Summary of Research
for NASA Grant NAG-1-1805

to

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1. **Introduction**

This grant supported a global atmospheric chemistry/transport modeling and data-analysis project devoted to: (a) development, testing, and refining of inverse methods for determining regional and global transient source and sink strengths for trace gases; (b) utilization of these inverse methods which use either the Model for Atmospheric Chemistry and Transport (MATCH) which is based on analyzed observed winds or back-trajectories calculated from these same winds for determining regional and global source and sink strengths for long-lived trace gases important in ozone depletion and the greenhouse effect; (c) determination of global (and perhaps regional) average hydroxyl radical concentrations using inverse methods with multiple "titrating" gases; and (d) computation of the lifetimes and spatially resolved destruction rates of trace gases using 3D models.

Important ultimate goals included determination of regional source strengths of important biogenic/anthropogenic trace gases and also of halocarbons restricted by the Montreal Protocol and its follow-on agreements, and hydrohalocarbons now used as alternatives to the above restricted halocarbons.

2. **Research Accomplishments**

We briefly summarize here research accomplishments over the period 1996 to the present supported in whole or in part by NASA Grants NAGW-474 (1996) and NAG-1-1805 (1997–1998). Most of the work has been published in seventeen papers in journals and three doctoral theses. The research accomplishments are divided conveniently into four sections devoted respectively to three-dimensional modeling; trace gas source and sink determinations; lifetime determinations; and parametric uncertainty analysis. A note on a relevant Workshop is also included here.

2.1 **Three-dimensional modeling**

For interpreting observational data and in particular for use in inverse methods, accurate and realistic chemical transport models are essential. Toward this end we have, in collaboration with NCAR scientists, successfully developed and tested a global three-dimensional Model for Atmospheric Transport and Chemistry (MATCH). This formed the doctoral thesis of MIT student Natalie Mahowald (Development of a three-dimensional chemical transport model based on observed winds and use in inverse modeling of the sources of CCl$_3$F, Ph.D. Thesis, MIT, 199 pages, 1996) and the work was published in three papers:


We also elucidated the effects of uncertainty of emissions estimates of CFCl₃ on 3D model predictions (specifically using the NCAR CCM2) concluding that transport errors are more significant than emission errors for this case. This was published in:


We examined the impact of the vertical profile of the horizontal wind in the troposphere and lower stratosphere on the vertical convective transport of chemical species. We used a dynamical cloud-ensemble model and found that the horizontal wind profile significantly affects the development of deep convection and thus the vertical flux of chemicals like (CH₃)₂S. The work is published in:


2.2 Time-variable regional source-sink determinations using inverse methods in 3D models

One of the major problems in atmospheric chemistry today involves the quantitative determination of trace gas emission and removal rates on regional as well as global scales. For example, the chemical and climatic importance of atmospheric CH₄ is readily recognized and ample evidence exists demonstrating an increase (albeit decelerating) in total global methane in recent years. However, estimates of the strengths of the individual regional surface sources of CH₄ which contribute to this global total are very uncertain.

In addition to the work on CCl₃F by Mahowald *et al.* (cited in Section 2.1), two new methods for estimating time varying fluxes of atmospheric trace gases using observations and 3D transport models have been investigated. One method used Kalman filtering to estimate inputs from a state-space model identified using unit-pulse response functions from the transport model. The method is new because no assumptions about initial conditions are required but deduced flux processes (e.g., chemical loss rates) must be linearly related to concentrations. Applied to AGAGE CCl₃F observations, the method is stable but estimated regional emissions were of poor accuracy due apparently to the inaccuracies in the ANU Lagrangian chemical transport model used in the analysis. This work by MIT postdoctoral scientist J. Mulquiney is published in:


In collaboration with researchers at Georgia Tech we also explored the use of the Kalman filter to deduce time-variable emissions. We conclude that an adaptive-iterative approach is the most accurate. This was published in:


2.3 Lifetimes and emissions of present and alternative halocarbons

Analysis of the extensive ALE/GAGE/AGAGE(AGA) observations (1978–present) of trace gases using our inverse methods with a 2D model was supported in part by this grant as well as by the separate AGA grant to MIT.

We have measured the atmospheric trend and deduced the lifetime of CHF$_2$Cl (HCFC-22) and thus obtained an independent estimate of OH concentrations $(11(5,-4) \times 10^5 \text{ cm}^{-3})$ in statistical agreement with that derived from CH$_3$CCl$_3$ (Prinn et al., 1995). This is published in:


We have also measured the trends and deduced the emissions of CF$_3$CHF$_2$ (HFC-134a), CCl$_2$FCH$_3$ (HCFC-141b) and CClF$_2$CH$_3$ (HCFC-142b). We estimate emissions in reasonable agreement with industry estimates for 134a and 141b but industry estimates are less than half those required to explain 142b observations. This is published in:


We also reported optimal estimates of lifetimes and/or emissions for the AGA-observed gases CFC$_1$ (CFC-11), CF$_2$Cl$_2$ (CFC-12), CCl$_2$FCCIF$_2$ (CFC-113), and CCl$_4$. These are published in:


2.4 Parametric uncertainty analysis

Uncertainty analysis for complex models has been hampered in the past by the computational demands of these models. This has prevented the large number of runs (e.g., $10^3$–$10^4$) required, for example, for the usual Monte Carlo approaches for models with many uncertain inputs or internal parameters. With support from this grant, we have developed at MIT a new powerful method for deducing the probability distribution functions (PDFs) of model outputs given the PDFs of uncertain inputs/parameters. The method uses expressions for model outputs which are polynomial chaos expansions of polynomials, whose weighting functions are the PDFs of the inputs, together with a formalism for identifying the specific input values (collocation points) for running the parent complex model to deduce the coefficients of the expansion. The new theory called the Probabilistic Collocation Method is published in:


This method has been applied to uncertainty analysis of the direct and indirect radiative forcing by anthropogenic sulfate aerosols. Parametric uncertainty dominates structural uncertainty and radiative forcing ranges from $-0.1$ to $-4.2$ and $-0.1$ to $-5.2$ Watt/m$^2$ for direct (13 uncertain inputs considered) and indirect (20 uncertain inputs considered) forcing respectively. This comprised the doctoral thesis of MIT student W. Pan (The role of aerosol effects in the troposphere: Radiative forcing, model response, and uncertainty analysis, Ph.D. Thesis, MIT, 259 pgs, 1996), and is published in two papers:


2.5 Workshop on inverse methods in global biogeochemical cycles

The growing realization of the power of inverse methods in studies of chemical fluxes led to the 1998 "Workshop on inverse methods in global biogeochemical cycles," organized by M. Heimann, D. Hartley, and P. Kasibhatla, and sponsored by IGAC (GIM), GAIM, the EU, and NASA. The PI was a member of the steering committee and gave the opening lecture entitled "The measurement equation for trace chemicals in fluids and solution of its inverse using optimal linear filtering." The lectures (including the PIs) from this 5 day Workshop in Heraklion, Crete, are now in press in *Geophysical Monographs*: