Nighttime Chemical Processing & Halogen Activation during CalNex 2010

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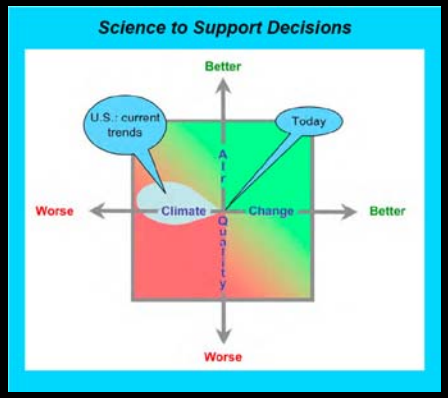
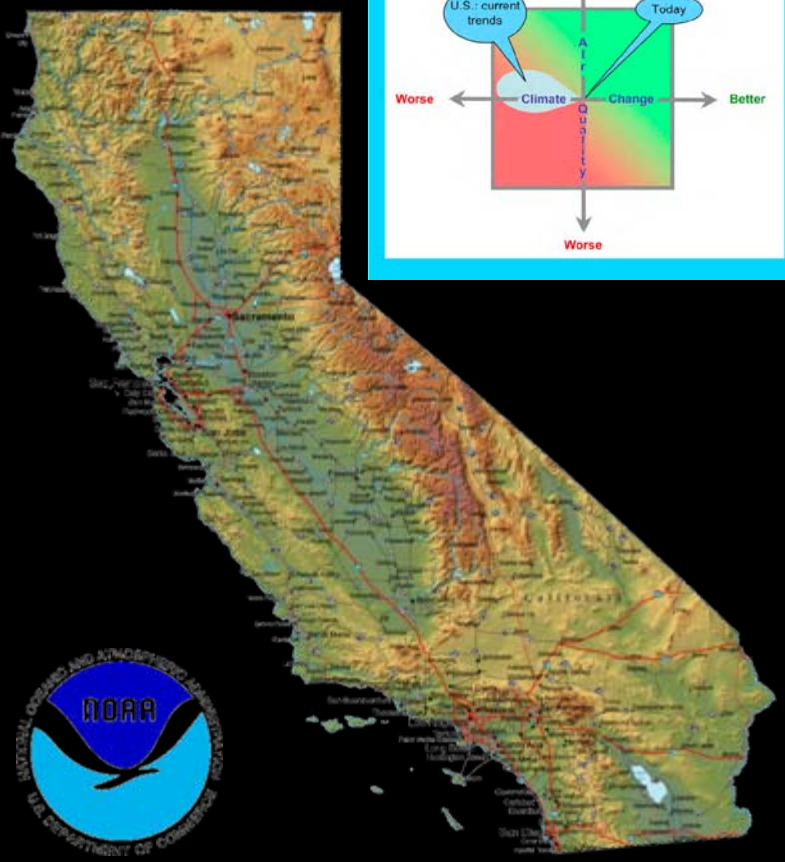
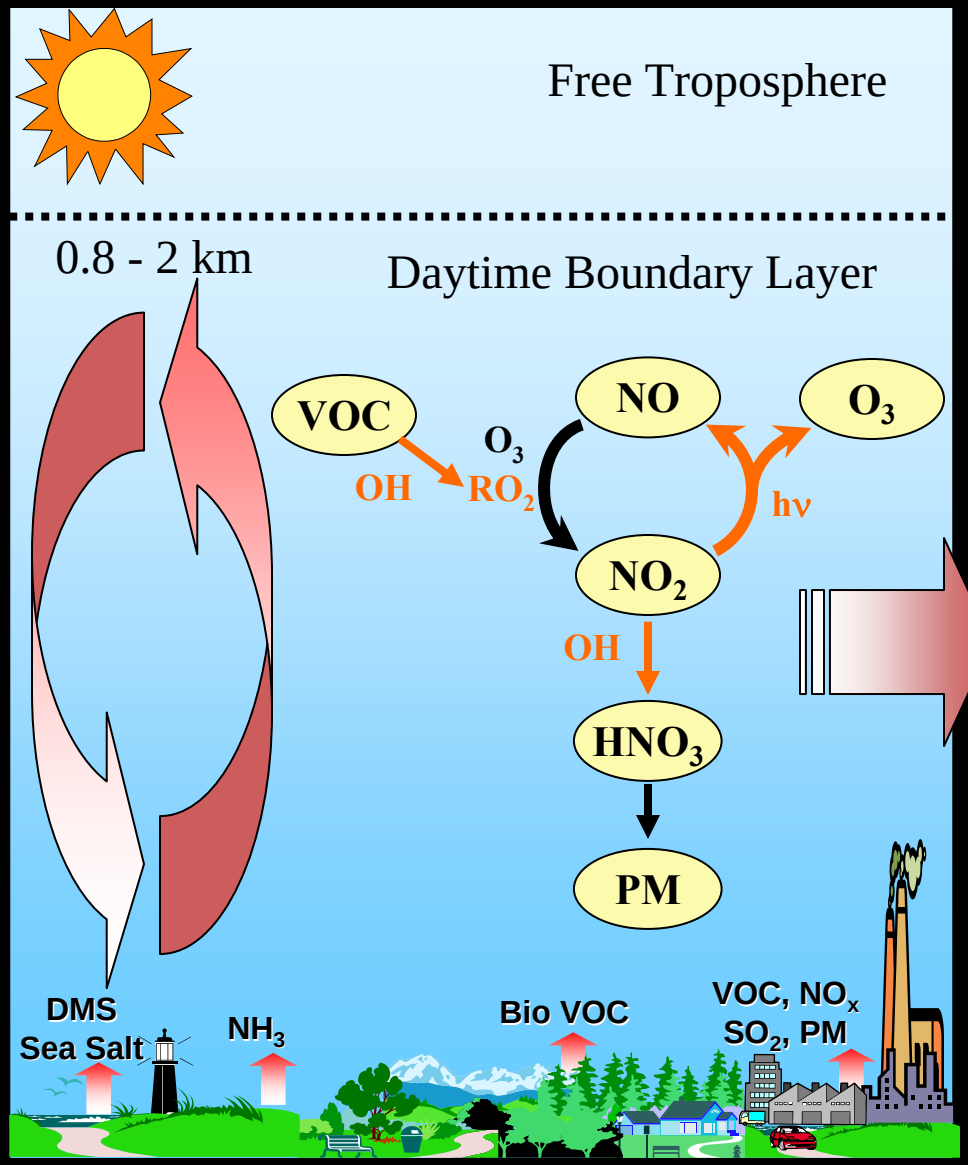


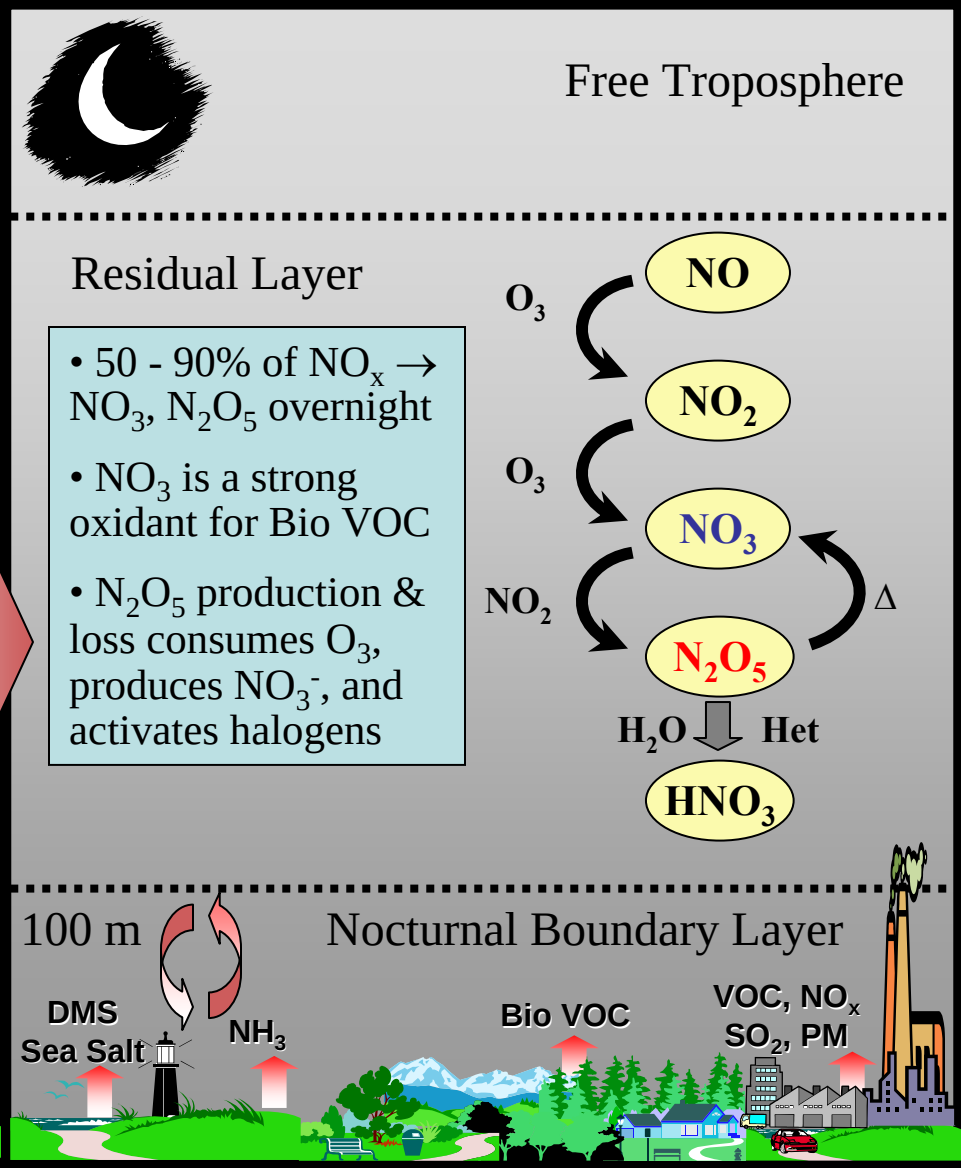


Outline

- Introduction - Role of nighttime processes in air pollution chemistry
- Overnight transport vs. loss of NO_x as N_2O_5
  - Next-day O_3 photochemistry
  - Nitrate aerosol
- Nighttime halogen activation from N_2O_5 uptake to sea salt aerosol

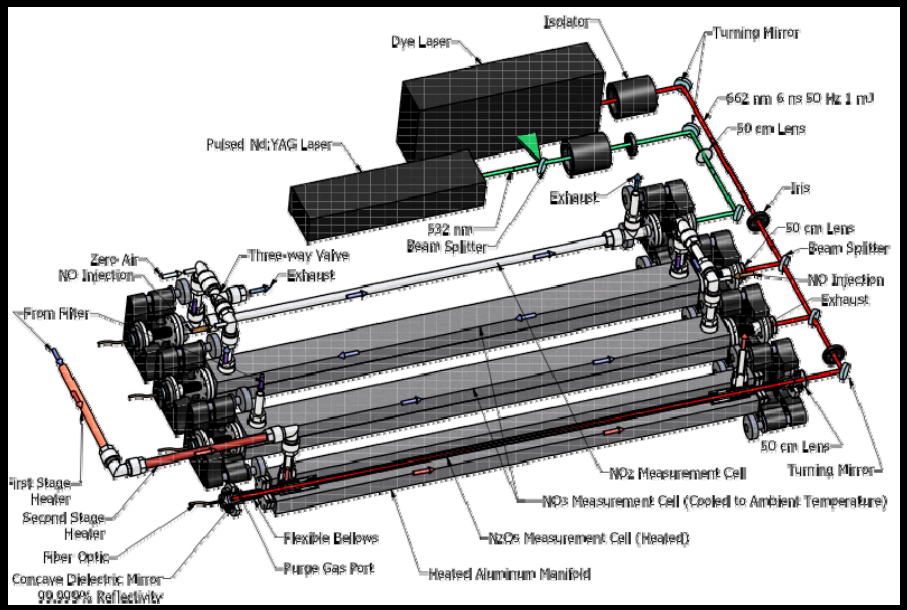
Diurnal Nitrogen Oxide Cycles

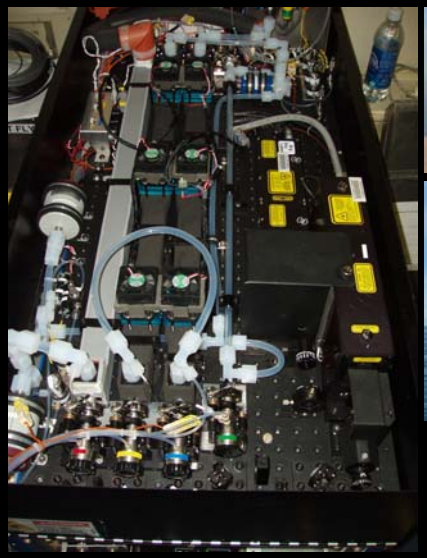




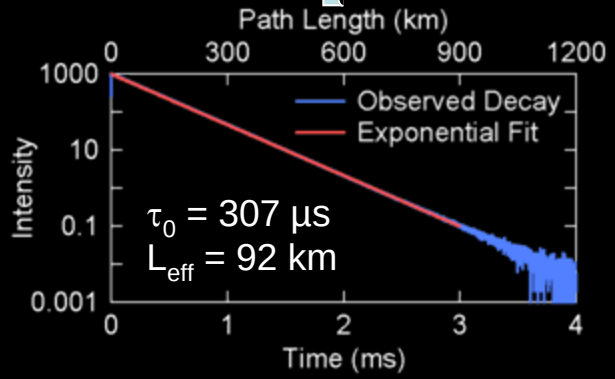
In-Situ NO_2, NO_3, N_2O_5 Instrument

"ARNOLD" = Airborne Ringdown Nitrogen Oxide Laser Detector





Pulsed Cavity Ring-down Spectroscopy



Measure first-order decay rate coefficient of light intensity from an optical cavity

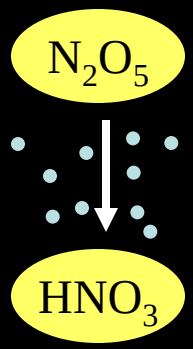
$\alpha_{min} \leqslant 10^{-10}$ cm^{-1}

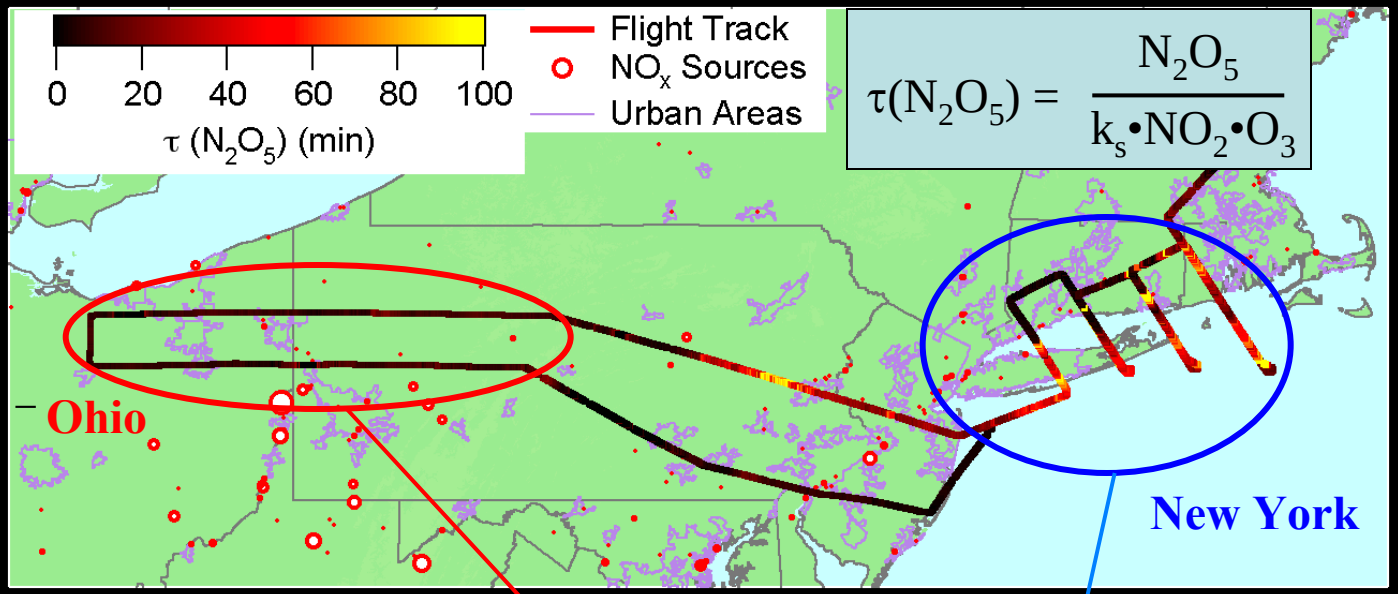
NO_2: 532-nm optical extinction
L.O.D. $\leqslant$ 0.1 ppbv @ 1 Hz
Accuracy = 5%

NO_3: 662 nm optical extinction
L.O.D = 0.2 - 2 pptv @ 1 Hz
Accuracy = 12%

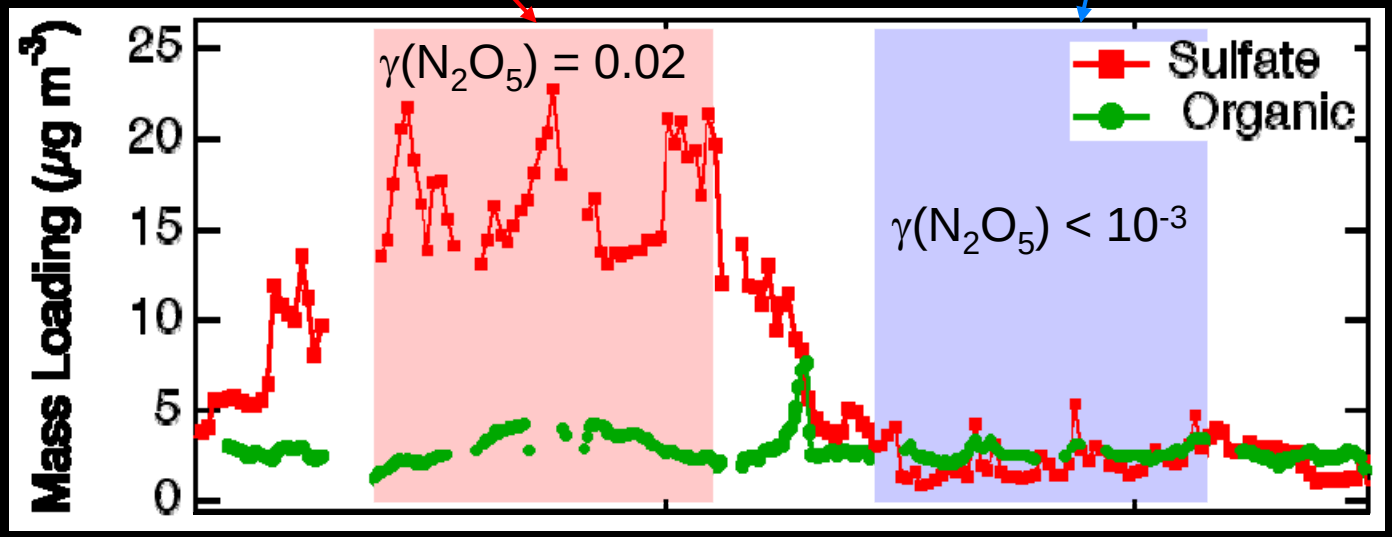
N_2O_5: Thermal conversion + 662 nm optical extinction
L.O.D. = 0.5 - 2 pptv @ 1 Hz
Accuracy = 10%

Variability in N_2O_5 Hydrolysis: Northeast U.S.





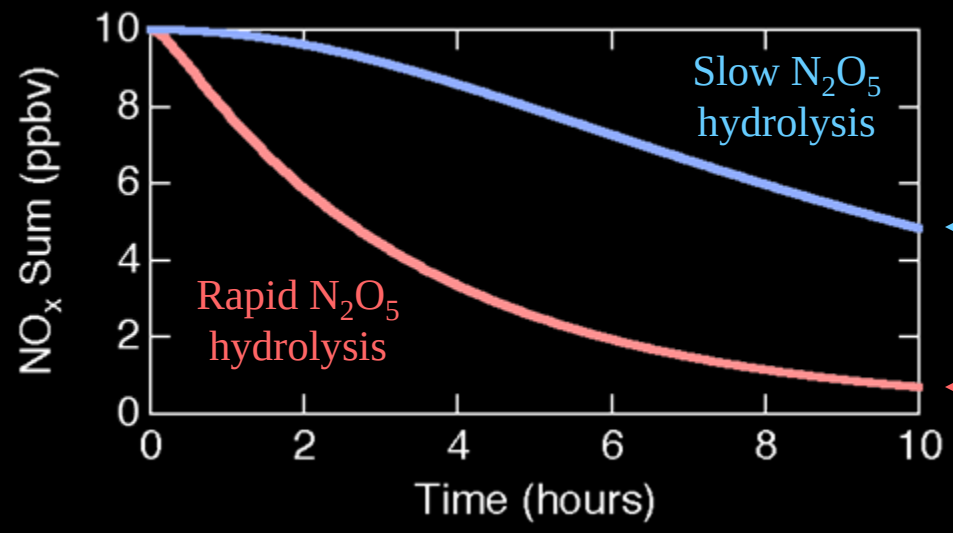
NO_x Chem



Aerosol

Regional variation in nighttime nitrogen oxide lifetime determined by amount and type of aerosol (e.g., sulfate vs. organic)

Effect on Next Day Ozone

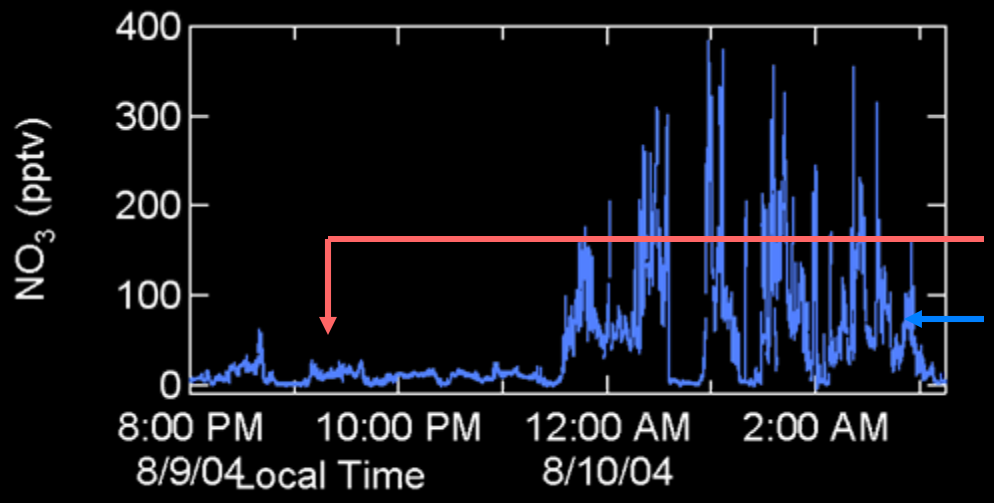


NO_x processing overnight

NO_x Sum = $NO_2 + NO_3 + 2\times N_2O_5$

50% $N_2O_5 \rightarrow NO_3 \rightarrow NO_x$

7% $N_2O_5 \rightarrow HNO_3$



Nocturnal Oxidative Capacity

Reactive VOC (e.g. alkenes, aldehydes)

$\gamma = 0.02$ τ(VOC) ~ 60 hours 15% loss

$\gamma < 0.001$ τ(VOC) ~ 6 hours 82% loss

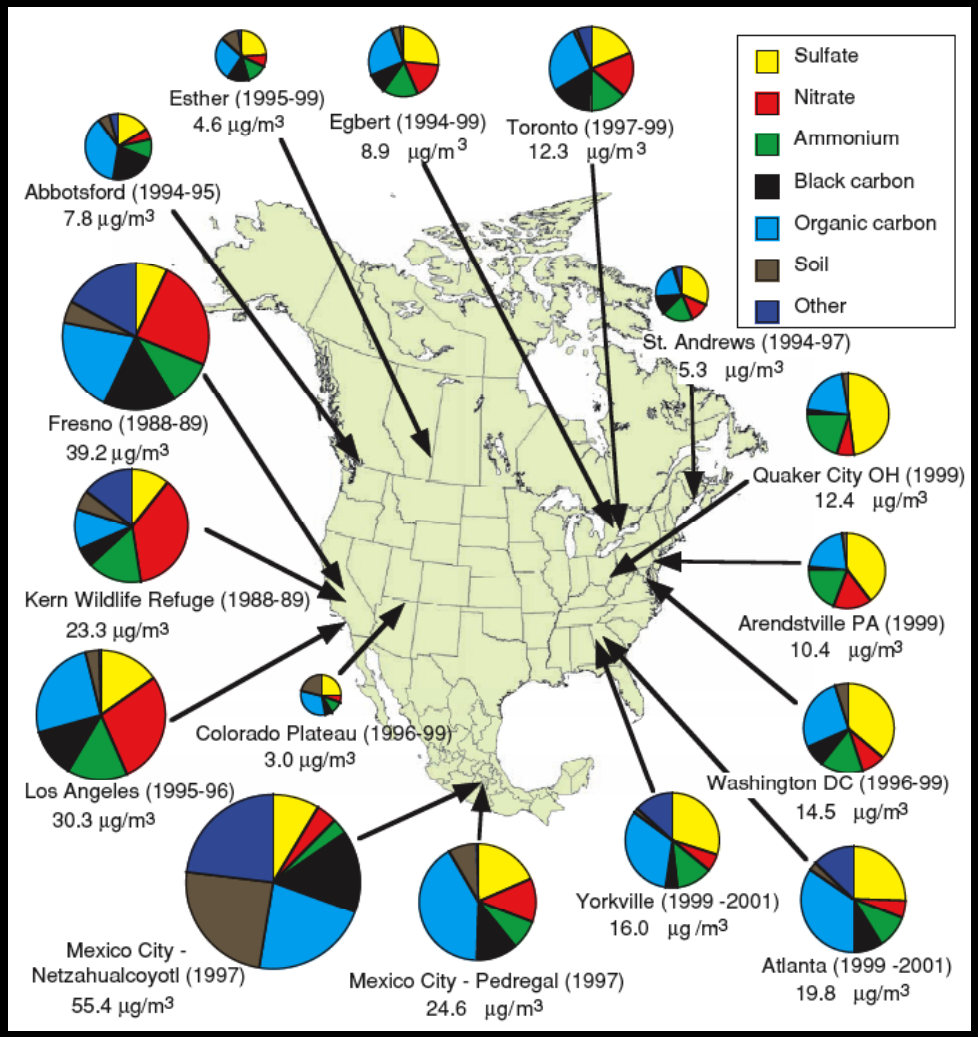
Variability in $\tau(N_2O_5)$ affects the 2 components of photochemical ozone

How Does this Affect California ?

- Daytime upslope flow / Nighttime drainage flow
- LA Basin is the receptor of its own emissions after nighttime transport
- Understanding chemical transformation within the return flow key to “background” ozone

- Nighttime return in vertically stratified atmosphere - study with P-3 and vertically resolved ground site
- Interbasin transport - Influence of overnight transport of LA emissions on Mojave Desert, San Joaquin Valley, etc.

Nitrate Aerosol and N_2O_5



Eastern U.S. SO_4^{-2} dominant
Western U.S. NO_3^- dominant

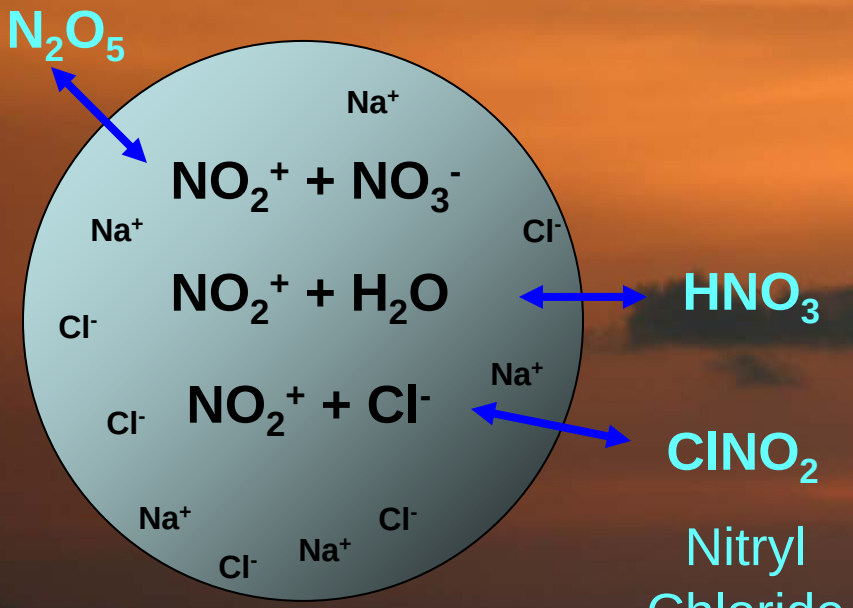
- Nighttime N_2O_5 hydrolysis a principal source of NO_3^-, and therefore nitrate aerosol, a key air quality issue in California

- Lab studies suggest NO_3^- aerosol *inhibits* uptake of N_2O_5. No conclusive field data on this effect.

$$N_2O_5\ (g) \rightleftharpoons NO_2^+\ (aq) + NO_3^-\ (aq)$$

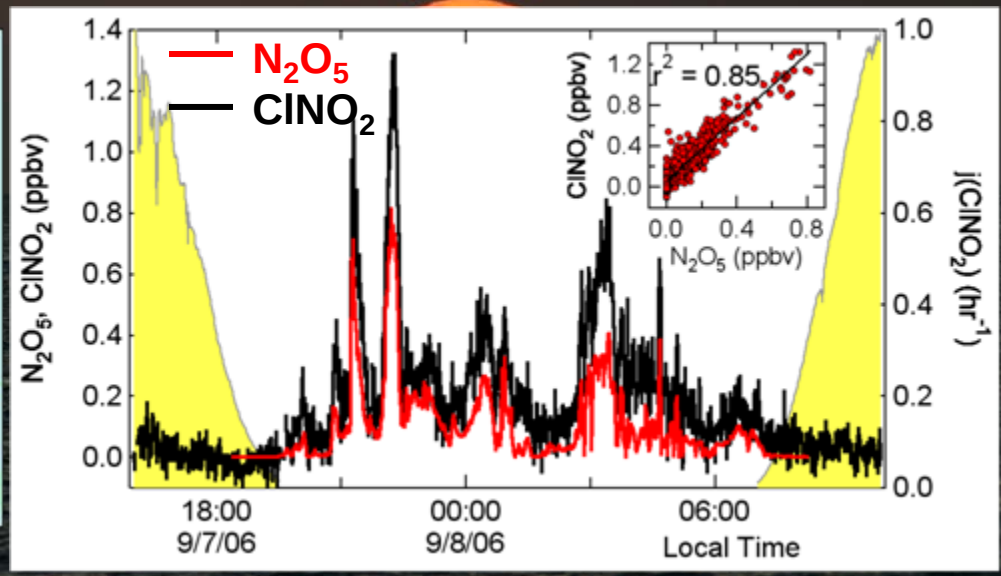
- Analysis of N_2O_5 uptake coefficients, $\gamma(N_2O_5)$, from P-3 flights in California will provide data on the interaction of N_2O_5 and nitrate aerosol

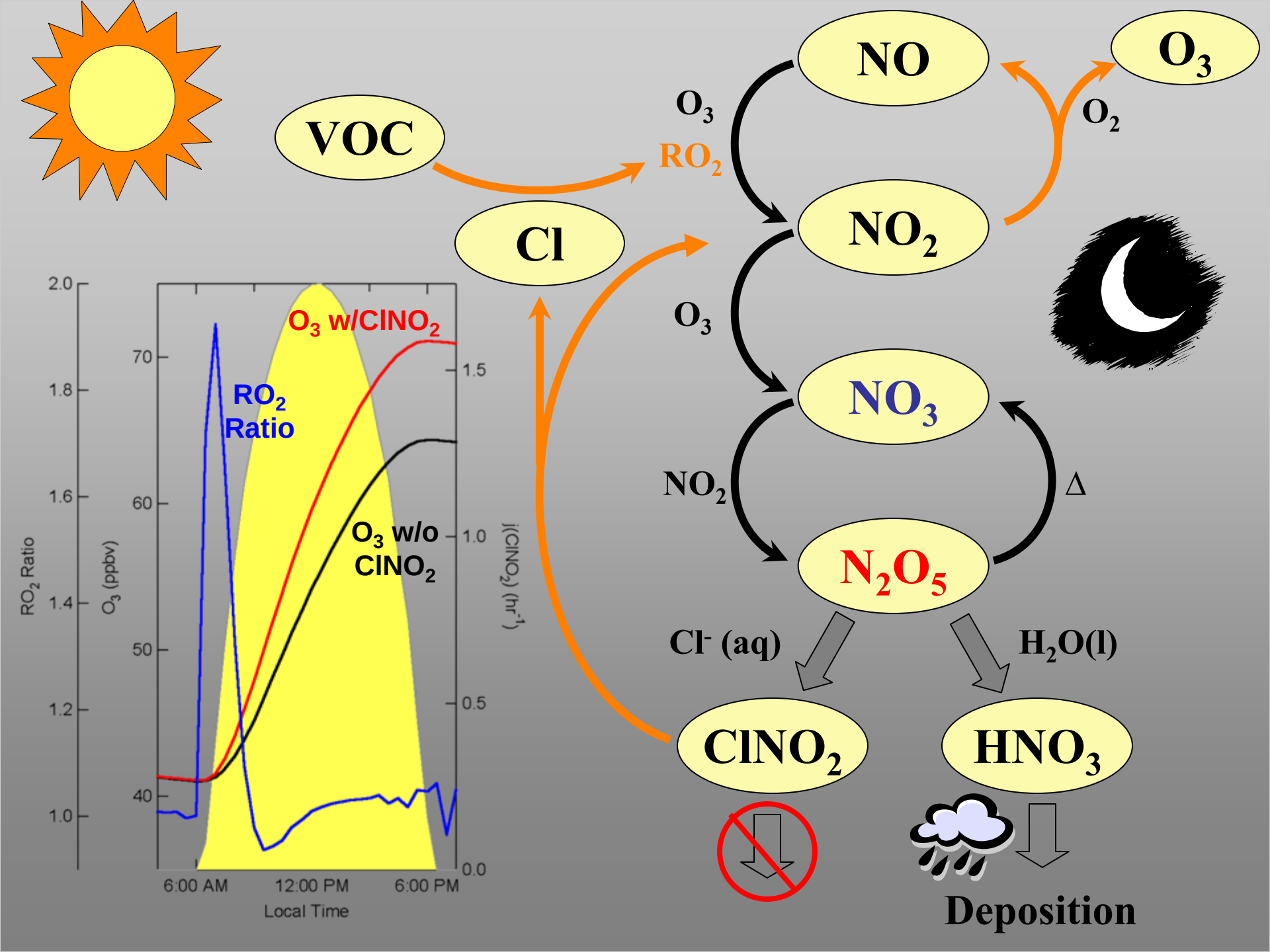
Nighttime Halogen Activation from NO_x and Sea Salt



Behnke et al., JGR 1997
$\Phi(ClNO_2) \approx 1$, $[Cl^-] \geq 1$ M

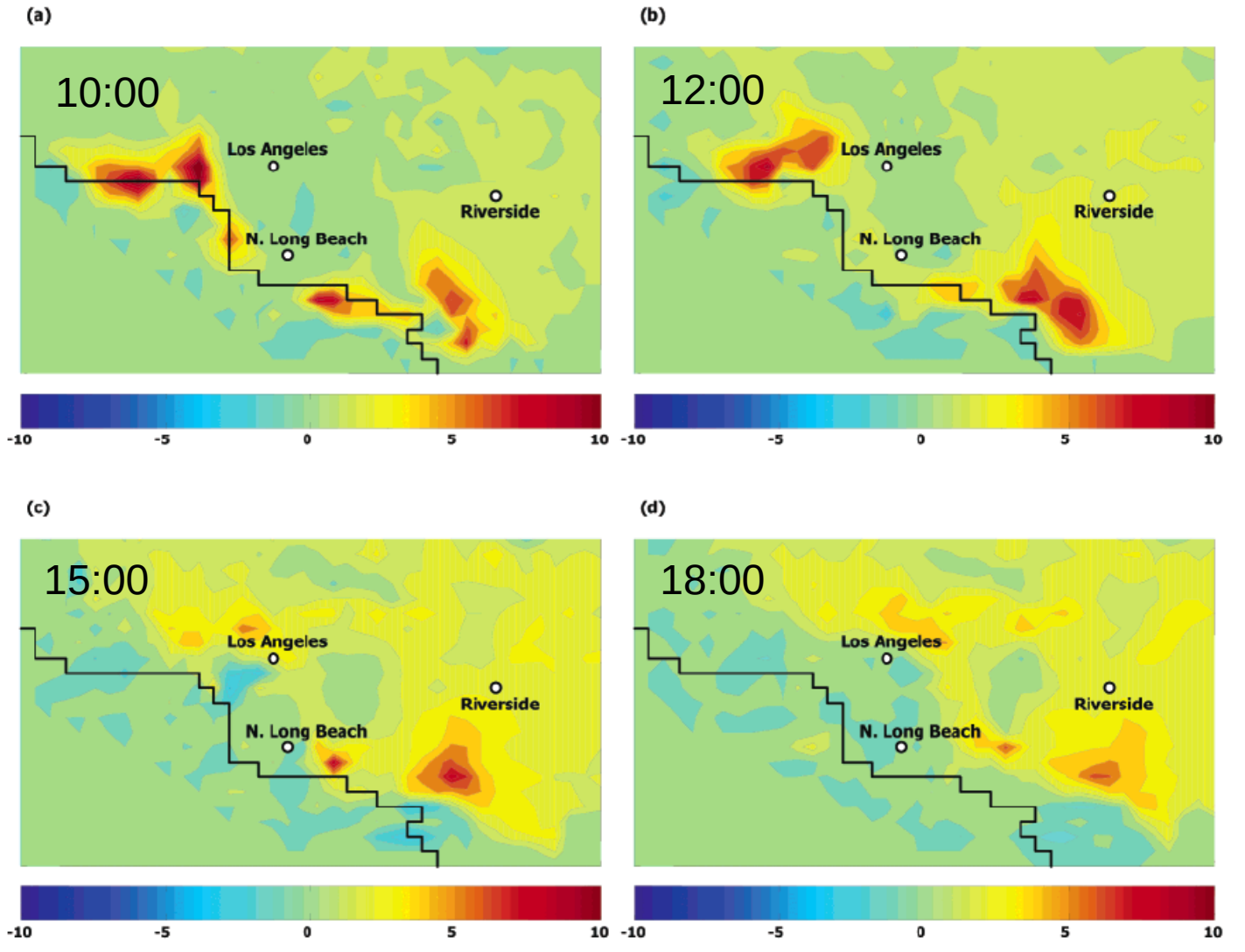
- Surprisingly high efficiency for $ClNO_2$: up to ~ 50% yield per NO_x oxidized
- Implies role for chloride-containing, submicron aerosol
- Acid displacement of HCl from sea salt & equilibration to submicron aerosol




VOC
Cl
RO_2
O_3
NO
O_2
O_3
NO_2
O_3
NO_3
NO_2
Δ
N_2O_5
Cl^- (aq)
$H_2O(l)$
$ClNO_2$
HNO_3
Deposition
O_3 w/$ClNO_2$
RO_2 Ratio
O_3 w/o $ClNO_2$
RO_2 Ratio
O_3 (ppbv)
$j(ClNO_2)$ (hr^{-1})
2.0
1.8
1.6
1.4
1.2
1.0
70
60
50
40
1.5
1.0
0.5
0.0
6:00 AM
12:00 PM
6:00 PM
Local Time

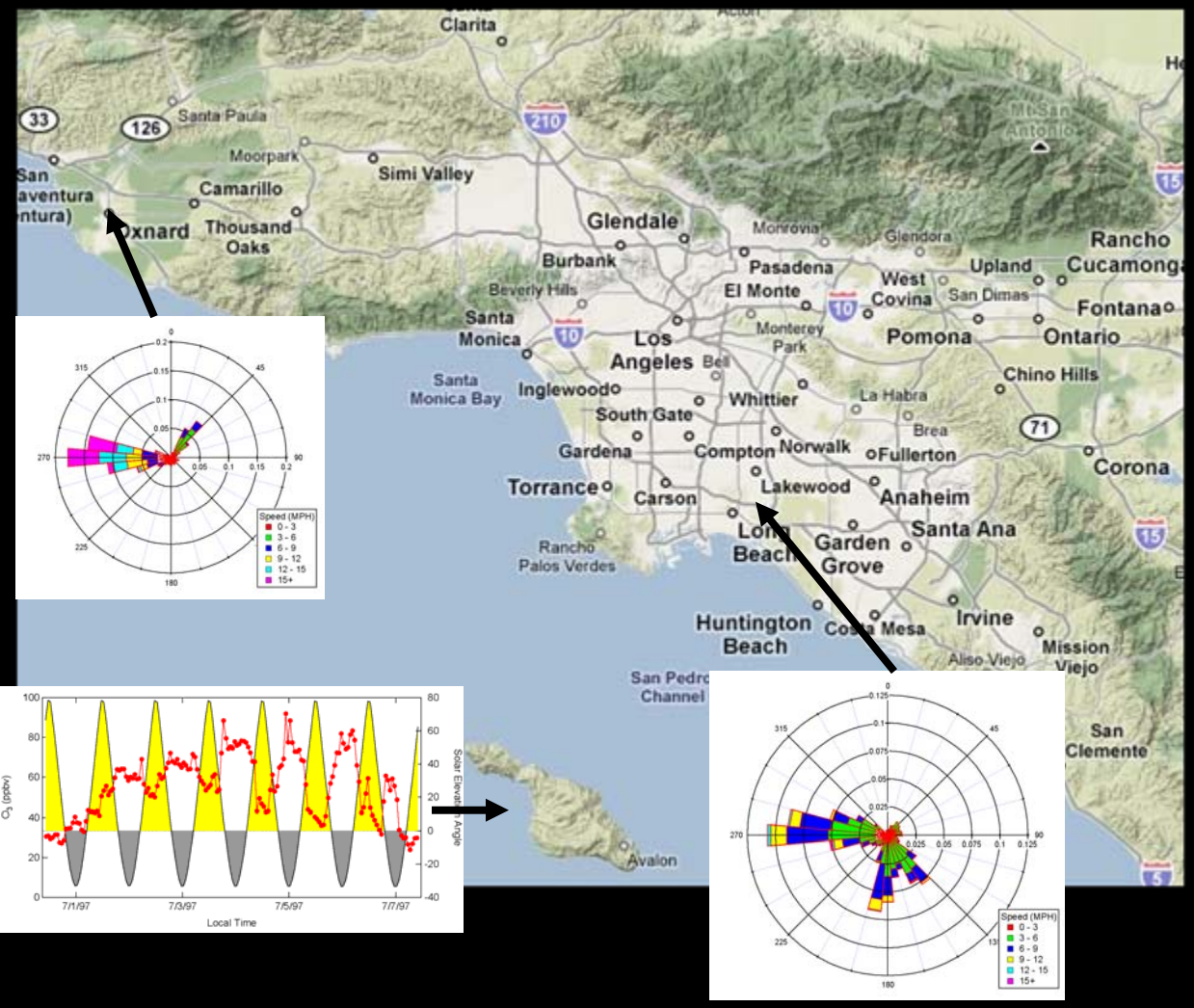
Impact on California Air Quality ?

Knipping & Dabdub, ES&T 2003



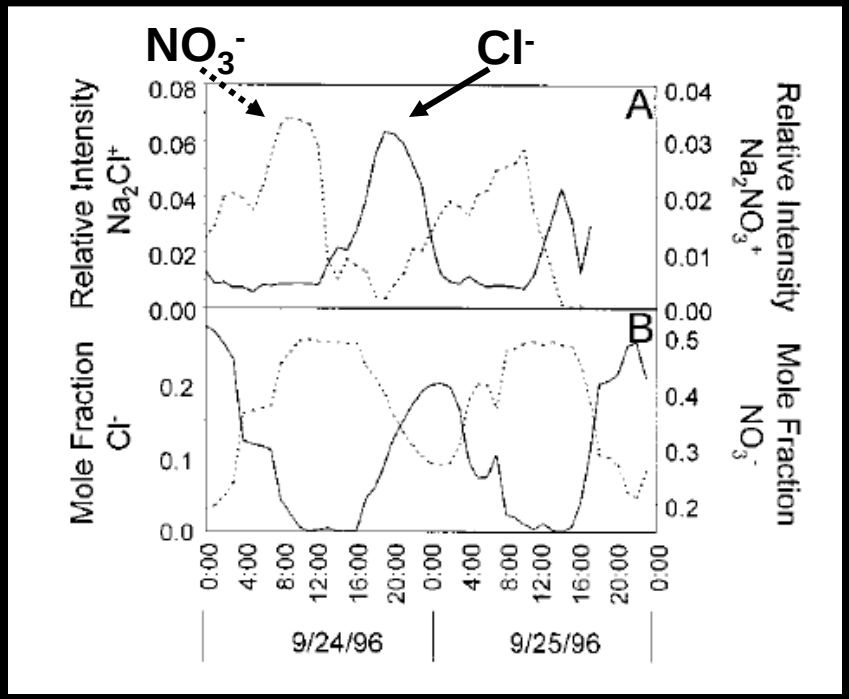
Cl production of similar magnitude increases background O_3 by several ppbv and peak O_3 by upt to 12 ppbv

Coastal Halogen Activation: NOAA R/V *Brown*



- Diurnal cycle at coast: Weak nighttime land breeze followed by strong daytime sea breeze (e.g. Shair *et al.*, Atmos Environ 1982)
- Coupling between diurnal cycles in both halogen activation chemistry and transport
- Shipping NOx: Large emission source in CA, known to be efficient halogen production source

Halogen Activation Aloft: P3



- Gard et al., Science (1998): Nearly complete displacement of Cl^- by NO_3^- in LA sea salt aerosol, with distinct diurnal pattern at Long Beach

- HCl should be a widespread Cl^- reservoir available for $ClNO_2$ production throughout the basin

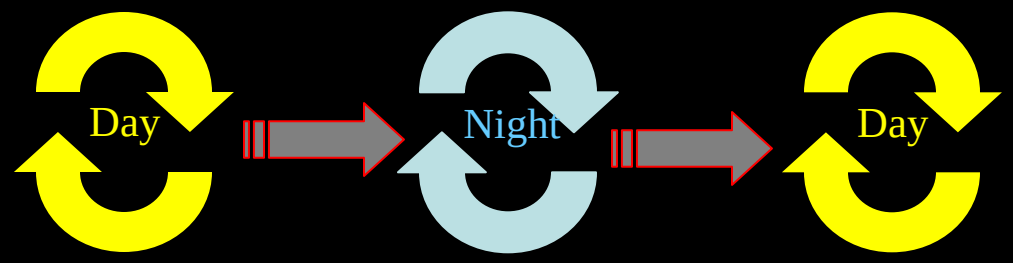
- P-3 flights surveying nighttime return flow and / or interbasin transport will investigate inland halogen activation

- Vertical stratification over urban areas will require this study to be carried out by aircraft over land

- Currently ***no field data*** on radical production and NO_x recycling from this process

Conclusions

- Nighttime conversion of $NO_x \rightarrow HNO_3$ affects next-day ozone photochemistry and secondary aerosol production

- Nighttime halogen activation affects radical and NO_x cycling

- NOAA P-3 and R/V *Brown* used to study interaction of this chemistry with transport patterns in LA and other air basins of California