TROPOSPHERIC CHEMISTRY STUDIES USING OBSERVATIONS FROM GOME AND TOMS

NASA Grant NAG1-2153

Final Report
For the period 1 January 1999 through 30 September 2002

Principal Investigator
Kelly Chance

January 2003

Prepared for
National Aeronautics and Space Administration
Washington, DC 20546

SMITHSONIAN INSTITUTION
ASTROPHYSICAL OBSERVATORY
CAMBRIDGE, MASSACHUSETTS 02138

Director: Irwin I. Shapiro

The Smithsonian Astrophysical Observatory is a member of the Harvard-Smithsonian Center for Astrophysics
Tropospheric Chemistry Studies Using Observations From GOME and TOMS: An ACMAP Proposal

Final Report NAG1-2153

Principal Investigator
Dr. Kelly Chance
Smithsonian Astrophysical Observatory
Atomic and Molecular Physics Division

Co-Investigators
Dr. Robert J.D. Spurr
Smithsonian Astrophysical Observatory
Atomic and Molecular Physics Division

Dr. Thomas P. Kurosu
Smithsonian Astrophysical Observatory
Atomic and Molecular Physics Division

Prof. Daniel J. Jacob
Department of Earth and Planetary Sciences and
Division of Engineering and Applied Science
Harvard University

Dr. James F. Gleason
Laboratory for Atmospheres
Atmospheric Chemistry and Dynamics Branch
NASA Goddard Space Flight Center
1 Research Objectives

To quantitatively determine trace gas and aerosol amounts from the Global Ozone Monitoring Experiment (GOME) and the Total Ozone Monitoring Experiment (TOMS) and perform chemical modeling studies which utilize these results. This includes:

1. Analysis of measurements from the GOME and TOMS instruments for tropospheric distributions of O₃ and HCHO; tropospheric enhancements of SO₂, NO₂, and aerosols associated with major sources; and springtime events of elevated BrO in the lower Arctic troposphere.

2. Application of a global 3-dimensional model of tropospheric chemistry to interpret the GOME observations in terms of the factors controlling the abundances of tropospheric ozone and OH.

The goals of the present research are:

1. To determine global climatologies of trace species associated with ozone chemistry in the stratosphere and troposphere.

2. To better understand the role of transport from the stratosphere, export from polluted continents, and large-scale photochemistry in determining the abundances of tropospheric ozone.

3. To analyze changes in tropospheric chemistry associated with perturbing events, including volcanic eruptions, large-scale fires, and polar springtime halogen enhancements.

4. To use HCHO as a photochemical tracer of OH chemistry and hydrocarbon reactivity in the troposphere.

2 Summary of Progress and Results

2.1 HCHO

We concentrated as a first priority on the capability to retrieve formaldehyde (HCHO) from GOME measurements in a stable fashion and with high precision. We have developed the ability to determine air mass factors (relating satellite-geometry slant column measurements to vertical column amounts) for arbitrary altitude distributions of HCHO. Our method combines
the use of the SAO multiple scattering model LIDORT [Spurr et al., 2001] with shape factors for the HCHO distribution calculated using the GEOS-CHEM 3-D model of tropospheric chemistry and transport, driven by assimilated meteorological data. We completed the initial study, to determine the HCHO over North America in July, 1996, including comparison of the measured HCHO with modeling results, and validation of the GEOS-CHEM shape factors against measurements from the Southern Oxidants Study and the North Atlantic Regional Experiment. Two publications resulted from this work [Chance et al., 2000; Palmer et al., 2001].

We then developed a methodology for deriving emissions of volatile organic compounds (VOC) using space-based column observations of HCHO, and applied it to data from the GOME satellite instrument over North America during July 1996. The HCHO column is related to local VOC emissions, with a spatial smearing that increases with the VOC lifetime. Isoprene is the dominant HCHO precursor over North America in summer, and its lifetime (~1 hour) is sufficiently short that the smearing can be neglected. We use GEOS-CHEM to derive the relationship between isoprene emissions and HCHO columns over North America, and use these relationships to convert the GOME HCHO columns to isoprene emissions. We also use the GEOS-CHEM model as an intermediary to validate the GOME HCHO column measurements by comparison with in situ observations. The GEOS-CHEM model including the GEIA emission inventory for isoprene provides a good simulation of both the GOME data ($r^2=0.69$, $n=756$, bias=+11%) and in situ summertime HCHO measurements over North America ($r^2=0.47$, $n=10$, bias=-3%). The GOME observations show high values over regions of known high isoprene emissions, and a day-to-day variability that is consistent with the temperature dependence of isoprene emission. Isoprene emissions inferred from the GOME data are 20% less than GEIA on average over North America and twice those from the US EPA BEIS2 inventory. The GOME isoprene inventory when implemented in the GEOS-CHEM model provides a better simulation of the HCHO in situ measurements than either GEIA or BEIS2 ($r^2=0.71$, $n=10$, bias=-10%). This work has produced one publication to date [Palmer et al., 2003].

A study of HCHO concentrations over North America for various seasons and years, over the lifetime of the GOME instrument, remains in progress. The study of the seasonal variation provides further testing and validation of the GEOS-CHEM model for predicting tropospheric chemistry and pollution. Detailed measurements, from individual orbits of GOME, indicate significant hot spots of production and possibly transport of HCHO and its progenitors. We will study the photochemistry and transport of individual episodes in order to understand the production and evolution of HCHO, and VOC emissions, in detail.
2.2 NO₂

We have developed a retrieval of tropospheric nitrogen dioxide columns from GOME that improves in several ways over previous retrievals, especially in the accounting of Rayleigh and cloud scattering [Martin et al., 2002b]. Slant columns, which are directly fitted without low-pass filtering or spectral smoothing, are corrected for an artificial offset likely induced by spectral structure on the diffuser plate of the GOME instrument. The stratospheric column is determined from NO₂ columns over the remote Pacific Ocean to minimize contamination from tropospheric NO₂. The air mass factor (AMF) used to convert slant columns to vertical columns is calculated from the integral of the relative vertical NO₂ distribution from GEOS-CHEM, weighted by altitude-dependent scattering weights computed with LIDORT, using local surface albedos determined from GOME observations at NO₂ wavelengths. The AMF calculation accounts for cloud scattering using cloud fraction, cloud top pressure, and cloud optical thickness from a cloud retrieval algorithm (GOMECAT). Over continental regions with high surface emissions, clouds decrease the AMF by 20-30% relative to clear-sky. GOME is almost twice as sensitive to tropospheric NO₂ columns over ocean than over land. Comparison of the retrieved tropospheric NO₂ columns for July 1996 with GEOS-CHEM values tests both the retrieval and the NOₓ emissions inventories used in GEOS-CHEM. Retrieved NO₂ columns over the United States, where NOₓ emissions are particularly well known, are within 18% of GEOS-CHEM columns and strongly spatially correlated ($r^2=0.78$, $n=288$, $p<0.005$). Retrieved columns show more NO₂ than GEOS-CHEM columns over the Transvaal region of South Africa, and industrial regions of the northeast United States and Europe. They are lower over Houston, India, eastern Asia, and the biomass burning region of central Africa, possibly because of biases from absorbing aerosols.

Inventory of Nitrogen Oxide Emissions Derived from Space-based Observations of NO₂ Columns.

We then constructed a global inventory of NOₓ emissions using top-down information from our retrieval of tropospheric NO₂ columns from GOME. We combine the top-down information with an a priori bottom-up inventory weighted by relative errors in the top-down and bottom-up sources. The a priori inventory is based on the Global Emission Inventory Activity (GEIA) and scaled to 1996-97. Our GOME NO₂ retrieval was further improved by accounting for scattering and absorption of radiation by aerosols. Absorbing aerosols can decrease the sensitivity of GOME to tropospheric NO₂ over biomass burning regions by 40%. The air mass factor calculation in the retrieval uses local relative vertical profiles (shape factors) of NO₂ from GEOS-CHEM using the a priori inventory; application of a globally uniform shape factor would introduce regional biases of up to 40% over industrial regions and a factor of 2 over remote regions. We use the GEOS-CHEM model to calculate the local relationship between NO₂ columns and NOₓ emissions. Monthly mean top-down errors in NOₓ emissions of 50% at $2° \times 2.5°$ resolution are
comparable to bottom-up errors over industrial regions and much better elsewhere. Global \( a \) posteriori errors are about half of \( a \) priori errors. Global annual land surface NO\(_x\) emissions for the \( a \) priori, a recent bottom-up inventory (EDGAR 3.0), and the \( a \) posteriori are 34.2, 36.2, and 35.1 Tg N yr\(^{-1}\) respectively. Local \( a \) posteriori NO\(_x\) emissions suggest underestimates of up to a factor of 2 near Johannesburg, Tehran, and Riyadh, up to 50% for Spain, Tokyo, and the Po Valley of Italy, and 25% for the eastern United States, as well as local overestimates of up to 50% for India and the biomass burning regions of central Africa and Brazil. The \( a \) posteriori inventory is more consistent with EDGAR than with the \( a \) priori. Anthropogenic \( a \) posteriori emissions are aseasonal despite seasonal variation in NO\(_2\) columns. A posteriori NO\(_x\) emissions provide evidence that soil NO\(_x\) emissions are underestimated for the western United States, Spain, the Sahel, and the Mediterranean coastal region.

2.3 BrO

Studies of tropospheric BrO, including background concentration and springtime events of elevated BrO in the lower Arctic troposphere are ongoing, in collaboration with the Georgia Institute of Technology.

3 Journal Publications


