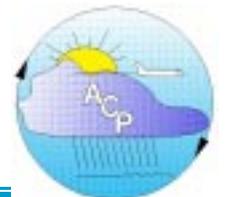


NARSTO '95 observations and modeling of oxidants and precursors

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Special thanks to:

- ACP Field Team
- The NARSTO-NE Project Coordination Office
- PNNL Atmospheric Modeling Group



Background: who, when, where, what,....

- **Argonne National Laboratory, Battelle Memorial Institute, the Environmental Measurements Laboratory, Brookhaven National Laboratory, Pacific Northwest National Laboratory**
- to investigate effects of mixing on surface chemistry (last year's emphasis)
- **to support NARSTO effort** to assess 3-dimensional pollutant distribution on episode days & develop data base for model evaluation (this year's emphasis)
-



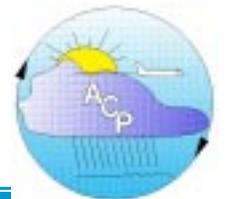
Within the analysis domain, during NARSTO '95...

- What was the source region for 'episode' days? Air mass age?
- How was local chemical production affected by ozone precursors (e.g. NO_x, PAN) advected into the domain?
- How did a column of air at the beginning of an 'episode' day differ from that on a non-episode day? Why?
- How do mixed layer characteristics affect ozone production?



Our Approach: observations + model evaluation = analysis tool

- Use field observations
 - ⇒ to assess column characteristics of ozone and precursor species via *in situ* measurements
 - ⇒ to formulate tentative hypothesis
- Model evaluation
 - ⇒ to assess model performance, strengths and weaknesses
- Model analysis of high ozone events
 - ⇒ to test hypothesis.
 - ⇒ to evaluate rates of key processes.
 - ⇒ to perform ‘what if’ sensitivity tests



Model Highlights

- **RAMS** with **4DDA** + nested grid
- outer grid: most of U.S. and southern Canada east of the Rocky Mtns, $\Delta x = 48$ km
- inner grid S. Quebec, eastern New York, eastern Penn., New Jersey and New England, $\Delta x = 12$ km.
- Third grid: Long Island, Connecticut, Rhode Island and w. Mass, $\Delta x = 3$ km

- **GChM** with condensed Lurmann, Lloyd and Atkinson chemistry with modifications for isoprene and updated kinetic/rate coefficients. 126 rxn, 64 species.

- **Local one dimensional approximation (“operator splitting”):**

Δ tot =

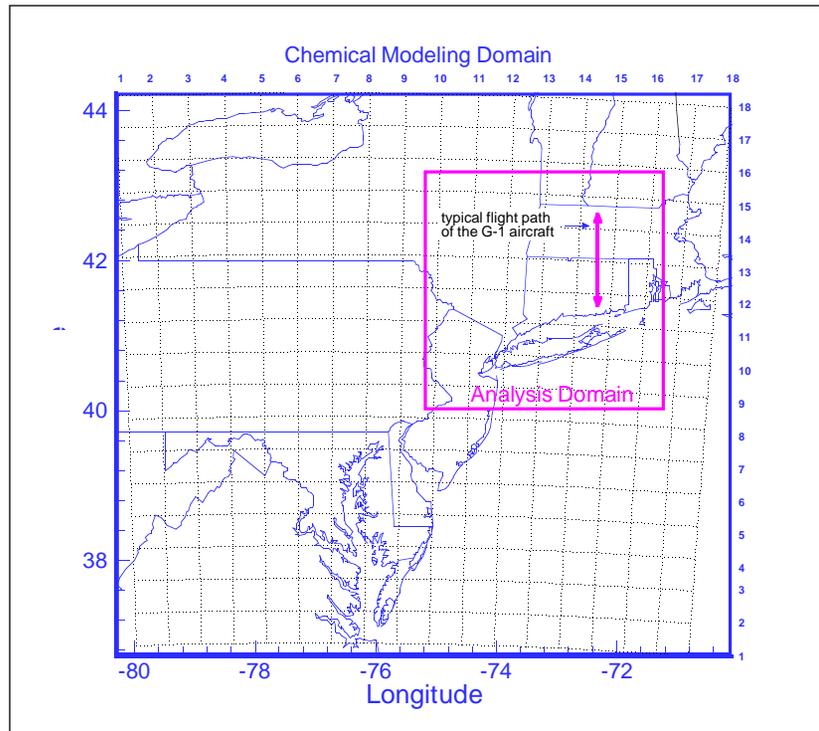
Δ chem + Δ xy-trans +

Δ z-trans + Δ DryDep +

Δ Emissions



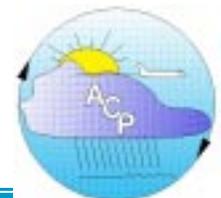
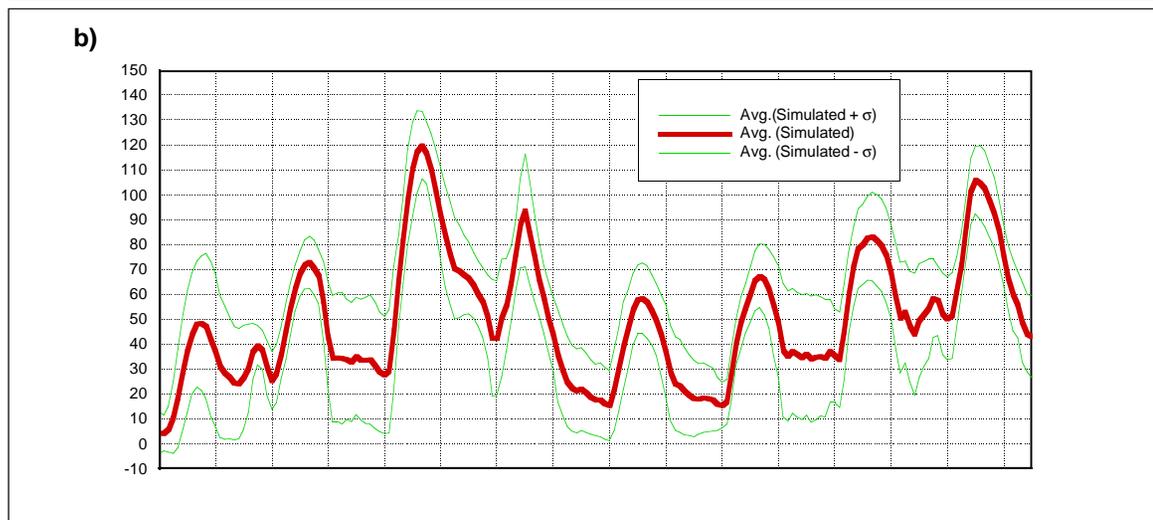
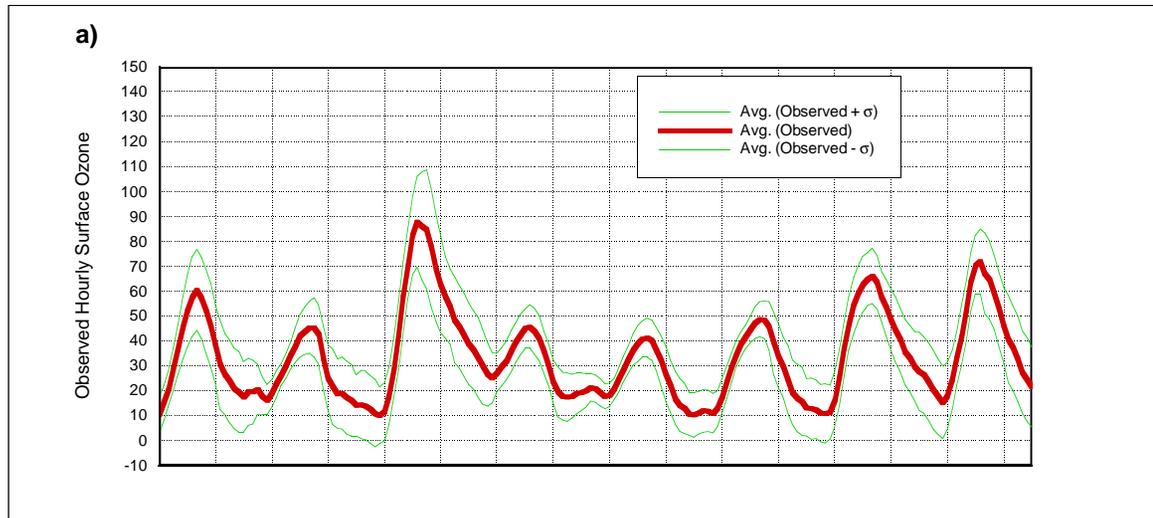
Modeling and Sampling Domain



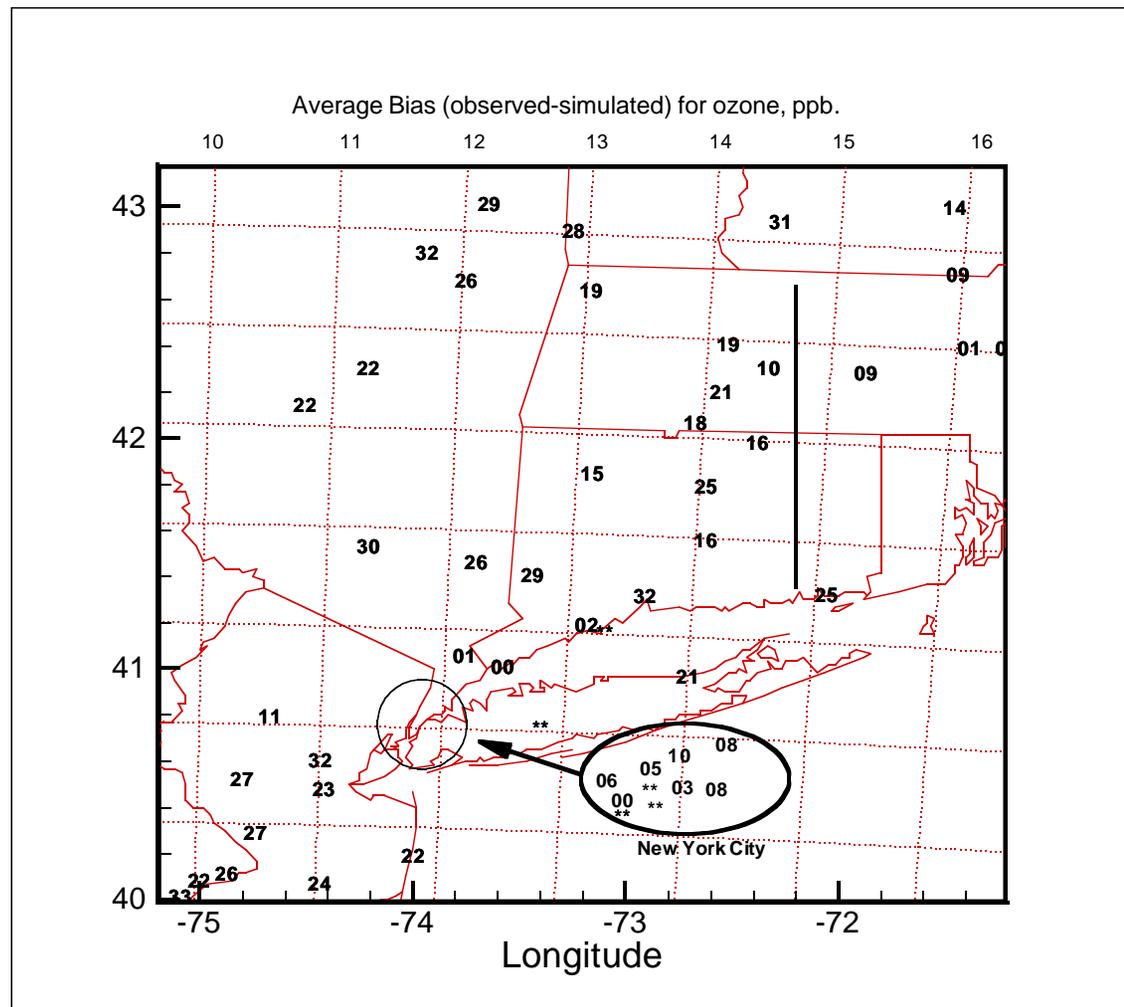
- NARSTO'95
- Airborne observations
August 30 - September 5
- Surface chemistry
- Additional radiosondes and
profiler coverage



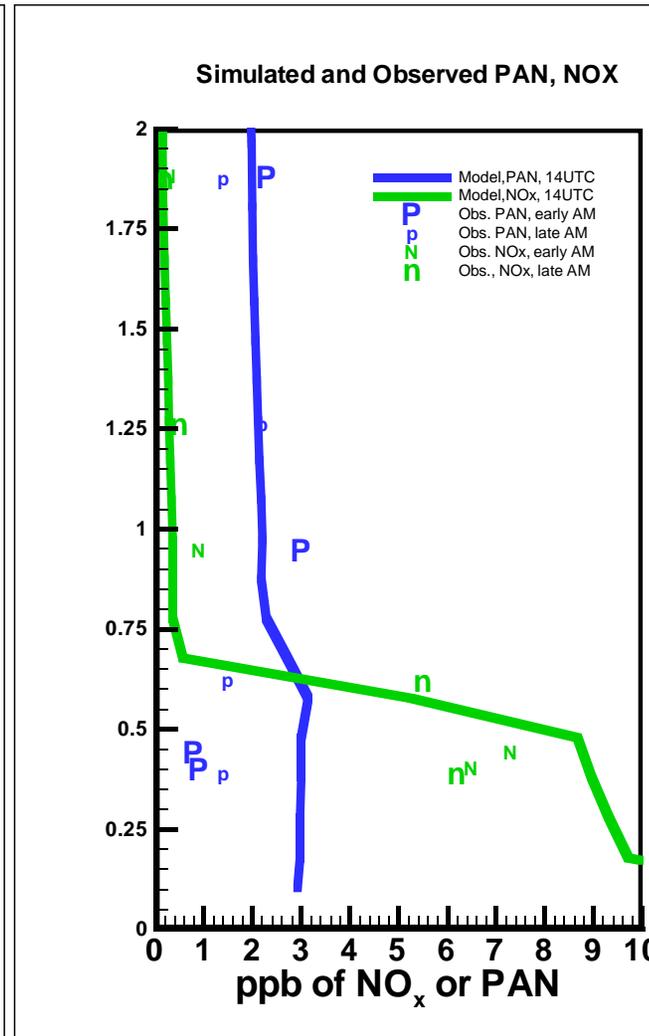
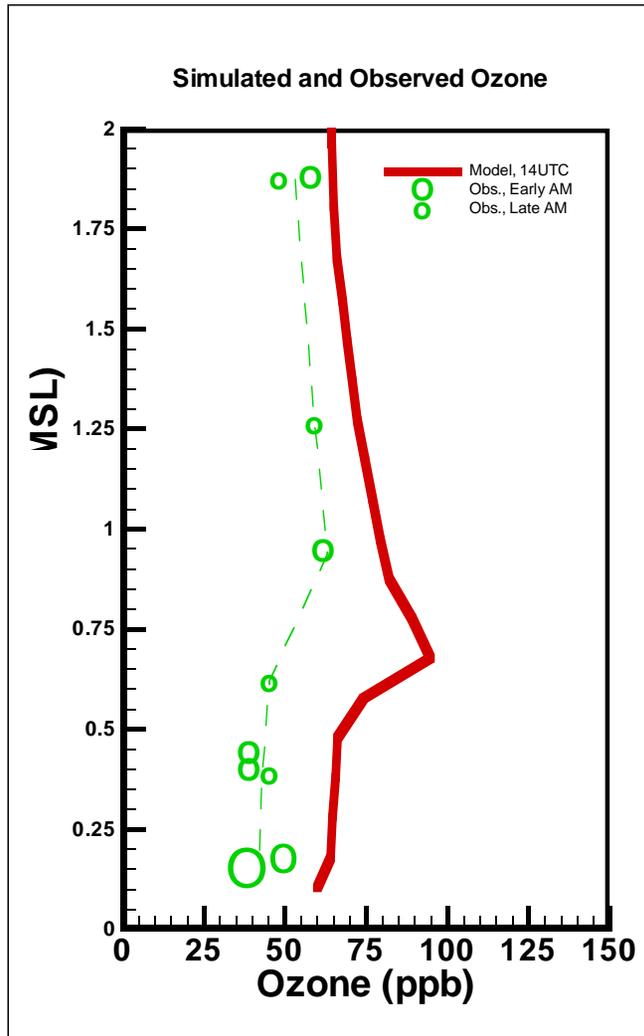
Surface ozone: **mean** and **std. deviation** Observed (top) and Simulated (bottom)



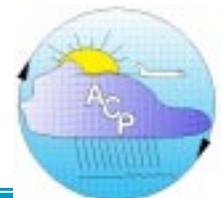
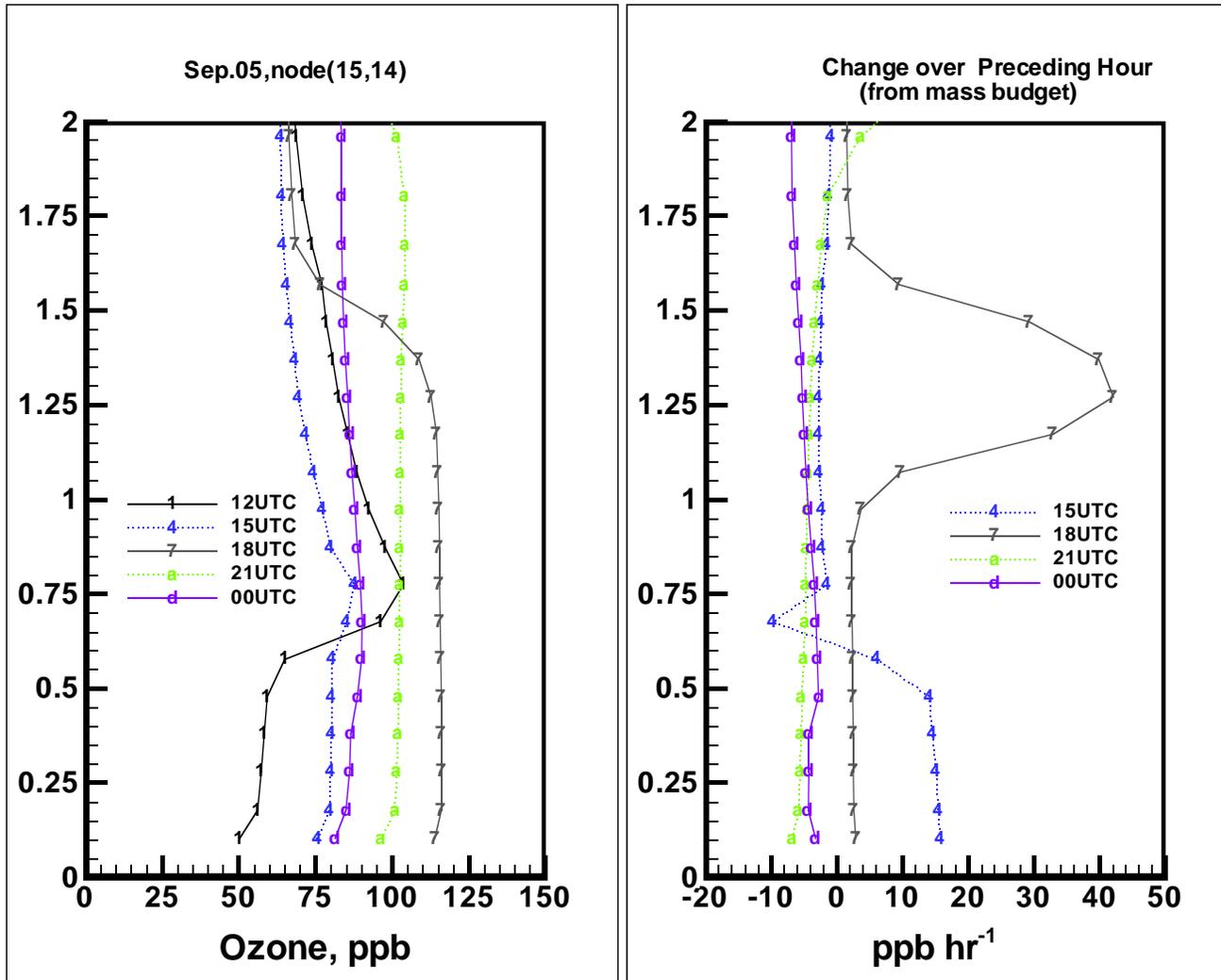
Average (simulated - observed) surface ozone



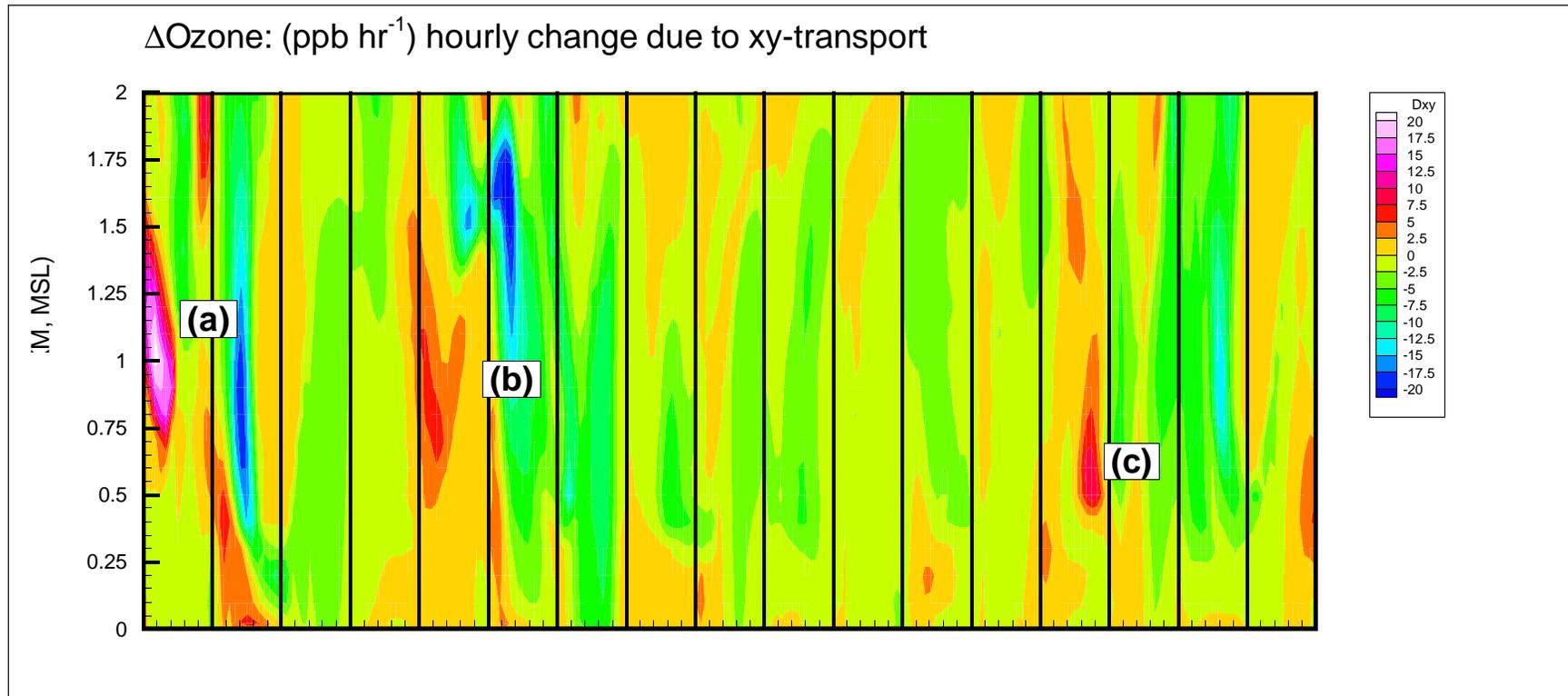
Ozone (Left), PAN & NO_x (right) Observed and Simulated, Sept. 5, 1995



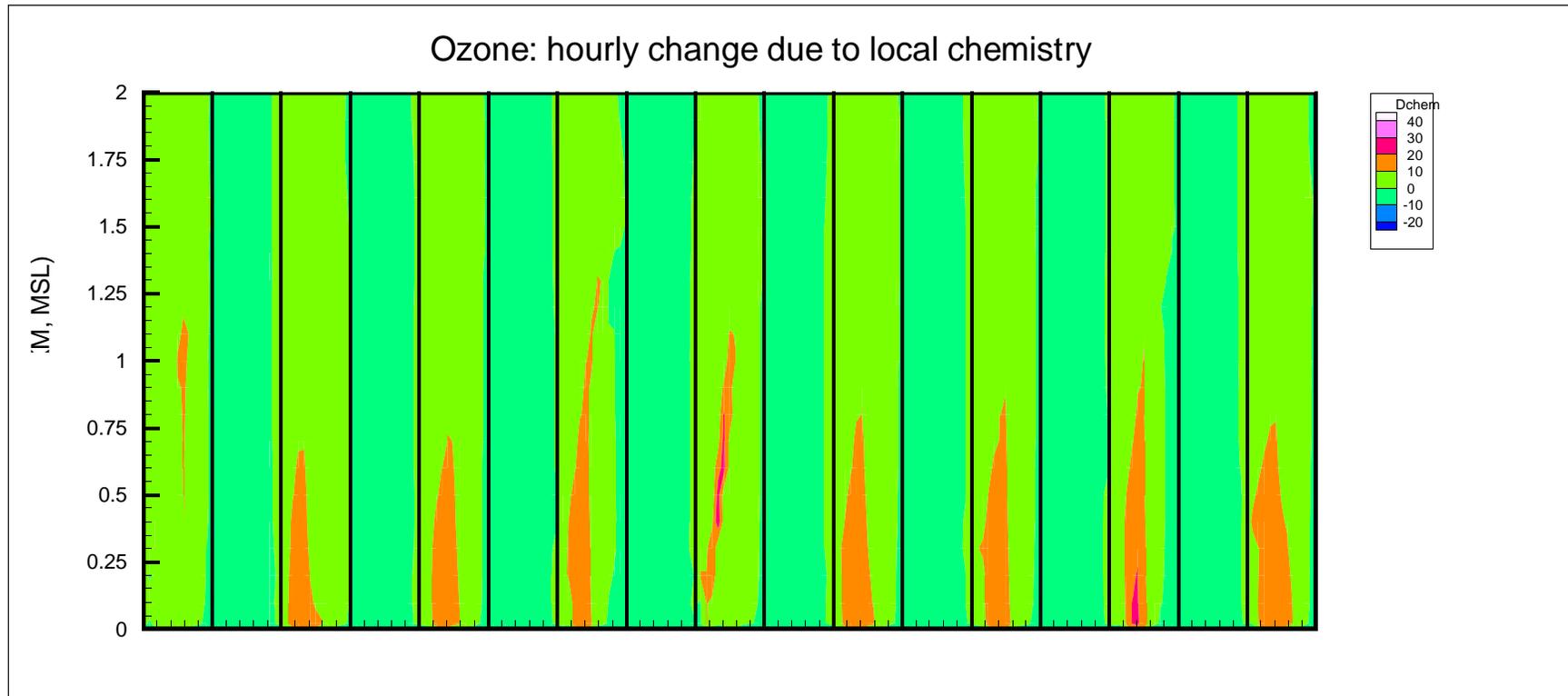
Mass Budget



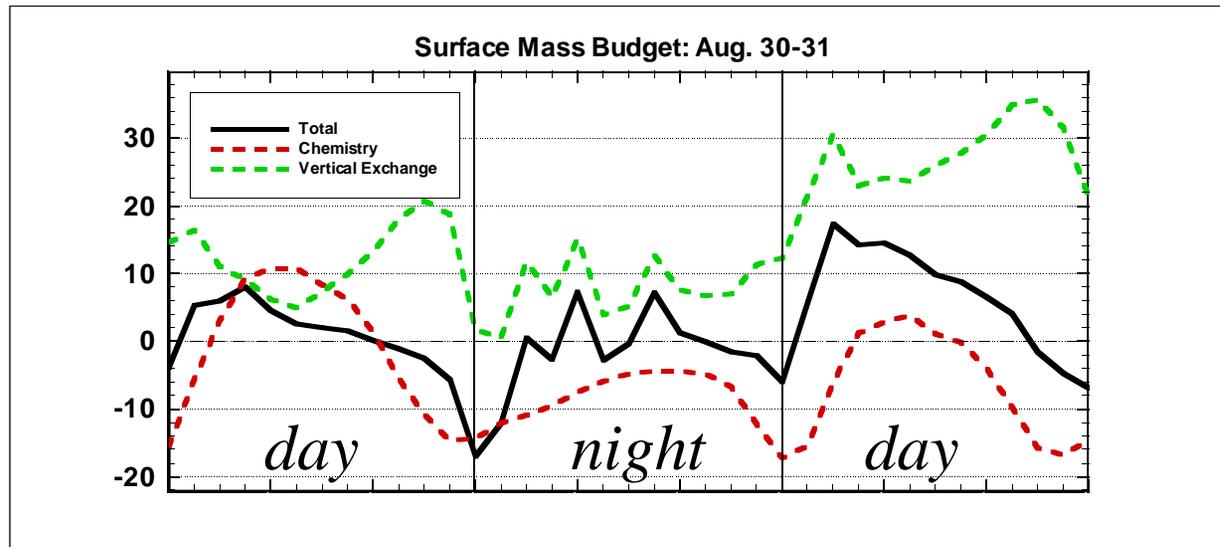
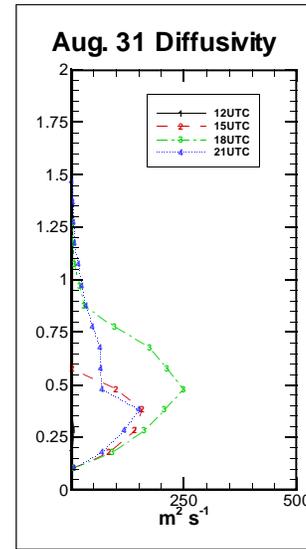
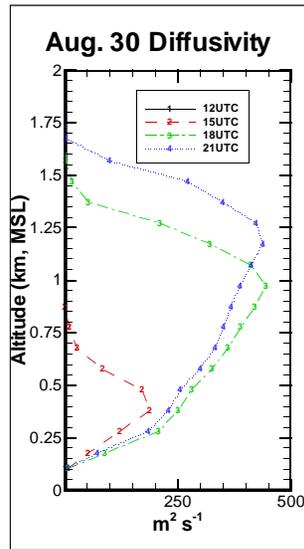
Role of Horizontal Transport (ppb hr⁻¹)



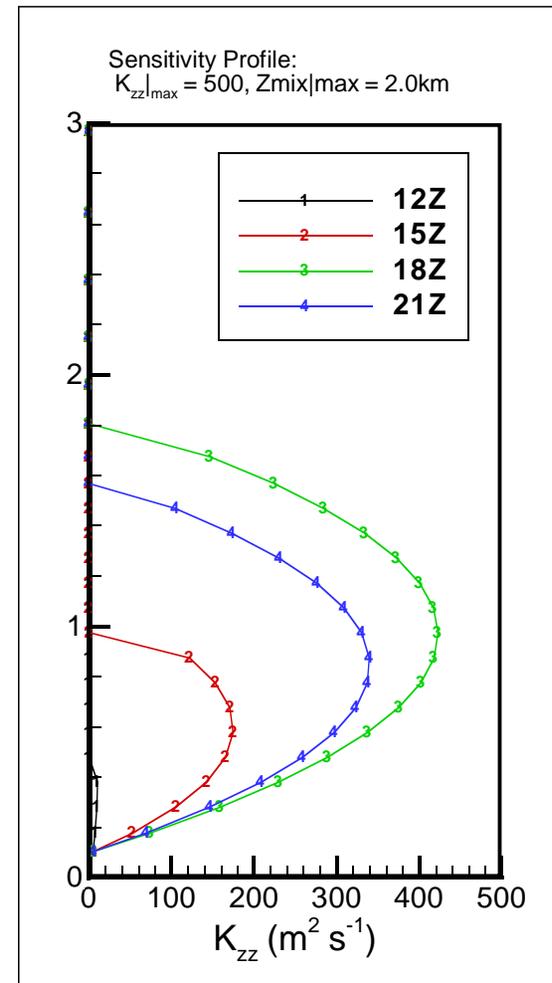
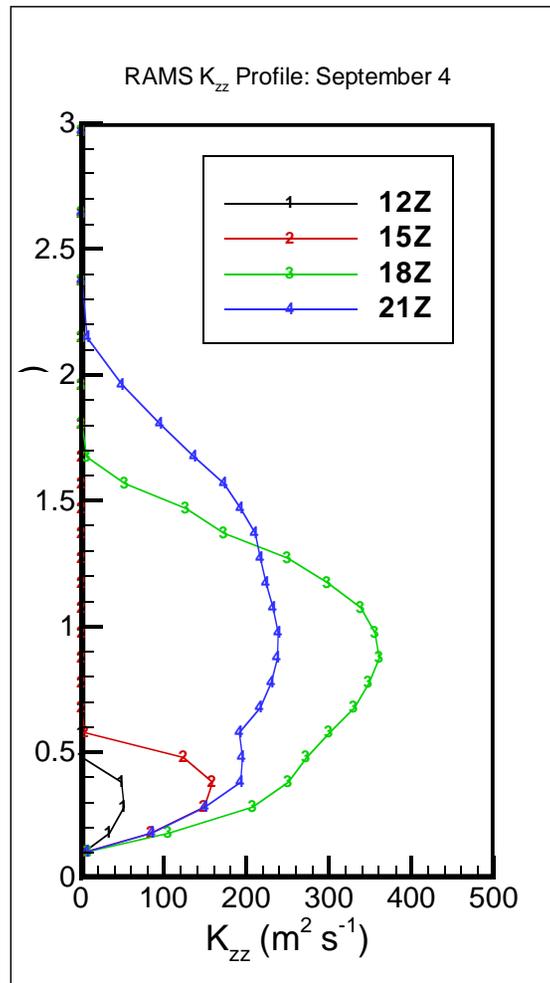
Role of Local Gas-phase Chemistry (ppb hr⁻¹)



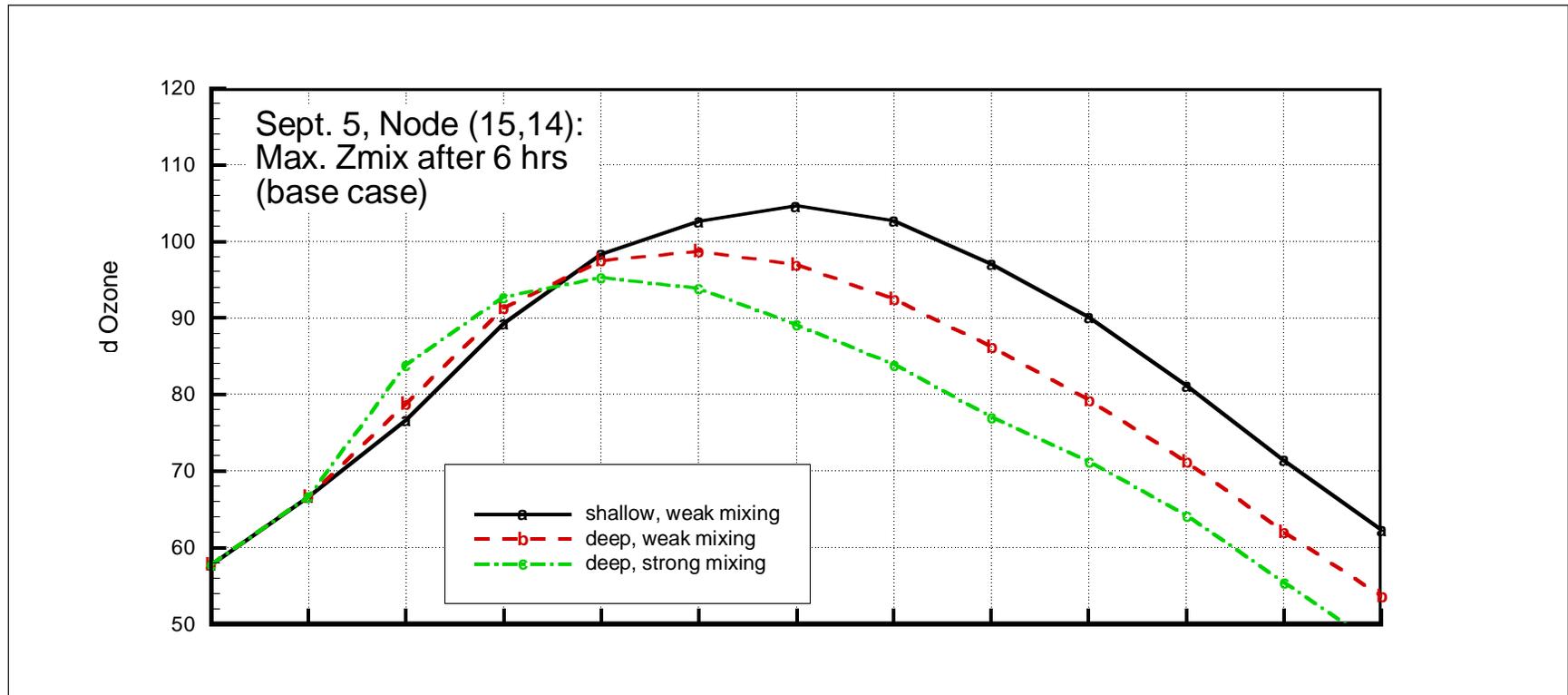
Mixed Layer Depth, Chemistry and Vertical Exchange



How Does Mixing Impact Surface Chemistry?



How Does Mixing Impact Surface Chemistry?



Summary of Results - I

I. The ‘age’ and ‘source region’ did not have a unique ‘clock time’ or ‘point or origin.’

- better characterized by a statistical distribution.
- Does not apply equally to short- and longer-lived species

II. Chemical production on episode days driven by local emissions

- Minimal horizontal exchange of reactive ozone predecessors.

III Column ozone on ‘episode’ days = 2x that on preceding non-episode days

- gradual build-up due to xy-transport ($\sim 1\text{-}3 \text{ ppb hr}^{-1}$ at surface; greater rate of increase aloft)



Summary of Results -II

IV Shallow daytime mixed layers result in reduced, or negative, surface chemical ‘production’ rates:

- high ozone concentrations develop above daytime sfc. layer and mix down

V Chemistry in shallow, weakly mixed (SWM) layer vs. deep, vigorously mixing (DVM) layer, same initial conditions:

	<u>SWM</u>	<u>DVM</u>
Peak [O ₃]	105 ppb	95 ppb
Time of peak:	3PM LST	1PM LST
[O ₃] near sunset	90 ppb	70 ppb

