

UT/LS: Science, needs, and some plans

A. R. Ravishankara

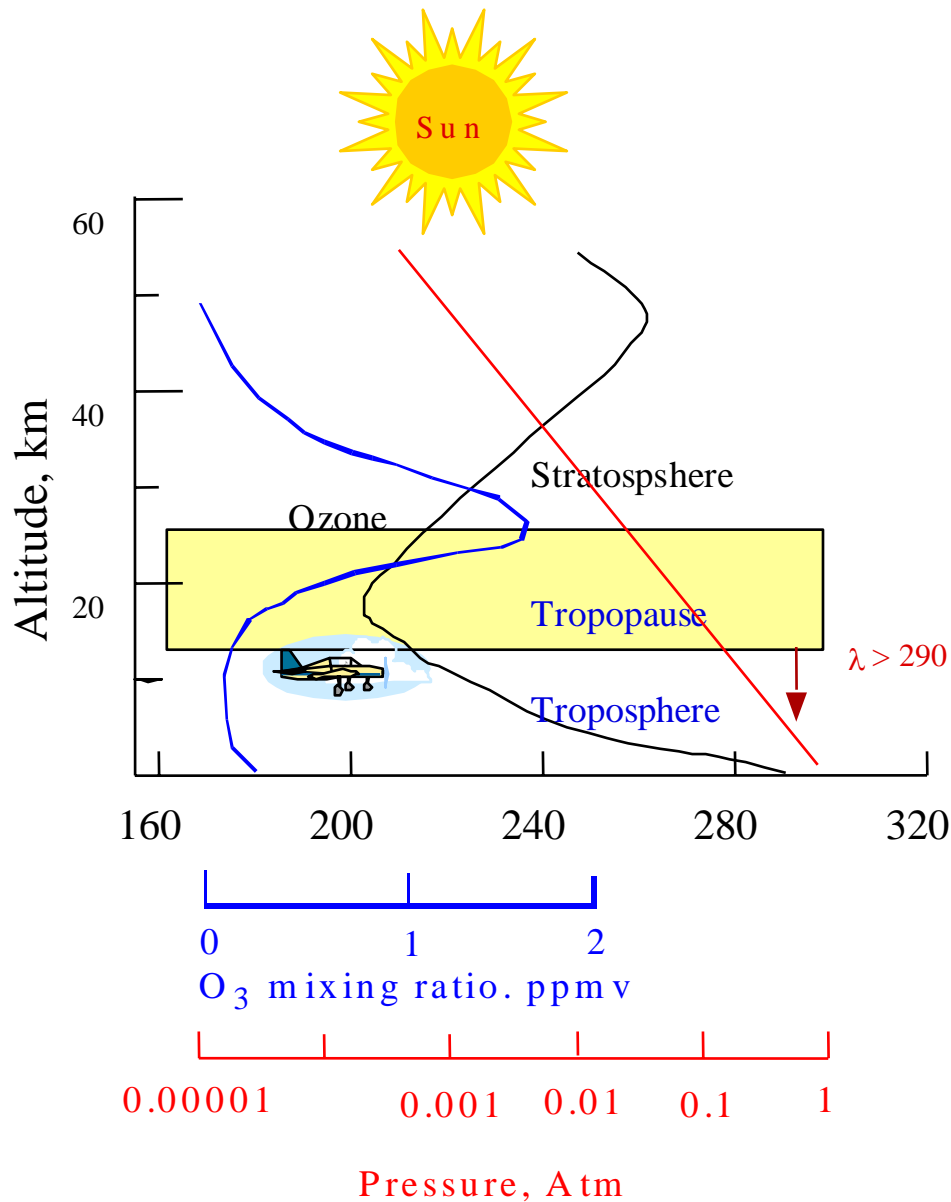
NOAA, Earth System Research Laboratory, Chemical Sciences Division

Boulder CO

Outline:

1. Special nature and importance of UT/LS (emphasis on UT in this talk)
2. Ozone in the upper troposphere- how to quantify its abundance and changes
3. Observationally based quantification of STE (flux)
4. Observationally based quantification of UT ozone production
5. Basic informational needs for calculating UT ozone production
6. Laboratory data needs- the SPARC-IGAC (AC&C)- Introp workshop
7. What AC&C is doing about trop ozone (> 5km)- modeling and observations
8. Summary

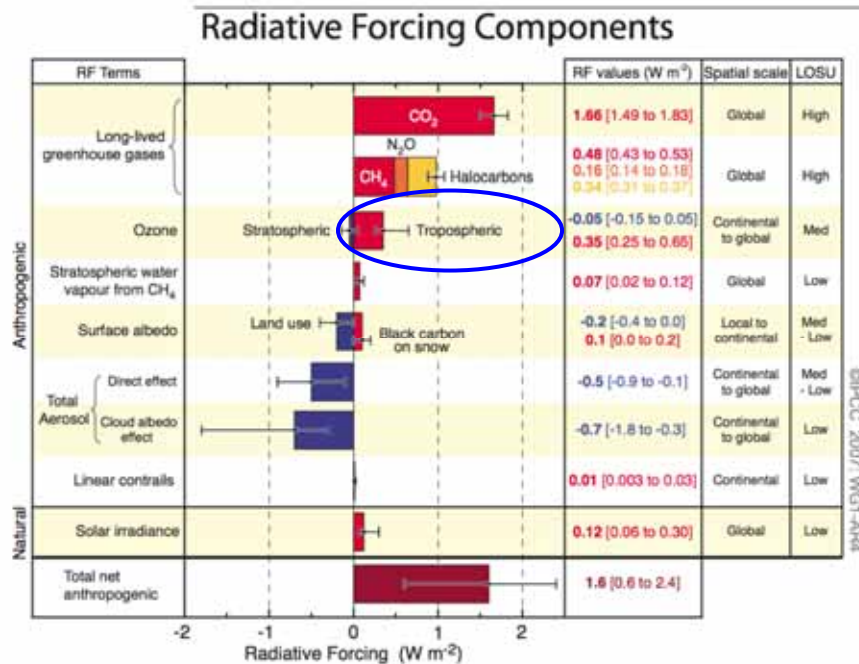
What is special about UT/LS



- Pressure is still high
- Temperature is low
- UV almost the same as in troposphere
- Mixing slower than in trop but not as “stratified” as strat
- Water vapor variable but low
- Far from pollution (?)
Aviation?
- Tropopause acts as a “transport barrier”
- What does the future hold?

Climate forcing by ozone

Global Mean Radiative Forcing (W m^{-2}) in 2005 relative to 1750 (IPCC 2006) Top of atmosphere instantaneous forcing- not at equilibrium



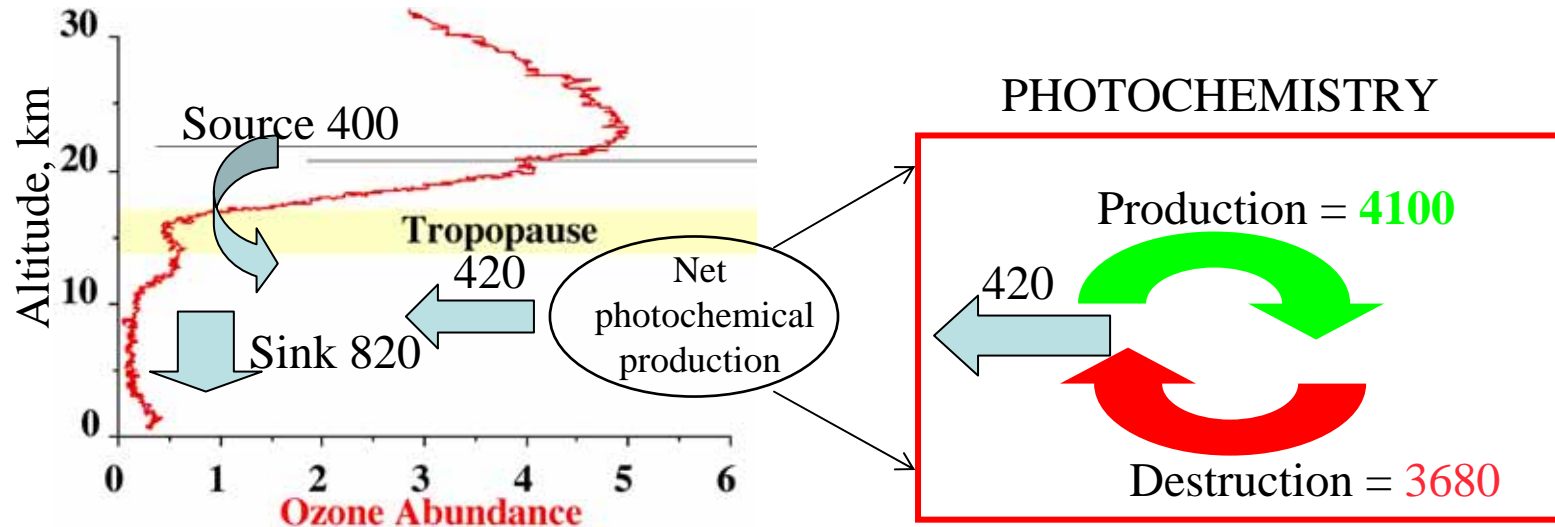
Forcing includes the “amplification” due to water vapor.

- The large uncertainty is due to uncertainties in short-lived forcing agents
- The forcing agents “interact” with each other! A change in one can lead to a change in the other... feedbacks! Ozone is a key player in the feedbacks.
- Reducing short-lived emissions is an option to “buy time”
- Impacts of climate change will be felt through short-lived species, e.g., ozone.

Key points (up front!)

- ❖ UT-LS is a special and KEY region
 - Importance for radiative budget and UT's special role, “entry and exit points for strat”, weather prediction, etc.
 - Emphasis commensurate with its importance(?)
 - **Ozone**, Water vapor, Aerosols, and clouds (your goals for IAGOS!)
- ❖ How well is the composition and influence understood? (My limited view-observations and process studies)
- ❖ Modeling is necessary (understanding past & predicting future). BUT, some **key quantities can be observationally quantified** and it is essential!
- ❖ Some examples and needs:
 - (1) Observational quantification of STE
 - (2) Observational quantification of O₃ production/production in UT (and other species)
 - (3) Process studies for quantification of chemical production and removal processes (and modeling of these processes/capturing them in global models)
 - (4) Deposition...
- ❖ Next step for AC&C- Phase II. Observations (“Time to think about it!”)

Ozone and Strat - Trop Exchange



Representative numbers!

Q: What are the contributions of local production and of stratosphere to tropospheric O₃

- Stratosphere/Troposphere exchange
- in-situ photochemical production
- Transport from other regions?
- Removal processes



Varies with z,
location, and season

Need to quantify strat/trop exchange

Need to quantify ozone production and loss terms

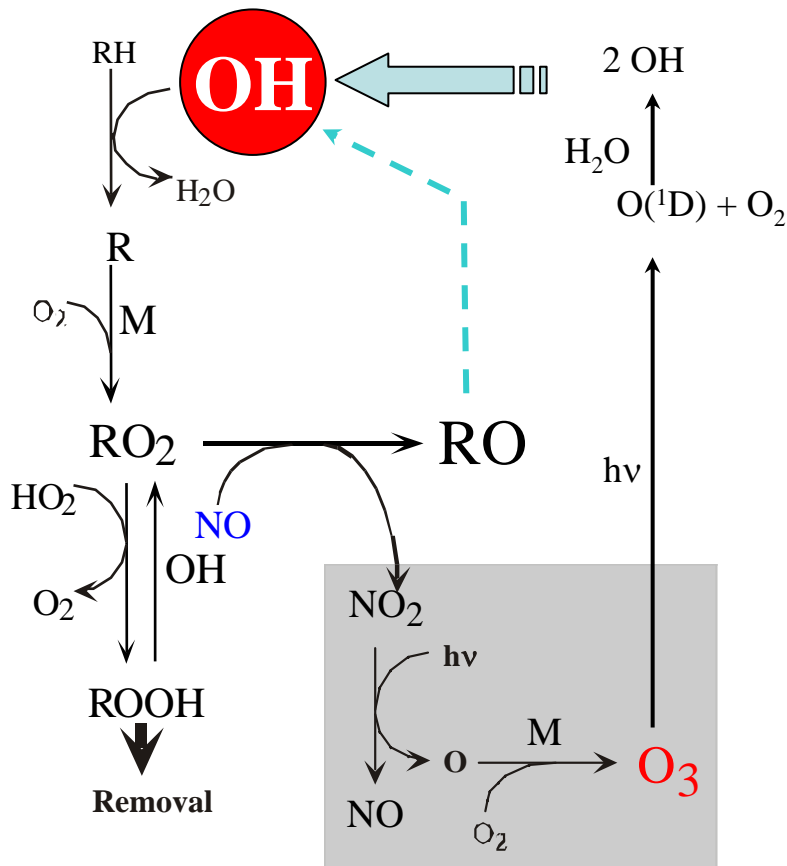
Evolving Model O₃ Budgets

Tendency Tg/yr	1995-2000 (12 studies)	2001-2005 (12 studies)	Accent 2005 (25 models)
STE	770	510	520
O ₃ Production	3450	4620	5060
O ₃ Loss	3440	4200	4560
Net Chemistry	50	420	500
Deposition	820	1000	1010
Burden /Tg	300	330	340
Lifetime /days	24	24	22.4

Courtesy: Oliver Wild

- Most recent calculations show more O₃ production, less STE, larger O₃ burden
- Does this reflect real changes in understanding or just different model specifications?

Tropospheric chemical ozone production



QuickTime™ and a decompressor are needed to see this picture.

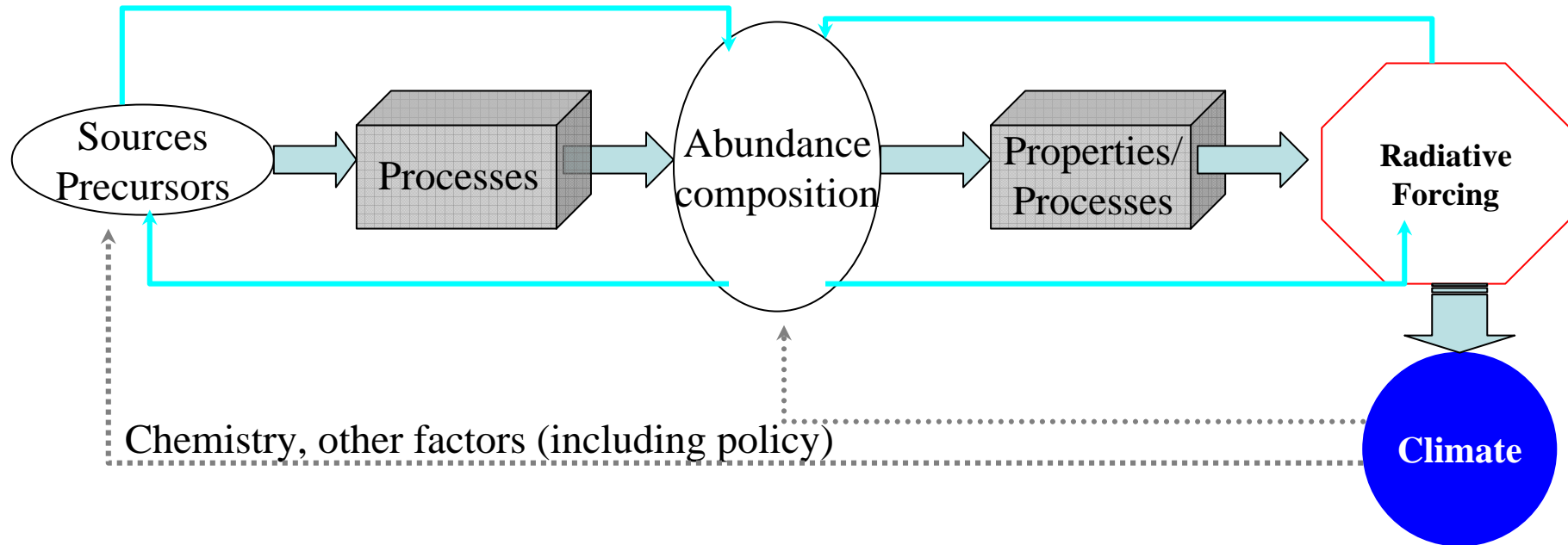
O₃ production method in troposphere is distinctly different from that in the stratosphere.

Tropospheric production rate of O₃ is very large!

Chemical production is a major contributor to tropospheric ozone budget.

How does it vary with location?

Quantification of abundances/fluxes from modeling and observations!



- Modeling the processes is a key way to get abundances and their influences- essential for prediction.
- Are there observational methods to derive the same information?

- How accurate are the calculated transport and chemical fluxes?
- How can these fluxes be observationally quantified?
- How well can we predict this in the future?
- Continued improvements of models---

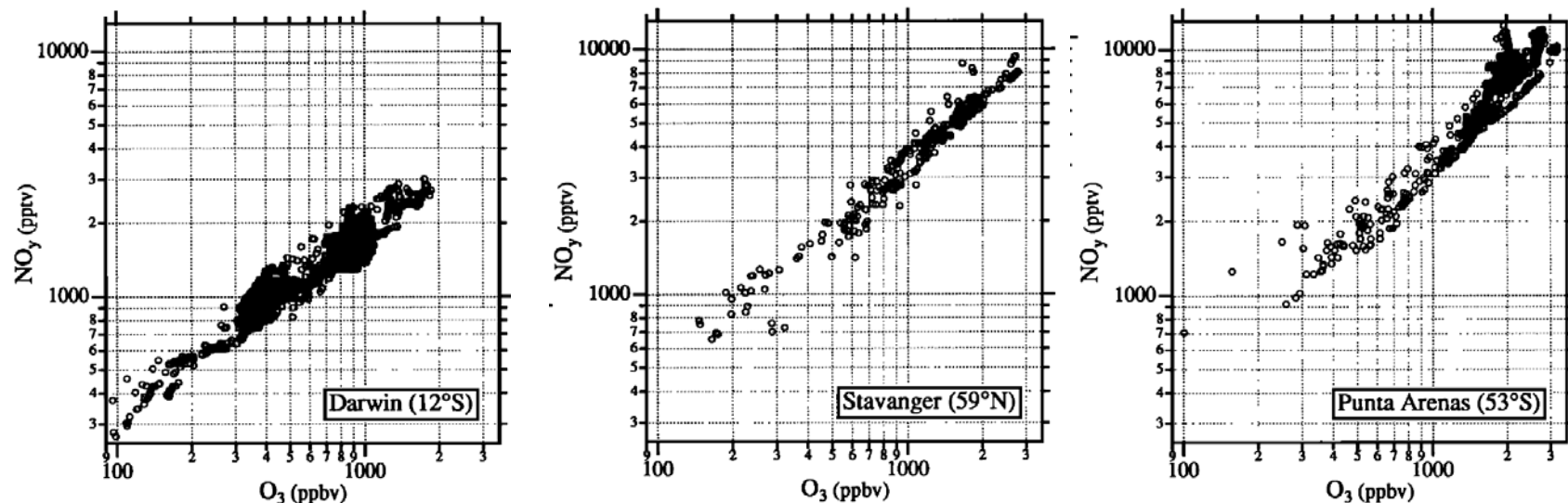
Quantification of STE of O₃ via observations

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 98, NO. D5, PAGES 8751-8773, MAY 20, 1993

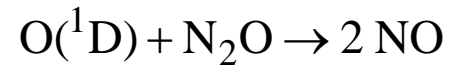
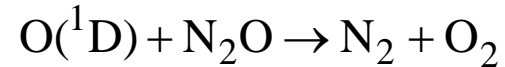
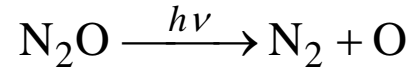
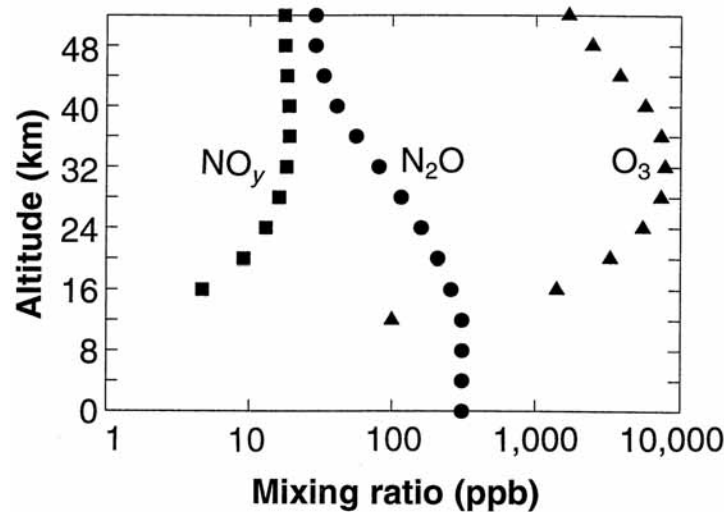
Reactive Nitrogen and Its Correlation With Ozone in the Lower Stratosphere and Upper Troposphere

D. M. MURPHY,¹ D. W. FAHEY,¹ M. H. PROFFITT,^{1,2} S. C. LIU,¹ K. R. CHAN,³
C. S. EUBANK,^{1,2} S. R. KAWA,^{1,2} AND K. K. KELLY¹

Lower stratospheric Ozone and NO_y are correlated, with the ratio of NO_y to O₃ of 0.0025 to 0.0040.



Quantification of STE of O₃, continued



Michael J. Prather, Time Scales in Atmospheric Chemistry: Coupled Perturbations to N₂O, NO_y, and O₃, Science 27 February 1998: Vol. 279. no. 5355, pp. 1339 - 1341

- NO_y in stratosphere comes almost exclusively from N₂O
- 8-17 Tg per year of N₂O is destroyed in the stratosphere and yields roughly 0.28 to 0.60 Tg per year of NO_y
- In a steady state atmosphere, this much NO_y is removed to trop.
- Therefore, flux of O₃ from the stratosphere to troposphere is 240- 820 Tg per year
- **Observational data (more tracers) will enable better flux calculations!**

Quantification of ozone production rates

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 111, D24S05, doi:10.1029/2006JD007306, 2006



Large upper tropospheric ozone enhancements above midlatitude North America during summer: In situ evidence from the IONS and MOZAIC ozone measurement network

O. R. Cooper,^{1,2} A. Stohl,³ M. Trainer,⁴ A. M. Thompson,⁵ J. C. Witte,⁶ S. J. Oltmans,⁴ G. Morris,⁷ K. E. Pickering,⁸ J. H. Crawford,⁹ G. Chen,⁹ R. C. Cohen,¹⁰ T. H. Bertram,¹⁰ P. Wooldridge,¹⁰ A. Perring,¹⁰ W. H. Brune,⁵ J. Merrill,¹¹ J. L. Moody,¹² D. Tarasick,¹³ P. Nédélec,¹⁴ G. Forbes,¹⁵ M. J. Newchurch,¹⁶ F. J. Schmidlin,¹⁷ B. J. Johnson,⁴ S. Turquety,¹⁸ S. L. Baughcum,¹⁹ X. Ren,⁵ F. C. Fehsenfeld,⁴ J. F. Meagher,⁴ N. Spichtinger,²⁰ C. C. Brown,⁹ S. A. McKeen,^{1,2} I. S. McDermid,²¹ and T. Leblanc²¹

Received 16 March 2006; revised 25 August 2006; accepted 21 September 2006; published 12 December 2006.

Provide insights into mechanisms and their contributions

Li et al. [2005] used the GEOS-CHEM model to simulate upper tropospheric ozone during July 2000.

Conclusions: the summertime upper level anticyclone traps anthropogenic pollution and lightning NO_x above the southern USA leading to an ozone maximum.

To force their model to agree with the five available ozonesondes from Huntsville they had to increase their lightning NO_x emissions by a factor of four.

Q. Li, et al., North American pollution outflow and the trapping of convectively lifted pollution by upper-level anticyclone, *J. Geophys. Res.*, 2005.

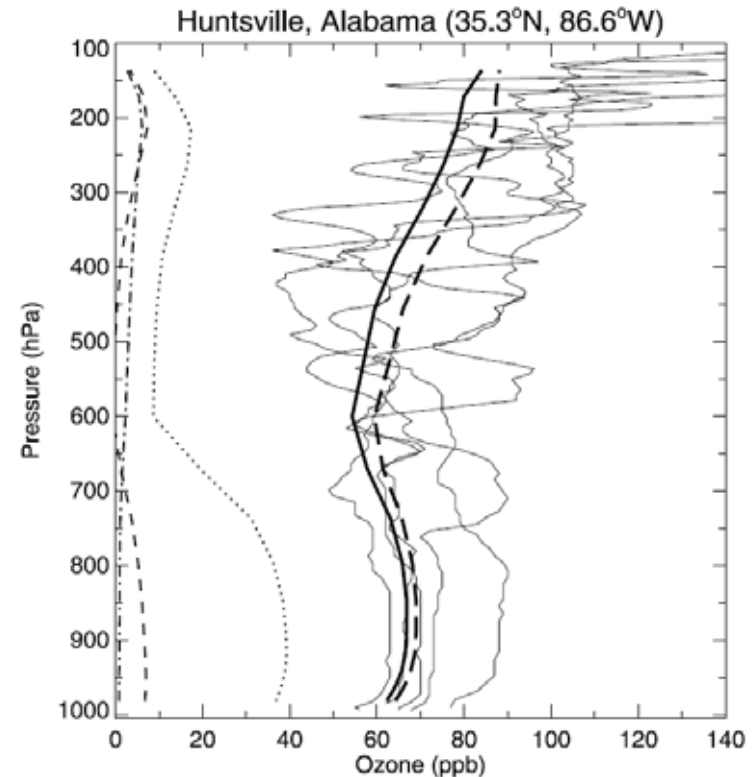
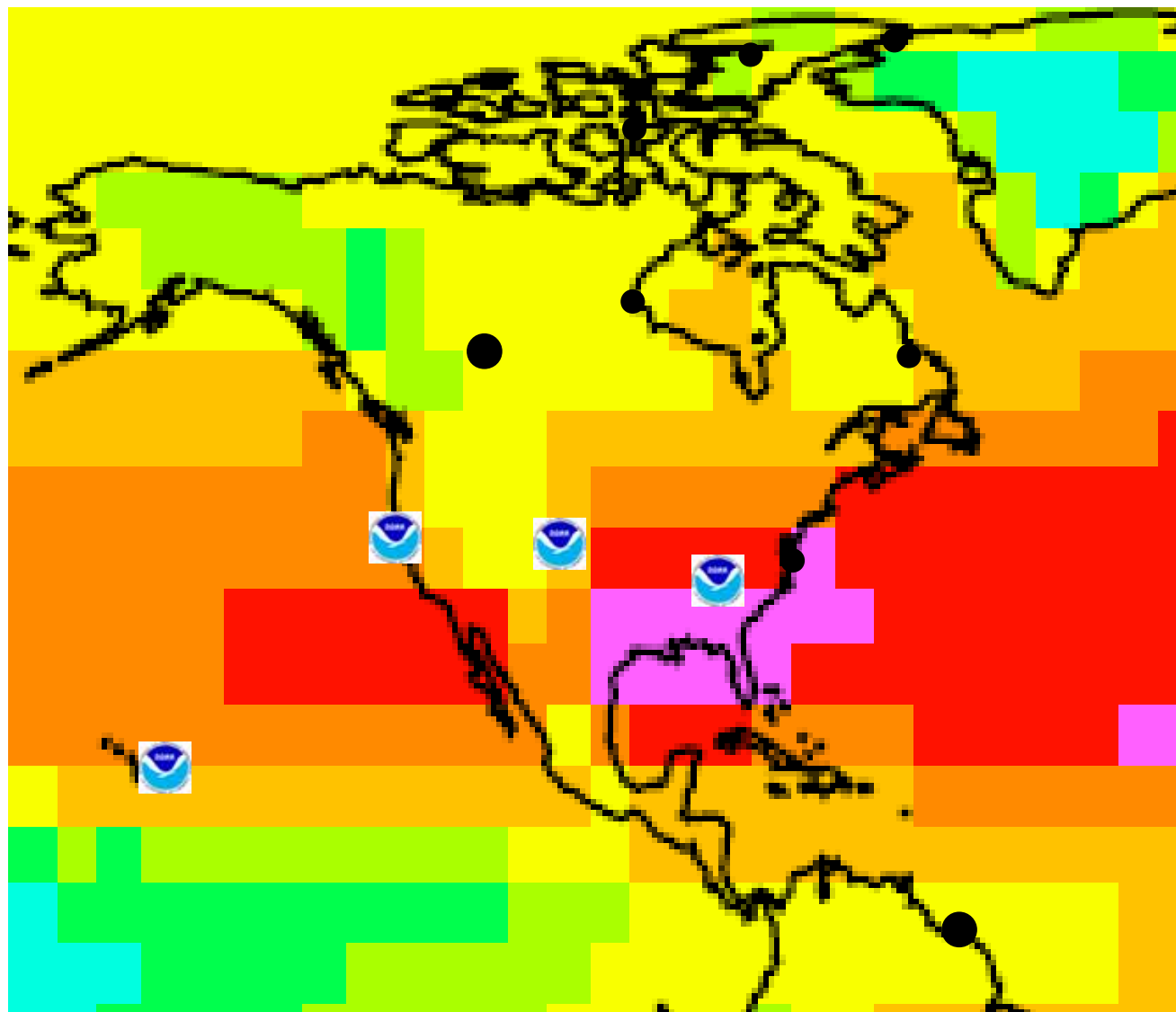
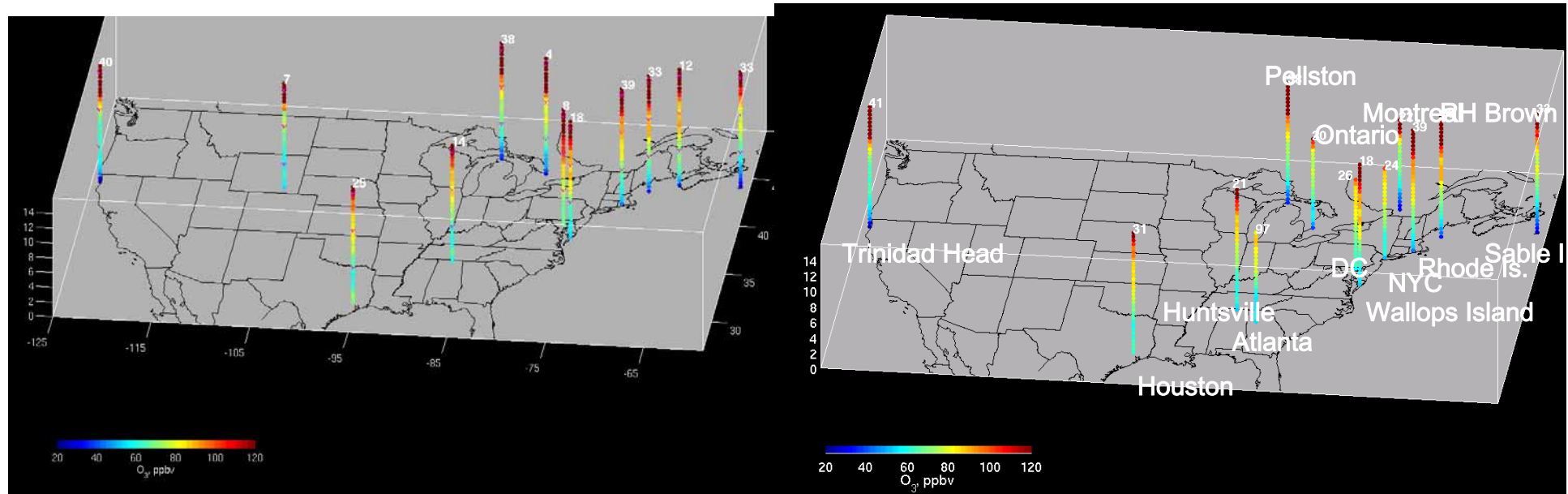


Figure 15. Vertical profiles of ozone concentrations at Huntsville, Alabama (86.6°W, 34.7°N) in July 2000. The thin solid lines are five ozonesonde soundings made during the month (1, 8, 15, 22, and 29 July) by *Newchurch et al.* [2003]. The thick solid line shows the model monthly mean values. The thin dotted, dashed, and dash-dotted lines show the simulated enhancements from North American anthropogenic, biogenic, and lightning emissions, respectively, as determined by difference with simulations where these emissions are shut off. The thick long dashes line shows the model monthly mean values from a simulation with lightning NO_x emissions over North America increased by a factor of four.



Prior to 2004 there were 12 ozonesonde sites in the Americas, north of the equator, launching only once-per-week.

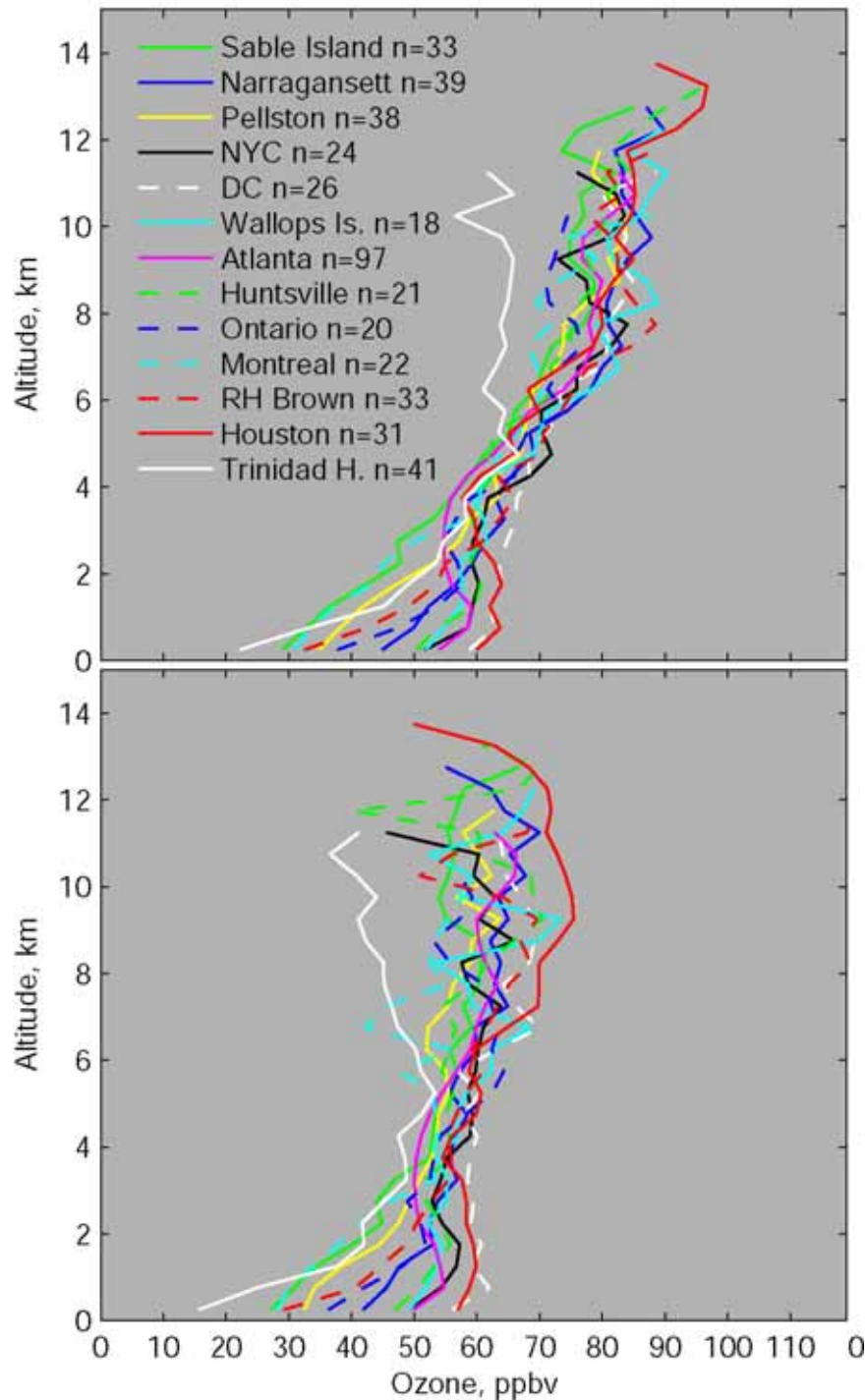
More extensive observations of vertical profiles



IONS - INTEX Ozonesonde Network Study

Thompson et al. (2007), IONS-04 (INTEX Ozonesonde Network Study, 2004): Perspective on Summertime UT/LS (Upper Troposphere/Lower Stratosphere) ozone over northeastern North America, *J. Geophys. Res.*

IONS and MOZAIC sites used in determining the trans-North America ozone distribution, July 1 – August 15, 2004 (469 total profiles)
The most extensive set of ozone measurements ever assembled for N. America



Median tropospheric ($PV < 1.0$) ozone profiles for all sites

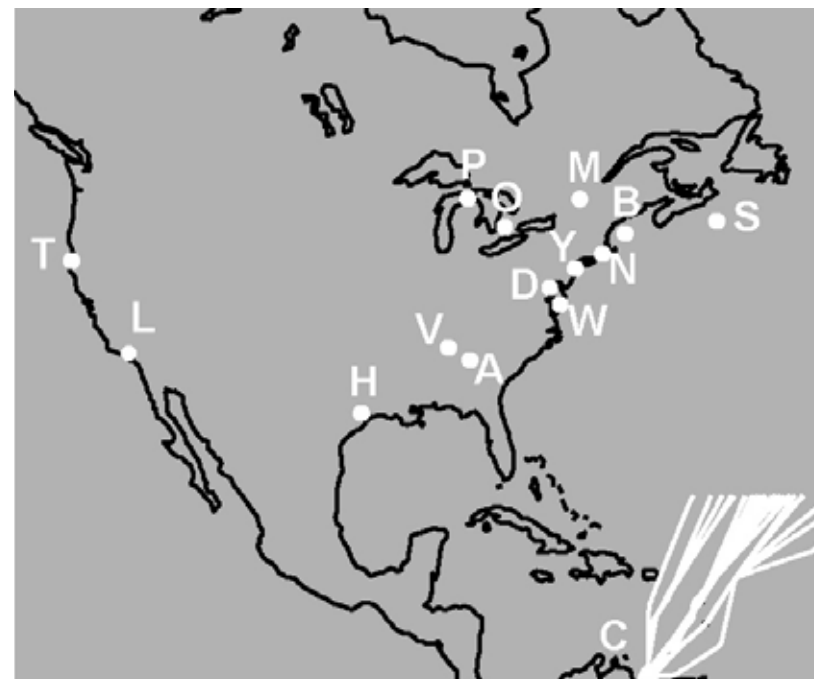
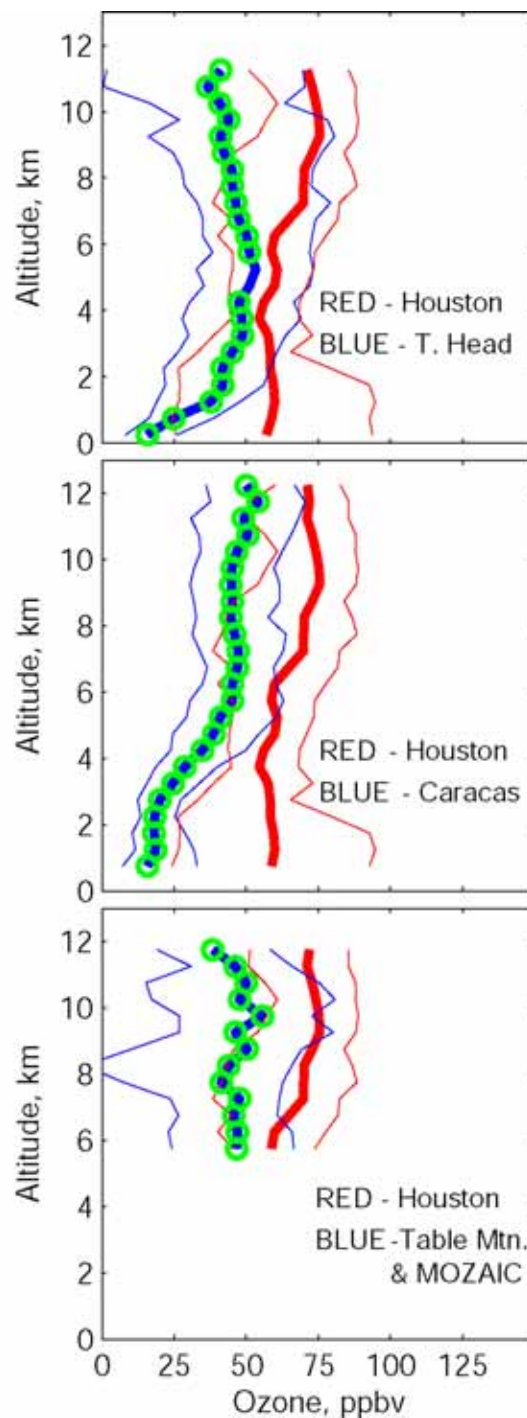
With stratospheric influence removed, as calculated by FLEXPART: ECMWF global wind fields; - 1x1 degree; 60 vertical levels; every 3 hours.

Ozone mixing ratio in stratosphere specified according to O_3/PV ratio.

Enable quantification of stratospheric fluxes?

62 MOZAIC flights to Caracas, Venezuela, 1999-2004

9 MOZAIC flights and 17 lidar profiles near Los Angeles, July 1 – Aug 15, 2004



In comparison to the 3 upwind sites, Houston has a 24 ppbv ozone enhancement in the upper troposphere.

Overall, eastern N. America has an upper tropospheric ozone enhancement of 16 ppbv.

Evidence for a recurring eastern North America upper tropospheric ozone maximum during summer

O. R. Cooper^{1,2}, M. Trainer², A. M. Thompson³, S. J. Oltmans², D. W. Tarasick⁴, J. C. Witte⁵, A. Stohl⁶, S. Eckhardt⁶, J. Lelieveld⁷, M. J. Newchurch⁸, B. J. Johnson², R. W. Portmann², L. Kalnajs⁹, M. K. Dubey¹⁰, T. Leblanc¹¹, I. S. McDermid¹¹, G. Forbes¹², D. Wolfe², T. Carey-Smith¹³, G. A. Morris¹⁴, B. Lefer¹⁵, B. Rappenglück¹⁵, E. Joseph¹⁶, F. Schmidlin¹⁷, J. Meagher², F. C. Fehsenfeld², T. J. Keating¹⁸, R. A. Van Curen¹⁹ and K. Minschwaner²⁰

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¹⁵Geosciences Department, University of Houston, USA

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¹⁸United States Environmental Protection Agency

¹⁹California Air Resources Board, USA

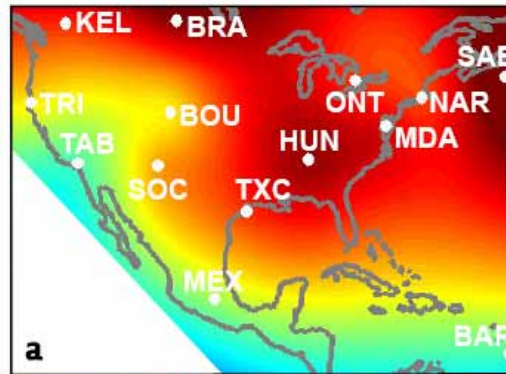
²⁰Department of Physics, New Mexico Institute of Mining and Technology, Socorro

Submitted to JGR, March 27, 2007

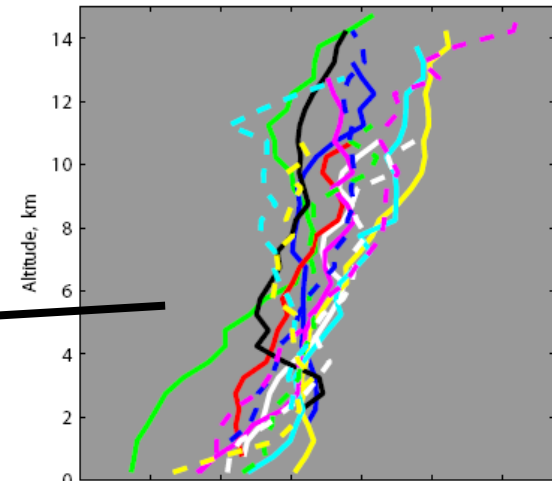
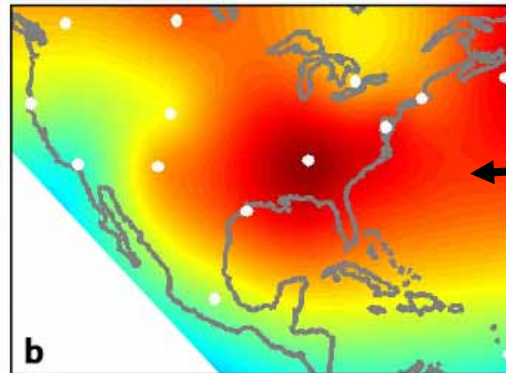
Revised June 29, 2007, Accepted July 19, 2007

Contoured ozonesonde data, median values, 10-11 km, August, 2006.

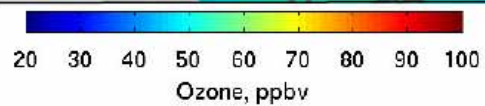
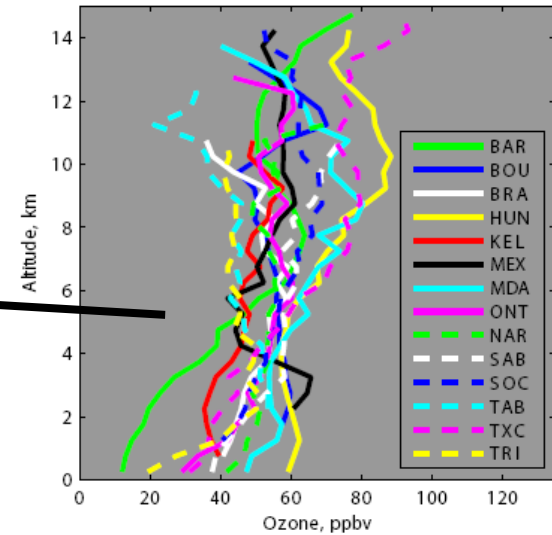
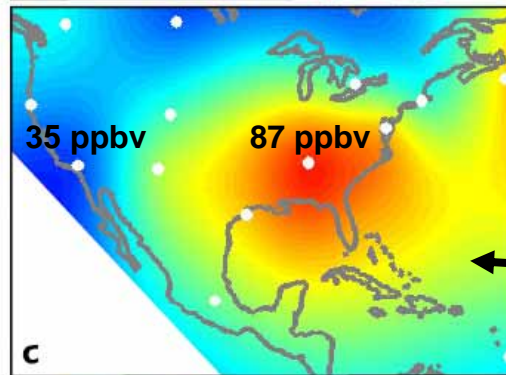
All data, regardless of location in troposphere or stratosphere.



Tropospheric data only.



FLEXPART calculated stratospheric ozone estimates removed.



Average ozone at 250 hPa, August 2006, as calculated by: ECHAM5/MESSy1 atmospheric chemistry general circulation model.

Ozone from all sources, tropospheric and stratospheric.

Ozone produced only in the stratosphere.

Ozone produced only in the troposphere.

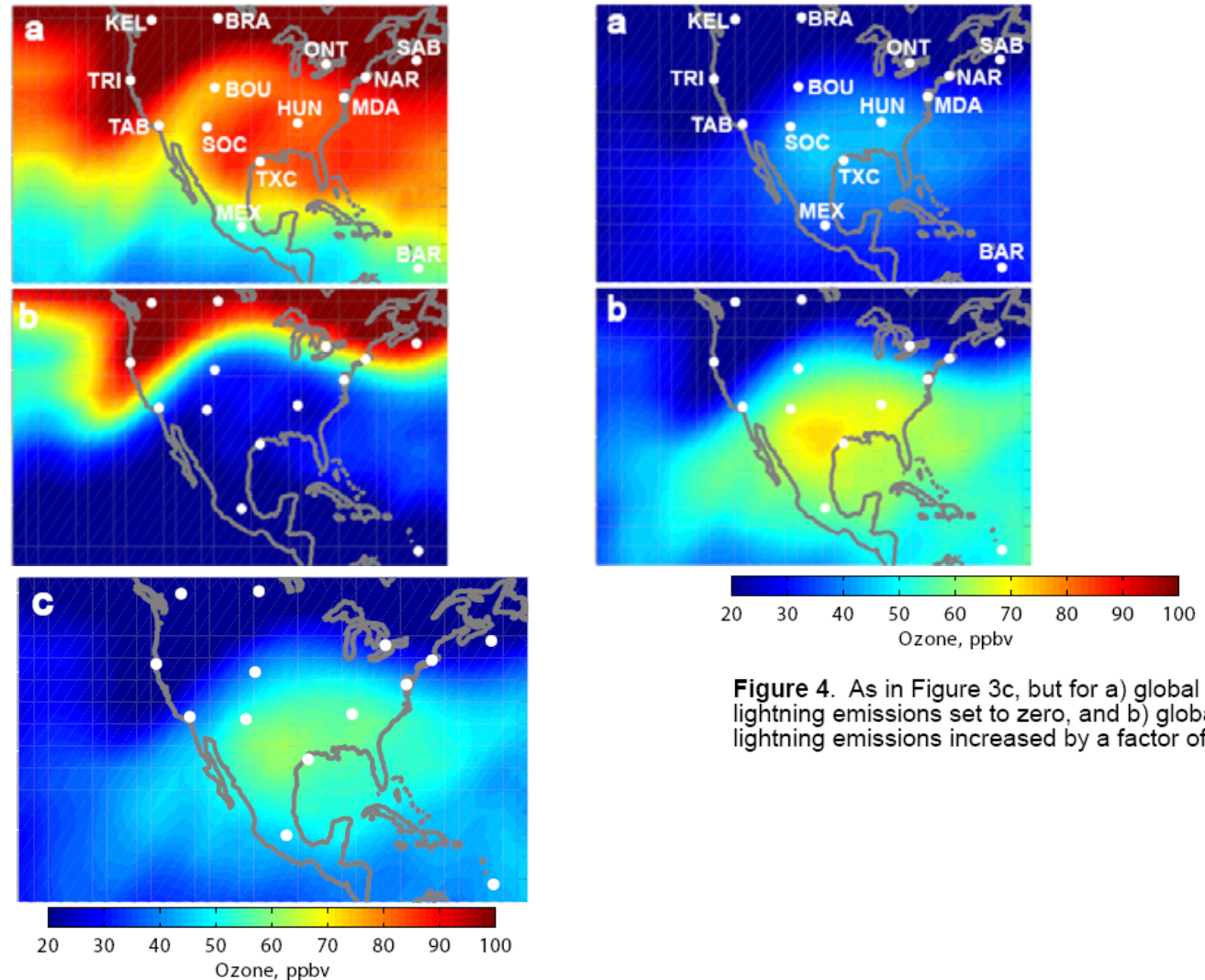
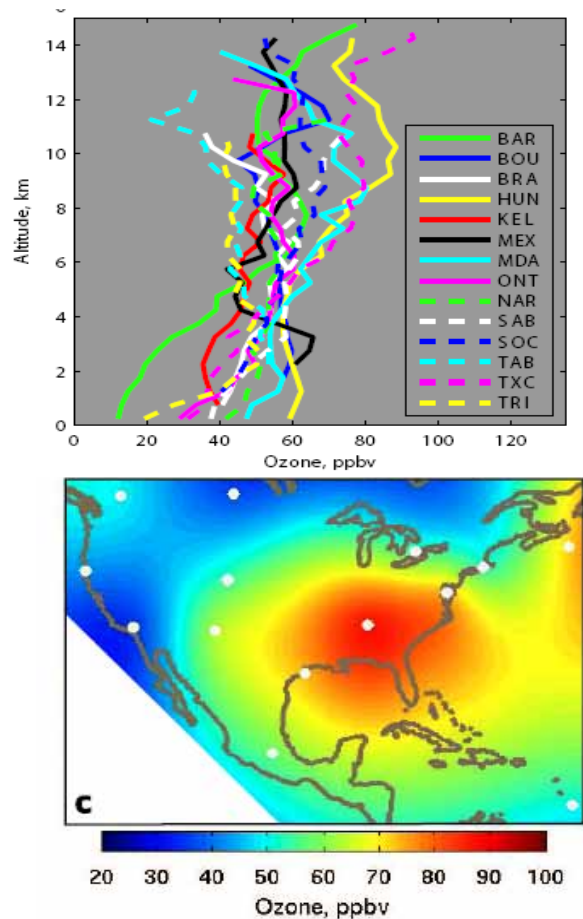


Figure 4. As in Figure 3c, but for a) global lightning emissions set to zero, and b) global lightning emissions increased by a factor of 3.

- Models capture the ozone production
- They are not necessarily quantitative in amount and locations

Upper trop. O₃ production over N. America

Average tropospheric ozone profile (top) and with stratospheric ozone removed at IONS 06 sites in Aug. 2006



Contours of ozone mixing ratio at 10-11 km

Modeling study predicted summer upper trop. ozone maximum over central U.S. Li, Q., et al. (2005), *J. Geophys. Res.*, 110, D10301, doi:10.1029/2004JD005039.

Observations of vertical profiles enabled quantification of the upper trop. Ozone amounts

Analysis of IONS 04 sonde data suggested that this maximum could have a significant contribution from lightning generated NO_x. Cooper, O., et al. (2006), *J. Geophys. Res.*, 111, doi:10.1029/2006JD007306.

IONS 06 strengthened the connection with lightning, showed the strength and persistence of the maximum, Strong year to year variation. Cooper O., et al. (2007), *J. Geophys. Res.*, 112, D23304, doi:10.1029/2007JD008710.

Observational needs for quantification

- It is possible to observationally quantify STE
 - other tracers? Products of stratospheric chemical degradation?
- Need such data for different regions (little data in SH), seasons
- Observations of vertical profiles key for quantification of ozone production and transport
- Such profiles also help confront models (of more and more complexity) with data
- Longer terms observations allow “quantification” of variability and change
- Many other applications for such data- assimilation, etc.

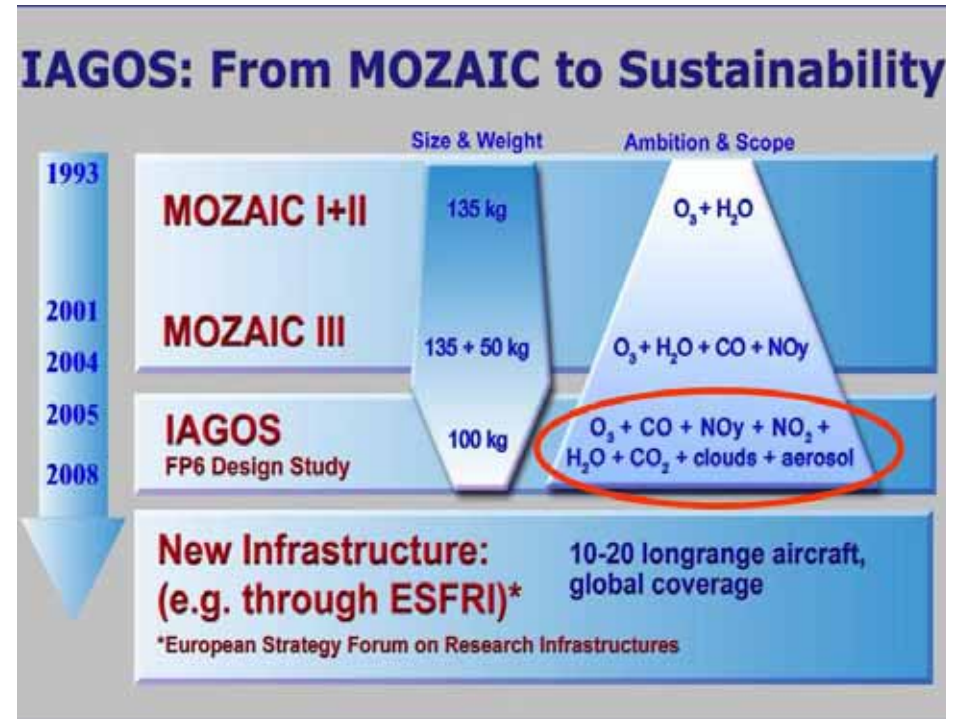
MOZAIC

Measurements of **O**Zone and water vapour by in-service **A**irbus air**C**raft



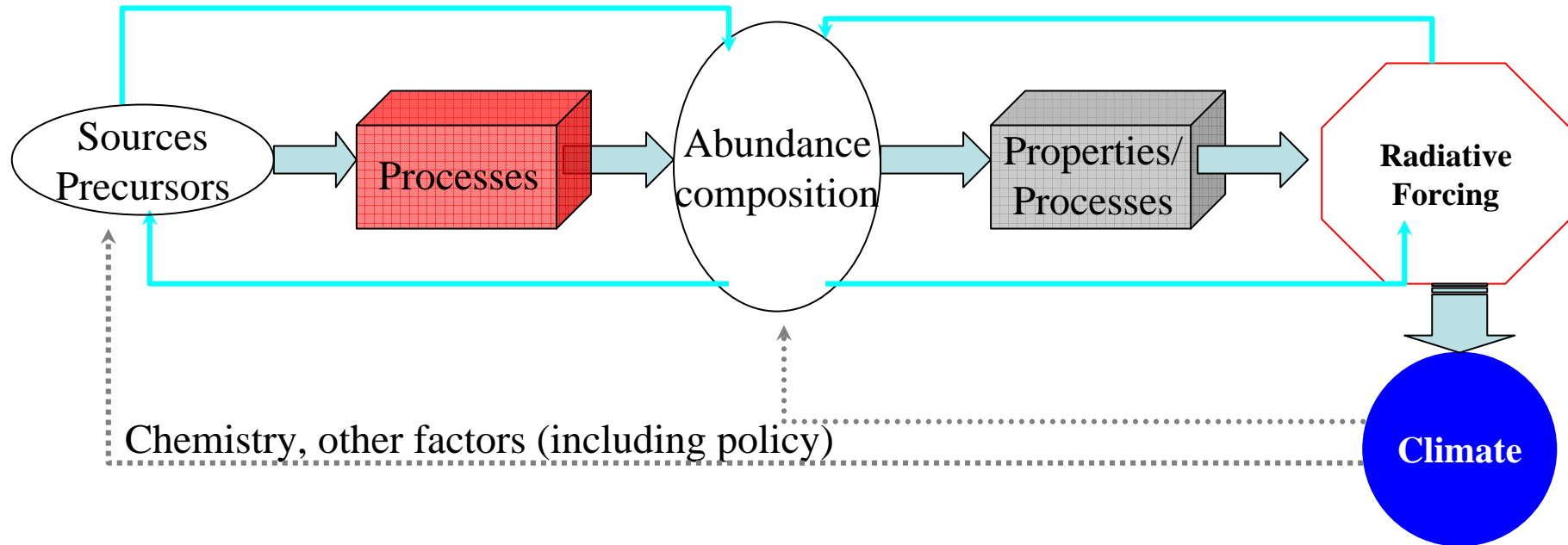
IAGOS

Integration of routine **A**ircraft measurements into a **G**lobal **O**bserving **S**ystem



- An important advance to observationally quantify ozone and other species.
- An important data set to confront models.

Quantification of individual steps in ozone production and loss



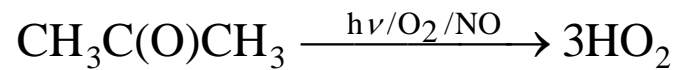
OH, NO_x, and “fuel” are key ingredients for production of O₃

Could HO_x be produced by processes other than the standard method?

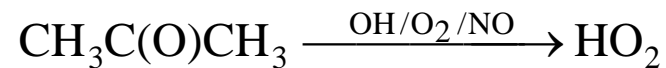
HO_x in the UT: Role of acetone

Net HO_x Production

- Photolysis



- OH Reaction



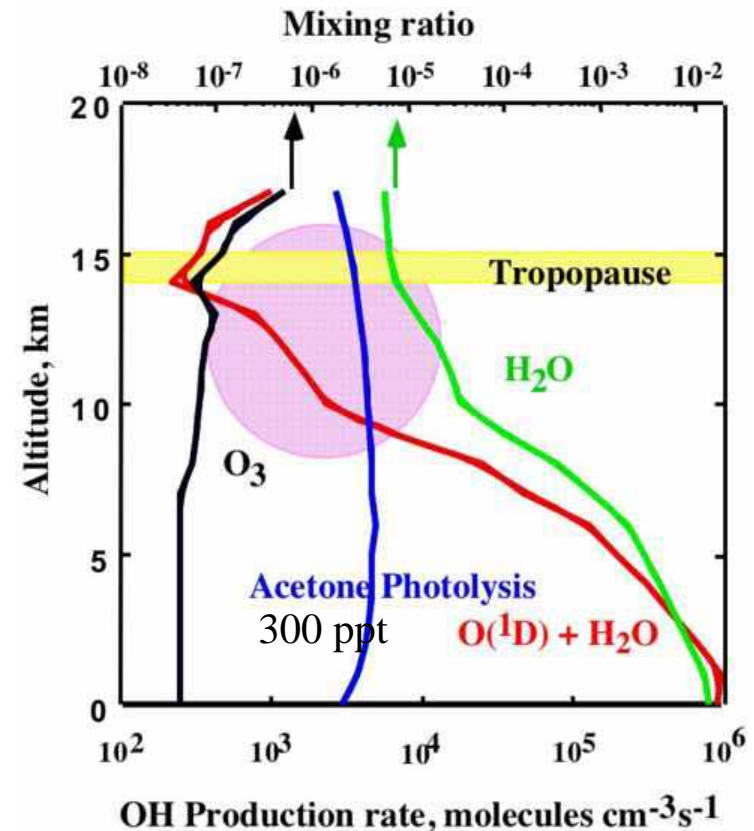
Upper Troposphere is dry

What is the abundance of water vapor

The contribution critically depends on

- rate coefficient for reactions
- Product of reactions
- Photolytic production of radicals

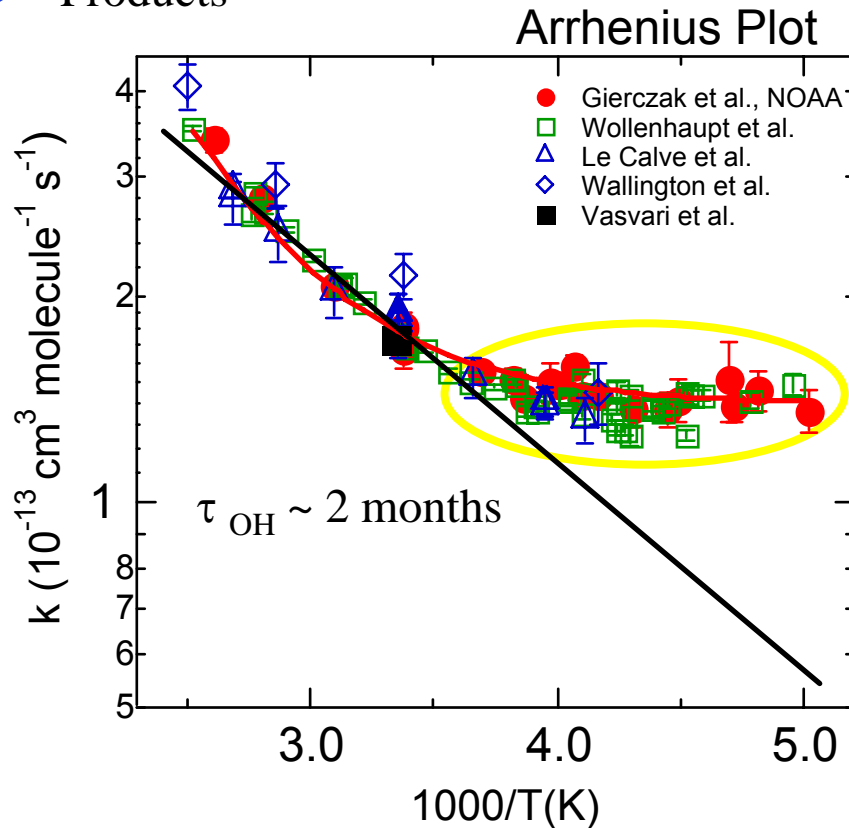
ALL AT APPROPRIATE T, PRESSURE, and COMPOSITION



Atmospheric Loss: OH Reactivity



- OH rate coefficient
- Products



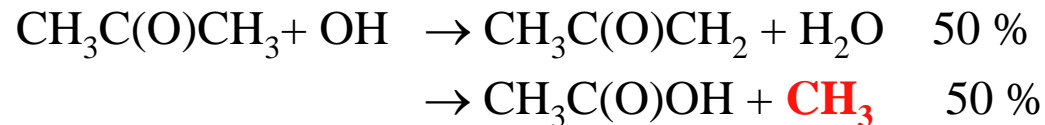
Curvature in Arrhenius plot makes a big difference at mid and upper trop temperatures!

Reaction of OH with acetone determines acetone lifetime and how much gets to the stratosphere.

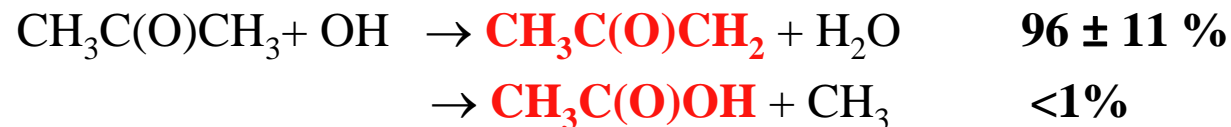
Could part of the acetone be lost before HO_x production?

OH Reaction Products - Atmospheric Impact

Wollenhaupt and Crowley, 2000



Direct detection of products:



- Branching Ratio: Independent of Temperature (237 - 353 K)
- Reaction occurs via H-abstraction pathway under all atmospheric conditions.
- ✓ $\text{CH}_3\text{C}(\text{O})\text{OH}$ is not produced
 - Degradation products stay in the atmosphere and lead to HOx

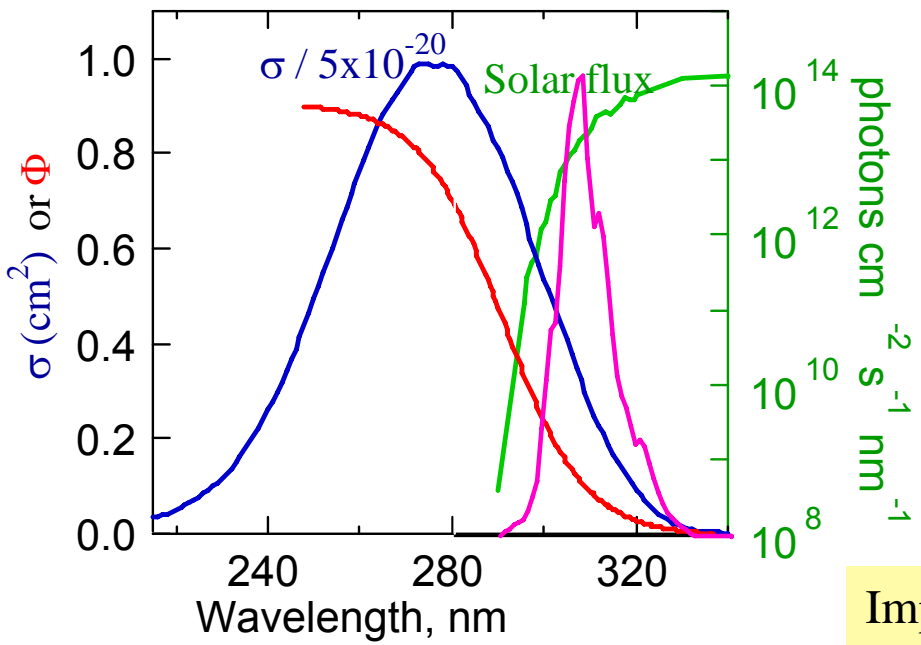
Atmospheric UV Photochemistry of acetone

$$J \text{ value} = \int \sigma(\lambda, T) \times \Phi(\lambda, [M], T) \times F(\lambda, z, \chi)$$

UV abs cross section Quantum yield Solar flux

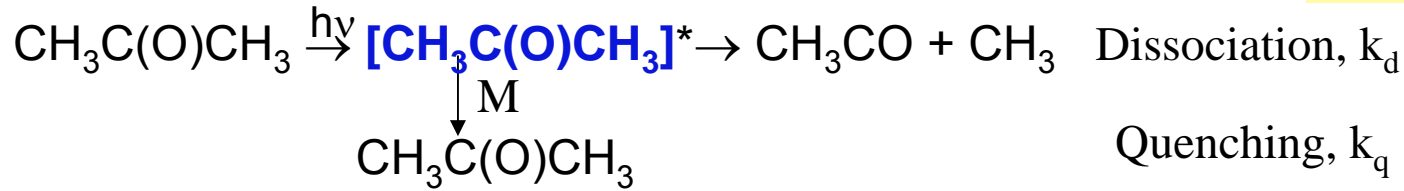
$$\Phi(\text{loss}) = \frac{\# \text{ of destroyed molecules}}{\# \text{ of photons absorbed}}$$

$$\Phi(\text{loss}) = \frac{\# \text{ of destroyed molecules}}{\# \text{ of photons absorbed}}$$



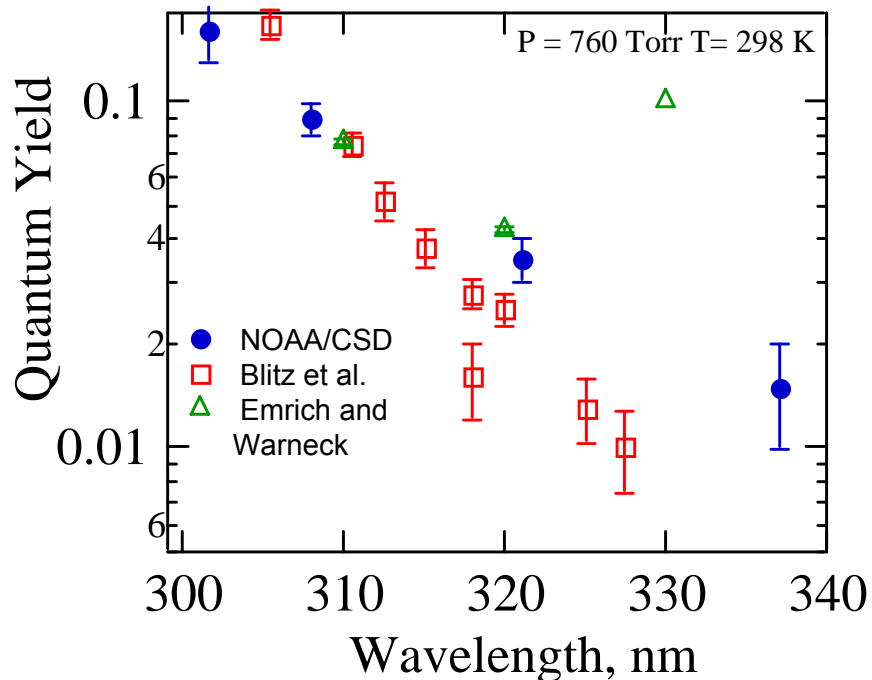
Important
λ range: 290-330
nm

Quantum yield, $\Phi(\lambda, [M], T)$



QY needs to be measured as function of $(\lambda, [M], T)$

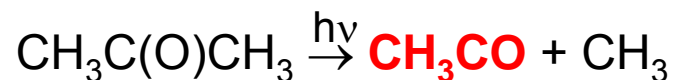
Quantum Yields from Earlier Studies



➤ Φ is small and σ is small--
difficult to measure

- Uncertainties in QY exist.
 - Impacts J
 - Impacts HOx production rate
- Primary products were not measured.

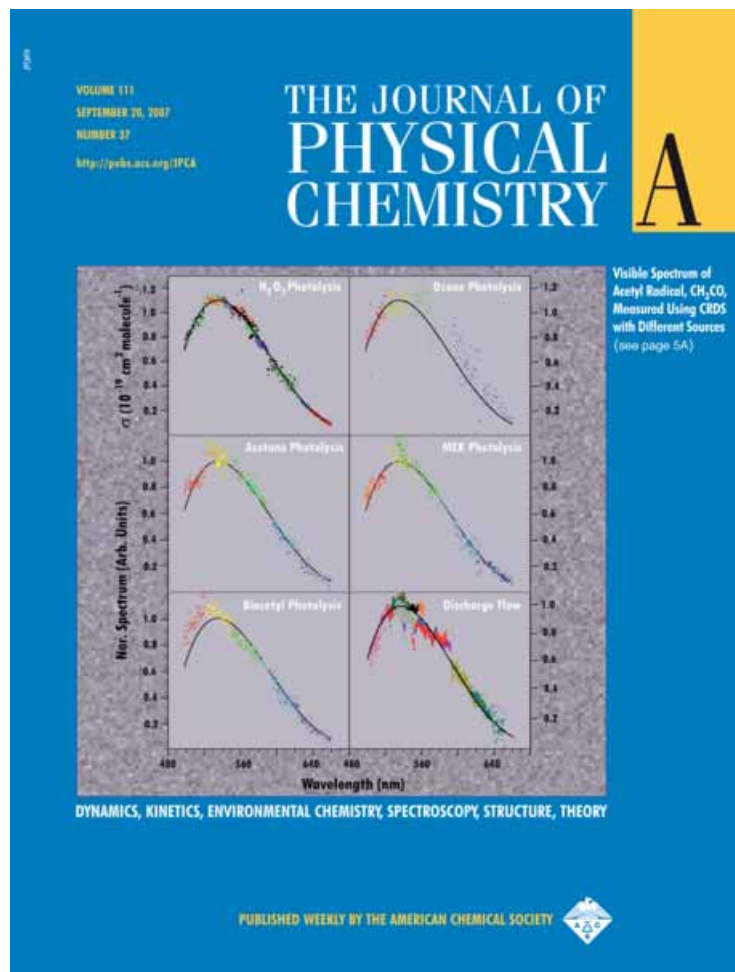
□ Detect the primary photolysis product, CH_3CO



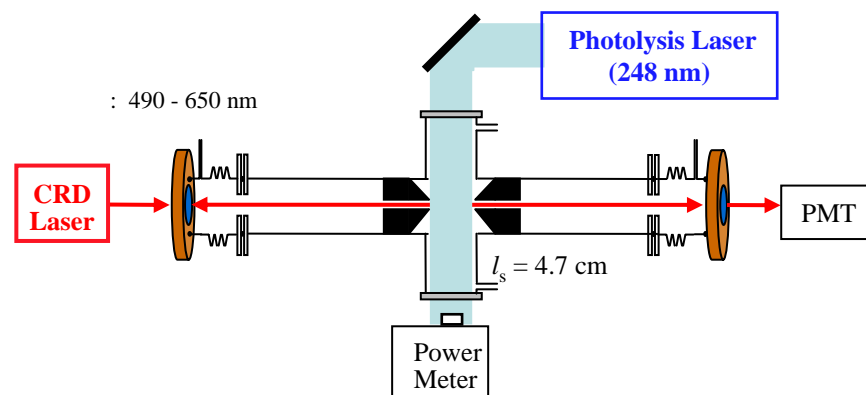
- Developed spectroscopic method.

Direct Sensitive Detection of the CH_3CO Radical

- CH_3CO Visible spectrum measured for the **first time**



Pulsed Laser Photolysis- Cavity Ring Down Spectroscopy



- New way to detect acetyl radical
- Enables direct measurement of a primary photolysis product

B. Rajakumar, J.E. Flad, T. Gierczak, A.R. Ravishankara, J.B. Burkholder, *J. Phys. Chem. A*, 111, 8950, 2007

Obtaining accurate lab data requires development of new tools

Data needs from laboratory studies

An examination of gaps in data on rates, products, and mechanisms of gas phase reactions

- What are the issues?
- What is the current state?
- What are the needs?
- How do we fulfill these needs?



Gas Phase Group
IGAC • SPARC • INTROP

Cambridge workshop • 19-20th June 2008 (UK)

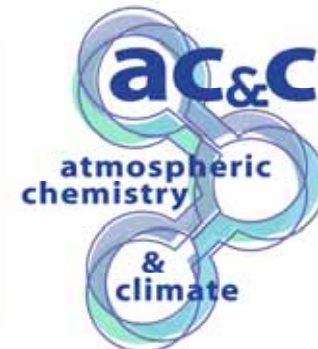


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SETTING SCIENCE AGENDAS FOR EUROPE



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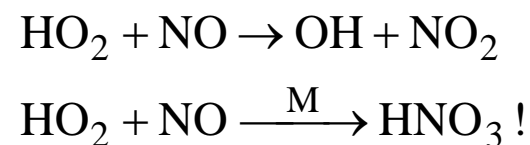
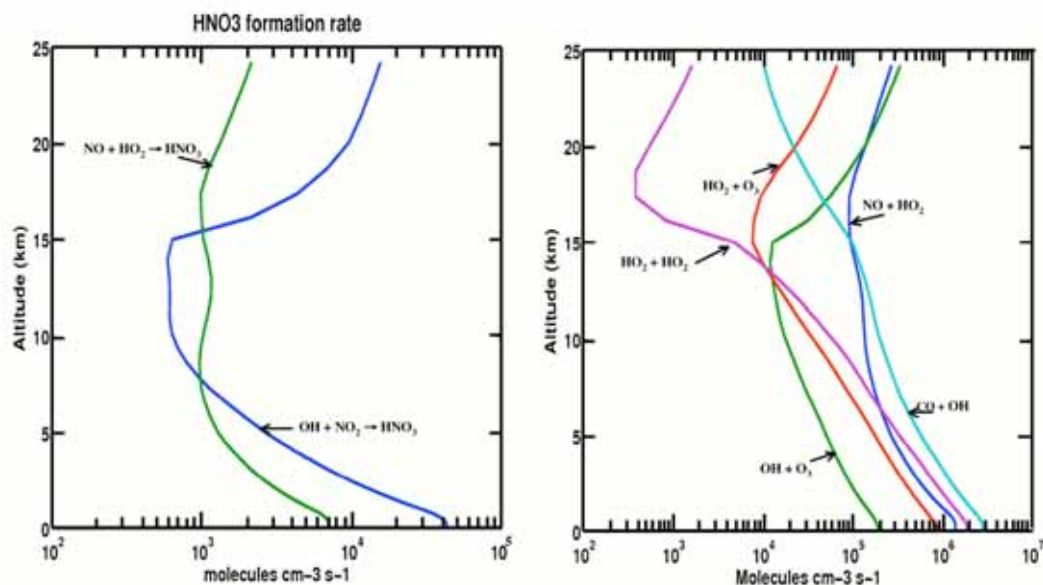
last update: 11/07/2008



Surprises in fundamental reactions abound!

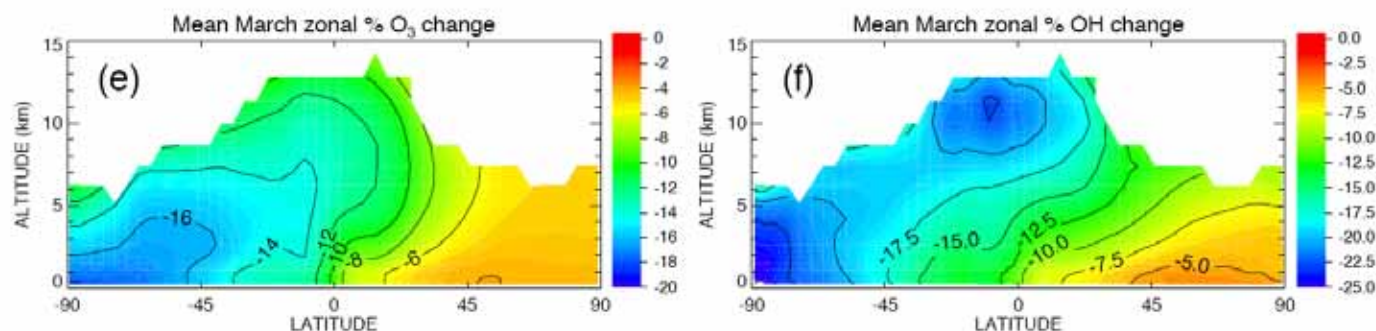
Impact of the new HNO₃-forming channel of the HO₂+NO reaction on tropospheric HNO₃, NO_x, HO_x and ozone

D. Cariolle^{1,2}, M. J. Evans³, M. P. Chipperfield³, N. Butkovskaya⁴, A. Kukui⁵, and G. Le Bras⁴
Atmos. Chem. Phys., 8, 4061-4068, 2008



Branching ratio for HNO₃ production measured

Confirmation studies essential!!



Laboratory data needs



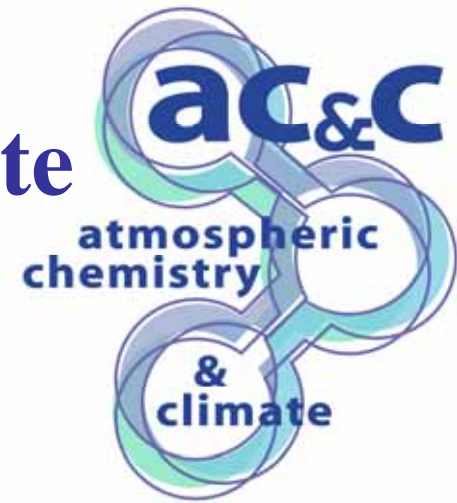
- Nitrogen oxides- key for chemical production of ozone
- Hydrocarbon oxidation rates and mechanisms (particle formation?)
- Radical production pathways and their quantification

Gas phase reactions- examples

- Rates of processes (e.g., $\text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3$)
 - Products (e.g., $\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$)
 - Rates (radicals, e.g., $\text{HO}_2 + \text{HO}_2$)
- Photochemistry (e.g., CH_3CHO , $\text{CH}_3\text{C}(\text{O})\text{CH}_3, \dots$)
 - Heterogeneous reactions and photochemistry on surfaces

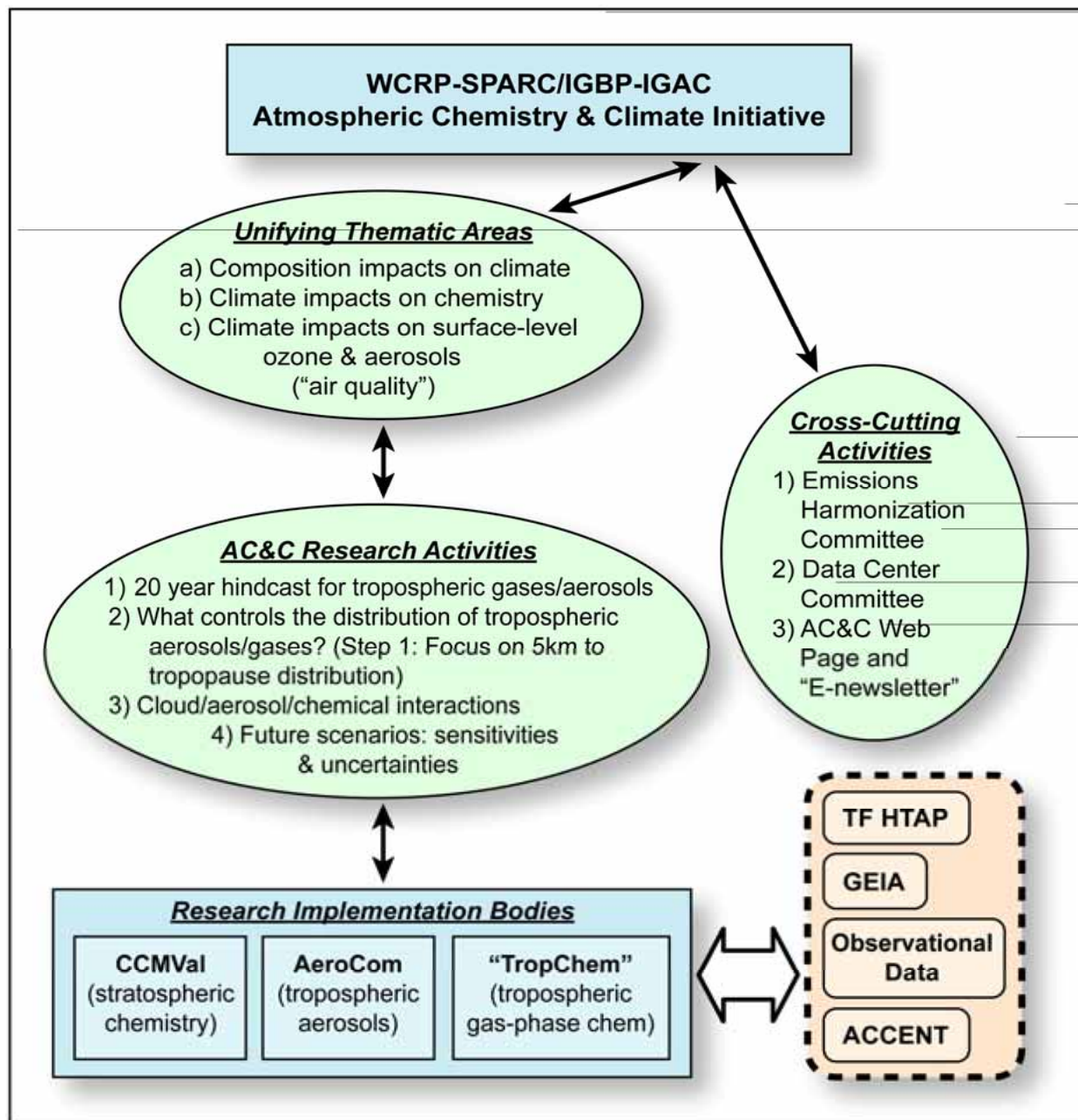
Report of the workshop is forthcoming in 2008

IGBP-IGAC/ WCRP-SPARC Atmospheric Chemistry & Climate Initiative



Phil Rasch & Sarah Doherty: IGBP-IGAC
A. R. Ravishankara, WCRP-SPARC

- Chemically active species:
 - Source of significant fraction of uncertainty in radiative forcing
 - Atmos concentrations change rapidly with changes in emissions*implications for science & policy*
- Understanding:
 - **what controls the distribution** of these species,
 - **their role in climate change,**
 - **how their distribution might change with climate,** and
 - **the coupling between climate and air quality***→ are all critical to effective climate change projections and to mitigation and adaptation decisions.*



AC&C Initiative, Activity 2: *Vertical Distributions*

José Rodriguez, Joyce Penner, Céline Mari



What controls distribution 5km-tropopause?:

- Advection by large-scale winds
- Convection
- Wet scavenging
- Dry Deposition
- Stratosphere-Troposphere Exchange (CCMval, SPARC)
- Chemistry
- In situ production of ozone precursors

➤ *Start off looking at **convection** and **scavenging** processes, as these are the most uncertain and biggest “knobs” in the models, in particular when looking at UT.*

AC&C Initiative, Phase 2: Atmospheric Observations



- A consistent set of observational data is essential for “testing” models
- Should include satellite and in-situ observations
- In-situ observations:
 1. Long term measurements of key constituents
 2. “sporadic” more extensive measurements (often done for process understanding).
 3. Spatial and temporal scales to be compatible with model outputs.

Summary

- UT/LS is an important region and requires greater scrutiny.
- Tropospheric ozone is an important chemical that needs special attention.
- There are observational approaches to quantifying
 - STE
 - Chemical Production
- Basic studies still needed to improve model inputs (and hence prediction capability) (Lab studies workshop)
- Atmospheric Chemistry and Climate (AC&C) has its Phase I on its way. Observational information will be a cornerstone for Phase II. AC&C is well positioned to examine UT/LS issues

Thank you for your
attention