Summary of Research
for NASA Grant NAG-1-1805

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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_3F, Ph.D. Thesis, MIT, 199 pages, 1996) and the work was published in three papers:

(1) Deducing CCl_3F emissions using an inverse method and chemical transport models with assimilated winds, N.M. Mahowald, P.J. Rasch, and R.G. Prinn, *J. Geophys. Res*, **102**, 28153–28168, 1997.

(2) Transport of ^{222}radon to the remote troposphere using the Model of Atmospheric Transport and Chemistry and assimilated winds from ECMWF and the National Center for Environmental Prediction/NCAR, N.M. Mahowald, P.J. Rasch, B.E. Eaton, S. Whittlestone, and R.G. Prinn, *J. Geophys. Res.*, **102**, 28139–28151, 1997.

(3) Representations of transport, convection, and the hydrologic cycle in chemical transport models: Implications for the modeling of short-lived and soluble species, P.J. Rasch, N.M. Mahowald, and B.E. Eaton, *J. Geophys. Res.*, **102**, 28127–28138, 1997.

We also elucidated the effects of uncertainty of emissions estimates of $CFCl_3$ 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:

(4) Evaluating chemical transport models; Comparison of effects of different CFC-11 emission scenarios, D.E. Hartley, T. Kindler, D.M. Cunnold, and R.G. Prinn, *J. Geophys. Res.*, **101**, 14381–14385, 1996.

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 effects the development of deep convection and thus the vertical flux of chemicals like $(CH_3)_2S$. The work is published in:

(5) Impact of the horizontal wind profile on the convective transport of chemical species, C. Wang and R.G. Prinn, *J. Geophys. Res.*, **103**, 22063–22072, 1998.

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 CH_4 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 CH_4 which contribute to this global total are very uncertain.

In addition to the work on CCl_3F 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 CCl_3F 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:

(6) A new inverse method for trace gas flux estimation 1. State-space model identification and constraints, J.E. Mulquiney and J.P. Norton, *J. Geophys. Res.*, **103**, 1417–1427, 1998.

(7) A new inverse method for trace gas flux estimation 2. Application to tropospheric $CFCl_3$ fluxes, J.E. Mulquiney, J.A. Taylor, A.J. Jakeman, J.P. Norton, and R.G. Prinn, *J. Geophys. Res.*, **103**, 1429–1442, 1998.

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:

(8) Optimizing an inverse method to deduce time-varying emissions of trace gases, D.E. Haas-Laursen, D.E. Hartley, and R.G. Prinn, *J. Geophys. Res.*, **101**, 22,823–22,831, 1996.

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_2Cl (HCFC-22) and thus obtained an independent estimate of OH concentrations ($11(+5,-4) \times 10^5$ cm^{-3}) in statistical agreement with that derived from CH_3CCl_3 (Prinn *et al.*, 1995). This is published in:

(9) Atmospheric trend and lifetime of chlorodifluoromethane (HCFC-22) and the global tropospheric OH concentration, B. R. Miller, J. Huang, R. F. Weiss, R. G. Prinn and P. J. Fraser, *J. Geophys. Res.*, **103**, 12237–13248, 1998.

We have also measured the trends and deduced the emissions of CF_3CHF_2 (HFC-134a), CCl_2FCH_3 (HCFC-141b) and $CClF_2CH_3$ (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:

(10) Calculated trends and the atmospheric abundance of 1,1,1,2-tetrafluoroethane, 1,1-dichloro-1-fluoroethane, and 1-chloro-1,1-difluoroethane using automated *in-situ* gas chromatography-mass spectrometry measurements recorded at Mace Head, Ireland, from October 1994 to March 1997. P.G. Simmonds, S. O'Doherty, J. Huang, R. Prinn, R. G. Derwent, D. Ryall, G. Nickless, and D. Cunnold, *J. Geophys. Res.*, **103**, 16029–16037, 1998.

We also reported optimal estimates of lifetimes and/or emissions for the AGA-observed gases $CFCl_3$ (CFC-11), CF_2Cl_2 (CFC-12), CCl_2FCClF_2 (CFC-113), and CCl_4. These are published in:

(11) Lifetime and emission estimates of 1,1,2-trichlorotrifluorethane (CFC-113) from daily global background observations June 1982–June 1994, P. Fraser, D. Cunnold, F. Alyea, R. Weiss, R. Prinn, P. Simmonds, B. Miller, and R. Langenfelds, *J. Geophys. Res.*, **101**, 12585–12599, 1996.

(12) GAGE/AGAGE measurements indicating reductions in global emissions of CCl_3F and CCl_2F_2 in 1992–1994, D. M. Cunnold, R. F. Weiss, R. G. Prinn, D. Hartley, P. G. Simmonds, P. J. Fraser, B. Miller, F. N. Alyea, and L. Porter, *J. Geophys. Res.*, **102**, 1259–1269, 1997.

(13) Global trends and emission estimates of carbon tetrachloride (CCl_4) from *in-situ* background observations from July 1978 to June 1996, P. G. Simmonds, D. M. Cunnold, R. F. Weiss, R. G. Prinn, P. J. Fraser, A. McCulloch, F. N. Alyea, and S. O'Doherty, *J. Geophys. Res.*, **103**, 16017–16028, 1998.

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:

(14) An efficient method of parametric uncertainty analysis of numerical geophysical models, Menner A. Tatang, Wenwei Pan, Ronald G. Prinn, Gregory J. McRae, *J. Geophys. Res.*, **102**, 21925–21932, 1997.

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:

(15) Uncertainty analysis of direct radiative forcing by anthropogenic sulfate aerosols, Wenwei Pan, Menner A. Tatang, Gregory J. McRae, and Ronald G. Prinn, *J. Geophys. Res.*, **102**, 21915–21924, 1997.

(16) Uncertainty analysis of indirect radiative forcing by anthropogenic sulfate aerosols, Wenwei Pan, Menner A. Tatang, Gregory J. McRae, and Ronald G. Prinn, *J. Geophys. Res.*, **103**, 3815–3823, 1998.

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*:

(17) Measurement equation for trace chemicals in fluids and solution of its inverse, Ronald G. Prinn, Geophysical Monographs (American Geophysical Union, P. Kasibhatla *et al.*, eds.), in press, 1999.