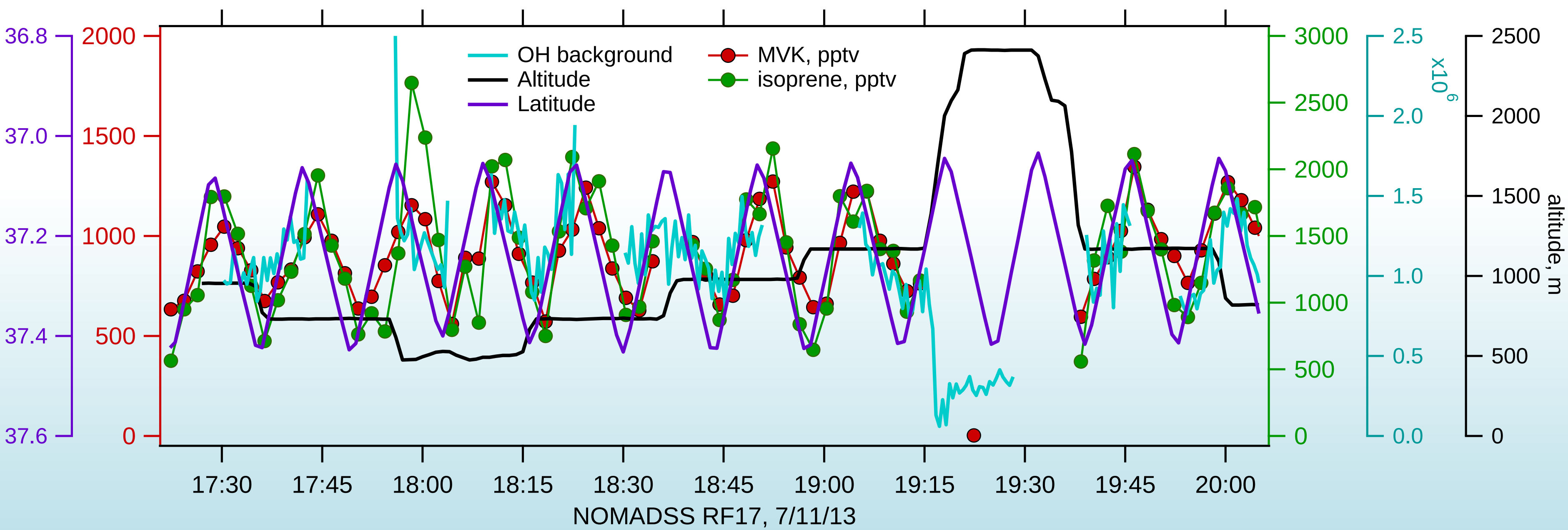


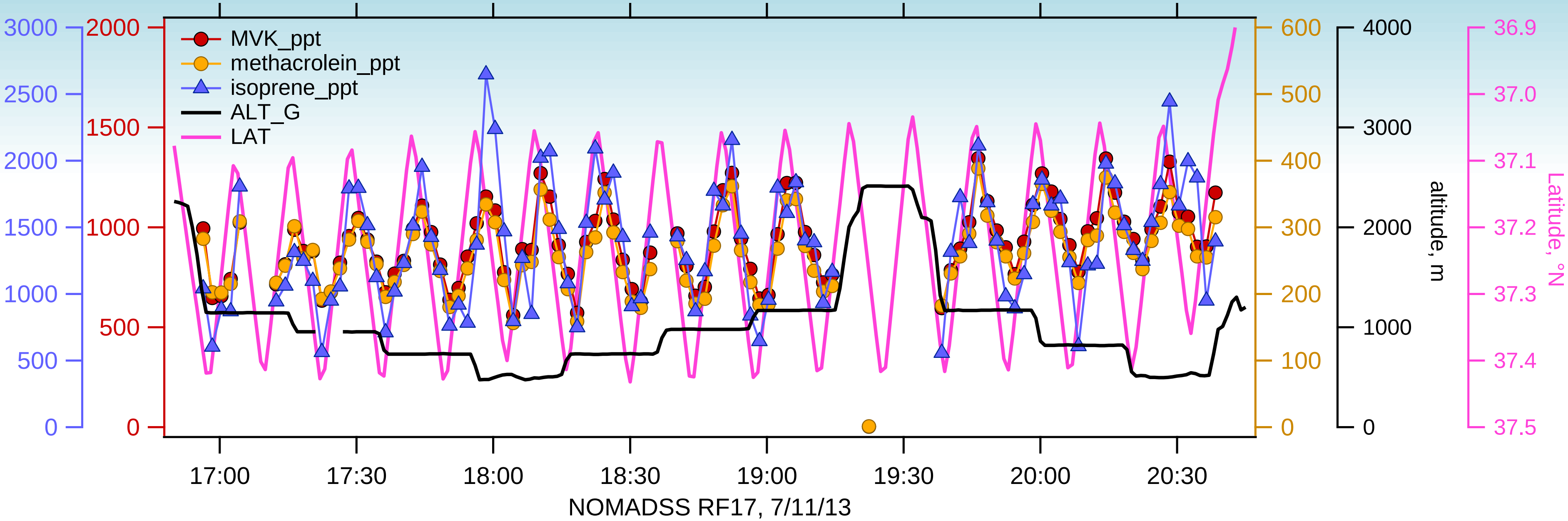
An overall increase in the OH "background" over the southern end of the race track shows an increase in oxidative capacity presumably due to the increase in biogenic activity leading to an increase in stabilized Criegee Intermediate, sCI, production.



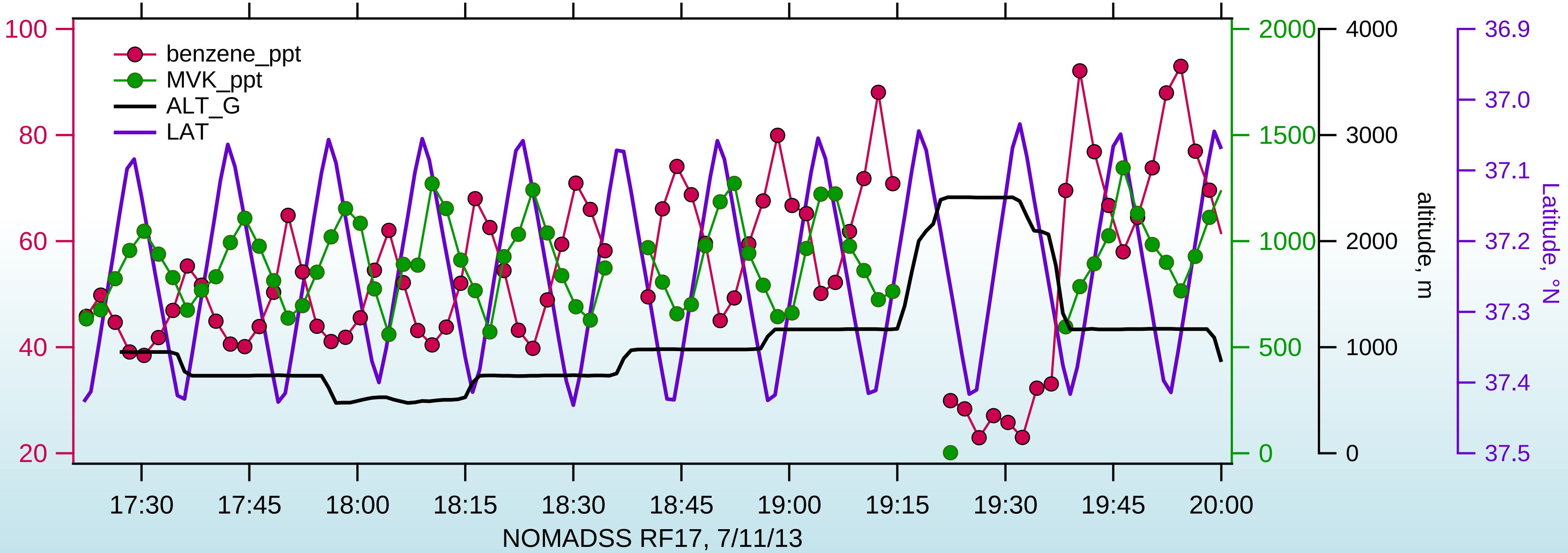
MVK_ppt
isoprene_ppt
ALT_G
a_pinene_ppt
X3_methylfuran_ppt
3500
3000
2500
2000
1500
1000
500
0
20
15
10
5
40
30
20
10
6000
5000
4000
3000
2000
1000
altitude, m
17:30
17:45
18:00
18:15
18:30
18:45
19:00
19:15
19:30
19:45
20:00
NOMADSS RF17, 7/11/13



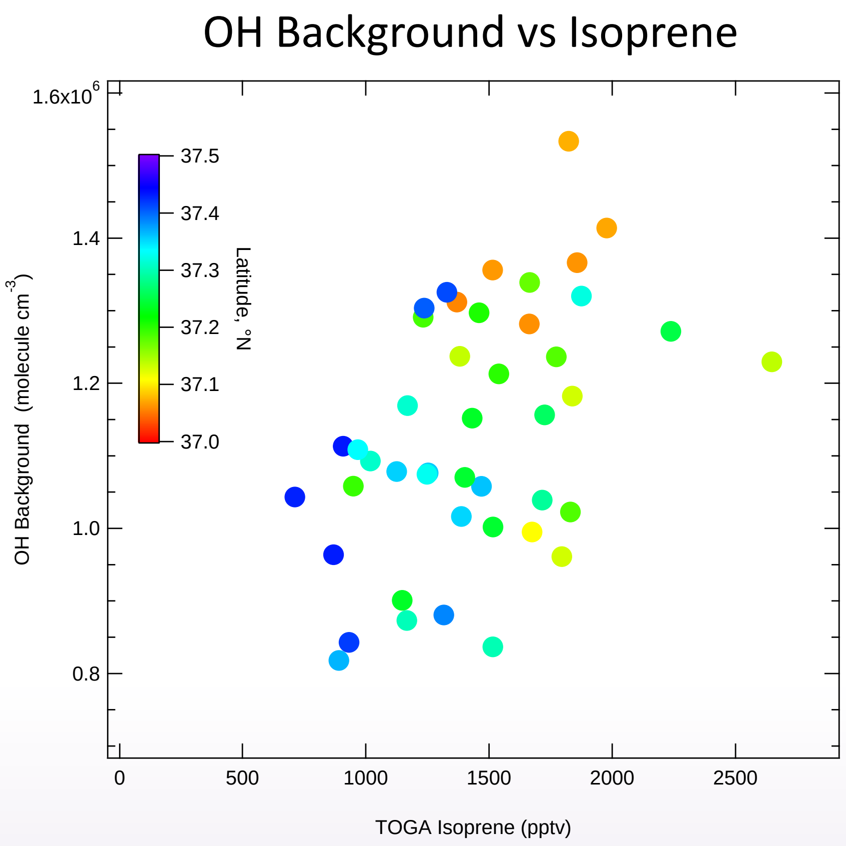
OH background
Altitude
Latitude
MVK, pptv
isoprene, pptv
36.8
37.0
37.2
37.4
37.6
2000
1500
1000
500
0
3000
2500
2.5
2.0
1.5
1.0
0.5
0.0
x10^6
altitude, m
17:30
17:45
18:00
18:15
18:30
18:45
19:00
19:15
19:30
19:45
20:00
NOMADSS RF17, 7/11/13

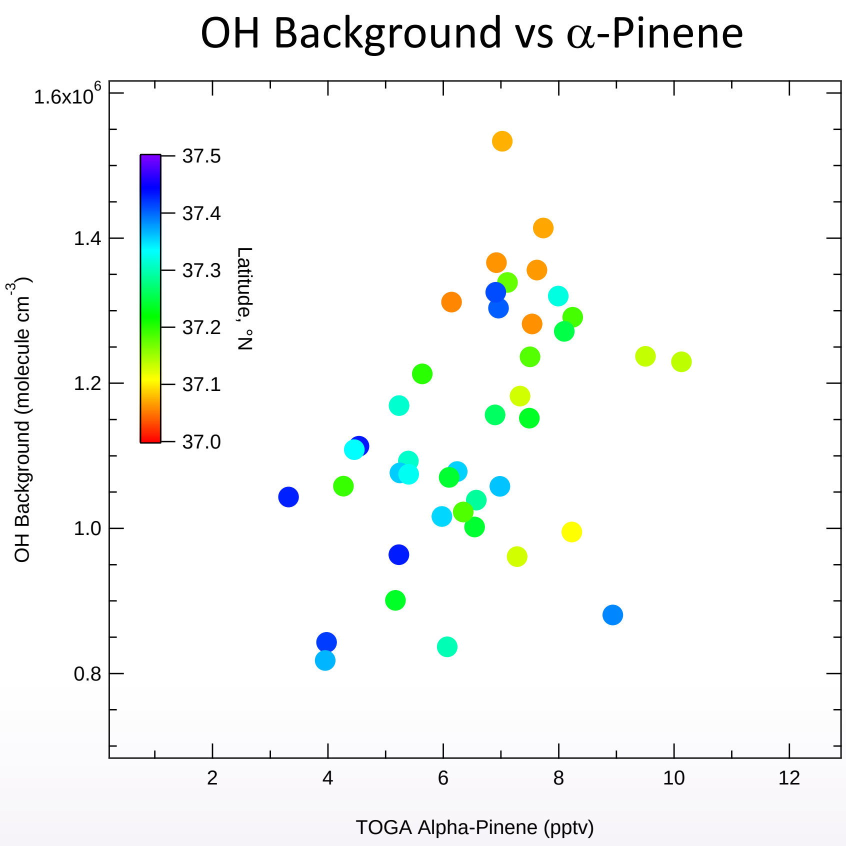


MVK_ppt
methacrolein_ppt
isoprene_ppt
ALT_G
LAT
3000
2500
2000
1500
1000
500
0
2000
1500
1000
500
0
600
500
400
300
200
100
0
4000
3000
2000
1000
0
altitude, m
36.9
37.0
37.1
37.2
37.3
37.4
37.5
Latitude, °N
17:00
17:30
18:00
18:30
19:00
19:30
20:00
20:30
NOMADSS RF17, 7/11/13

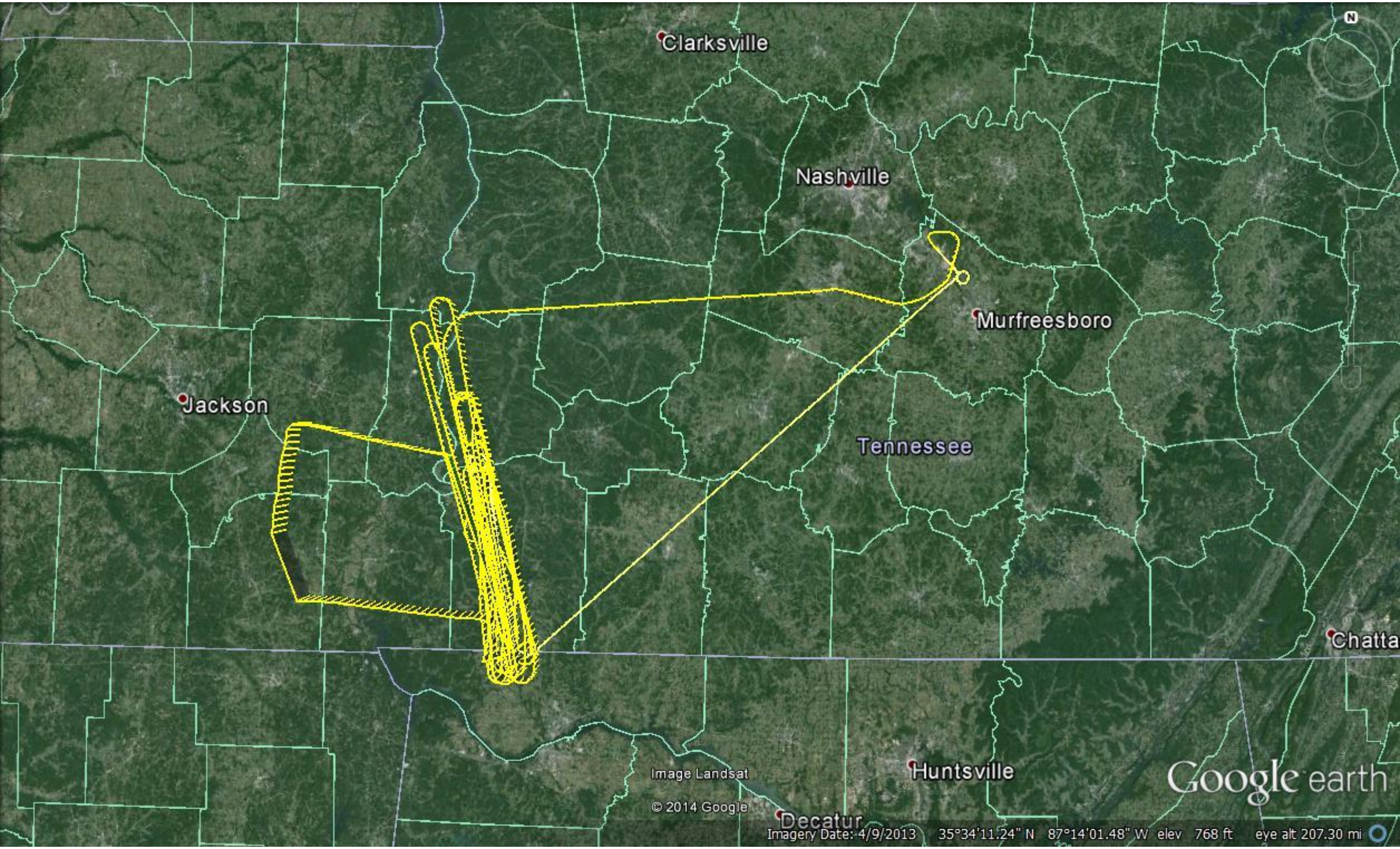


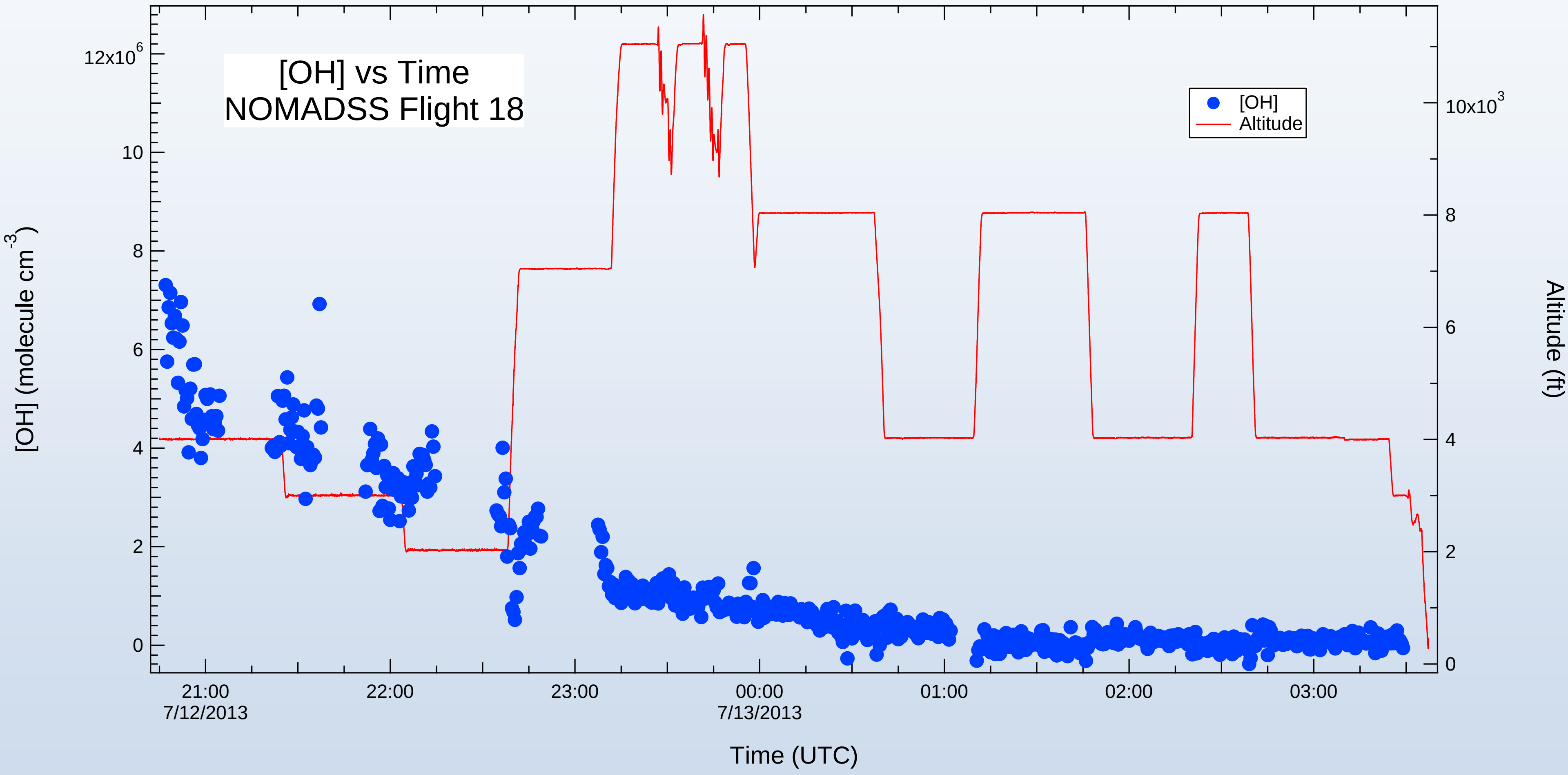
benzene_ppt
MVK_ppt
ALT_G
LAT
100
80
60
40
20
2000
1500
1000
500
0
4000
3000
2000
1000
0
altitude, m
36.9
37.0
37.1
37.2
37.3
37.4
37.5
Latitude, °N
17:30
17:45
18:00
18:15
18:30
18:45
19:00
19:15
19:30
19:45
20:00
NOMADSS RF17, 7/11/13


OH Background vs Isoprene
1.6x10^6
1.4
1.2
1.0
0.8
OH Background (molecule cm^-3)
37.5
37.4
37.3
37.2
37.1
37.0
Latitude, °N
0
500
1000
1500
2000
2500
TOGA Isoprene (pptv)

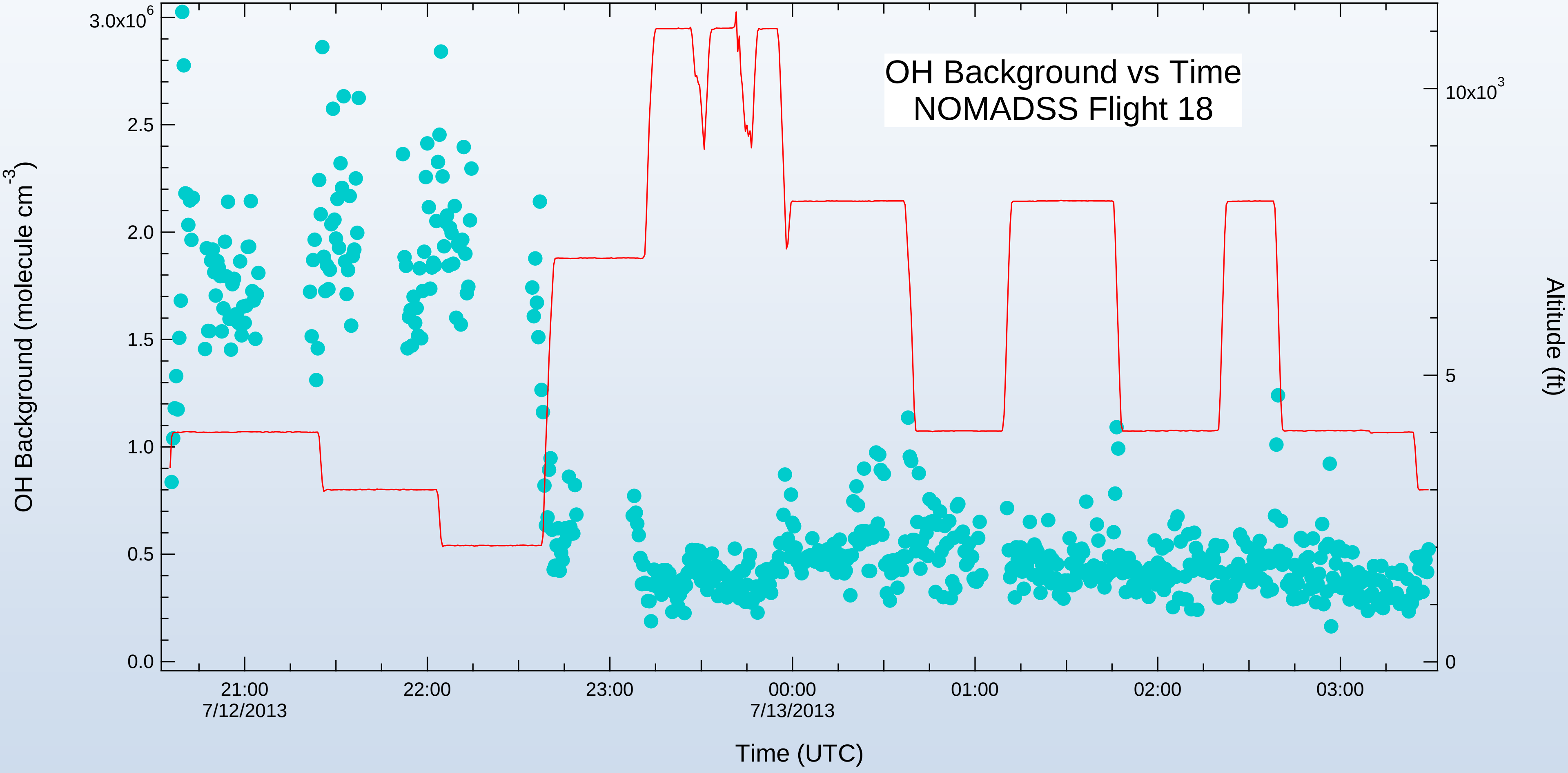

OH Background vs α-Pinene
1.6x10^6
1.4
1.2
1.0
0.8
OH Background (molecule cm^-3)
37.5
37.4
37.3
37.2
37.1
37.0
Latitude, °N
2
4
6
8
10
12
TOGA Alpha-Pinene (pptv)

NOMADSS Flight 18 Flight Track



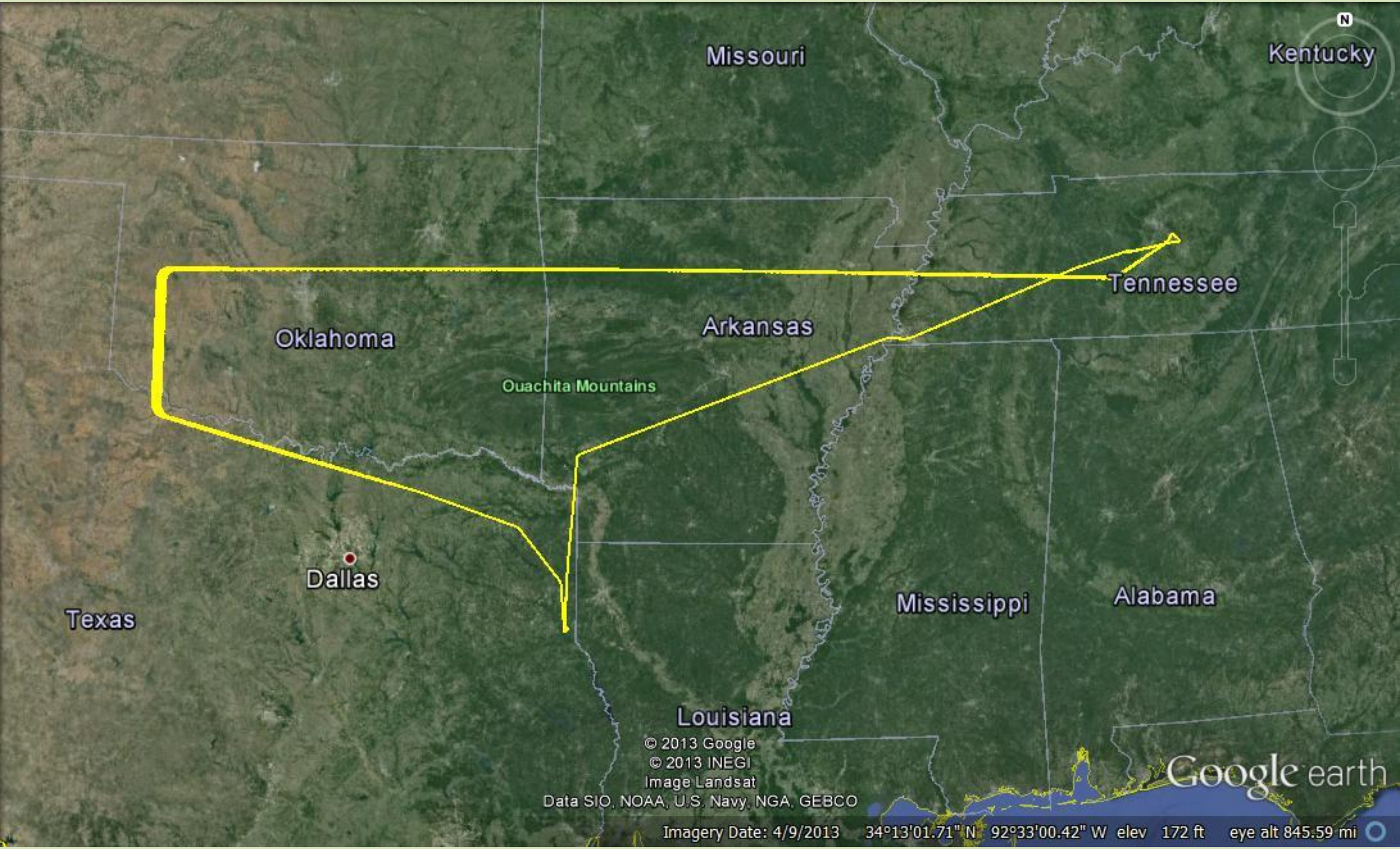


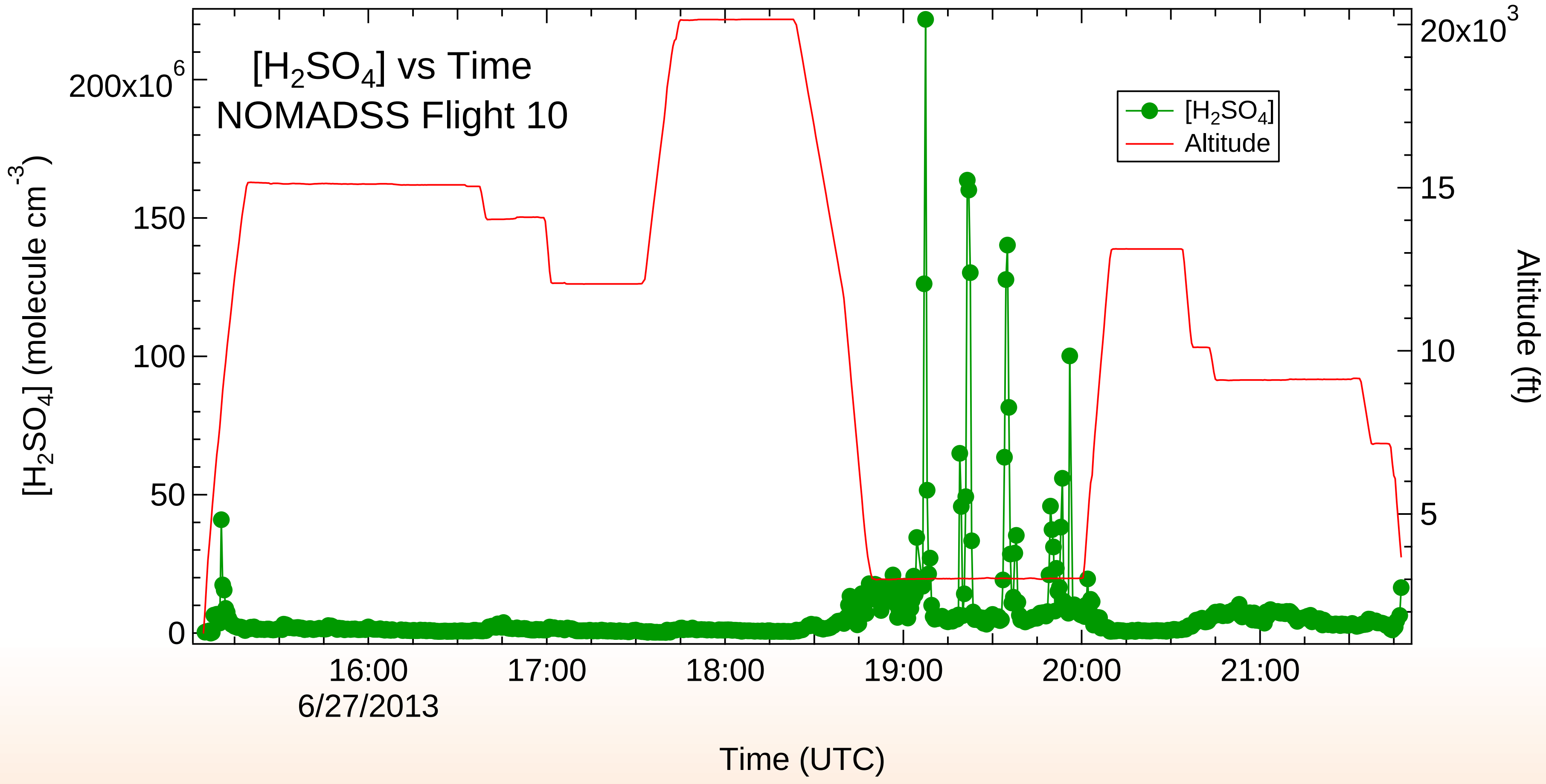
[OH] vs Time
NOMADSS Flight 18
[OH]
Altitude
12x10^6
10
8
6
4
2
0
[OH] (molecule cm^-3)
10x10^3
8
6
4
2
0
Altitude (ft)
21:00
7/12/2013
22:00
23:00
00:00
7/13/2013
01:00
02:00
03:00
Time (UTC)



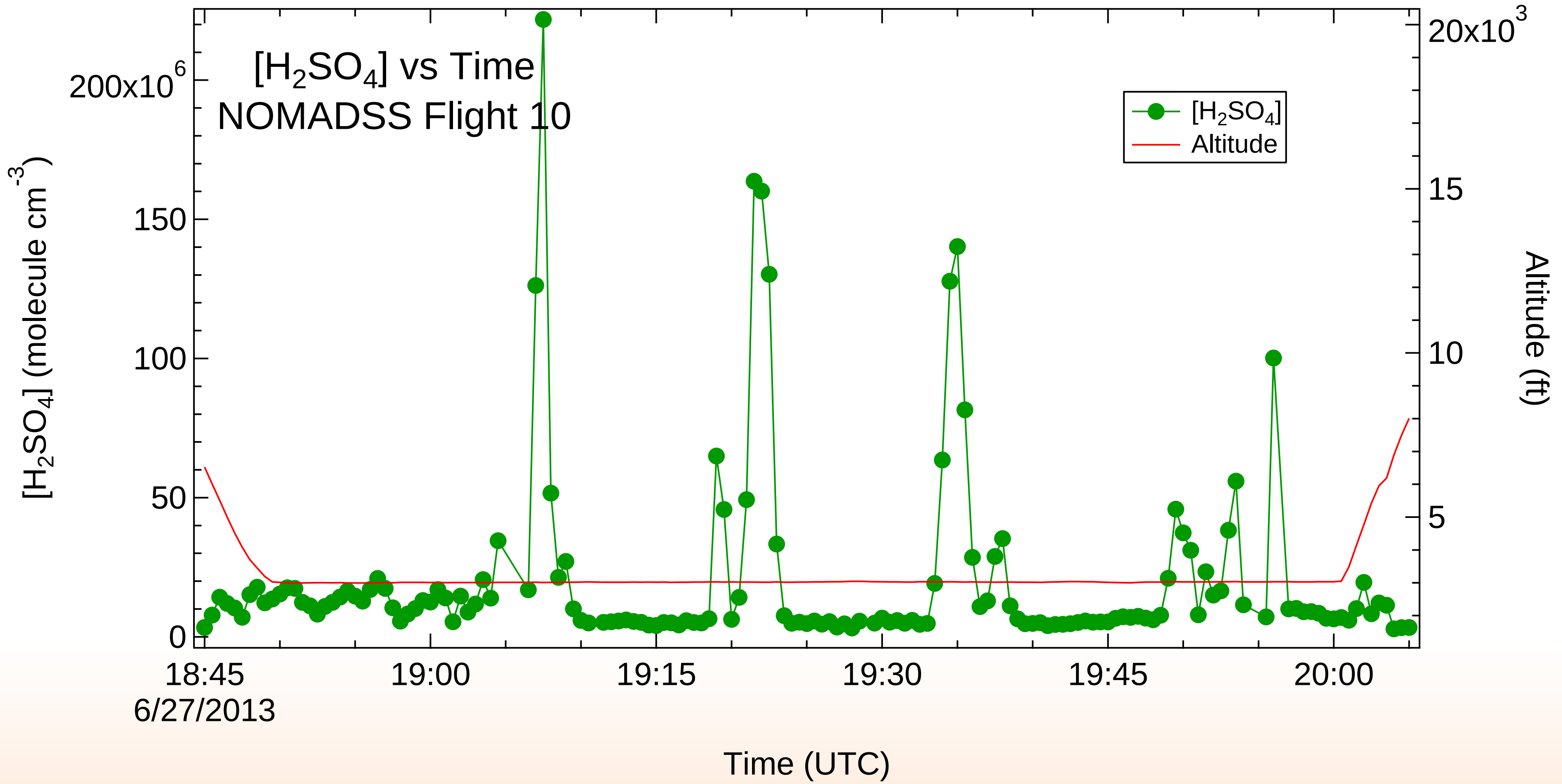
OH Background vs Time
NOMADSS Flight 18
OH Background (molecule cm^-3)
3.0x10^6
2.5
2.0
1.5
1.0
0.5
0.0
Altitude (ft)
10x10^3
5
0
21:00
7/12/2013
22:00
23:00
00:00
7/13/2013
01:00
02:00
03:00
Time (UTC)

NOMADSS Flight 10 Flight Track



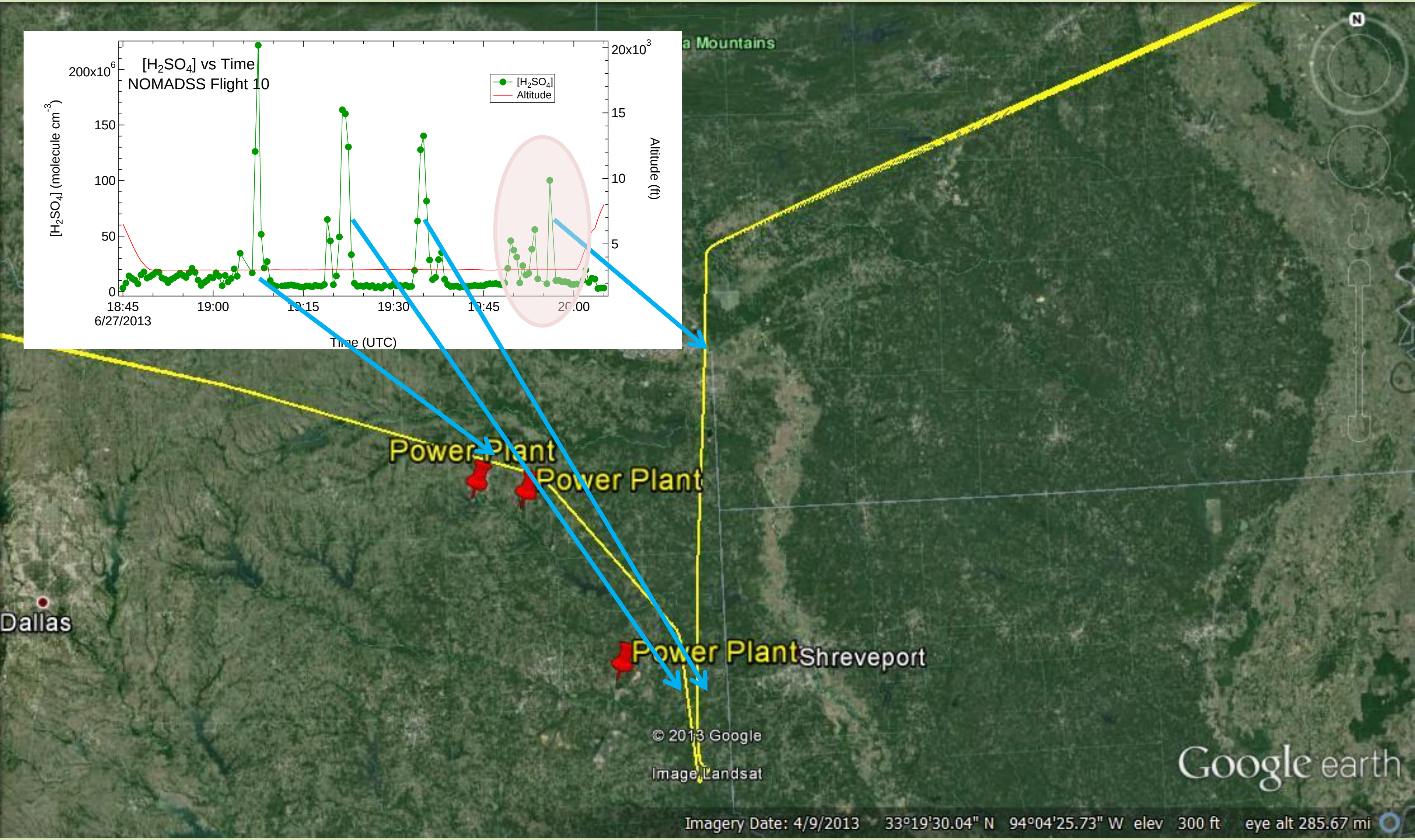


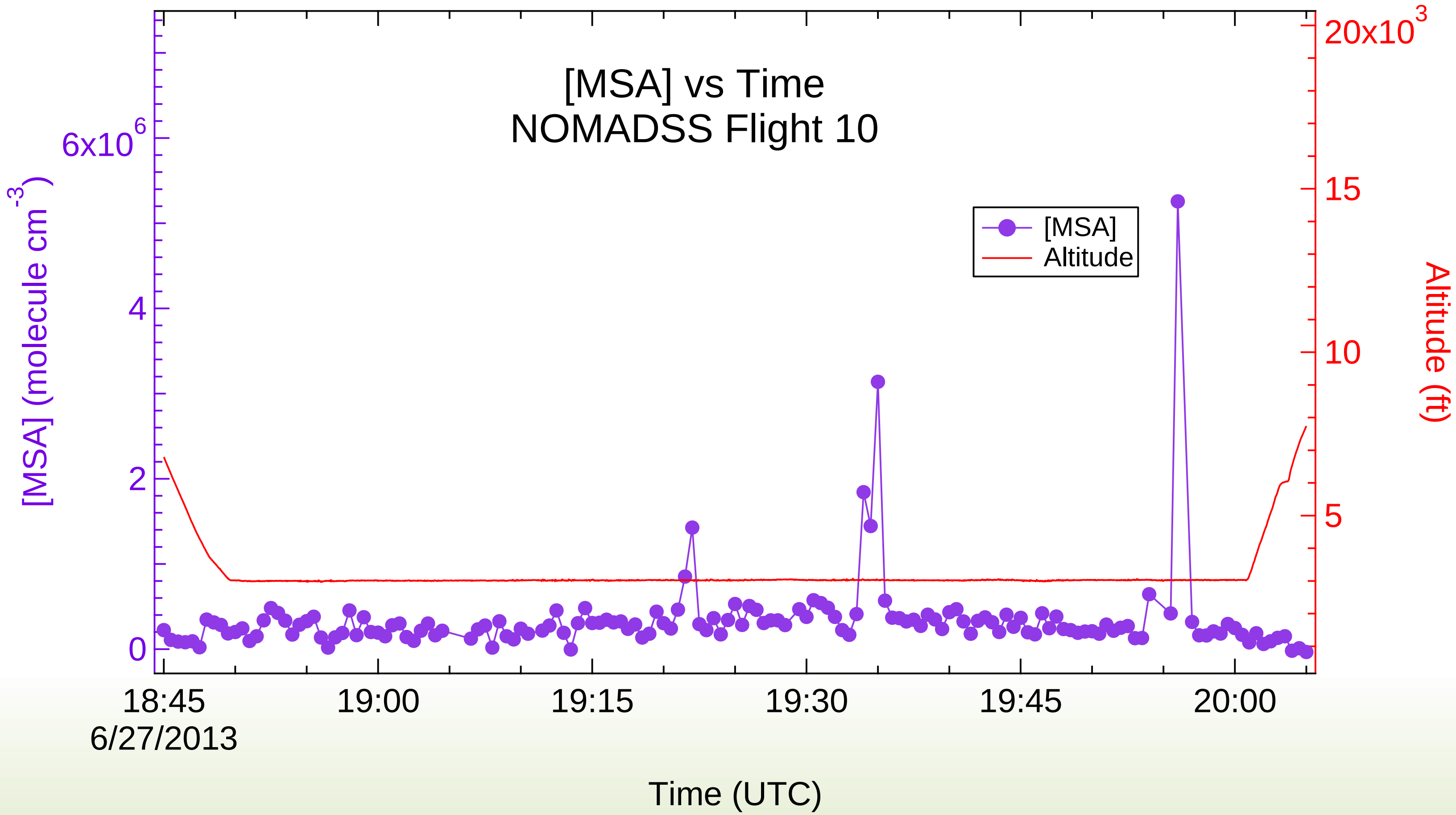
[H2SO4] vs Time
NOMADSS Flight 10
[H2SO4]
Altitude
200x10^6
150
100
50
0
20x10^3
15
10
5
[H2SO4] (molecule cm^-3)
Altitude (ft)
16:00
6/27/2013
17:00
18:00
19:00
20:00
21:00
Time (UTC)



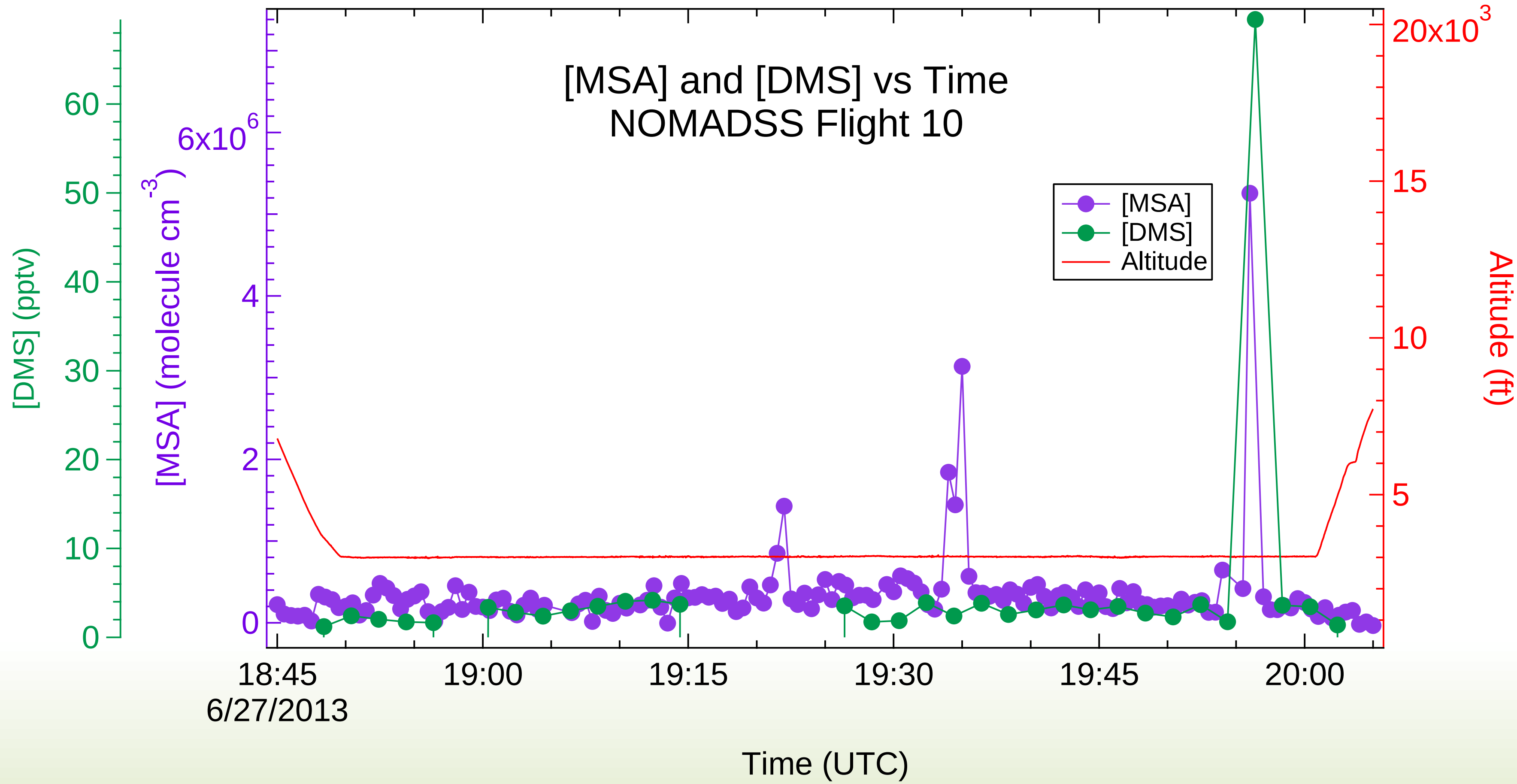
[H2SO4] vs Time
NOMADSS Flight 10
[H2SO4]
Altitude
200x10^6
150
100
50
0
20x10^3
15
10
5
[H2SO4] (molecule cm^-3)
Altitude (ft)
18:45
6/27/2013
19:00
19:15
19:30
19:45
20:00
Time (UTC)

NOMADSS Flight 10

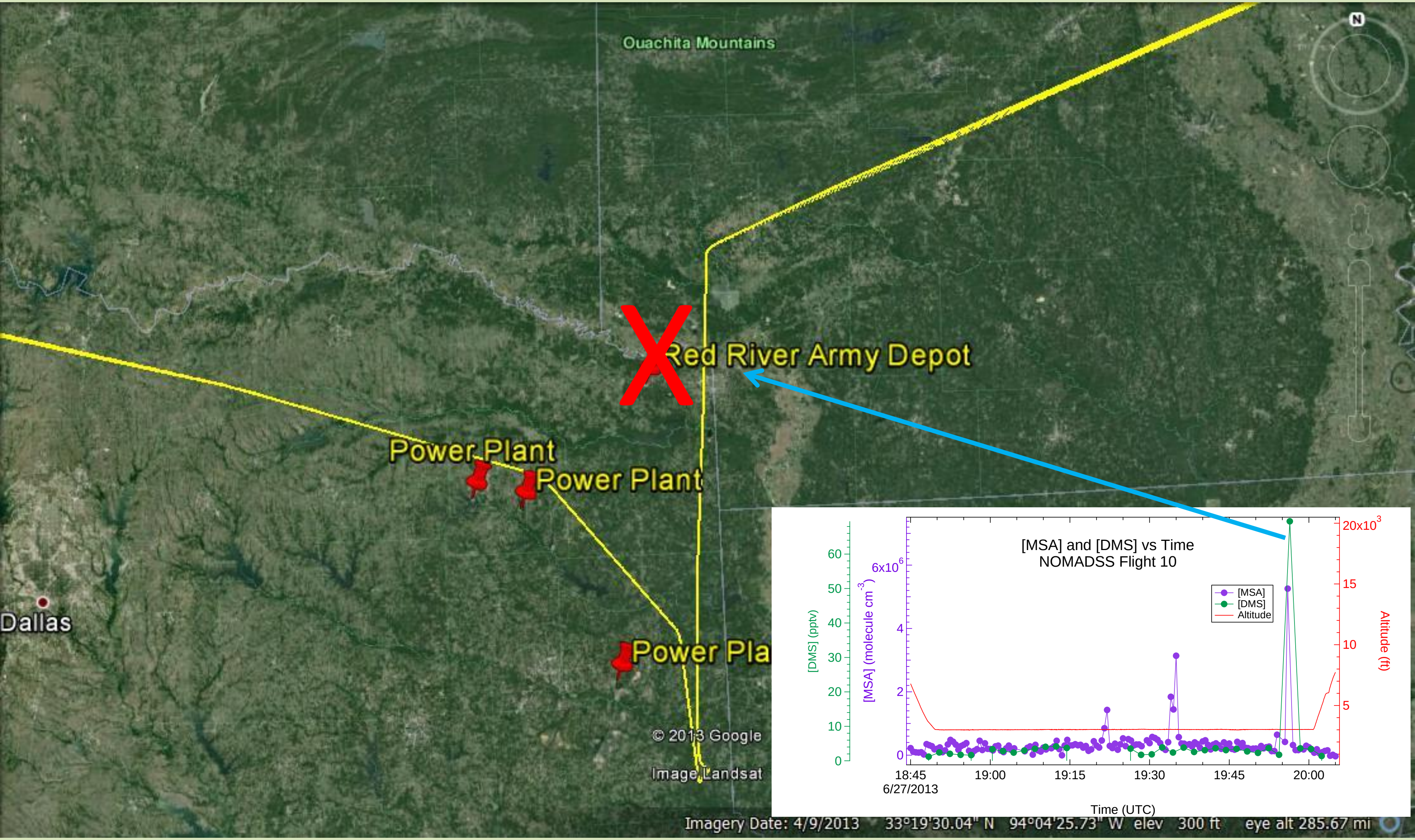




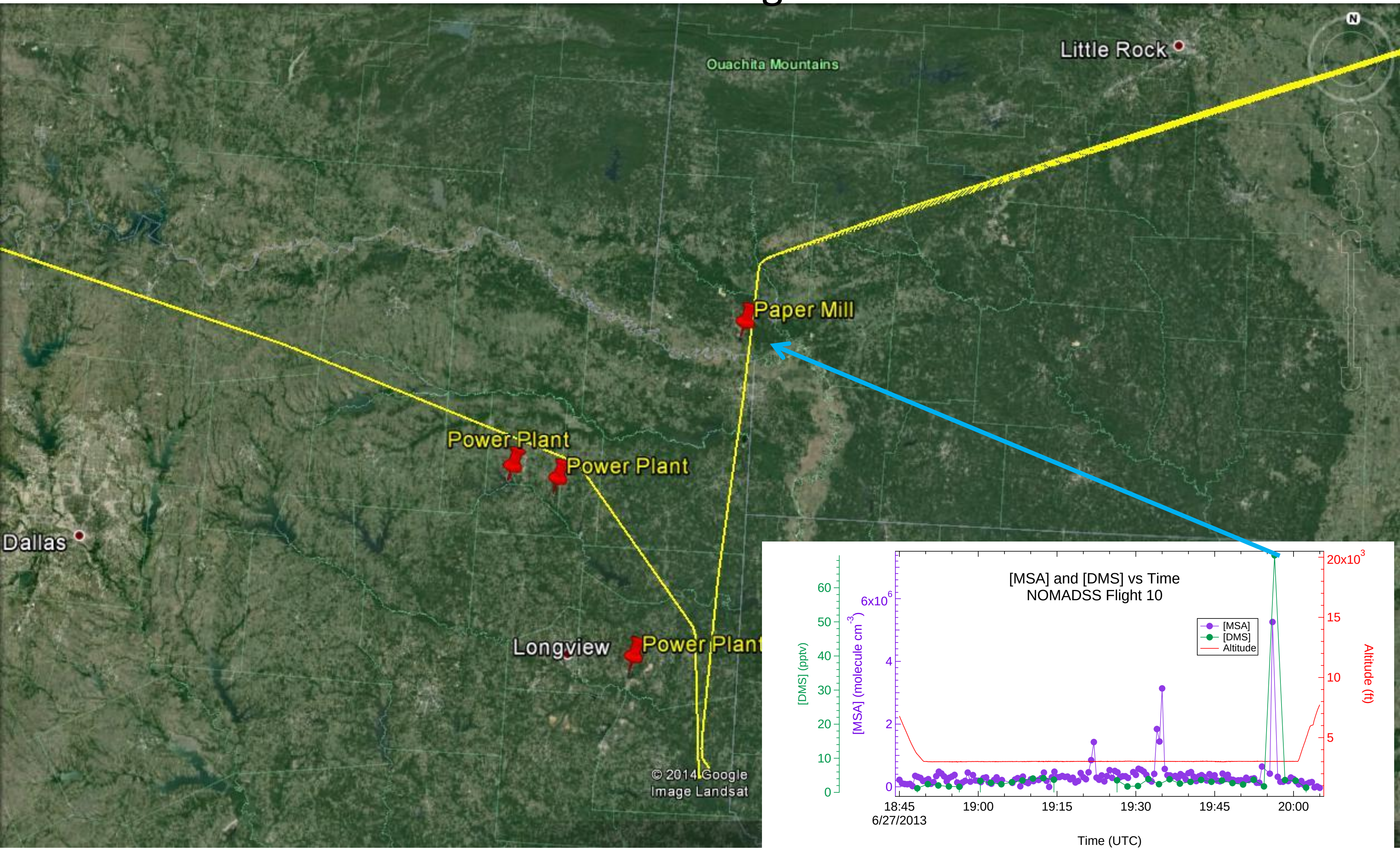
[MSA] vs Time
NOMADSS Flight 10
[MSA]
Altitude
6x10^6
4
2
0
[MSA] (molecule cm^-3)
20x10^3
15
10
5
Altitude (ft)
18:45
6/27/2013
19:00
19:15
19:30
19:45
20:00
Time (UTC)


[MSA] and [DMS] vs Time
NOMADSS Flight 10
[MSA]
[DMS]
Altitude
[DMS] (pptv)
[MSA] (molecule cm^{-3})
Altitude (ft)
0
10
20
30
40
50
60
2
4
6x10^{6}
5
10
15
20x10^{3}
18:45
6/27/2013
19:00
19:15
19:30
19:45
20:00
Time (UTC)

NOMADSS Flight 10



NOMADSS Flight 10



Domtar Nacoosa Paper Mill

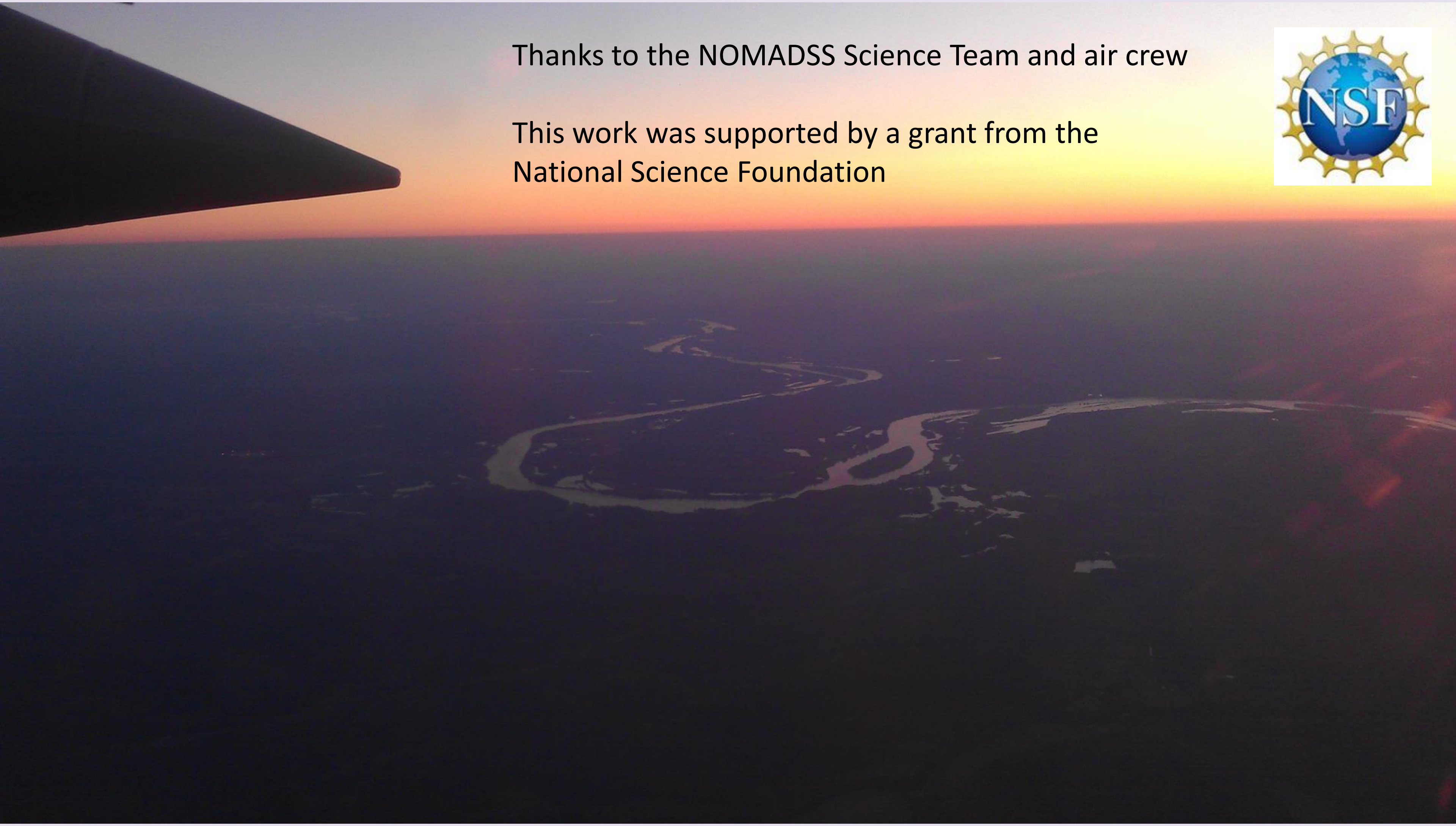
Summary

☺ Oxidants and oxidation products were observed during NOMADSS ☺

- Mid-day BL [OH] ~2-4 x 10^6 molecule cm^{-3}. [OH] > 1 x 10^{7} in urban outflow
- Power plant plume encounters showed elevated levels of both SO_2 and H_2SO_4
  H_2SO_4 > 5 x 10^7 molecule cm^{-3}. Largest concentration > 2 x 10^8 !!!
- Measurements near Texarkana, AR showed a continental source of DMS as well as it's oxidation product MSA. Probably source – Domtar paper mill in Ashdown, Arkansas.
- OH "Background" measurements over a forest south of St. Louis showed an increase in oxidants capable of oxidizing SO_2, but do not react with propane – sCI. Increase in oxidative capacity due to biogenic activity.

Future Work

- Box modeling of sulfur chemistry
- Mercury oxidation chemistry
- HONO chemistry



Thanks to the NOMADSS Science Team and air crew

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