Airborne Measurements of Nitryl Chloride and Implications for Chlorine Activation in the South Coast Air Basin of California

J.M. Roberts; S.S. Brown; W.P. Dubé; J. Neuman; J.B. Nowak; C.A. Brock; A.M. Middlebrook; R. Bahreini; T.B. Ryerson; I.B. Pollack; P.R. Veres; A.K. Cochran; C. Warneke; J.A. de Gouw

Introduction to $ClNO_2$ chemistry: what do we know about it so far

Measurements aboard the NOAA WP-3 During CalNex 2010

What does this tell us about $ClNO_2$ formation chemistry

Photo: Sarah Lance

sea salt

$$N_2O_{5(g)} + Cl^-_{(aq)} \Rightarrow ClNO_{2(g)} + NO_3^-{}_{(aq)}$$

$$ClNO_2 + h\nu \Rightarrow Cl + NO_2$$

Finlayson-Pitts, et al., 1989

<u>The Chemistry Requires</u>

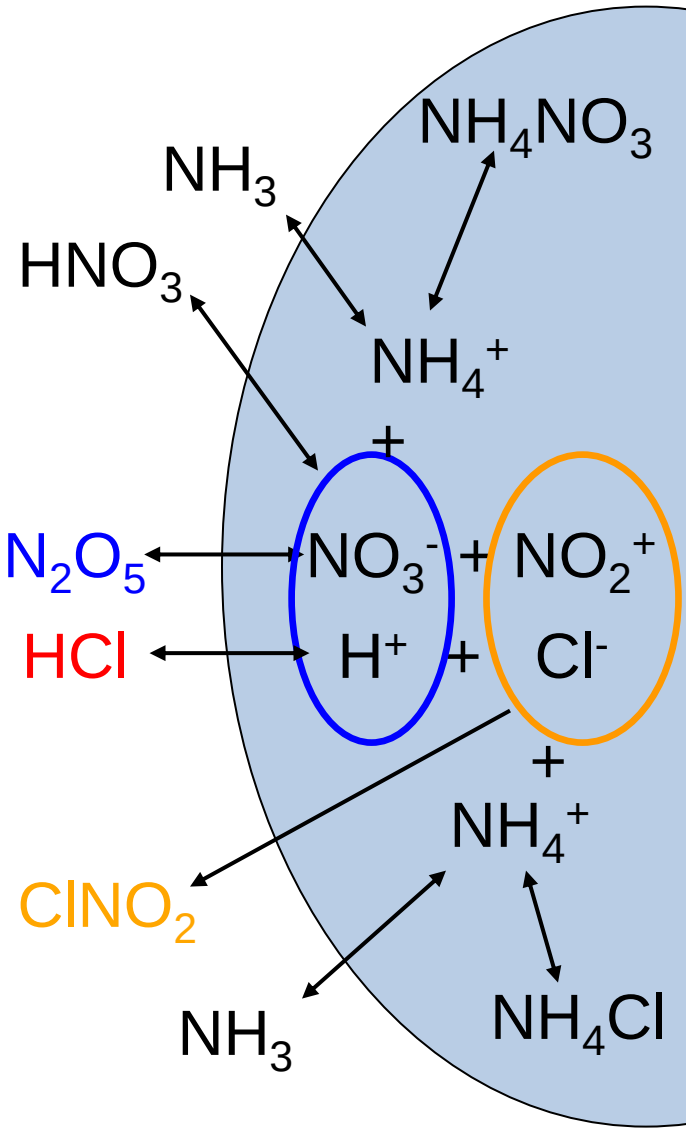
N_2O_5 (NO_2, O_3, Time,)

Efficient N_2O_5 uptake

Aerosol Surface Area

Aerosol Chloride

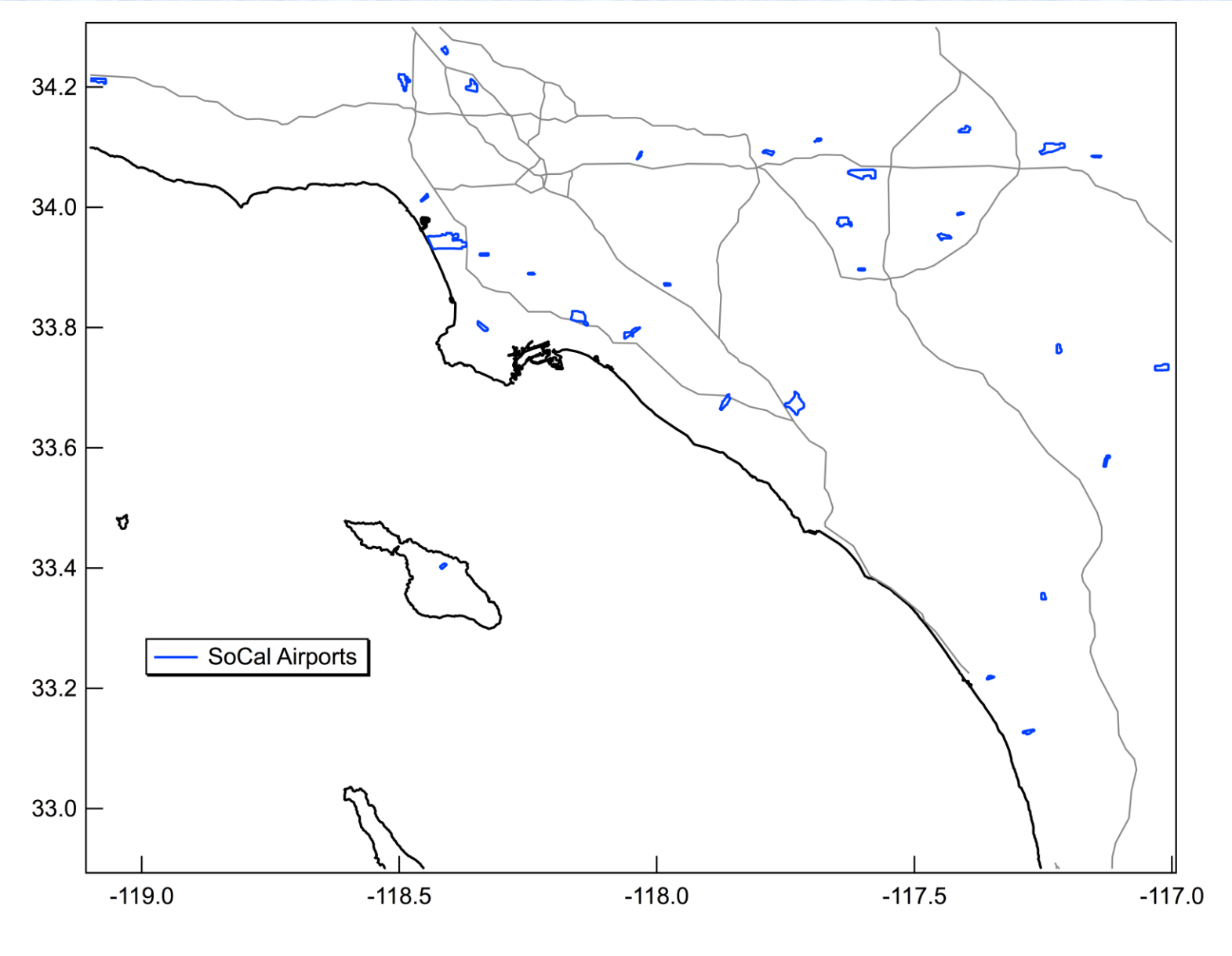
Source of Soluble Chloride to Aerosol



NOAA 43RF

$ClNO_2$	Iodide ion CIMS	Jim Roberts, Andy Neuman, John Nowak
NO_3, N_2O_5	CaRDS	Steve Brown, Bill Dube, Nick Wagner
NO_y, NO_2, NO, O_3	Chemiluminescence	Tom Ryerson, Ilana Pollack
NH_3	CIMS;	John Nowak
HNO_3	CIMS;	Andy Neuman
Aerosol Chemistry	C-ToF AMS;	Ann Middlebrook, Roya Bahreini
Aerosol Surface Area	NMASS/UHSAS	Chuck Brock

NOAA P3 Flight patterns for May 24, 30, 31 and June 2, 3, 2010 Night Flights



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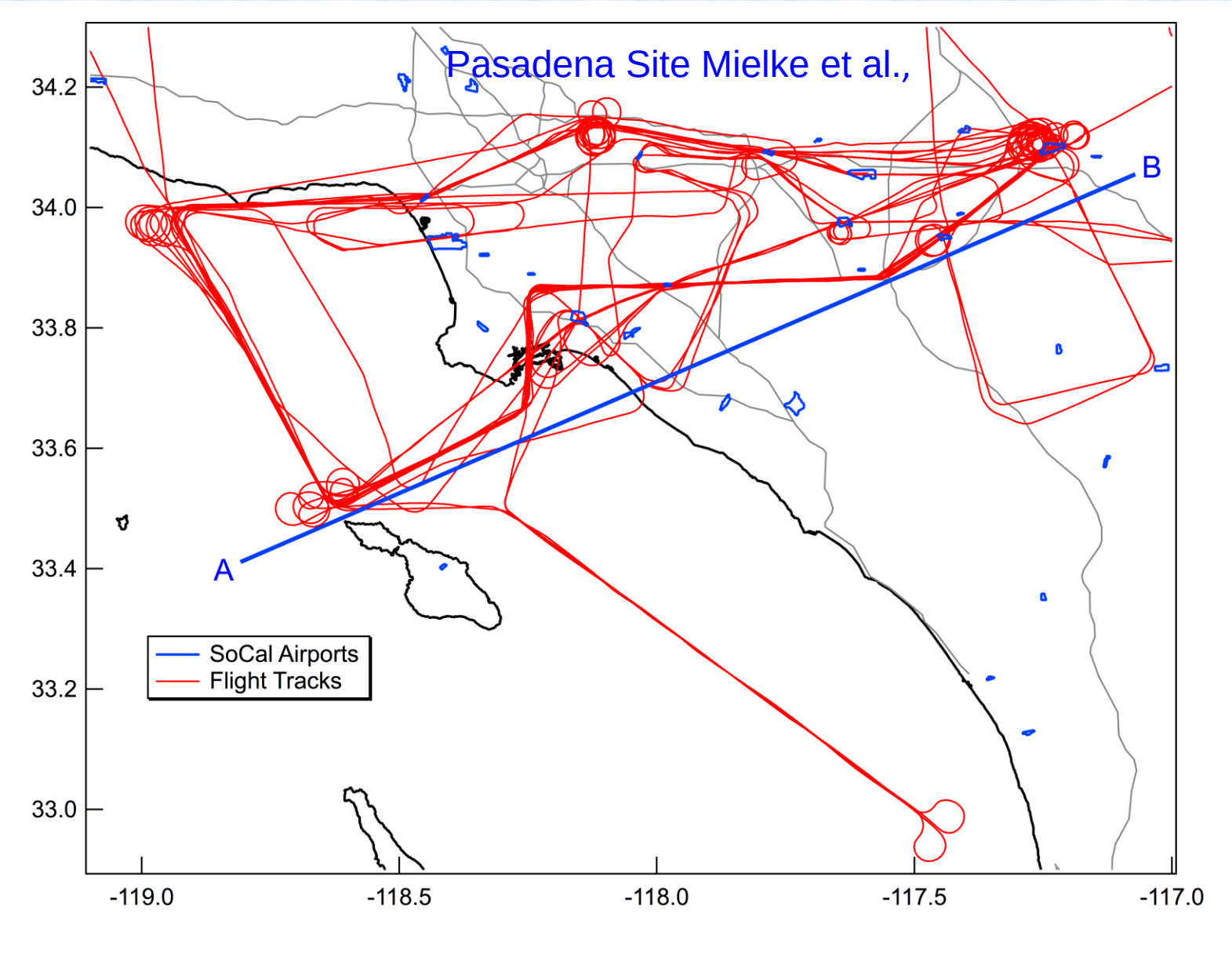
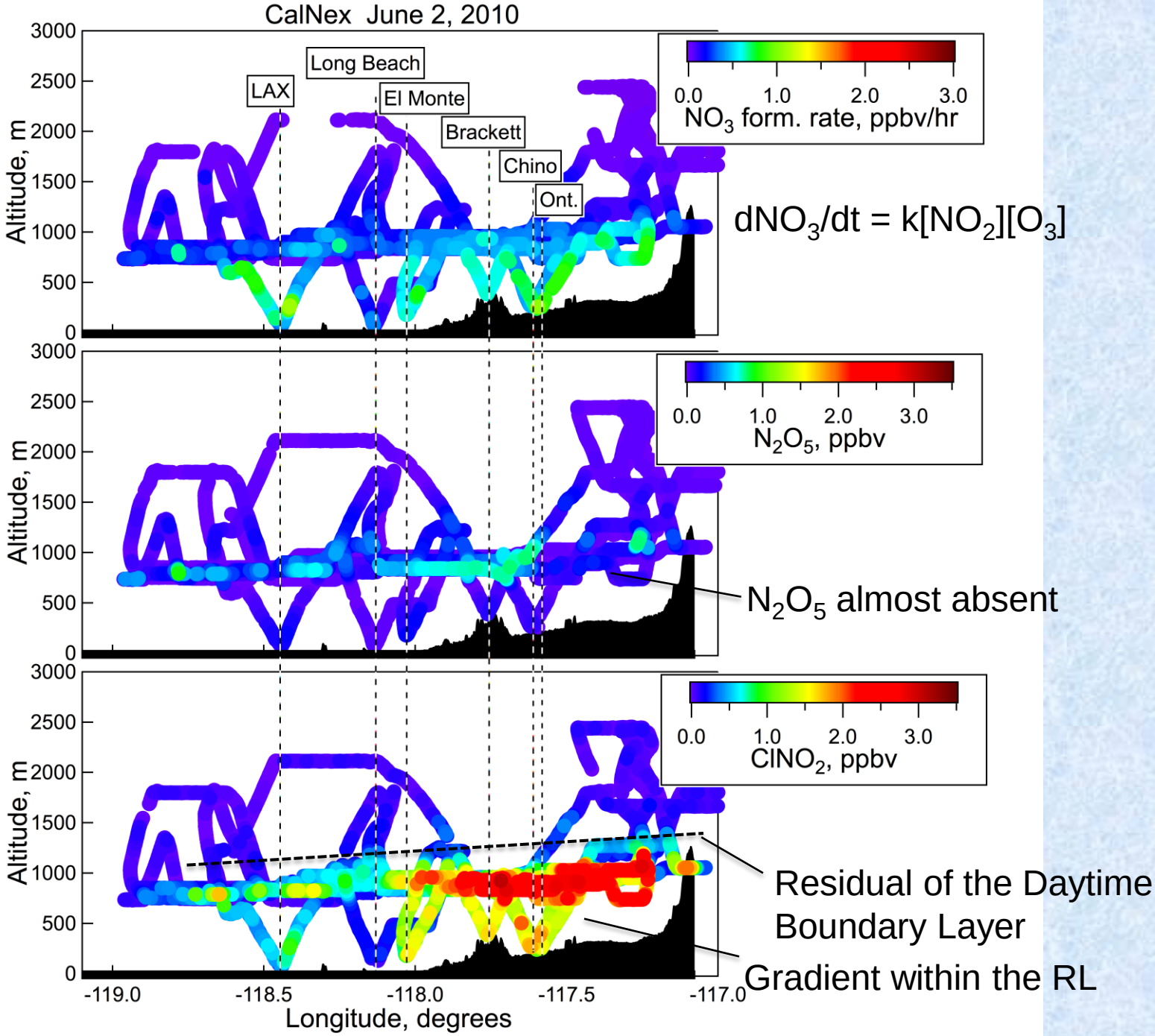


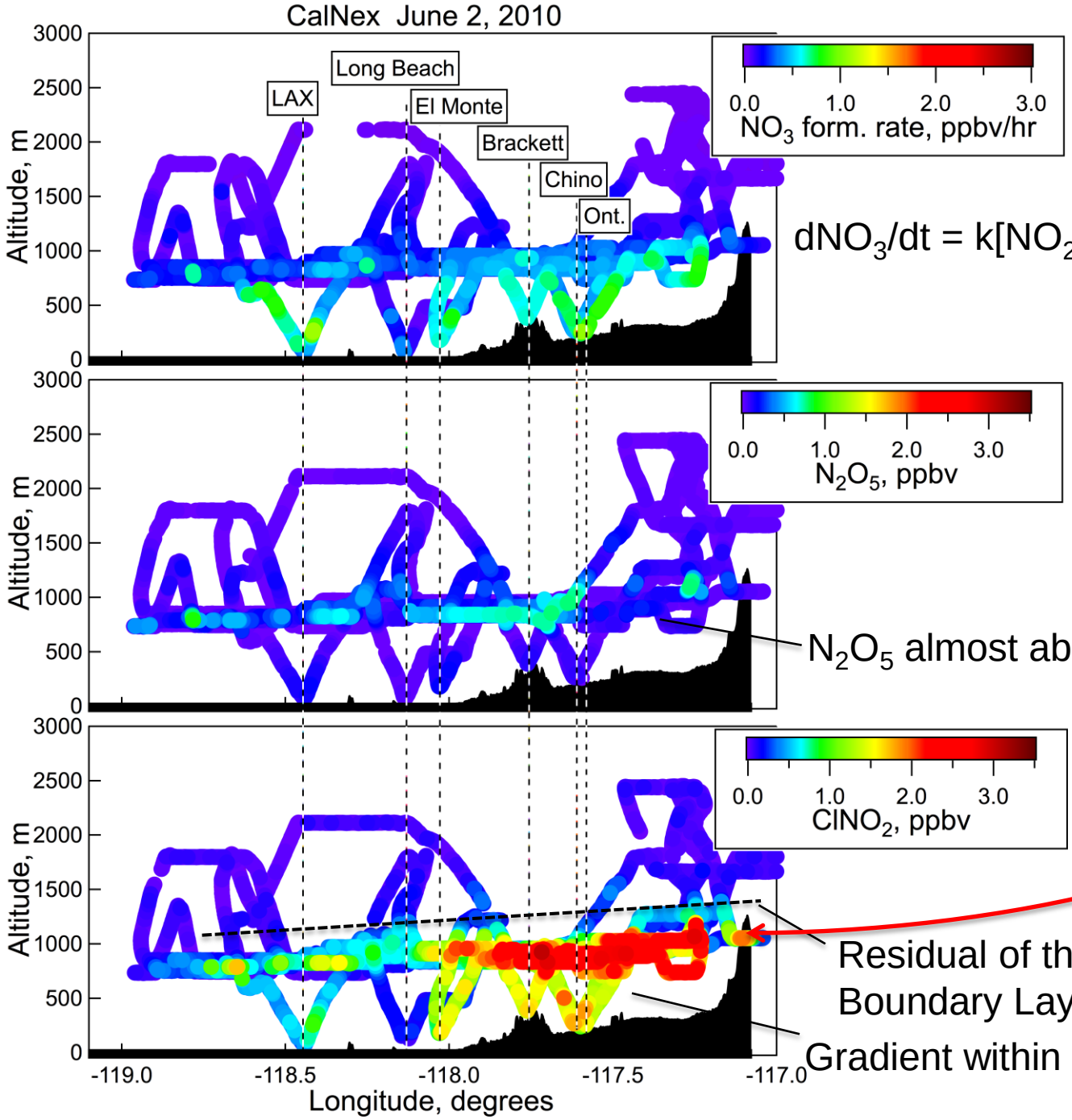


$dNO_3/dt = k[NO_2][O_3]$

N_2O_5 almost absent

Residual of the Daytime Boundary Layer

Gradient within the RL



$dNO_3/dt = k[NO_2][O_3]$

Ozone Production

$ClNO_2 + h\nu \Rightarrow Cl + NO_2$

$Cl + RH \Rightarrow RO_2$

$RO_2 + NO \Rightarrow RO + NO_2$

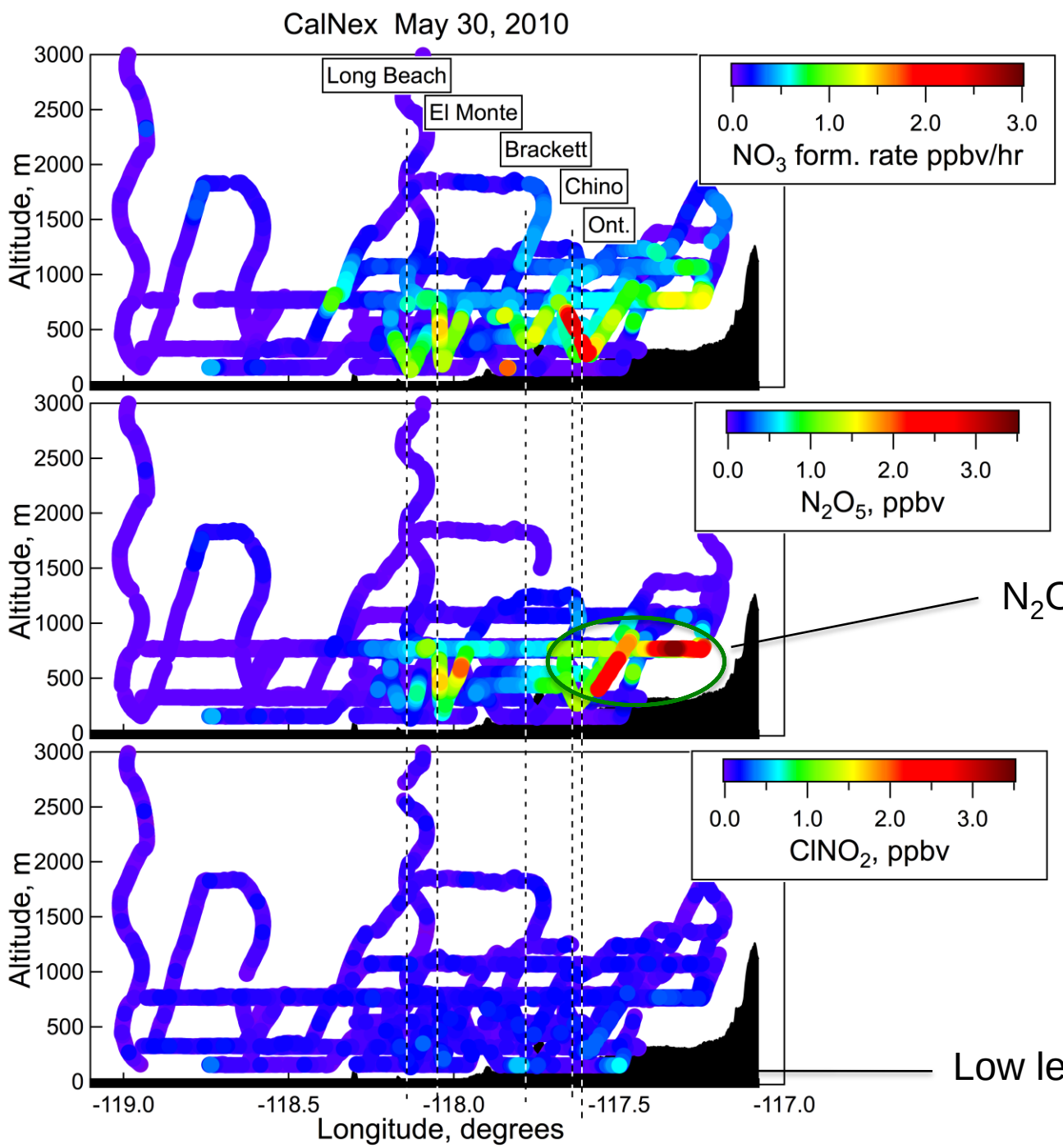
$RO + O_2 \Rightarrow HO_2 + OVOC$

$HO_2 + NO \Rightarrow NO_2 + OH$

N_2O_5 almost absent

Residual of the Daytime Boundary Layer

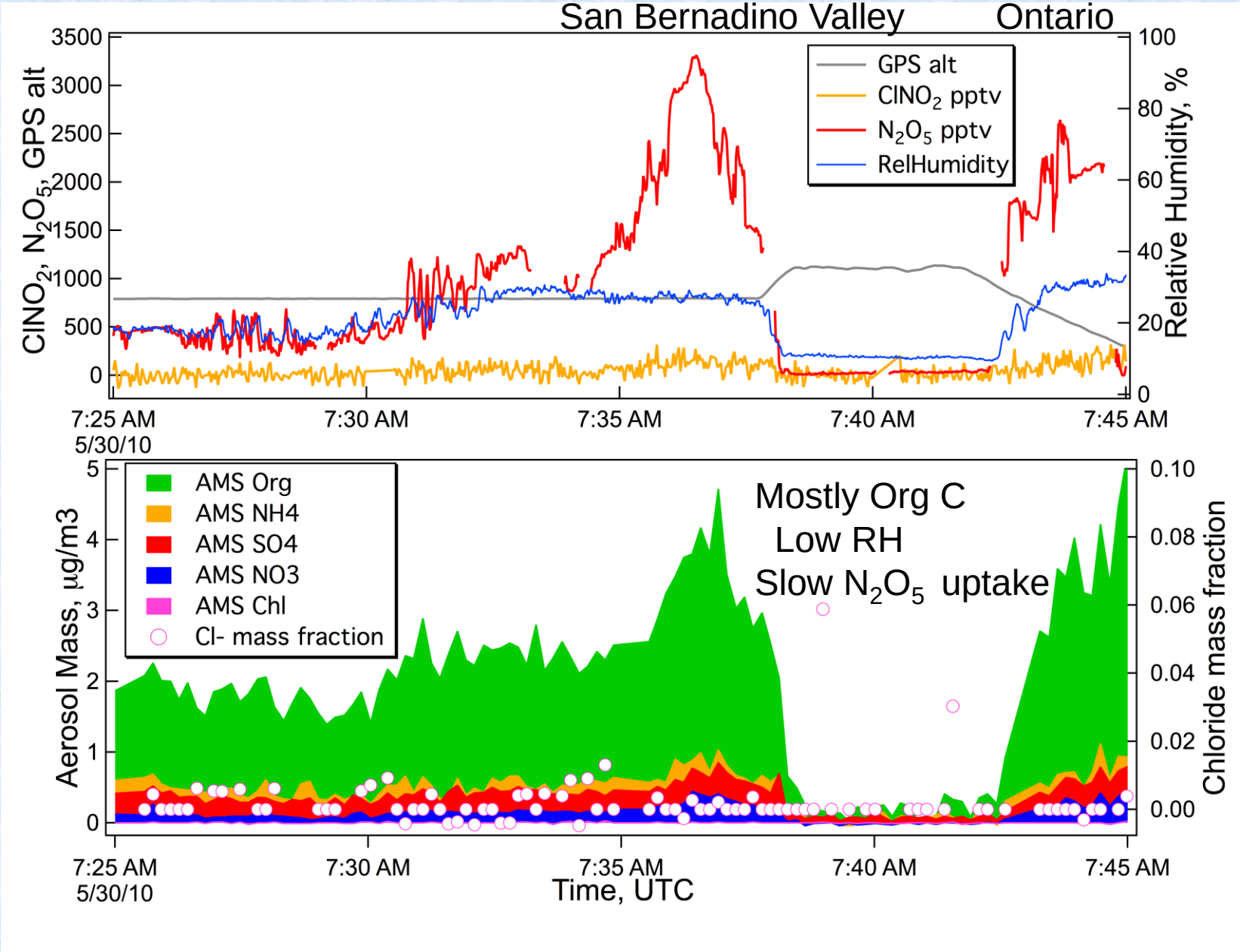
Gradient within the RL

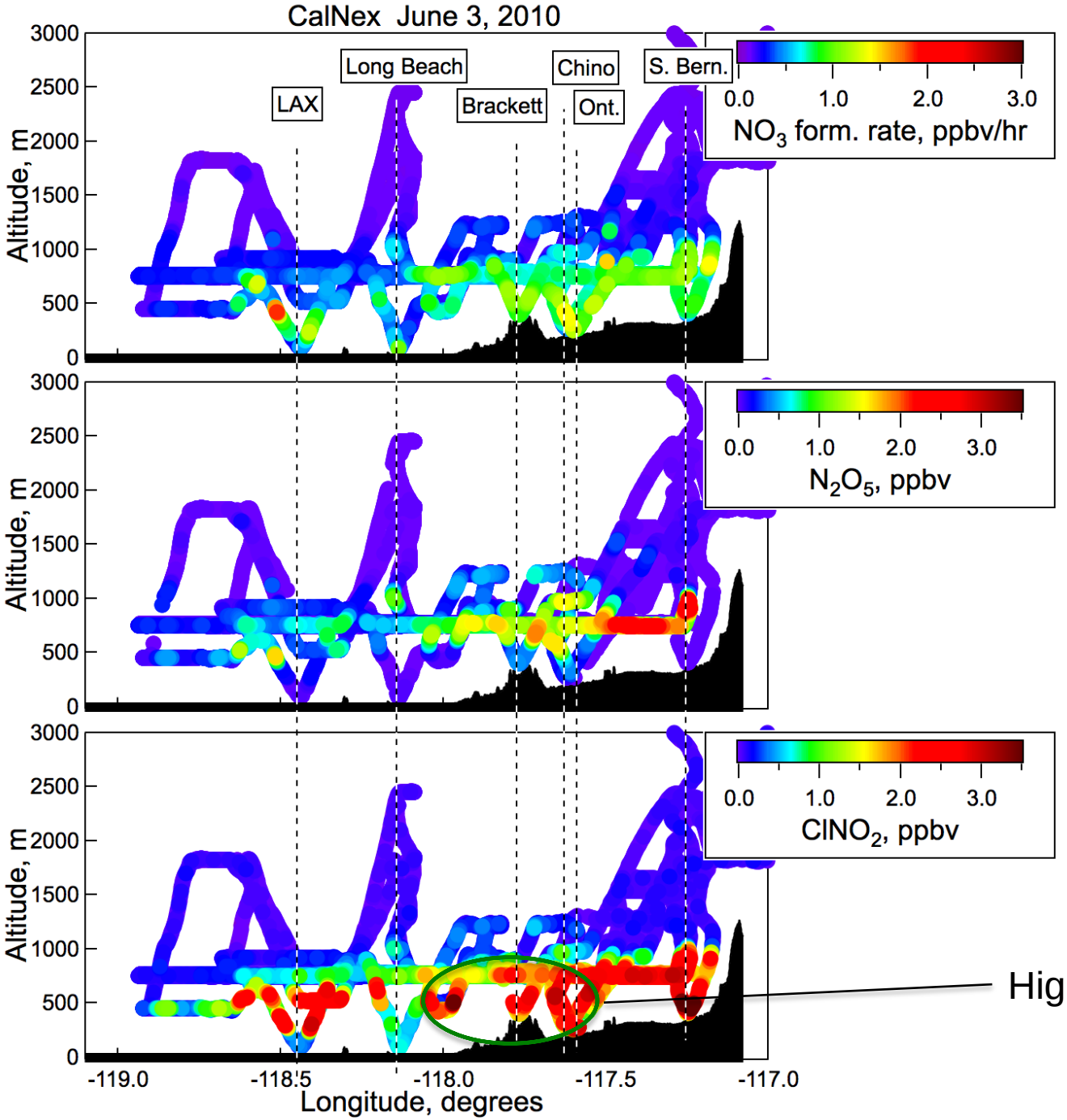


N_2O_5, but not much $ClNO_2$

Low level leg over the Ocean

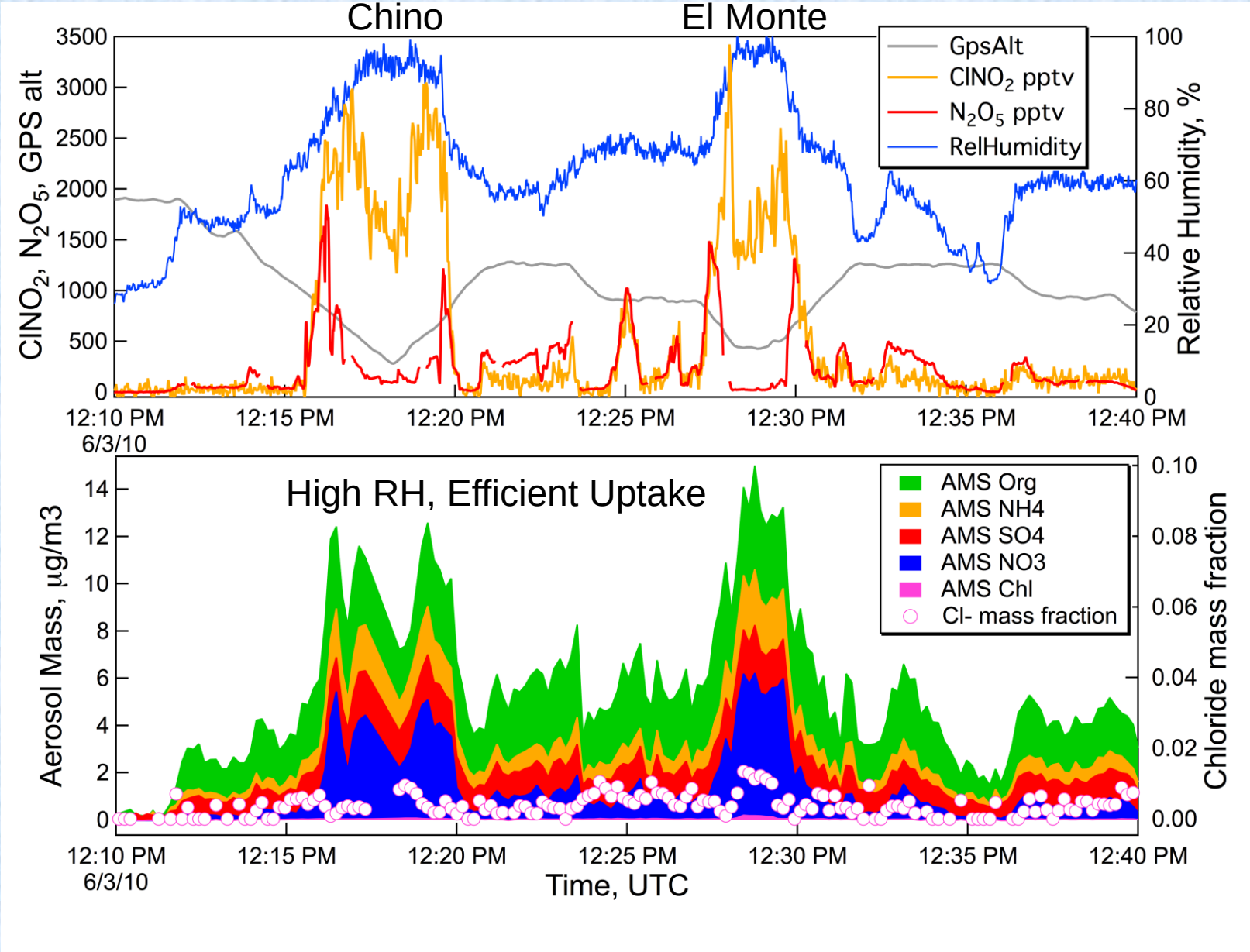
May 30, 2010 Flight –N_2O_5 High, almost no $ClNO_2$



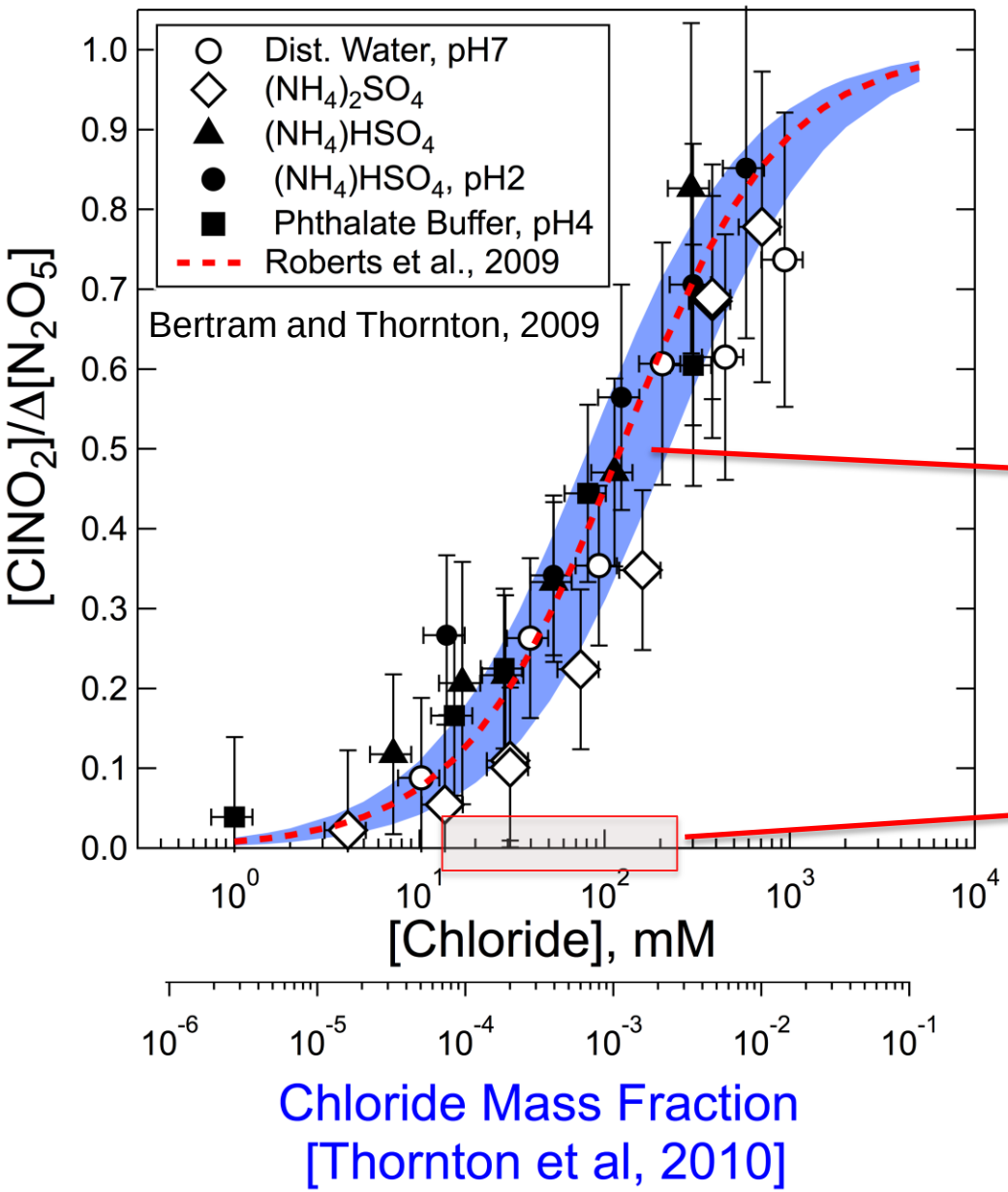


High $ClNO_2$ close to ground

June 3, 2010 Flight – High $ClNO_2$ close to the ground



Reaction efficiency vs. particle chloride



$N_2O_5 \Leftrightarrow NO_2^+ + NO_3^-$

$NO_2^+ + Cl^- \Rightarrow ClNO_2$

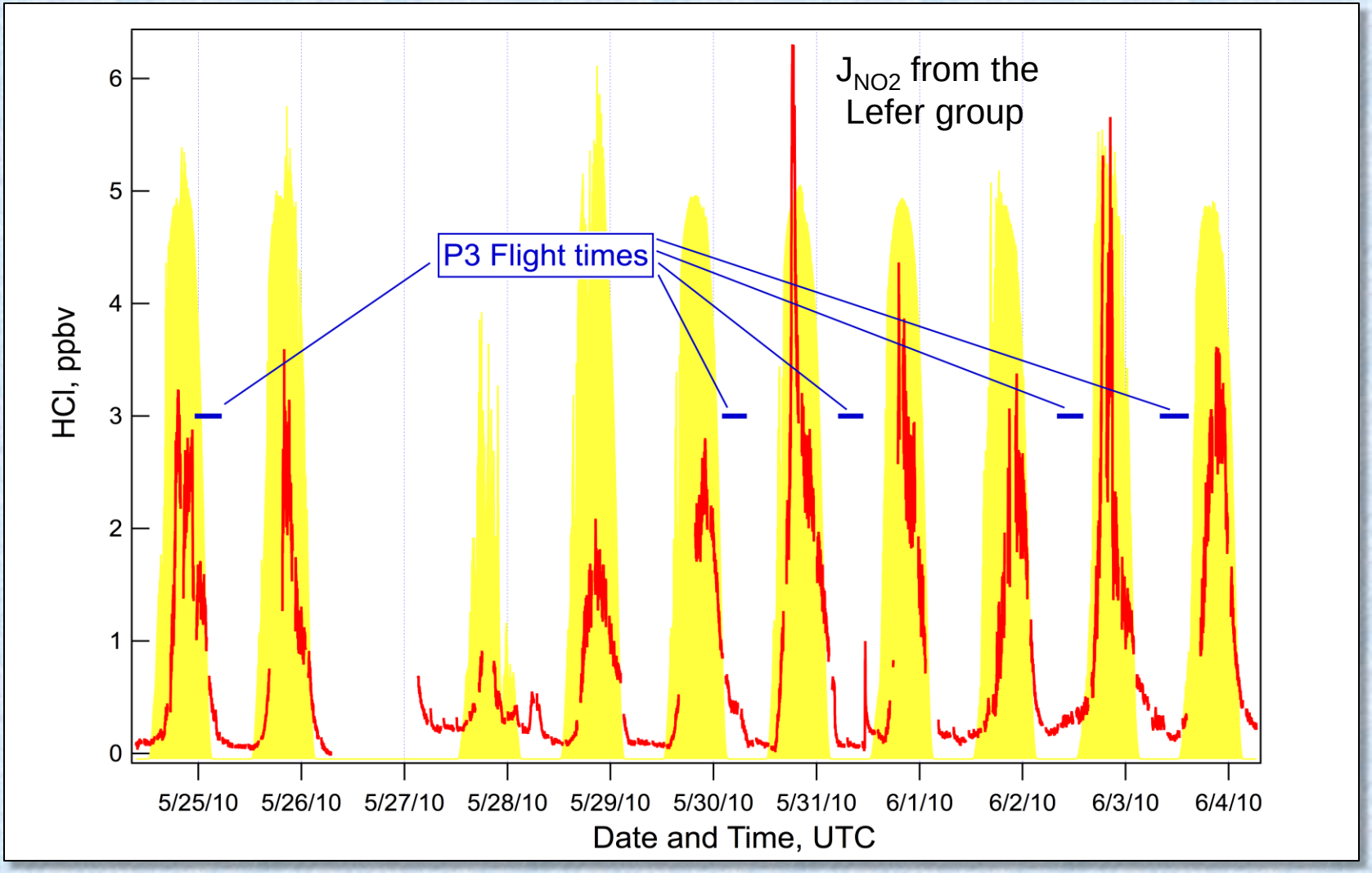
$NO_2^+ + H_2O \Rightarrow HNO_3 + H^+$

in the particle

The chemistry is efficient even at modest [Cl-]

Low [Cl^-] difficult to measure by AMS

Mass balance requires a gas phase source of soluble chloride
HCl measurements at the Pasadena ground site



If mid-day HCl is somewhat characteristic of the Daytime PBL then the Residual Layer has 2-6 ppbv HCl (see also Eldering, et al., *Atmos. Environ.*, **25A**, 2091, 1991)

Trevor VandenBoer et al., P21 - Thursday

Box model of N_2O_5 to $ClNO_2$ conversion

R1 $NO + O_3 \Rightarrow NO_2 + O_2$

R2 $NO_2 + O_3 \Rightarrow NO_3$

R3 $NO_3 + NO_2 \Leftrightarrow N_2O_5$

R4 $N_2O_5 + Cl^-_{(aerosol)} \Rightarrow ClNO_2 + HNO_3$

R5 $N_2O_5 + H_2O_{(aerosol)} \Rightarrow 2HNO_3$

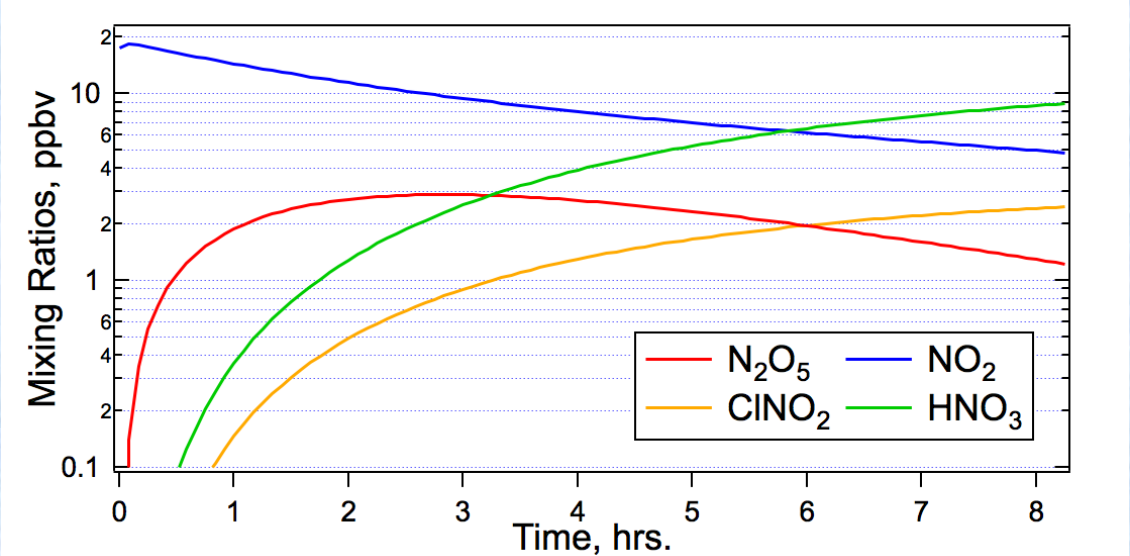
R6 $NO_3 + NO \Rightarrow 2NO_2$

$N_2O_5 + H_2O \Leftrightarrow NO_2^+(H_2O) + NO_3^-$

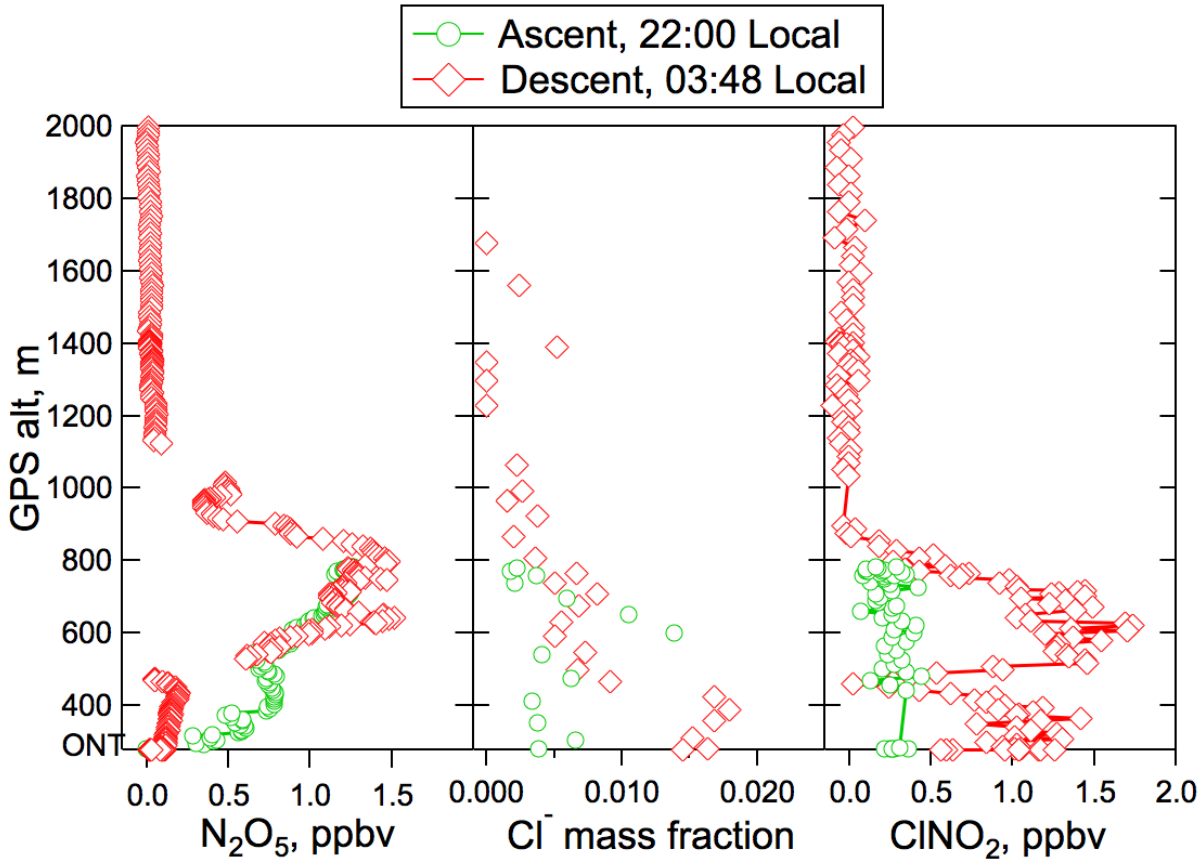
Sum: Total uptake rate
Ratio: Reaction efficiency

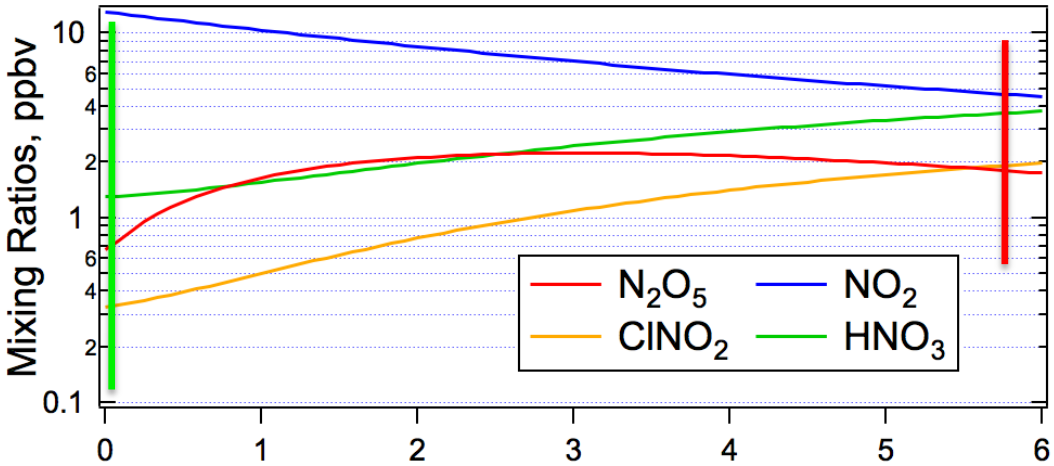
Initialize with ambient measurements
Adjust R4 and R5 to match N_2O_5 and $ClNO_2$ at end time
Calculate N_2O_5 uptake and $ClNO_2$ formation efficiency

Example Output



May 31, 2010 Flight



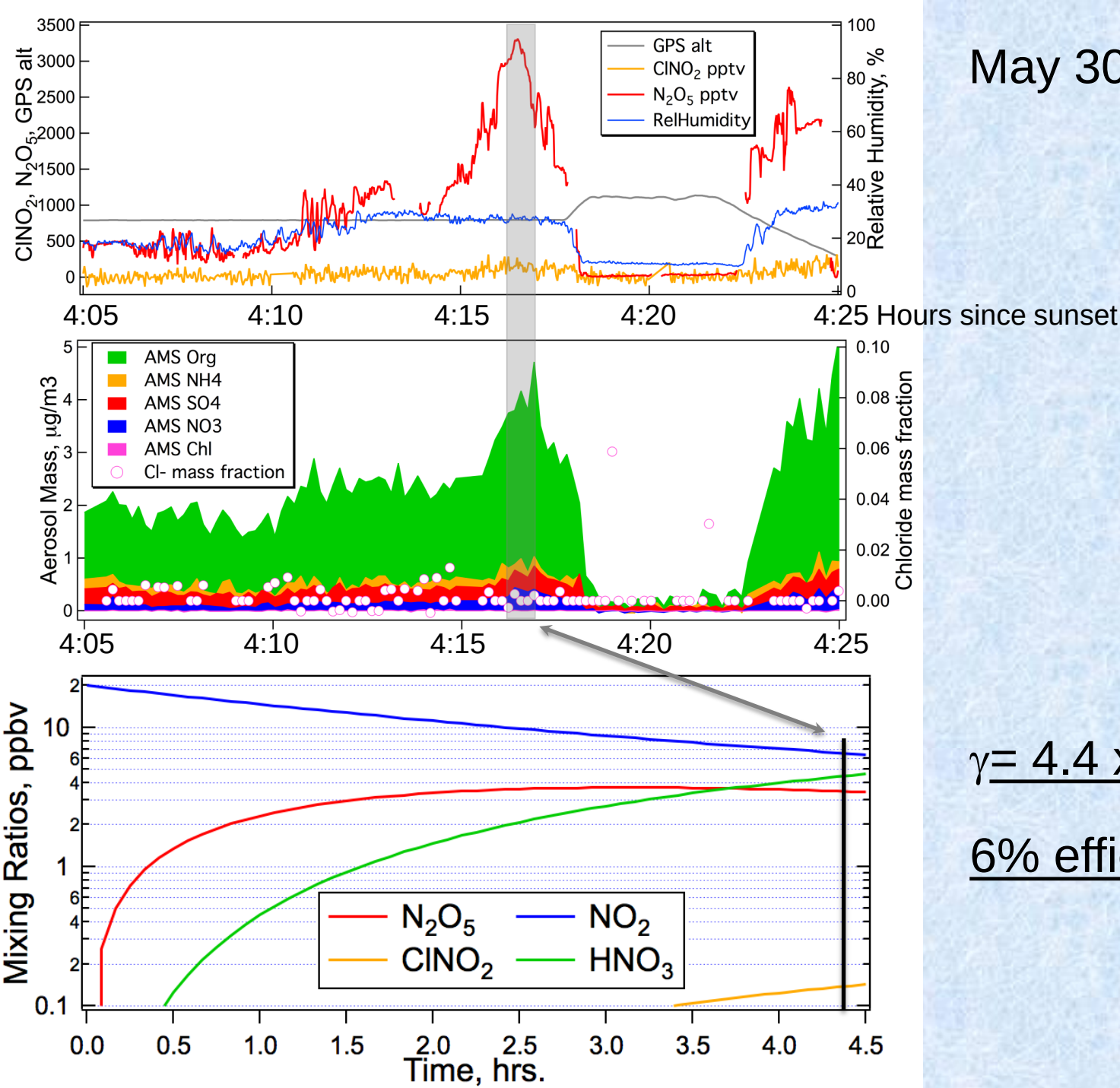


Ascent
vs
Descent

$\gamma = 3.3 \times 10^{-3}$

80% efficiency

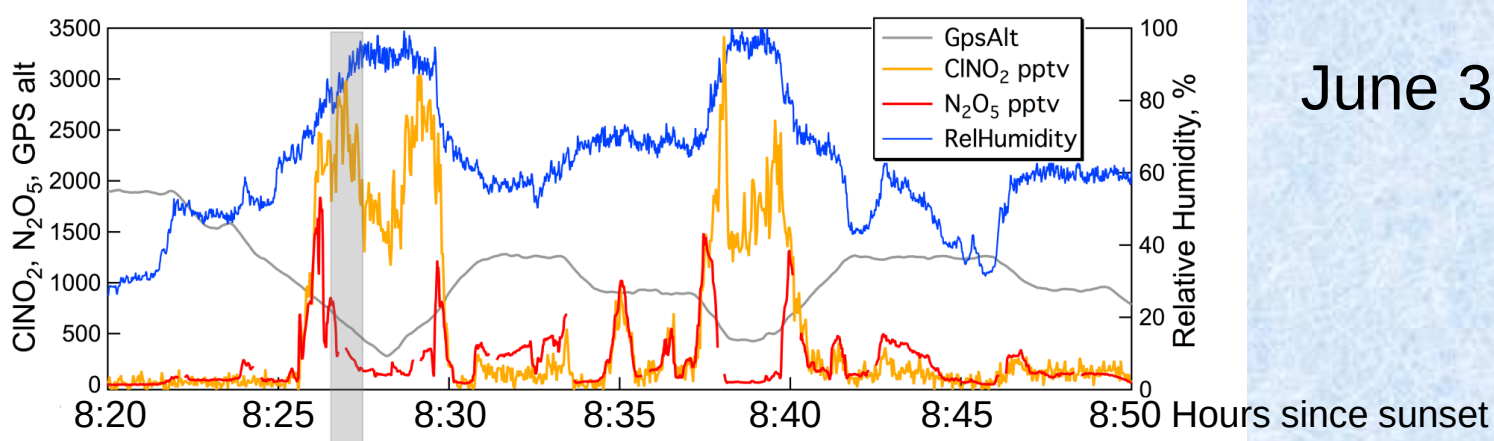
May 30, 2010 Flight

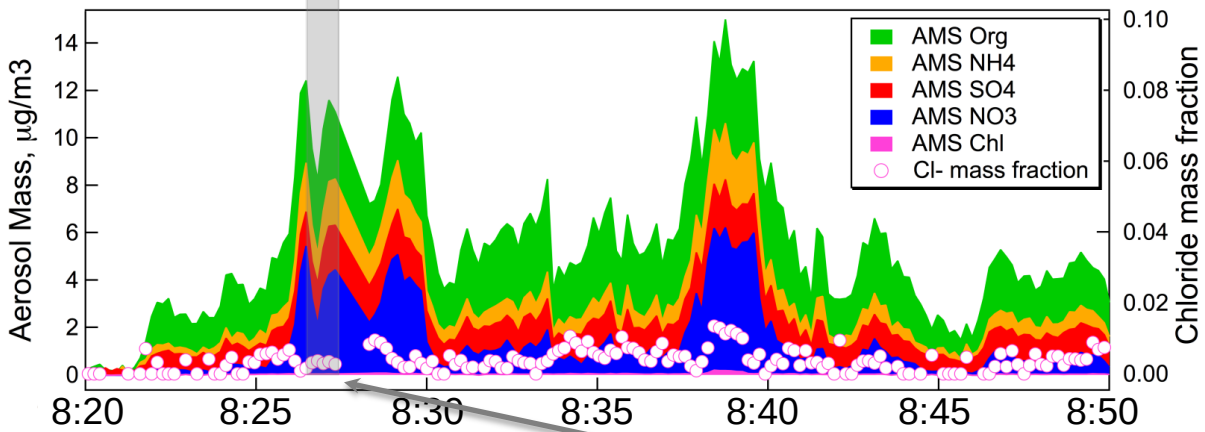


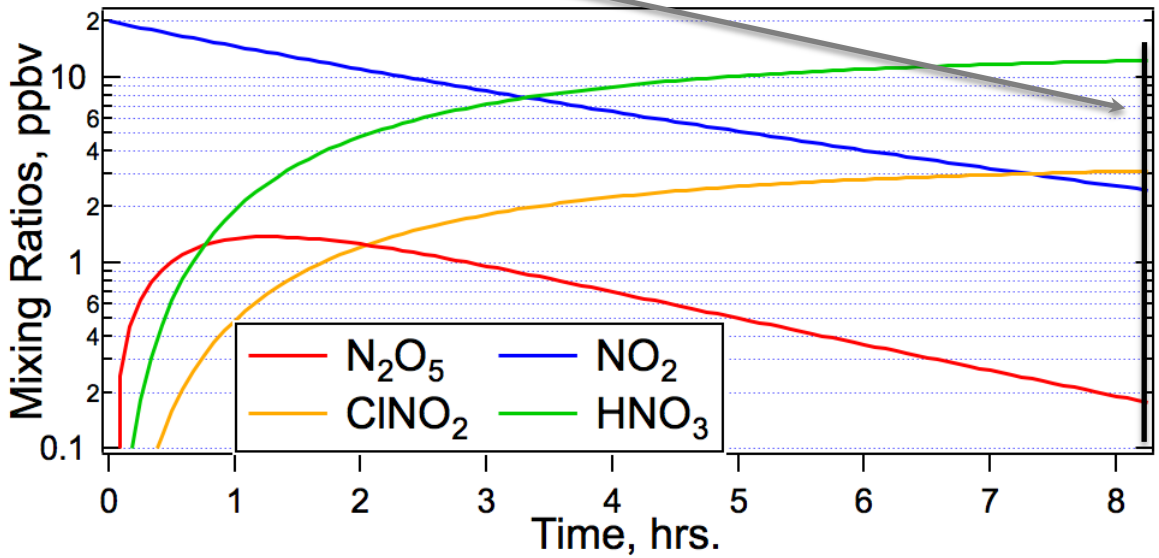
$\gamma = 4.4 \times 10^{-3}$

6% efficiency

June 3, 2010 Flight







$\gamma = 2.8 \times 10^{-2}$

44% efficiency

What does this tell us about uptake coefficients.

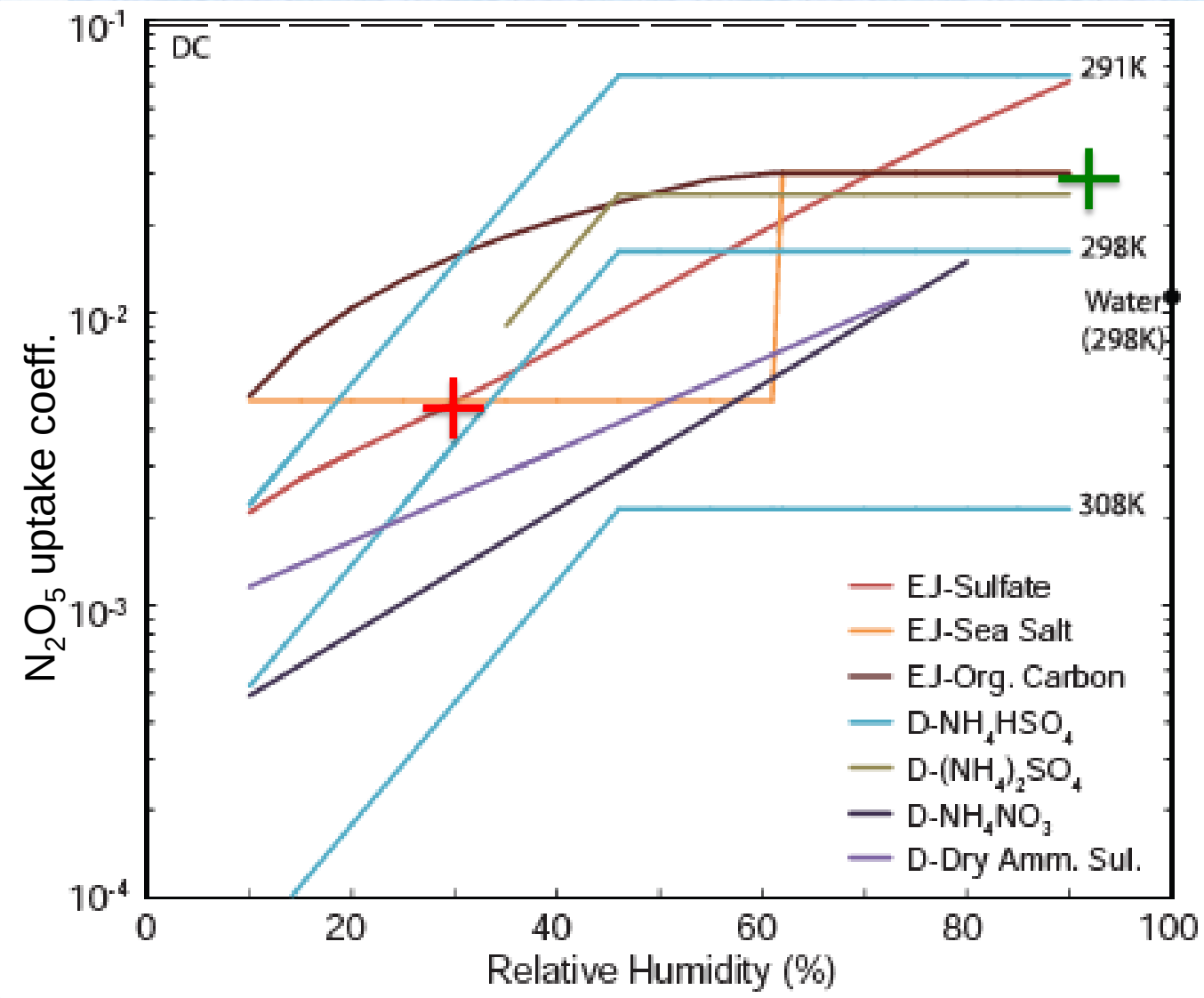


Figure 15. Chang et al., Aer. Sci. Technol., 45, 655-685, 2011.

Conclusions

$ClNO_2$ is often abundant in the nighttime residual layer, measured mixing ratios were up to 3.7 ppbv.

There is often enough aerosol surface area and chloride in the LA Basin to make the chemistry reasonably efficient.

Low $ClNO_2$ production seems to be related to low N_2O_5 uptake due to low RH and low aerosol chloride.

Box model runs make much more HNO_3/NO_3^- than is measured

Further Work/Problems/Unknowns

Nitrogen and Odd-Oxygen Balances
O_3 production from Cl atom Chemistry
Soluble Chloride Inventory