CHEMICAL TRANSFORMATION AND LONG-RANGE TRANSPORT

I. INTRODUCTION

It is now clear that "background" concentrations of many trace gases and aerosols are elevated above their pre-industrial levels by continental emissions that circulate globally before they are removed. It has been known since the inception of atmospheric studies that chemical transformations determine the amount and properties of atmospheric constituents.

Long-range transport of air pollutants is important for air quality management because it affects the local concentrations of ozone, aerosols and Hazardous Air Pollutants (HAPS). Polluted air transported into a receptor location during a local or regional pollution event can potentially push a local area over its air quality standard, and the elevation of average background levels by long-range transport limits the local pollution that can be tolerated before exceeding the local standard. Long-range transport affects the current concentrations of, and hence the climate forcings by, ozone and aerosols on regional to global scales, and how these forcings have evolved over the decades since the industrial revolution. Chemical transformations determine the impact of a given species on air quality and climate change issues, the properties of the relevant species and their removal from the atmosphere. Therefore, we need clear understanding of the transport and chemical transformations for understanding the current state of air quality and climate change, as well as predicting and projecting the future evolution of these issues.

Our understanding of the long-range transport effects on air quality and climate change is dependent upon our ability to develop accurate chemical transport models on hemispheric scales. One of the most important limitations on our ability to develop these models is a still-imperfect understanding of the chemical and physical processes that affect trace gas and aerosol concentrations and properties during transport. NOAA conducts intensive ground-based, ship-based and airborne field campaigns and maintains remote and regional background monitoring stations to characterize the concentrations of ozone, aerosols and HAPS for comparison with models. Insightful analysis of these field data combined with focused laboratory studies develop the detailed process understanding that must be incorporated into models.

II. KEY ACHIEVEMENTS INCLUDE: (last 4 years)

- ESRL authors played major roles in developing the comprehensive, unified picture of the importance of intercontinental transport of air pollution presented in two recent reviews [*Stohl*, 2004; *LRTAP*, 2007]. This work provides a clearer picture and identifies gaps in our understanding of the role this phenomenon plays in climate change and air quality issues.
- ESRL scientists successfully organized and led the 2004 ICARTT study [*Fehsenfeld et al.*, 2006]; it included the IGAC sponsored ITCT Lagrangian 2K4 study and involved four research aircraft based in North America, the Azores and Europe to sample polluted air masses several times during transport across the North Atlantic. This study provided the first Lagrangian experiment in the free troposphere on intercontinental scales and enabled better characterization of chemical transformation by quantitatively accounting for mixing and deposition processes during transport.
- ESRL scientists have developed an understanding of atmospheric transport of pollution plumes, and have incorporated that understanding into models to the extent that transport of pollution plumes can be modeled to a semi-quantitative level over 1000's of km (e.g., Figure 1) [*de Gouw et al.*, 2006].

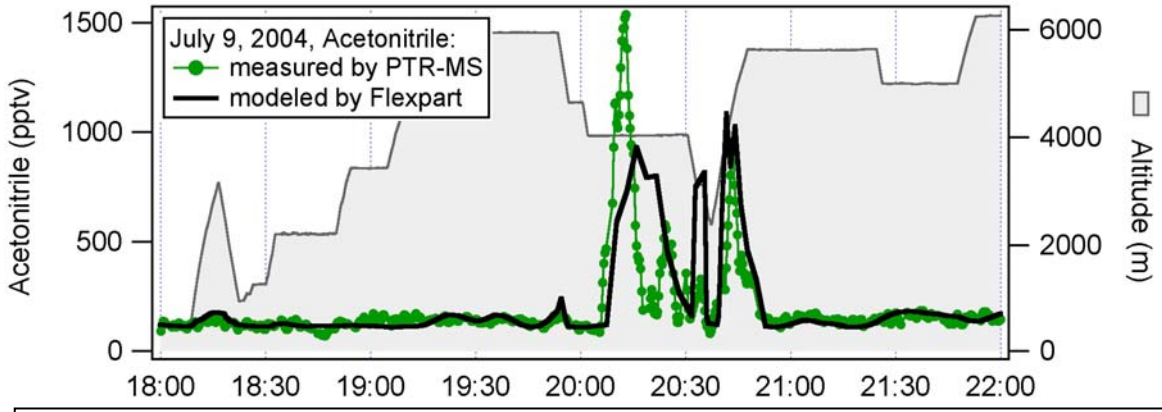

Figure 1: Large forest fire plume from Alaska intercepted by the NOAA WP-3D aircraft several thousand km downwind from the source. Measured acetonitrile (CH_3CN), a tracer for biomass burning, is compared with that predicted by the Lagrangian transport model FLEXPART.

- ESRL scientists conducted a suite of laboratory studies that addressed questions regarding key chemical transformation processes in the atmosphere. 3D models have incorporated the results into for better climate and air quality prediction. These studies include:
  - A new atmospheric nucleation model [*Lovejoy et al.*, 2004, *Kazil and Lovejoy*, 2004] was developed, which predicts widespread new particle formation throughout the mid and upper troposphere via ion-induced nucleation of sulfuric acid and water. *Brock et al.* [2004] observed new particle formation of nearly pure sulfuric acid in the mid troposphere over the North Pacific Ocean, a process that is closely related to the laboratory work. Such synergistic interaction between laboratory work and analysis of field data leads to rapid and efficient advancement in our understanding of atmospheric processes.
  - Our understanding of the atmospheric photochemistry of acetone has been greatly improved. A measurement technique that enabled the direct detection of the important $CH_3C(O)$ free radical was developed, and a host of rate coefficient and photochemical parameters have been determined [*Gierczak et al.*, 2003; *Talukdar et al.*, 2003; *Rajakumar et al.*, 2007].
- Quantifying the sensitivity of global OH abundance to interannual changes in the atmospheric environment provides a critical test to global models, especially when these models are used to project future trace-gas atmospheric abundances and environmental impacts in an atmosphere with potentially very different chemical and physical characteristics. ESRL scientists studied long-lived trace gases to infer mean global abundances of the hydroxyl radical (OH) (Figure 2), and found that interannual variations in the global OH abundance are generally on the order of a few

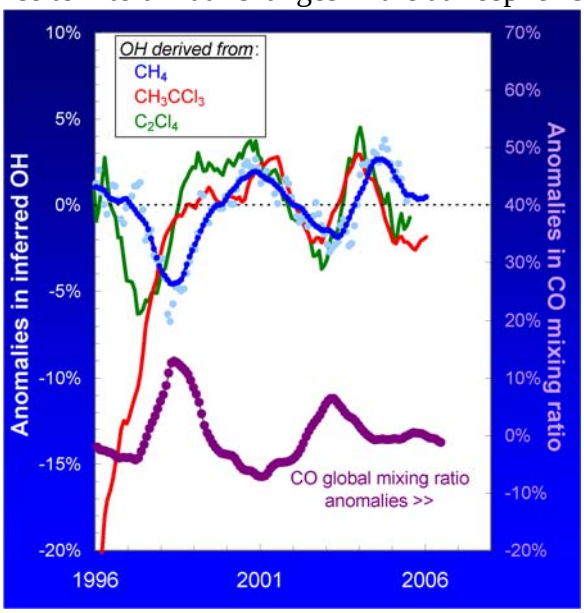

Figure 2: Anomalies in atmospheric OH inferred from measured atmospheric variations of three trace gases. The largest inferred changes for OH are anti-correlated with anomalies in global mixing ratios of CO, a strong global sink for OH

percent, suggesting that global OH abundances are fairly highly buffered against large, short-term changes. These improved estimates increase our ability to accurately gauge the environmental effects and longevity of certain ozone-depleting gases, some non-CO_2 gases that influence the climate (CH_4, and HFCs), and HAPs.

III. PAYOFFS INCLUDE:

- Understanding the levels of HAPs transported into North America helps US airshed managers to understand for which HAPs regional or local action could provide meaningful reductions of cancer risks, and for which compounds risk mitigation would require action on broader or international scales. Data from NOAA's remote and regional background monitoring stations demonstrate that average background concentrations of some HAPs reaching the US due to long-range transport from the west exceed 1-in-a-million cancer benchmark concentrations [*McCarthy et al.*, 2006].
- Improvement of climate and air quality models requires improved understanding of the distributions and trends in radiatively and chemically important trace species and aerosols and of the processes that shape those distributions and trends. The analyses of data sets collected in the intensive field campaigns and baseline monitoring conducted by NOAA/ESRL have led to significant advances in this understanding, and the data sets themselves provide invaluable benchmarks for further testing of the models [e.g., *Oltmans et al.*, 2004; *Li et al.*, 2005; *Gloor et al.*, 2007].

IV. FUTURE PLANS INCLUDE:

- Conduct the Aerosol, Radiation and Cloud Processes affecting Arctic Climate (ARCPAC) study, a NOAA Climate Forcing Program Project for the International Polar Year 2008. This study will characterize anthropogenic aerosols transported to the Arctic, their direct radiative effects, their impact on cloud radiative properties there, and their transformation and removal within the Arctic. This information is needed to understand the very rapid regional climate change in the Arctic, as evidenced by the Arctic ice melting more rapidly than expected.
- Increase our understanding of processes and transport influences on trace gases impacting the US west coast. This will include planning and executing the CalNex 2010 study in California, in collaboration with the California Air Resources Board and the California Energy Commission, and augmenting the ongoing regular profiling of the atmosphere above sites on the west coast. This work will address the impacts of trans-Pacific transport of aerosols, and the CalNex field study will particularly emphasize the interactions between air quality and climate change issues.
- Develop the best possible characterization of the decadal trends in marine tropospheric ozone over the eastern Pacific along the North American west coast. This is a region immediately downwind of the largest, nearly source-free region of the Northern Hemisphere, which is being impacted by rapidly increasing emissions of ozone precursors from Asia. Elucidating these trends is critical to understanding the impact of anthropogenic emissions on the tropospheric ozone budget.
- A high altitude mountain site will be added to the Trinidad Head Baseline Observatory to better characterize the distribution and trends in radiatively and chemically important trace species and aerosols reaching North America above the marine boundary layer. The resulting data sets will allow for better inputs to climate and air quality models that focus on regional North American impacts.

Selected Publication Highlights

Brock, C.A., P.K. Hudson, E.R. Lovejoy, A. Sullivan, J.B. Nowak, L.G. Huey, O.R. Cooper, D.J. Cziczo, J.A. de Gouw, F.C. Fehsenfeld, J.S. Holloway, G. Hübler, B.G. Lafleur, D.M. Murphy, J.A. Neuman, D.K. Nicks, Jr., D.A. Orsini, D.D. Parrish, T.B. Ryerson, D.J. Tanner, C. Warneke, R.J. Weber and J.C. Wilson (2004), Particle characteristics following cloud-modified transport from Asia to North America, Journal of Geophysical Research, 109, D23S26, doi:10.1029/2003JD004198.

de Gouw, J.A., C. Warneke, A. Stohl, A.G. Wollny, C.A. Brock, O.R. Cooper, J.S. Holloway, M. Trainer, F.C. Fehsenfeld, E.L. Atlas, S.G. Donnelly, V. Stroud and A. Lueb (2006), Volatile organic compounds composition of merged and aged forest fire plumes from Alaska and western Canada, Journal of Geophysical Research, 111, D10303, doi:10.1029/2005JD006175.

Fehsenfeld, F.C., G. Ancellet, T.S. Bates, A.H. Goldstein, R.M. Hardesty, R. Honrath, K.S. Law, A.C. Lewis, R. Leaitch, S. McKeen, J. Meagher, D.D. Parrish, A.A.P. Pszenny, P.B. Russell, H. Schlager, J. Seinfeld, R. Talbot and R. Zbinden (2006), International Consortium for Atmospheric Research on Transport and Transformation (ICARTT): North America to Europe–Overview of the 2004 summer field study, Journal of Geophysical Research, 111, D23S01, doi:10.1029/2006JD007829.

Gierczak, T., M. K. Gilles, S. Bauerle, and A. R. Ravishankara (2003), Reaction of hydroxyl radical with acetone. 1. Kinetics of the reactions of OH, OD, and ^{18}OH with acetone and acetone-d_6, *J. Phys. Chem. A, 107*, 5014-5020.

Gloor, M., E. Dlugokencky, C. Brenninkmeijer, L. Horowitz, D.F. Hurst, G. Dutton, C. Crevoisier, T. Machida, and P. Tans (2007), Three-dimensional SF6 data and tropospheric transport simulations: Signals, modeling accuracy, and implications for inverse modeling, *J. Geophys. Res., 112*, D15112, doi:10.1029/2006JD007973.

Kazil, J., and E. R. Lovejoy (2004), Tropospheric ionization and aerosol production: A model study, Journal of Geophysical Research, 109, doi:10.1029/2004JD004852.

Li, J., D. M. Cunnold, H.-J. Wang, R. F. Weiss, B. R. Miller, C. Harth, P. Salameh, and J. M. Harris (2005), Halocarbon emissions estimated from Advanced Global Atmospheric Gases Experiment measured pollution events at Trinidad Head, California, *J. Geophys. Res., 110*, D14308, doi:10.1029/2004JD005739.

Lovejoy, E.R., J. Curtius and K.D. Froyd (2004), Atmospheric ion-induced nucleation of sulphuric acid and water, Journal of Geophysical Research, 109, D08204, doi:10.1029/2003JD004460.

LRTAP, *Hemispheric Transport of Air Pollution 2007,* Air Pollution Studies No. 16, United Nations, New York and Geneva, 2007

McCarthy, M.C., H.R. Hafner, and S.A. Montzka, Background concentrations of 18 Air Toxics for North America (2006), *J. Air & Waste Manage. Assoc*., 56, 3-11,.

Oltmans, S. J., B. J. Johnson, J. M. Harris, A. M. Thompson, H. Y. Liu, C. Y. Chan, H. Vömel, T. Fujimoto, V. G. Brackett, W. L. Chang, J.-P. Chen, J. H. Kim,L. Y. Chan, and H.-W. Chang (2004), Tropospheric ozone over the North Pacific from ozonesonde observations, *J. Geophys. Res.*, *109*, D15S01, doi:10.1029/2003JD003466.

Rajakumar, B., J. E. Flad, T. Gierczak, A. R. Ravishankara, and J. B. Burkholder (2007), The visible absorption spectrum of the CH_3CO radical, *J. Phys. Chem. A*, *111*, 8950-8958.

Stohl, A., *Intercontinental Transport of Air Pollution, The Handbook of Environmental Chemistry*, O. Hutzinger, ed., Springer-Verlag, 2004.

Talukdar, R. K., T. Gierczak, D. C. McCabe, and A. R. Ravishankara (2003), Reaction of hydroxyl radical with acetone. 2. Products and reaction mechanism, *J. Phys. Chem. A*, *107*, 5021-5032.