DEVELOPING THE ADJOINT OF ISORROPIA TO EQUIP CMAQ-ADJ

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1. INTRODUCTION

Atmospheric aerosols significantly influence quality of life today and shape the evolution of Earth's climate. These solid or liquid particles suspended in the air alter the radiative heat balance of Earth directly by absorbing and scattering solar radiation and indirectly by enhancing cloud formation and reflectivity (Trenberth, et al., 2009). Additionally, their interactions with light reduce visibility, a measure of air quality (Altshuller, et al., 1984). Furthermore, extensive epidemiological evidence suggests that particulate air pollution increases cardiovascular deaths as well as pulmonary problems (Dockery, 2001). In an effort to understand mechanisms of climate change and to optimize methods of improving air quality, atmospheric models have been developed to elucidate the effects of natural and anthropogenic emissions of chemicals and particles into the atmosphere.

Across this broad spectrum of climate and health effects, inquiries impossible to make via observation or experiment due to the relevant time scale or spatial range have become feasible with the application of chemical transport models (CTMs) as investigative tools. New policies intended to improve air quality and reduce climate change have been implemented in large part because of the results of atmospheric modeling (Craig, et al., 2008). Nevertheless, improvements are still needed in the applicability of regional air quality models and in the accuracy of global climate models, especially with regard to aerosols (Forster, et al., 2007).

A promising means of refining atmospheric modeling is using the increasingly large sets of observational data from satellites, monitoring sites, and field campaigns. Inverse modeling is one method of extracting meaningful and specific information out of vast and heterogeneous observational datasets. In the last thirty years, measurements of atmospheric composition including aerosol abundance and type have become much more robust and dense due to increasing satellite technology and coverage (e.g., CALIPSO, MODIS) (Remer, et al., 2005, Vaughan, et al., 2004). CTMs rely heavily upon input information such as initial or boundary conditions and emissions rates that are often uncertain and unreasonable to assess directly. Therefore, application of inverse modeling of aerosols to vast and heterogeneous data gathered by satellites as well as field missions would assist in refining CTMs and increasing their predictive accuracy (Hartley and Prinn, 1993, Kurokawa, et al., 2009, Muller and Stavrakou, 2005). An efficient method of inverse modeling with atmospheric aerosol observations is necessary for optimizing these parameters (Henze and Seinfeld, 2007). Such tools can also be employed to calculate efficiently the extent to which various sources contribute to a given location's atmospheric composition. This type of information provides a means of answering a long-standing inquiry that has developed into the field of source apportionment with the most quantitative, physically-based methods available.

2. METHODOLOGY

2.1 Background

CTMs solve the atmospheric diffusion equation (eq. 1) based on supplied boundary and initial conditions (Seinfeld and Pandis, 2006).

$$\frac{\partial C_i}{\partial t} = -\mathbf{u}\cdot\nabla C_i + \frac{1}{\rho}\nabla\cdot(\rho K\nabla C_i) + R_i + E_i \quad (1)$$

The concentration of species *i*, C_i, at a given time, *t*, and location is determined by the advection of the species due to wind with speeds,

u, from a meteorological model; the diffusion through air given its density, ρ, and the diffusivity, **K**, of each species *i*; the consumption and production of species *i* through reactions, R_i; and the emissions, E_i, respectively. Given this framework, a formulation appropriate for discussion of the inverse problem is $\mathbf{y} = \mathbf{F}(\mathbf{x}) + \varepsilon$, where observations of atmospheric concentrations, ***y***, equal the sum of the operation of the CTM, ***F***, on the vector, ***x***, of model parameters influencing predicted concentrations and the observation and model error, ε.

For developing an inverse model with atmospheric observations, considering a linearization of the model about a point $\mathbf{x_0}$ is convenient and satisfactory assuming that **F**(**x**) is linear within the bounds of the observation error, ε (eq. 2) (Rodgers, 2000)

$$\begin{aligned}\mathbf{y} - \mathbf{F}(\mathbf{x_0}) &= \frac{\partial \mathbf{F}(\mathbf{x})}{\partial \mathbf{x}}(\mathbf{x} - \mathbf{x_0}) + \varepsilon \\ &= \nabla_x \mathbf{F}(\mathbf{x})(\mathbf{x} - \mathbf{x_0}) + \varepsilon\end{aligned} \tag{2}$$

where $\nabla_{\mathbf{x}}\mathbf{F}(\mathbf{x})$ is the kernel or tangent linear model of the function. The aim, then, is to solve an inverse problem with noise, or error, associated with both the ambient observations and the model predictions. Prior knowledge about the state of the atmosphere, **x**, and the degree of error, ε, can be expressed quantitatively with more or less uncertainty. Given this noisy inverse problem, Bayes' theorem provides a formalism by which the model can be inverted to update the *a priori* state (i.e., estimated) of the atmosphere with information from the observation in order to establish the *a posteriori* estimate of the atmosphere if a probability distribution function is assumed for the model state vectors and the observation information. The Gaussian distribution is suitable for describing the error associated with many processes and is amenable to algebraic manipulation; additionally, it retains the minimum amount of information a distribution function can given only mean and variance information (Rodgers, 2000). Therefore, it is frequently applied in the inverse modeling of atmospheric chemistry (Hartley and Prinn, 1993, Kopacz, et al., 2009, Tarantola, 1987).

Reducing the error-weighted mismatch between the *a priori* estimate of the state vector to the true state as well as the error-weighted mismatch between the observation and the model predictions requires minimizing the scalar-valued cost function, *J*(**x**) (eq. 3) (Rodgers, 2000).

$$\begin{aligned}J(\mathbf{x}) = &(\mathbf{F}(\mathbf{x}) - \mathbf{y})^T \mathbf{S}_{\mathbf{\Sigma}}^{-1}(\mathbf{F}(\mathbf{x}) - \mathbf{y}) \\ &+ \gamma(\mathbf{x} - \mathbf{x_a})^T \mathbf{S}_{\mathbf{a}}^{-1}(\mathbf{x} - \mathbf{x_a})\end{aligned} \tag{3}$$

where $\mathbf{x}_a$ and $\mathbf{S_a}$ denote the *a priori* values of the state vector and the model covariance matrix, respectively; $\mathbf{S}_{\mathbf{\Sigma}}^{-1}$ denotes the observational error covariance matrix; and γ denotes the regularization parameter that controls the extent to which the observations or *a priori* estimate constrains the solution (Kopacz, et al., 2009). By minimizing the cost function with respect to the state vector (i.e., $\nabla_{\mathbf{x}} J(\mathbf{x}) = 0$), statistically optimal agreement between observations and predictions of the model as well as the revised *a priori* estimate of the state vector and the true state vector can be obtained (Kopacz, et al., 2009). Efficiently adjusting model parameters to achieve the minimization of the cost function (i.e., eq. 4) constitutes the solution of the inverse problem.

$$\begin{aligned}\nabla_{\mathbf{x}} J(\mathbf{x}) = &2(\nabla_{\mathbf{x}}\mathbf{F}(\mathbf{x}))^T \mathbf{S}_{\mathbf{\Sigma}}^{-1}(\mathbf{F}(\mathbf{x}) - \mathbf{y}) \\ &+ 2\gamma \mathbf{S}_{\mathbf{a}}^{-1}(\mathbf{x} - \mathbf{x_0}) = 0\end{aligned} \tag{4}$$

In the last two decades, minimization of the cost function to determine better estimates of atmospheric composition has been pursued in at least two manners. Analytical solutions to $\nabla_{\mathbf{x}} J(\mathbf{x}) = 0$ have been extensively applied to reconcile emissions of trace gases with observations (Kaminski, et al., 1999b, Levelt, et al., 1998, Mendoza-Dominguez and Russell, 2001, Patra, et al., 2003); however, computational limitations on the number of parameters that can be optimized have driven the field beyond this method in an effort to better understand emissions that vary on smaller spatial and temporal scales. Adjoint operators can be applied to minimize the cost function without computational constraints on the number of parameters to be optimized (Cacuci, 1981, Marchuk, 1977, Tarantola, 1987).

Variational data assimilation in the fields of meteorology and oceanography began employing adjoints two decades ago (Courtier and Talagrand, 1987, Navon, 1998, Talagrand and Courtier, 1987), and inverse modeling of atmospheric gases has since been accomplished through the application of adjoints (Elbern, et al., 2000, Hakami, et al., 2007, Hakami, et al., 2006, Kaminski, et al., 1999a, Kurokawa, et al., 2009, Martien and Harley, 2006, Muller and Stavrakou, 2005, Zhang, et al., 2009, Zhang, et al., 2008). Most recently, adjoints have been a focus of

developments in the atmospheric modeling field with regard to aerosol emissions which have high spatial and temporal variability (Dubovik, et al., 2008, Hakami, 2005, Henze, et al., 2007, Yumimoto, et al., 2008). The primary motivation for development of an aerosol adjoint is that it can overcome the limitations of other approaches to minimizing the cost function.

Recently, implementations of global adjoints of CTMs, including aerosol, have proved successful due to the capability of this method to optimize significantly more model parameters than the analytical method at computational times comparable to forward model executions (e.g., Dubovik, et al., 2008, Henze, et al., 2009). Optimization of the state vector occurs iteratively in a solution-seeking algorithm such as the steepest descent method wherein

$$\mathbf{x_{n+1}} = \mathbf{x_n} - \delta_n \nabla_{\mathbf{x_n}} J \qquad (5)$$

with a step size of δ_n is iterated until the change in the state vector is sufficiently small (Rodgers, 2000). To do so, the observations that have been translated into model observation space are fitted to the model prediction values in accordance with the cost function (eq. 3) in four dimensions across an interval of time, $t = 0 \ldots T$ (Rodgers, 2000). Practically, the steps involved are execution of the forward model (i.e., a typical model run) in which values are saved at particular time points and subsequent integration of the adjoint model backwards in time. The primary computational savings arise from the adjoint model operating on the forcing term (i.e., $(\mathbf{F}(\mathbf{x}) - \mathbf{y})$) directly rather than a relying on a recalculation of the Jacobian at each time step. Due to this operation, only matrix by vector multiplications are required rather than vector by matrix multiplications. These distinctions provide the necessary efficiency for optimizing such high-resolution model parameters as aerosol emissions and boundary conditions.

2.2 ISORROPIA Adjoint

Development of the adjoint of ISORROPIA (Nenes, et al., 1998, 1999) is carried out within the model framework of CMAQ-ADJ, the adjoint of the Community Multiscale Air Quality (CMAQ) model (Byun and Schere, 2006), an internationally employed regulatory model maintained by the EPA. Hakami et al. developed the adjoint of the gas phase processes captured by the CMAQ model (2007), providing a framework within which an adjoint of aerosol properties would be of profound relevance. The modular nature of the CMAQ forward model allows one to treat it as individual box models (Hakami, et al., 2007); in this sense, the box model for the thermodynamics, chemistry, and dynamics of aerosol species has not yet been treated in its adjoint.

The key components of atmospheric aerosol are water, inorganic salts, crustal minerals, organics, and trace metals (Seinfeld and Pandis, 2006). Inorganic species constitute about 25 to 50% of the dry mass of the particle depending on the air mass, wherein ammonium (NH_4^+), sodium (Na^+), sulfate (SO_4^{2-}), bisulfate (HSO_4^-), nitrate (NO_3^-), and chloride (Cl^-) are the most abundant species (Heitzenberg, 1989). In areas where dust contributes significantly to the aerosol loading, crustal species such as Ca^{2+}, K^+, and Mg^{2+} are also significant constituents, which can perturb equilibria of other species and are important for accurate modeling of aerosol composition and size distributions (Ansari and Pandis, 1999). In the atmosphere and for small aerosol sizes, thermodynamics govern the partitioning of these species which can exist as gases, as solutes in the aerosol water, or as precipitated salts. Modeling the complex phase diagram that describes this behavior requires optimization of nonlinear (local) convex problem (Fountoukis and Nenes, 2007). Of the models developed to describe these states of aerosol precursors and species, CMAQ primarily makes use of ISORROPIA's description of the behavior of deliquesced aerosol; therefore, the adjoint of ISORROPIA has been developed for these aspects of the inorganic thermodynamic equilibrium model.

3. PRELIMINARY RESULTS

The adjoint of ISORROPIA consists of the original code supplemented with additional calculations to produce sensitivity values as well as transformations to allow these sensitivities to be traced through the code in reverse order. Due to the complexity of such a task, the ISORROPIA code was manipulated for processing with the automatic differentiation tool TAPENADE (Hascoet and Pascual, 2004), which produced augmented code. In cases where the derivative was not traceable through the original mathematical solution, alternate solution algorithms have been developed and verified against the original solutions. Evaluation of the adjoint consists of comparing its sensitivities against finite difference

sensitivities for the range of atmospherically relevant concentrations and conditions. The preliminary results in Figure 1 demonstrate the capability of this approach to treat the complex solution algorithm of the ISORROPIA models.

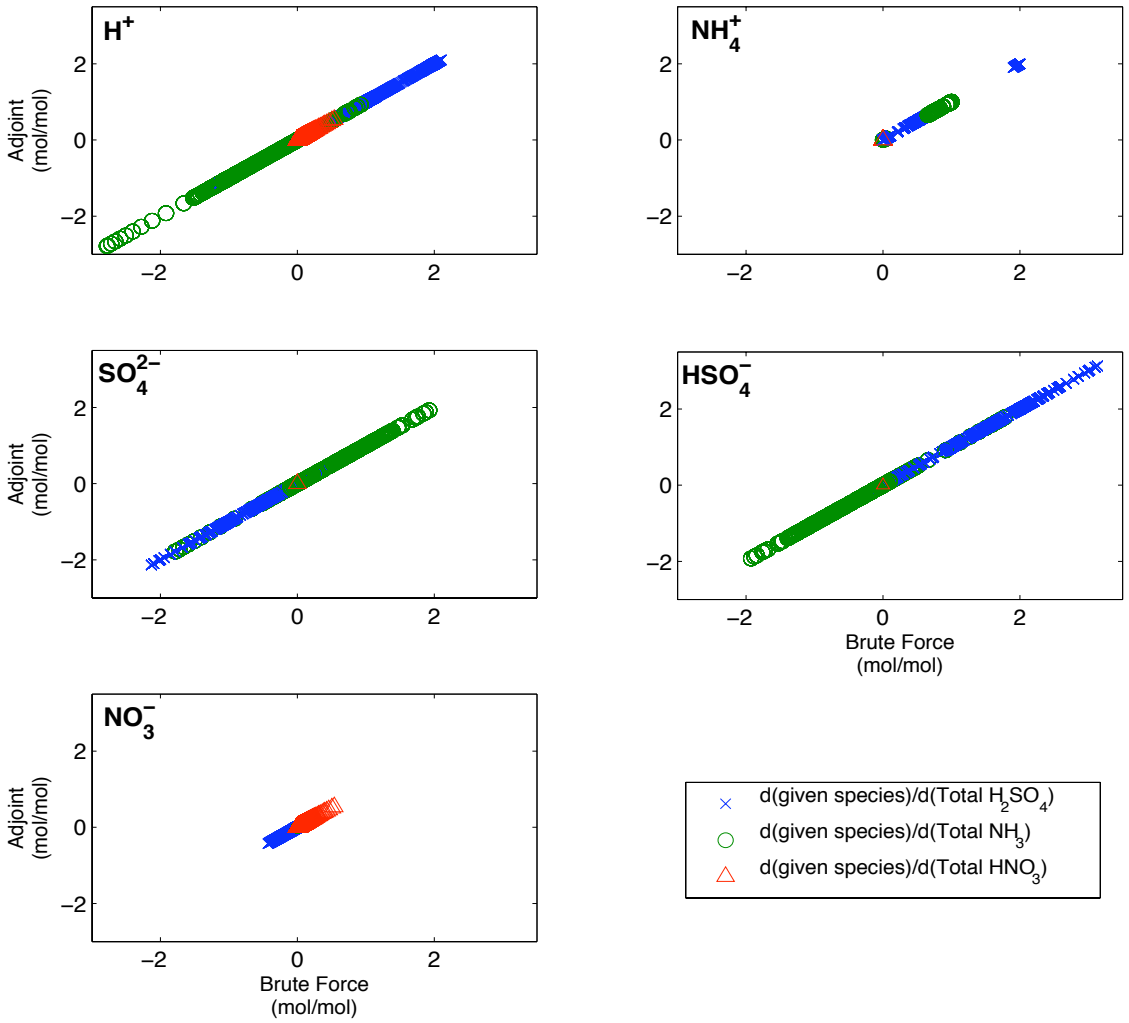

Figure 1. Comparison of the sensitivity results from the brute force method (i.e., central finite difference) and the adjoint method. The brute force results have been filtered to exclude non-physical sensitivities resulting from algorithmic shifts. The results span the range of atmospherically relevant concentrations of total sulfate, nitrate, and ammonia present in an air mass in ratios such that the aerosol phase is sulfate rich and the range of relative humidities that are treated properly by ISORROPIA (i.e., 5% to 95%).

4. CONCLUSIONS

Development of the adjoint of ISORROPIA (Nenes, et al., 1998, 1999) required the implementation of the automatic differentiation tool, TAPENADE (Hascoet and Pascual, 2004), and manual manipulation of the code to make it suitable for processing. The resulting adjoint code should be capable of producing sensitivities in agreement with central finite difference sensitivities for the range of concentrations except in cases in which the brute force method is incapable of capturing the physical behavior due to the structure of the algorithm. The sensitivities calculated by the adjoint are that of the deliquesced species (i.e., output of the forward model) to the total concentrations of species present (i.e., the input to the forward model).

Coupling the completed adjoint of ISORROPIA with CMAQ-ADJ will provide the adjoint of a regional chemical transport model including its treatment of inorganic aerosol species and their gaseous precursors. This tool should prove useful for source apportionment as well as reconciliation of emissions inventories with observations of aerosol from satellites and field campaigns.

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