Ozone Production: A Field Study to Evaluate Tropospheric Photochemical Mechanisms (a survey of accomplishments, 1994-1997)

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General Goals

- To use airborne geophysical and chemical observations for the development and evaluation of hypotheses describing the fate of tropospheric oxidants.
- Recent objectives
  - Verification of Cl_2 levels in the nighttime marine boundary layer
  - participation in the 1996 NARSTO-NE field campaign
  - Analysis of observations taken during the 1995 SOS field study

Key Personnel

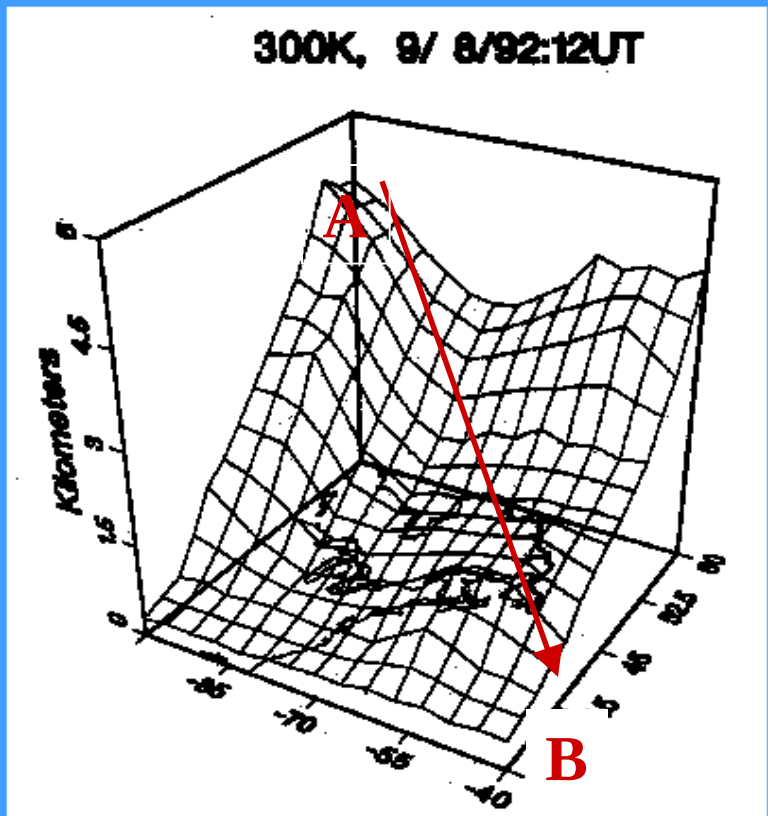
- Rich Barchet
  - aircraft operations manager
- Carl Berkowitz*
  - program design, data analysis
- Xindi Bian
  - numerical modeling
- Elaine Chapman
  - chemical mechanisms and analysis
- Chris Doran
  - boundary layer modeling and analysis
- Dick Easter
  - numerical analysis and modeling
- Jerome Fast
  - boundary layer modeling
- Barbara Finlayson-Pitts
  - University of California at Irvine.
- Bob Hannigan
  - aircraft operations
- John Hubbe
  - aircraft operations, data reduction
- Vic Morris
  - aircraft operations
- Will Shaw
  - boundary layer analysis
- Chet Spicer
  - Battelle Columbus Laboratory
- Mike Warren
  - aircraft operations
- Shiyuan Zhong
  - regional scale meteorological analysis

*Principal investigator

Observations of Ozone Within and Above the Marine Boundary Layer During NARE '92

Principal Investigators: C. M. Berkowitz and E. G. Chapman

- Aircraft profiles of ozone taken hundreds of kilometers east of the North American coast frequently showed an abrupt transition at the top of the marine boundary layer (m.b.l.)
  - Values within m.b.l. were of order 20-30 ppb
  - Values above m.b.l. were of order 60-70 ppb
- Since these profiles were observed under westerly flow (from North America), values aloft were tentatively identified as anthropogenic in origin, coming from the continental boundary layer
- Subsequent analysis showed elevated ozone levels above m.b.l. were natural, originating from mid-troposphere
  - isentropic surfaces (**see figure**) indicate strong subsidence from ~6 km at high latitudes (A), down to ~1 km over sampling site (B).



Key Reference: Berkowitz, C. M., K. M. Busness, E. G. Chapman, J. M. Thorp, and R. D. Saylor, "Observations of Depleted Ozone within the Boundary Layer of the Western North Atlantic," *J. Geophys. Res.*, 100(D6), 11483-11496, 1995

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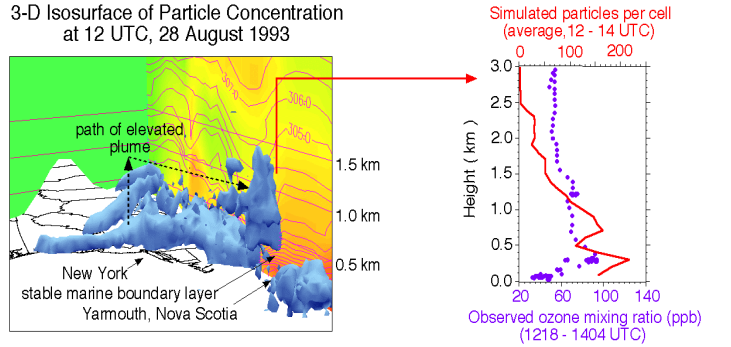
The Influence of Regional-Scale Atmospheric Circulations on Chemical Mixing over the Western North Atlantic

Principal Investigators: J. D. Fast and C. M. Berkowitz

- How old are pollution plums along the east coast? Where do they come from?
- How well do simulated time of transit estimates compare with estimates from field observations?
- Approach:
  - use aircraft observations from NARE '93 to construct a series of profiles (ozone, temperature, aerosols, etc.) for a one-month period
  - Use RAMS to drive a Lagrangian particle dispersion model; particle distribution was used as a surrogate for high/low ozone mixing ratios as a function of altitude
  - Tag particles for point of origin and time of release to evaluate age and source region
- Results:
  - observed layering well replicated by simulations
  - mix of chemicals due to convective processes over land lofting urban material into the free troposphere followed by transport within cyclonic synoptic circulations (**see figure**) makes identification of source region a statistical feature: no single source region is the sole contributor
  - complex circulations imply that plume age is not a good measure of transport distance, and therefore not a good indicator of source region

Mesoscale Dispersion Modeling System used to Determine Atmospheric Processes Associated with Ozone Layers during NARE in 1993



- *within 350 m of the surface, particles are transported by near-surface westerly winds within the marine boundary layer*
- *above 350 m, particles are lifted by convective boundary layer processes and subsequently transported by southwesterly winds over the marine boundary layer*

Atmospheric Studies in Complex Terrain Program and Atmospheric Chemistry Program — *Pacific Northwest National Laboratory*

Key Reference: Fast, J.D. and C. M. Berkowitz, "A Modeling Study of Boundary-Layer Processes Associated with Ozone Layers Observed During the 1993 NorthAtlantic Regional Experiment," *J. Geophys. Res.* 101(D22), 28683-28699, 1996

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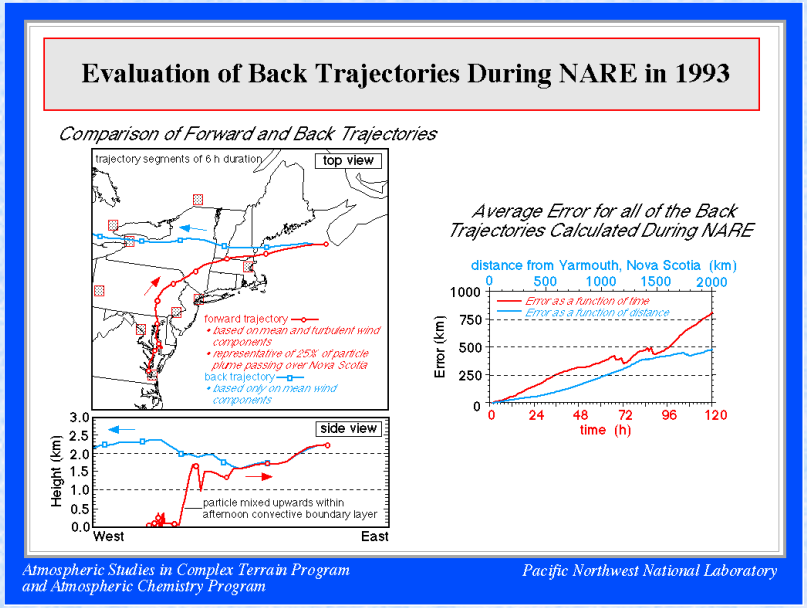
Evaluation of Back Trajectories Associated with Ozone Transport During the 1993 North Atlantic Regional Experiment

Principal Investigators: J.D. Fast and C. M. Berkowitz

- Back trajectories have long been a standard tool in air-quality studies for characterizing source/receptor relationships
- The effects of diffusion on these trajectories cannot be incorporated into back trajectories because turbulence is an irreversible process
- Question: how large is the error introduced into backward trajectories using laminar winds, relative to forward trajectories in a turbulent environment?
- Approach:Compare *forward* trajectories using mean and turbulent wind components derived from RAMS with data assimilation, against *back* trajectories based on only mean wind components**.**
- Results: The divergence between techniques is significant (**see figure**). The right side of the figure shows the errors in the back trajectories gradually grow with distance so that the average absolute error is 500 km at distance of 1500 km from Yarmouth



Key Reference: Fast, J.D. and C.M. Berkowitz "Evaluation of Back Trajectories Associated with Ozone Transport During the 1993 North Atlantic Regional Experiment," *Atmos. Environ.* 31(6): 825-837., 1997.

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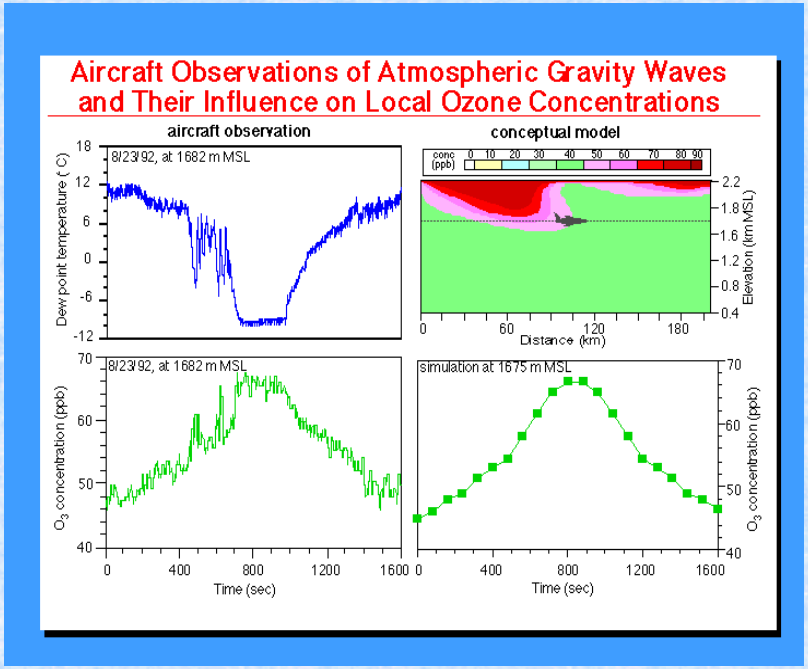
Aircraft Observations of Possible Gravity Waves and Associated Ozone Maximum

Principal Investigators: X. Bian, S. Zhong and C. M. Berkowitz

- A number of localized maxima in ozone were observed when the DOE research aircraft was sampling at constant altitude several hundred kilometers offshore from the east coast of North America (**see figure: bottom left**)).
- Question: Is the origin of these localized maxima natural (stratospheric, as indicated by drop in dewpoint; **see figure: top left**) or anthropogenic?
- Hypothesis: the absence of co-pollutants (e.g., CO SO_2) indicated a natural source. The postulated mechanism was that the aircraft was flying through an atmospheric perturbation associated with internal gravity waves trapped in a stable boundary layer
- Evaluation of Hypothesis: a relatively simple gravity wave model was coupled with a transport model, and initialized using conditions measured prior to the assumed 'fly through' of the perturbation. The model results agreed quite well with the subsequent observations (see figure).



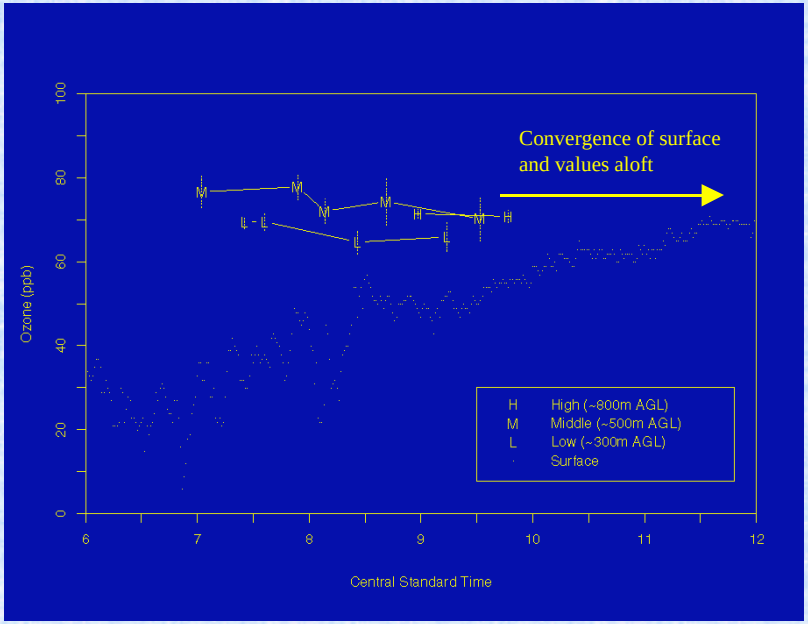
Key Reference: Bian, X., C. M. Berkowitz and S. Zhong, "Aircraft Observations of the Effects of Internal Gravity Waves on Ozone Over the Western North Atlantic," *J. Geophys. Res.* 101(D20), 26017-26021.

Pacific Northwest National Laboratory

The Role of Mixing on the Vertical Distribution of Oxidants and Reactive Hydrocarbons

Principal Investigators: C. M. Berkowitz and W. J. Shaw

- Hypothesis: The evolution of vertical mixing resulting from daily changes in boundary layer turbulence will cause significant variations in surface oxidant concentrations regardless of the photochemistry.
- Measurement Campaign: wind profiler observations and airborne measurements were used to produce a detailed description of the mixed layer development after sunrise at the 1995 Southern Oxidant Study's (SOS) site west of Nashville, TN.
- Results:
  - ozone values aloft mixed to surface(**see figure** H, M and L indicate sampling altitude)
  - the arrival of surface hydrocarbons at a given altitude coincided with a dramatic reduction in the slope of the correlation between ozone and NO_y
  - an order of magnitude increase was measured aloft in isoprene with the onset of turbulence.



Key Reference: Berkowitz, C. M. and W. J. Shaw, "Airborne Measurements of Boundary-Layer Chemistry During the SOS: A Case Study," *J. Geophys. Res* 102(D11); 12795-12804, 1997.

Pacific Northwest National Laboratory

A New Modeling System for the Analysis of Observations from ACP Field Campaigns

Principal Investigators: C. M. Berkowitz, J. D. Fast, R. C. Easter, E. G. Chapman

- ACP needs a tool to analyze measurements from regional scale field studies such as the NARE or NARSTO.
- Profiler technology allows refined measurements of boundary layer features; this data should be used in the simulations
- The Tool: the Regional Atmospheric Modeling System (RAMS) with 4-dimensional data assimilation provides mesoscale fields of winds, vertical diffusivities, temperature and moisture, to a chemical kinetic/transport code presently using a modified mechanism developed by Lurmann, Lloyd and Atkinson.
- Preliminary Results: comparison of observed (**Figure 1**) vs. predicted (**Figure 2**) ozone during NARE '93
- Present applications: analysis of layering observed during NARSTO '95 and '96 field campaigns

Key Reference: Berkowitz, C. M., J.D. Fast and E. G. Chapman, "An Analysis of Ozone Events During NARE 1993," Atmospheric Chemistry Program Monthly Update 7(10), U.S. Dept. of Energy, Washington, DC., 1993.

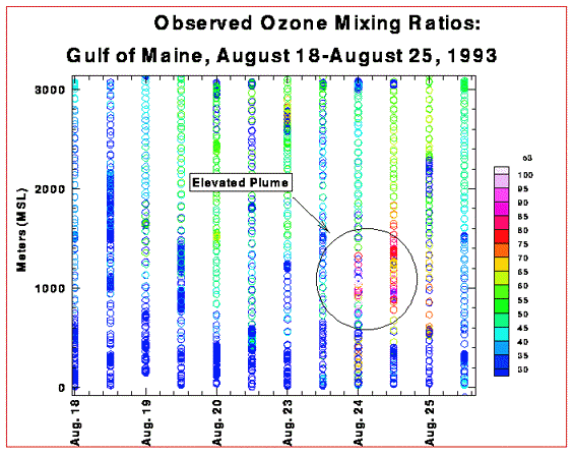


Figure 1

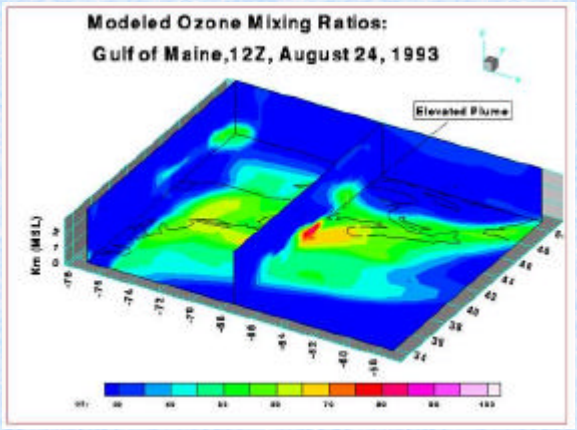


Figure 2

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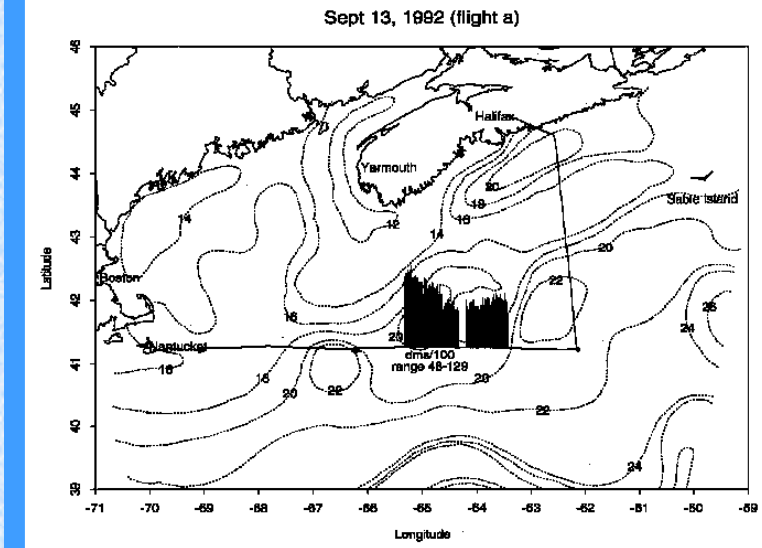
Airborne Measurements of DMS Over the Western North Atlantic

Principal Investigators: Chet W. Spicer and E.G Chapman

- Theoretical considerations developed during the last decade, and supported by certain field observations, suggest that cloud formation over remote areas of the ocean regions may be related to local gas-to-aerosol conversion processes
- A key species in these reactions is dimethylsulfide (DMS), present in seawater as a result of biological processes involving marine organisms
- No simple relationships have been found between DMS in seawater and other variables (such as salinity, solar radiation, etc.), thus precluding confident extrapolation of DMS data to locations, seasons, and time for which no data exist
- During the 1992 NARE campaign, ACP scientists used a tandem mass spectrometer modified for aircraft sampling to measure DMS over the western North Atlantic (**see figure**); an increase in DMS was found to be associated with pools of warm ocean water



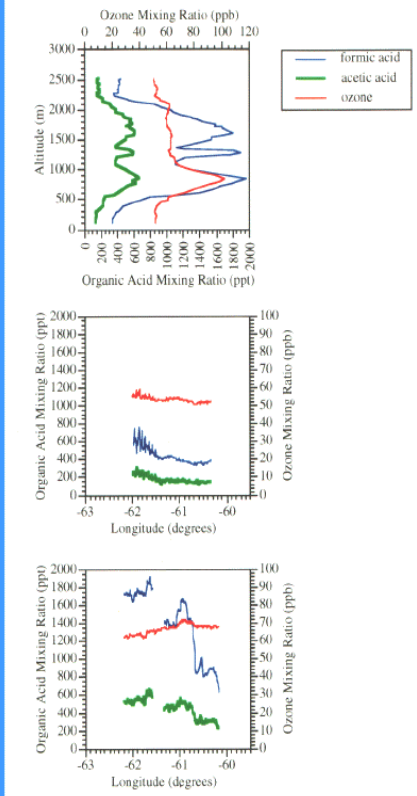
Key Reference: Spicer, C. W., D. V. Kenny, E. G. Chapman K. M. Busness, and C. M. Berkowitz, "Observations of Dimethylsulfide Over the Western North Atlantic Using an Airborne Tandem Mass Spectrometer', *J. Geophys. Res.* 101(D22), 29137-29147, 1996.

Pacific Northwest National Laboratory

Continuous Airborne Measurements of Organic Acids Over the Western North Atlantic

Principal Investigators: C. W. Spicer and E. G. Chapman

- Very few measurements of organic acids above the earth's surface have been made, despite their important contribution to precipitation acidity in remote regions of the world.
- Past measurements were hampered by the fact that earlier measurement technologies integrated over space and time, severely limiting data resolution.
- ACP scientists were able to make point measurements using a tandem mass spectrometer that was specially modified for aircraft sampling **(see figure)**
- Considerable temporal, vertical and horizontal variability was found for gaseous formic and acetic acids; modeling efforts will be needed to determine the major sources and sinks of these acids.



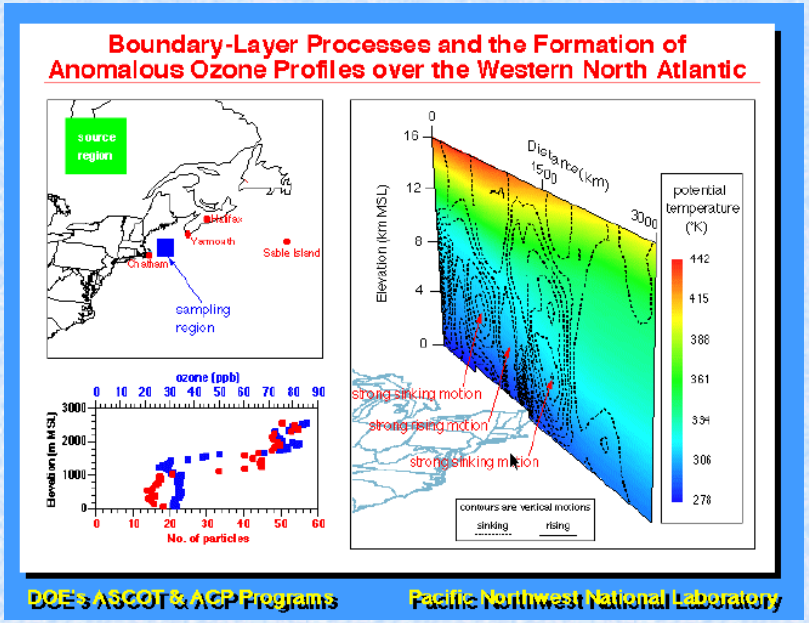
Key Reference: Chapman, E.G., D. V. Kenny, K. M. busness, J. M. Thorp, and C. W. Spicer, "Continuous Airborne Measurements of Gaseous Formic and Acetic Acids Over the Western North Atlantic," *Geophys. Res. Let.* 22(4), 405-408, 1995.

Pacific Northwest National Laboratory

Boundary-Layer Processes and the Formation of Anomalous Ozone Profiles over the Western North Atlantic

Principal Investigators: J. C. Doran, S. Zhong, C. M. Berkowitz

- Aircraft profiles taken near the coasts of New England and Nova Scotia frequently displayed a sudden increase of ozone at altitudes of ~ 1km.
- These discontinuities corresponded closely with the heights of layers of air over the ocean whose temperature variations with height suggested a region of vigorous vertical mixing.
- Question: how well can these discontinuities in ozone profiles be explained by *non-chemical*, boundary-layer processes?
- Method: A particle dispersion model was used in conjunction with the RAMS code (run with data assimilation) to simulate trajectories of nonreactive tracer particles as they are transported and dispersed by the mean and turbulent wind fields generated by the model.
- Results: The resulting distribution of particles resulted in a complex pattern of vertical mixing that accounted for much of the observed structure of the ozone profiles (**see figure**).

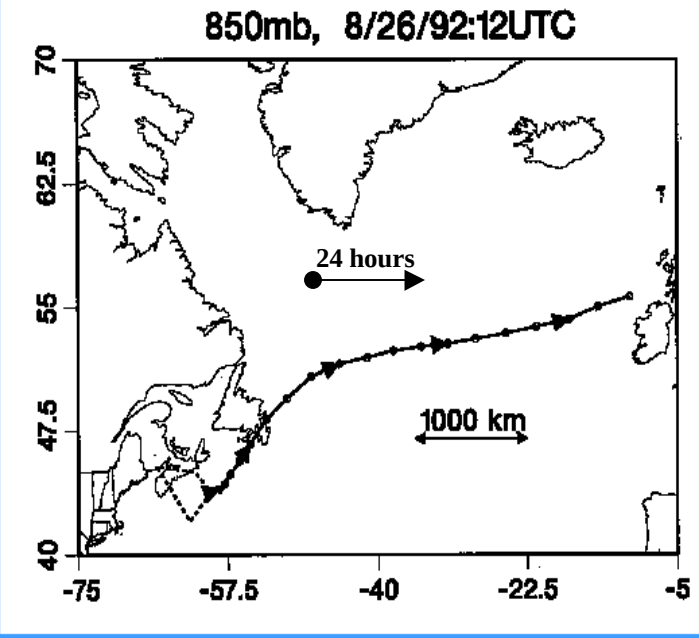


Key Reference: Doran, J.C., S. Zhong, and C. M. Berkowitz, "Meteorological Factors Affecting Ozone over the North Atlantic," *J. Geophys. Res.* 101(D22), 28701-28710

Transport Patterns Associated with the Export of Ozone over the Western North Atlantic

Principal Investigator: C. M. Berkowitz

- Concentrations of tropospheric ozone are generally associated with a combination of transport from the stratosphere and local tropospheric formation mechanisms involving a complex set of reactions between NO_x, hydrocarbons and sunlight.
- Measurements taken by the DOE G-1 aircraft identified high pollution levels in advance of eastward moving cyclonic systems.The ozone flux associated with these systems was estimated to be on the order of 1 gigamole per 24-hour cyclonic event, a value much higher than the previously estimated daily mean value.
- These same systems appear capable of causing rapid air mass transit between North America and Europe; in at least one case (**see figure**), trans-Atlantic transport following a pollution event was estimated to occur in less than 5 days.

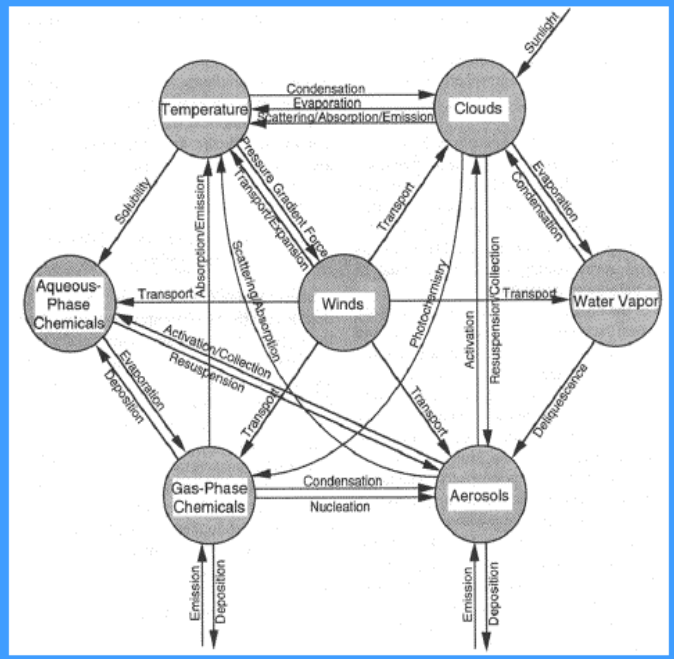


Key Reference: Berkowitz, C. M., P. Daum, C. W. Spicer and K. M. Busness, "Synoptic Patterns Associated with the Flux of Excess Ozone to the Western North Atlantic," *J. Geophys. Res*. 101(D22) 28923-28933., 1996

The Current State and Future Direction of Eulerian Models in Simulating Tropospheric Chemistry

Principal Investigators: C. M. Berkowitz, R. C. Easter, S. J. Ghan, and L. R. Leung

- A workshop was held at PNNL in 1994 to identify features of the next generation of tropospheric chemistry models. The rationale for holding the workshop at this time was anticipation of easily accessible computer hardware and recently developed numerical algorithms. These two categories of new tools were anticipated to allow atmospheric scientists to address questions that were previously not possible because of computational limitations.
- An illustration of the complexity of the processes that would ideally be considered is shown in the **attached figure**. Each circle contains a key parameter for the calculation of air pollution levels.
- Gas-phase chemicals, while often thought of as 'the end product' of air pollution models, effect air temperature and often lead to the formation of new aerosols. The next generation of air quality models must be able to take into account all of these interactions.



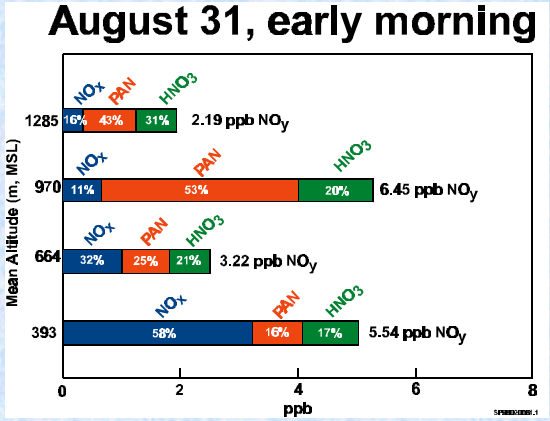
Key Reference: Peters, L. K., C. M. Berkowitz, G. R. Carmichael, R. C. Easter, G. Fairweather, S. J. Ghan, J. M. Hales, L. R. Leung, W. T. Pennell, F.A. Potra, R. D. Saylor, and T.T. Tsang, "The Current State and Future Direction of Eulerian Models in Simulating the Tropospheric chemistry and Transport of Trace Species; A Review," *Atmos. Environ.* 29(2), 189-222, 1995

Pacific Northwest National Laboratory

The Formation Mechanism and Chemical Characteristics of Elevated Photochemical Layers over the Northeast United States

Principal Investigators: C. M. Berkowitz and J. D. Fast

- Residual layers of pollutants had been detected by previous investigators using a more limited measurement capability than is available on the DOE G-1 aircraft..
- Flights over the northeast (**see figure: top right**) during days with high pollution levels resulted in more complete analysis of the composition of these layers **(bottom figure**).
- Subsequent analysis with detailed boundary layer models suggests that these layers are created when pollutants are lofted into the upper part of the mixed layer through afternoon convective mixing in urban centers on previous days. They were subsequently transported overnight into the Connecticut region
- Elevated layers of pollutants are then entrained into the growing convective boundary layer, degrading surface air quality. These layers were detected only on days with elevated pollution levels.



Key Reference: Berkowitz, C. M., J.D. Fast, S.R. Springston, R. J. Larsen, C.W. Spicer, P.V. Doskey, J. M. Hubbe and R. Plastridge, "The Formation Mechanism and Chemical Characteristics of Elevated Photochemical Layers over the Northeast United States," *J. Geophys. Res*. (in press), 1998.

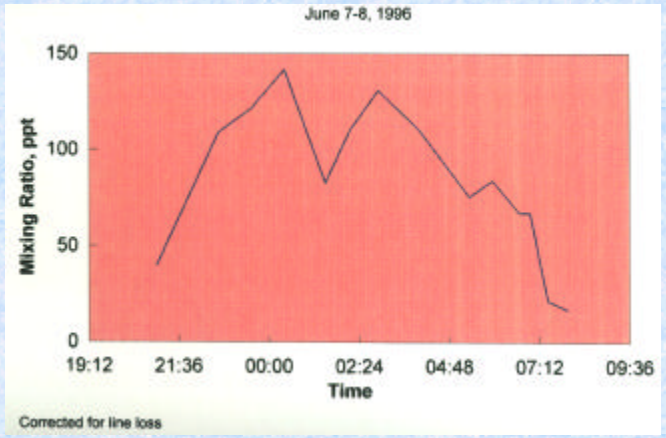
Pacific Northwest National Laboratory

Molecular Chlorine in the Marine Boundary Layer: First Measurements

Principal Investigators: E. G. Chapman, C. W. Spicer, and B. J. Finlayson-Pitts

- Chlorine is known to play an important role in stratospheric. However its role in the troposphere is less certain due to the lack of information about its concentration.
- The presence of molecular chlorine was conclusively demonstrated for the first time by ACP scientists using a tandem mass spectrometer on board the DOE G-1 research aircraft (**top right figure**)
- The measurements, taken at the tip of Long Island (**bottom right figure**) detected concentrations of molecular chlorine far in excess of concentrations predicted for a low-pollution marine environment. These levels could not be explained by known reactions, indicating that a "missing source" could exist.
- Working in their laboratory, UC/Irvine scientists have since identified a new source of molecular chlorinesuggesting the generation of significant quantities can come from the eaction of ozone with sea salt in light.

Key Reference: Spicer, C.W., E.G. Chapman, B. J. Finlayson-Pitts, R.A. Plastridge, J. M. Hubbe, J. D. Fast, and C. M. Berkowitz, "Observations of Enhancec Molecular Chlorine Concentrations in Coastal Air," *Nature* (in review), 1998.



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