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1. INTRODUCTION

Analysis of data collected from aircraft platforms in the troposphere represents a significant challenge for atmospheric chemistry modelers. Successful application of box photochemical models in analysis of data from the Airborne Antarctic Ozone Experiment and Airborne Arctic Stratospheric Expedition campaigns spurred considerable interest in application of these models with data collected from aircraft platforms in the lower stratosphere (Salawitch et al. 1994; Wennberg et al. 1994). Box models have also been used widely and with various degrees of success to analyze data collected in the troposphere by the DC-8 and other aircraft (Davis et al. 1996; Jacob et al. 1996).

The box models have traditionally been applied in the "equilibrium mode" and the "steady-state mode," each applicable for a set of species and/or meteorological conditions. Each of these approaches suffers from significant limitations. Box photochemical models applied in equilibrium mode are useful for calculating short-lived radicals, which themselves are often difficult to measure; thus, model verification is a difficult task. Steady-state calculations must be applied for carefully chosen locations and times to avoid processes that could affect the air parcel. Mixing times in the troposphere are often much shorter than the 10-30 days required to establish the steady state needed in the chemical model.

These limitations have led to the application of air parcel trajectory modeling in the troposphere. This type of modeling follows the chemical and dynamical history of an air parcel for 5-10 days, and the steady-state assumption is not required. The dynamical history of the air parcel is often described in terms of kinematic trajectory obtained from a mesoscale forecast model simulation, such as MM5 (Fuelberg et al. 1996). However, photochemical air parcel trajectory calculations are fraught with uncertainties, including problems in prescribing initial trace gas conditions for air parcels, uncertainties in the trajectories themselves, and uncertainties in trace gas data measured from the aircraft platform (Rodriguez et al. 1992).

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We are developing an enhanced version of the photochemical air parcel trajectory model that allows for improvement in the prescription of initial air parcel conditions and has superior predictive capabilities. This effort involves the development of a TLM (tangent linear model) and an adjoint for the TLM. Though adjoint methods for correcting initial conditions have become prevalent in the meteorological modeling community, their application in atmospheric chemistry modeling has not been explored (Errico 1997). We have formulated a TLM for our photochemical air parcel trajectory model and have tested the differences between the basic nonlinear version and linear versions of the model with a host of initial conditions to determine suitability for application to atmospheric chemistry problems (Kotamarthi et al. 1999).

As a result of our TLM/adjoint photochemical trajectory calculations, we can evaluate different scenarios of long-range transport of ozone and other key trace gases. Issues such as *in situ* production of ozone along the trajectory path, as opposed to local production in the source region and subsequent transport, can be addressed. By forcing agreement only with trace gases from key sources, the modeled radical mixing ratios of such gases as OH/HO_2 can be used to verify the chemistry in the model and identify possible missing reactions or sources.

2. TRAJECTORY PHOTOCHEMICAL MODEL

In the trajectory model, a zero-dimensional (0-D) photochemical model is moved along a trajectory described either by results from a forecast meteorology model for the region or from interpolated wind, temperature, and dew point fields from the 4-D data assimilation analysis provided by the National Center for Environmental Prediction. The trajectories derived from the latter data tend to be isentropic (Merrill 1996), while those from models can be kinematic (Fuelberg et al. 1996).

Time-dependent evolution of the chemical species in the box model is calculated from a starting point for the trajectory (usually 10 days before the sampling time and at the location of the aircraft platform) to the point were the measurements of trace gas concentrations were made. Trace gases from the ambient air surrounding the air parcel are either assumed to be at the same concentration or are prescribed, for instance from a global chemical-transport model. The former

case allows for no mixing of the trajectory air parcel with surrounding air, whereas in the latter case the air parcel is allowed to mix with a constant mixing coefficient. Additional constraints include column ozone from the Total Ozone Mapping Spectrometer along the trajectory path for radiative flux calculations and the presence of clouds above and below the trajectory from meteorological maps prepared for the mission. The cloud coverage data can probably be obtained more easily and accurately from satellite data products such as the International Satellite Cloud Climatology Project; we are exploring this option further.

The 0-D box photochemical model has options for using two different chemical schemes. The first version, based on the Lawrence Livermore National Laboratory-University of Illinois 2-D zonal average model (Kotamarthi et al. 1999), has 72 species, 132 thermal reactions and 52 photolysis rates. The model has full representation of CH_4, C_2H_6, and C_3H_8 chemistries, along with a condensed set of reactions for isoprene, C_2H_4, and C_3H_6. The model is capable of treating heterogeneous chemistry and includes N_2O_5, $BrNO_3$, and $ClNO_3$ reactions on sulfate aerosol. In addition, it has a full representation of ClO_x, BrO_x, HO_x, and NO_x chemistries of relevance to the stratosphere and troposphere. The second version uses the RACM (Regional Atmospheric Chemistry Mechanism) of Stockwell et al. (1997), but it has no halogen chemistry (Kotamarthi et al. 2001). The photolysis rates are calculated by using a 2-stream radiative transfer model with 128 bins for calculating absorption cross sections from 170 nm to 450 nm (Grant et al. 1987). The chemical integrator has the option of working with either the Gear method (Hindmarsh 1983) or the SMVGEAR II method (Jacobson and Turco 1994), suited for vector machine computing.

The major drawbacks of this method are the lack of knowledge of the initial conditions of the air parcel, the undefined nature of the box traveling along the trajectory, and the possible unreliability of trajectory paths in contact with convective mixing situations. We are working to develop a new version of the model, partially to overcome some of these difficulties and also to make the calculations more constrained and reliable by using tropospheric trace gas measurements from remote satellite platforms.

3. ANALYSIS USING THE TLM OF THE PHOTOCHEMICAL TRAJECTORY MODEL

We are developing an enhanced version of the trajectory photochemical model to account for some of its deficiencies and to automate the process of improving the initial model conditions. The objective of this approach is to minimize a cost function J,

$$J[x(t_0)] = \Sigma \, W[x(t_r)-x^m(t_r)]^2 , \qquad (1)$$

where $x(t_0)$ is a vector of dimension N representing the initial conditions of the model, $x(t_r)$ is the nonlinear model (NLM) solution at time t_r, $x^m(t_r)$ is the measurement of the model state at time t_r, and W is the $N \times N$ matrix of suitable weights for each of the n variables (Zou et al. 1993; Bischof 1994). In our example we choose 10 trace gases as key to our calculations; thus, the weighting matrix is of size 10×10, and $x^m(t_r)$ represents measured gas concentrations at the end of the trajectory. The set of initial conditions derived by this process will be the ones best able to describe the measured mixing ratios.

The steps for implementing this scheme involve the development of a TLM and its adjoint. The TLM of the basic model (the nonlinear 0-D photochemical model described above) is the first-order derivative of all the variables with respect to selected perturbations in initial conditions. This, for instance, can be considered the first-order term of a Taylor series expansion of the derivative of the prognostic/diagnostic/parameter variable in the model with respect to a small perturbation in the initial condition of, for example, ozone. The TLM runs forward along with the NLM. The adjoint of the TLM integrates the equations backward in time.

We have used ADIFOR, a software programming tool developed at Argonne National Laboratory (Bischof et al. 1996), to develop the TLM. This programming tool is a kind of compiler that operates on FORTRAN 77 codes to automatically generate code to obtain the partial derivative of the specified dependent variables with respect to a set of all specified independent variables or parameters. This tool eliminates the need for hand coding and modifying thousand of lines of code, common to a chemistry box model. Additions to the parameter list and hence additional code for calculating the derivatives can be generated with minimum effort. Scientists at Argonne have gained extensive knowledge on the use of this package for varied applications and have expressed willingness to collaborate with us to develop our application.

Version 3.0 of ADIFOR has the facility of reverse-mode differentiation, enabling calculation of the adjoint of the model. The backward operation mode is still under testing, and suitable optimization routines are being explored to find the minimum of equation (1). Figure 1 shows results generated with the TLM in a test for effects on ozone of a perturbation in the initial ozone conditions. The y-axis represents the difference between NLM and TLM as follows:

$$\frac{NLM \, (O_3) - TLM \, (O_3)}{NLM \, (O_3)} \qquad (2)$$

Here NLM stands for the original nonlinear model, and ozone mixing ratios are expressed in parts per billion.

Figure 1 (top) shows results for three different values for the perturbation of ozone, 1%, 0.5%, and 10%, for low-NO_x conditions. The figure indicates that the TLM produces results similar to the NLM for this particular set of initial conditions. Because the adjoint of the TLM is used for the backward-in-time integration, the TLM must reproduce the NLM results as closely as possible. For high-NO_x conditions (Figure 1, bottom), the NLM and TLM results deviate after about 40 hr. As the chemistry becomes progressively nonlinear, the differences between the TLM and NLM are likely to increase. Thus, in this example relevant chemical data would be required at about 40 hr for the reverse-mode calculations and hence the adjoint.

5. ACKNOWLEDGEMENT

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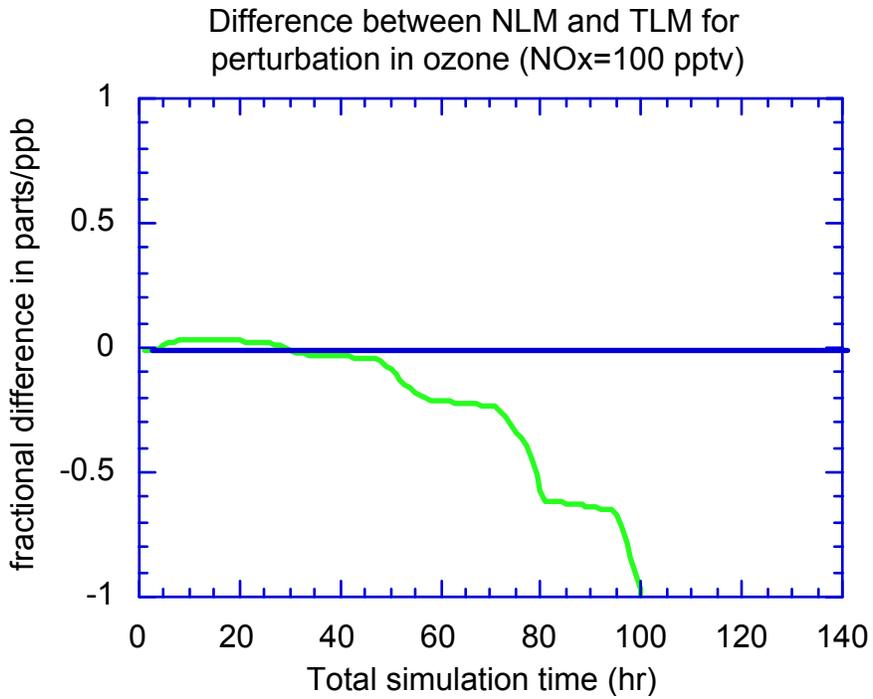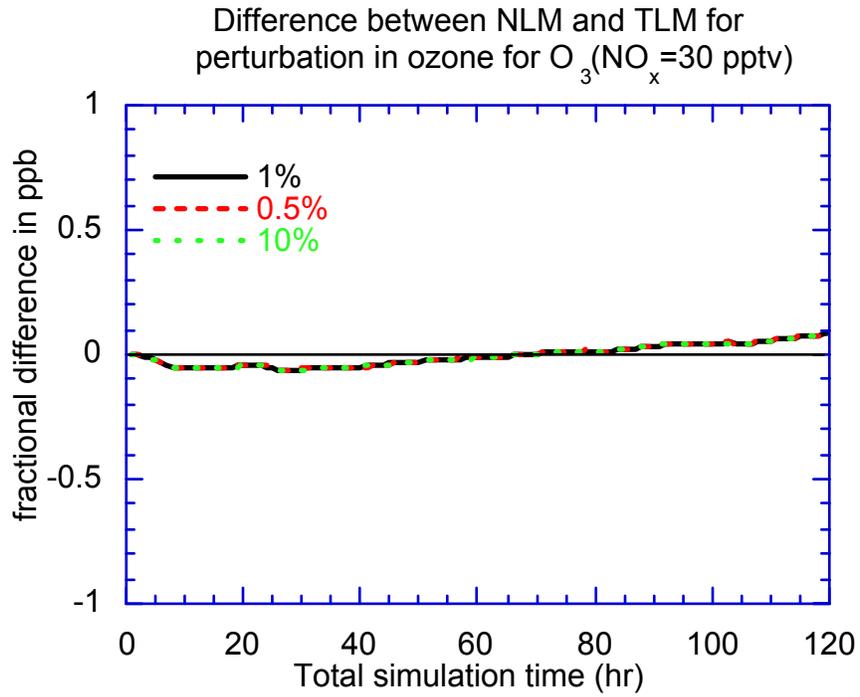
Figure 1. Top: The difference between the original nonlinear trajectory photochemical model (NLM) and the tangent linear model (TLM) of predicted ozone as a fraction of the ozone generated with the NLM model for low-NO_x conditions. Bottom: The same results for higher-NO_x conditions in the plume.