# Application of the complex step method to chemistry-transport modeling
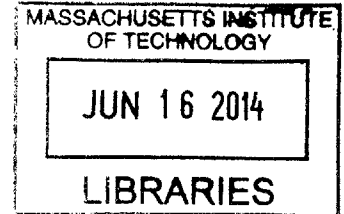
by

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B.S. Aerospace Engineering
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1

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## ABSTRACT

Sensitivity analysis in atmospheric chemistry-transport modeling is used to develop understanding of the mechanisms by which emissions affect atmospheric chemistry and composition, to quantify the marginal impact of emissions on air quality, and for other applications including improving estimates of emissions, developing fast first order air quality models, and validating adjoint models. In forward modeling sensitivities have predominantly been calculated using the finite difference approach, i.e. where the results of two separate simulations are subtracted. The finite difference approach incurs truncation and cancellation errors, which mean that exact sensitivities cannot be calculated and even approximate sensitivities cannot always be calculated for a sufficiently small perturbation (e.g. for emissions at a single location or time). Other sensitivity methods can provide exact sensitivities, but require the reformulation of non-linear steps (e.g. the decoupled direct method) or the adjointing of entire codes (partly automatically and partly manually). While the adjoint approach is widely applied and has significant utility in providing source-oriented information, in some applications the receptor-oriented information of forward approaches is needed. Here we apply an alternative method of calculating sensitivities that results in receptor-oriented information as with the finite difference approach, requires minimal reformulation of models, but enables near-exact computation of sensitivities. This approach – the complex step method – is applied for the first time to a complete atmospheric chemistry-transport model (GEOS-Chem). We also introduce the idea of combining complex-step and adjoint sensitivity analysis (for the first time in any context to our knowledge) to enable the direct calculation of near-exact second order sensitivities.

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# Table of Contents

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# List of Figures

# CHAPTER 1 – INTRODUCTION

Sensitivity analysis is the study of how the outputs of a model are affected by changes in the values of the inputs (Morgan and Henrion, 1990). In the context of atmospheric chemistry-transport models (CTMs), this typically entails computing the change in a species concentration with respect to a change in a species emission. The EPA recommends that sensitivity analysis be "used early and often" in the development and validation of computational models of the environment (EPA, 2009). Sensitivity analysis is also applied in the development of rapid surrogate models of more complex CTMs and in the analysis of potential air quality policies (e.g. Ashok et al., 2013). It is used both in determining which model parameters can be excluded from a particular class of problem (due to relatively low sensitivity), and for developing the parameters used by surrogate models. Sensitivity analysis is used in combination with uncertainty analysis to attribute uncertainty in outputs of models to uncertainty in their inputs (Beck et al., 1994). This informs users on the confidence that can be placed in models.

## 1.1. Sensitivity methods implemented in CTMs

The major classes of sensitivity methods implemented in CTMs are 1) the finite difference (FD) method, 2) the adjoint method, 3) the decoupled direct method (DDM), and 4) the Green's function method (GFM).

The FD is the most common sensitivity method used with CTMs because it is relatively straightforward to implement (van Keulen et al., 2005). The FD method in CTMs has been extensively used in climate and air quality sensitivity problems (Fry et al., 2012; Kohler et al., 2008; Naik et al., 2005; Stevenson et al., 2004) as well as in validating the implementation of the adjoints, e.g. GEOS-Chem (Henze et al., 2007).

The FD method is based on running a CTM twice: one simulation to obtain the reference results and another simulation with a perturbed input variable. The two results are then post processed to obtain sensitivities. The FD approximation is given by

$$f'(x_0) \cong \frac{f(x_0 + \Delta) - f(x_0)}{\Delta},$$ (1)

where $x_0$ is the reference value of the input variable and $\Delta$ is the perturbation. Relating to CTMs, $f$ is the result of the CTM (e.g. the concentration of a chemical species at a location), $x_0$ is an input to the CTM (e.g. an emission) and $f'(x_0)$ is the sensitivity of the result with respect to the input.

A drawback of the FD method is that there is a tradeoff between truncation and cancelation errors (Martins et al., 2003; Squire and Trapp, 1998; van Keulen et al., 2005). The truncation error is associated with non-linearity (i.e. ignoring the higher order terms) and is reduced by decreasing $\Delta$. However, at some decrease in $\Delta$ the cancelation error increases because, in finite precision, the reference and perturbed results become indistinguishable (resulting in "noisy" results). In practice this limits the calculation of sensitivities in CTMs to sufficiently large perturbations, which may be of a magnitude to incur truncation errors depending on the non-linearity of the specific problem. More on the FD method is presented in Appendix A

The DDM has been used in computing first order sensitivities in air quality models (Dunker et al., 2002) and higher order sensitivities (HDDM, Hakami et al., 2003; Hakami et al., 2004). The DDM method and the adjoint method are similar because they are both derived by differentiating the original code (i.e. algorithm differentiation) of the model and both produce near-exact sensitivities. The difference is that the DDM is a forward sensitivity method and the adjoint is an inverse method. The DDM method entails reformulating and recoding the extensive parts of the model in which non-linear responses can occur (e.g. chemistry and advection), because equations for sensitivities have different forms to those for concentrations in these cases.

The GFM has been used by Vuilleumier et al. (1997) to study "the temporal dependence of $O_3$ concentrations on the $NO_x$ concentrations". The GFM was designed to be a fast sensitivity analysis method (Rabitz et al., 1983), although it incurs numerical errors and errors that are introduced by the choice in step size (Vuilleumier et al., 1997), similar to the FD method. The GFM is not in widespread use.

The adjoint method is based on reverse differentiation of the forward code and then integrating the sensitivities backwards. This results in computing the sensitivity of one output of the CTM with respect to all the inputs by performing one run of the adjoint model. This has significant utility in applications where many inputs are assessed relative to their impact on one output, such as determining the spatiotemporal locations where emissions reductions result in the greatest total population exposure to a pollutant. Adjoint approaches are not useful where the distribution of impacts from an emissions change is required.

The adjoint method in GEOS-Chem has been implemented by Henze et al. (2007) and has been extensively used in air quality and climate studies (Henze et al., 2012; Bowman and Henze, 2012; Gilmore et al., 2013; Koo et al., 2013). As a particular example, Turner et al. (2012) used the adjoint sensitivity method in GEOS-Chem to estimate the impact on concentrations due to contributions of local versus distant emissions. The adjoint of GEOS-Chem is a combination of continuous and discrete adjoint code created by both manually implementing the code and by use of automatic adjoint generating tools such as Tangent and Adjoint Model Compiler (TAMC, Giering and Kaminski, 1998) the Kinetic PreProcessor (KPP, Sandu et. al. 2003; Damian et. al. 2002; Daescu et. al. 2003)

In theory, a main benefit of the adjoint is that the sensitivities are exact. As it is currently implemented, the adjoint of GEOS-Chem can compute sensitivities with respect to scaling factors of emissions, absolute values of emissions, initial concentrations and (more recently) reaction rate constants (GEOS-Chem Adjoint User's Guide (gcadj.v35)). The main drawback of the adjoint is that "the practical implementation of this approach can be challenging" (Giles et al., 2000). Also, because it is based on the forward code it means that for each update and further development of the forward model, the adjoint code must be updated accordingly to reflect the changes in the forward model. Both of these drawbacks are similar to the DDM approach. The adjoint approach also provides source-oriented information, which is advantageous in some applications while there are others where receptor-oriented information (as provided with the FD method) is needed. Further discussion on forward and inverse sensitivities is provided in Appendix B.

## 1.2. Motivation for the complex step method

As has been described forward methods retain information on the spatiotemporal distribution of the impact and lose information on the spatiotemporal distribution of the sources. In contrast, inverse methods retain information on the spatiotemporal distribution of the sources and lose information on the spatiotemporal distribution of the impact. Depending on whether the required result of the sensitivity analysis is a spatiotemporal distribution of impacts or a spatiotemporal distribution of sources, one may need to perform a forward sensitivity analysis, an inverse sensitivity analysis or both. Because of this, in CTMs such as GEOS-Chem, inverse sensitivity methods and forward sensitivity methods can be considered complements of each other and therefore there is need for both. However, while the adjoint method results in exact computation of source-oriented sensitivities, there is no accurate way of calculating receptor-oriented sensitivities in GEOS-Chem, and the exact DDM (applied to other models) incurs the drawbacks of reformulating and rewriting significant portions of the code.

There have also been studies that highlight the importance of computing second order sensitivities. Hakami et al. (2004) states that "addition of higher-order information to the analysis allows more reliable prediction of the response beyond its linear range, particularly when nonlinear behavior is expected". For example, Woody et al. (2011) and Koo et al. (2013) suggest that background emissions could change the air quality impacts attributable to aviation. Currently, the only method of computing second order sensitivities in GEOS-Chem is by performing FD sensitivities on the adjoint model which means that second order sensitivities are subject to the tradeoff between cancelation and truncation errors.

We propose application of the complex step (CS) sensitivity method to chemistry-transport modeling as an alternative forward sensitivity method that will mitigate the cancelation errors of the FD method, yielding near-exact first order sensitivities without the implementation drawbacks of the DDM or GFM. We also propose the idea of mixing CS and adjoint analysis to enable calculation of mixed source-receptor-oriented near-exact second order sensitivities. These can also answer applied questions such as "how will changes in ammonia emissions affect the

impact of aviation on air quality?" – which has utility in policy analysis contexts (Koo et al., 2013).

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# CHAPTER 2 – THE COMPLEX STEP METHOD

The CS sensitivity method is a numerical differentiation technique based on the properties of complex numbers. The idea of using complex numbers to compute derivatives was first introduced by Lyness and Moler (1967) and Lyness (1967). The initial description of how to use complex variables to obtain first and higher order derivatives was based on Cauchy's Theorem but the method was complicated and computationally intensive and was only put into practice after Squire and Trapp (1998) "developed an elegant, simple expression based on complex-step differentiation to compute first-order derivatives of an analytic function" (Lantoine et al., 2012).

Until now the CS method has been implemented in multidisciplinary sensitivity analysis (Newman et al., 1998) and for computational fluid dynamics problems (Anderson et al., 1999). It has also been used in validating the adjoint of the aerosol thermodynamic model ISSOROPIA (ANISORROPIA, Capps et al. 2012) and other adjoint implementations because of its accuracy in results (Martins et al., 2002; Giles et al., 2000).

This is to the best of our knowledge the first time the CS sensitivity method has been implemented in a chemistry-transport model such as GEOS-Chem and also the first time that second order sensitivities are computed by using the complex step method in combination with an adjoint model in any application.

## 2.1. Mathematical description

The CS method is explained by considering the Taylor series expansion of a real function $f$ around a reference point $x_0$,

$$f(x) = f(x_0) + f'(x_0)(x - x_0) + \frac{1}{2!}f''(x_0)(x - x_0)^2 + \frac{1}{3!}f^{(3)}(x_0)(x - x_0)^3 + \cdots, \qquad (2)$$

By substituting the real variable $x$ by a complex variable, $x = x_0 + ih$, where $x_0$ is a reference, $i = \sqrt{-1}$ and $h$ is an arbitrary real number we obtain

$$f(x_0 + ih) = f(x_0) + f'(x_0)(x_0 + ih - x_0) + \frac{1}{2!}f''(x_0)(x_0 + ih - x_0)^2 + \frac{1}{3!}f^{(3)}(x_0)(x_0 + ih - x_0)^3 + \cdots. \qquad (3)$$

This can be further simplified to

$$f(x_0 + ih) = f(x_0) + if'(x_0)h - \frac{1}{2!}f''(x_0)h^2 - \frac{1}{3!}if^{(3)}(x_0)h^3 + \cdots. \quad (4)$$

Taking the imaginary part of the left-hand side and right-hand side, rearranging and dividing through by $h$ we obtain

$$f'(x_0) = \frac{\text{Im}\{f(x_0+ih)\}}{h} + O(h^2), \quad (5)$$

where $O(h^2)$ terms of order $h^2$ or higher. This indicates that in the limit of $h \to 0$ the first derivative of the function is

$$f'(x_0) = \frac{\text{Im}\{f(x_0+ih)\}}{h}. \quad (6)$$

Equation (6) reveals the most important benefit of using the CS method. Although at relatively large complex steps, $h$, the derivative suffers from truncation error there is no subtraction as in the case of the finite difference method. This means that after decreasing the complex step size to a certain threshold, the sensitivities are computed within machine precision as there is no cancelation error. In theory the CS method can compute forward sensitivities as accurately as the adjoint method and the DDM. In practice some margin would be allowed for, so we term this a "near-exact" method as the step size (as will be shown) can be orders of magnitude smaller than is possible with the FD method.

## 2.2.   Implementation of the GEOS-Chem XPLEX

The CS method applied to GEOS-Chem, which we name GEOS-Chem XPLEX, is useful for computing: 1) sensitivities including validation of adjoints, 2) changes due to perturbations, and 3) second order sensitivities.

### 2.2.1.   CS sensitivities in GEOS-Chem XPLEX

Because it is not practical to compute all the sensitivities of the outputs with respect to all the inputs by applying an imaginary complex step to one variable at a time, we apply imaginary complex steps to multiple input variables simultaneously. To explain the meaning of doing this, we perform a Taylor series analysis on a function that depends on multiple variables. If we

substitute in Equation (2) the variable $x$ and $x_0$ by vectors $\mathbf{x} = [x_1, x_2, \ldots, x_n]$ and $\mathbf{x_0} =$ $[x_{0,1}, x_{0,2}, \ldots, x_{0,n}]$ respectively, the Taylor series expansion of a multiple variable function is

$$f(\mathbf{x}) = f(\mathbf{x_0}) + \frac{1}{1!}\sum_{j=1}^{n}\frac{\partial f(\mathbf{x})}{\partial x_j}(x_j - x_{0,j}) + \frac{1}{2!}\sum_{j=1}^{n}\sum_{k=1}^{n}\frac{\partial^2 f(\mathbf{x})}{\partial x_j \partial x_k}(x_j - x_{0,j})(x_k - x_{0,k}) + \frac{1}{3!}\sum_{j=1}^{n}\sum_{k=1}^{n}\sum_{l=1}^{n}\frac{\partial^3 f(\mathbf{x})}{\partial x_j \partial x_k \partial x_l}(x_j - x_{0,j})(x_k - x_{0,k})(x_l - x_{0,l}) + \cdots$$

(7)

By substituting in Equation (7) the variable $\mathbf{x}$ with the complex variable vector $\mathbf{x} = [x_{0,1} + ih, x_{0,2} + ih, \ldots, x_{0,n} + ih]$ we obtain

$$f(\mathbf{x}) = f(\mathbf{x_0}) + \frac{1}{1!}\sum_{j=1}^{n}\frac{\partial f(\mathbf{x})}{\partial x_{0,j}}ih - \frac{1}{2!}\sum_{j=1}^{n}\sum_{k=1}^{n}\frac{\partial^2 f(\mathbf{x})}{\partial x_{0,j}\partial x_{0,k}}(ih)^2 + \frac{1}{3!}\sum_{j=1}^{n}\sum_{k=1}^{n}\sum_{l=1}^{n}\frac{\partial^3 f(\mathbf{x})}{\partial x_{0,j}\partial x_{0,k}\partial x_{0,l}}(ih)^3 + \cdots$$

(8)

Dividing through by $h$, taking the imaginary part and rearranging Equation (8) we find that

$$\frac{\text{Im}\{f(\mathbf{x})\}}{h} = \sum_{j=1}^{n}\frac{\partial f(\mathbf{x})}{\partial x_{0,j}} + O(h^2).$$

(9)

As the complex-step size $h$ decreases, the imaginary part of the function divided by the complex step $h$ represents the summation of the partial derivatives of the function with respect to the inputs which were given a complex step. In other words, it is interpreted as the marginal cumulative impact of $\mathbf{x}$ on $f$. For example, let $\mathbf{x}$ be the emissions of $NO_x$ at all times $(t)$ and all grid locations $(s)$, $\mathbf{x} \equiv E_{NO_x}\big|_{s,t} + ih$, and $f$ the concentration of $PM_{2.5}$ at a particular grid point location. By using the CS method we compute the marginal impact of the global $NO_x$ emissions on the concentration of $PM_{2.5}$ at that particular grid cell. This is the interpretation of inputting a uniform complex step to a set of input variables. Note that, if $h$ is sufficiently small, the CS method does not affect the background since the information on sensitivity is kept in the imaginary part of the variables.

### 2.2.2. Change due to input perturbations

The CS method can also be used to compute the change of the output function due to a perturbation in a variable or a set of variables without altering the background reference case. The only modification that needs to be done is to multiply the imaginary complex step by the respective perturbation of the variables.

19

Multiplying the imaginary complex steps of $\mathbf{x}$ in Equation (9) by the respective real perturbations we obtain $\mathbf{x} = [x_{0,1} + i\,h\,\delta x_{0,1}, x_{0,2} + i\,h\,\delta x_{0,2}, \dots, x_{0,n} + i\,h\,\delta x_{0,n}]$ where $\delta x_{0,j}$ represents the perturbation in $x_{0,j}$. After manipulating the resulting equation, taking the imaginary part and dividing through by $h$ we obtain

$$\frac{\text{Im}\{f(\mathbf{x})\}}{h} = \sum_{j=1}^{n} \frac{\partial f(\mathbf{x})}{\partial x_{0,j}} \delta x_{0,j} + O(h^2) \approx \delta f(\mathbf{x}).$$

(10)

In Equation (10) each sensitivity, $\frac{\partial f(\mathbf{x})}{\partial x_{0,j}}$, is multiplied by each perturbation of the inputs, $\delta x_{0,j}$, which effectively results in computing a change in $f$ due to all perturbations (e.g. emissions at all locations), under the assumption that $\delta x_{0,j} \ll x_{0,j}$. Note that $\delta x_{0,j}$ may be different for each index, $j$. For example we can compute the change in the concentration of $PM_{2.5}$ due to global aviation $NO_x$ emissions under the assumption that aviation $NO_x$ emissions are a small perturbation to the background $NO_x$ (Barrett et al. 2010). This example is shown in more detail in section 3.3. of this paper. Another example is that temperature can be perturbed such that the impact of a marginal temperature change on atmospheric chemistry will be retained in the imaginary part of the complex concentrations, which is given Appendix G.

### 2.2.3. CS-Adjoint: Second order sensitivities

We propose a new numerical method of computing second order sensitivities in GEOS-Chem XPLEX by applying the complex step sensitivities in combination to the adjoint sensitivities. This is appealing because both the adjoint and the CS sensitivities can be computed within machine precision and the implementation on the CS sensitivity requires minimal changes to the original code.

The idea is that the CS method computes sensitivities of outputs with respect to an input or a set of inputs and the adjoint computes sensitivities of a cost function with respect to all the individual inputs. Therefore, the imaginary component of the CS-Adjoint result will be

$$\frac{\text{Im}\left\{\frac{\partial J}{\partial x_{0,k}}\right\}}{h} = \sum_{j=1}^{n} \frac{\partial}{\partial x_{0,j}} \left(\frac{\partial J}{\partial x_{0,k}}\right) + O(h^2) \overset{\lim_{h \to 0}}{=} \sum_{j=1}^{n} \frac{\partial^2 J}{\partial x_{0,j} \partial x_{0,k}} = \frac{\partial}{\partial x_{0,k}} \sum_{j=1}^{n} \frac{\partial J}{\partial x_{0,j}}.$$

20

where $J$ is the cost function of the adjoint, $\frac{\partial J}{\partial x_{0,k}}$ is the result of the adjoint, $x_{0,k}$ is an individual input, $x_{0,j}$ represent the inputs which had imaginary complex steps and $O(h^2)$ are the higher order terms. In the limit of $h$ going to zero, Equation (11) can be interpreted as how does $x_{0,k}$ impact the sensitivity of the cost function with respect to the vector $\mathbf{x} = [x_{0,1} + ih, x_{0,2} + ih, \ldots, x_{0,j} + ih, \ldots, x_{0,n} + ih]$. An example application of Equation (11) is given in section 3.2. of this paper.

### 2.2.4. Coding

We implemented the CS method in GEOS-Chem. In principle implementation of the CS method is as simple as converting all the real variables in the code to complex variables. In practice this necessitated our defining a new variable type "XPLEX" with the operator and function properties required for the CS method, as discussed further in Appendix C. Nonetheless the implementation of the CS method with the XPLEX variable type is significantly simpler than the development of an adjoint or a DDM implementation (Giles et al., 2000). We named our modified version of the code GEOS-Chem XPLEX. Implementation of the CS method in different programming languages is presented by Martins et al. (2003).

For for the proposed CS-Adjoint method, we replaced all real variables in the adjoint of GEOS-Chem with the XPLEX variable type.

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# CHAPTER 3 – RESULTS

In this section of the paper we show 1) comparisons between the CS, FD and adjoint sensitivities 2) application of the CS method in GEOS-Chem XPLEX and 3) our proposed CS-Adjoint approach to computing second order sensitivities.

## 3.1. First order sensitivities

We performed a comparison between the CS sensitivities and the FD and adjoint sensitivities. We computed the 24-hr average sensitivities of concentrations of nitrogen oxides ($NO_x$), ozone ($O_3$), fine particulate matter ($PM_{2.5}$) and three of the species of $PM_{2.5}$ [ammonium ($NH_4^+$), nitrates ($NO_3^-$) and sulfates ($SO_4^{2-}$)] with respect to $NO_x$ emissions at 11 grid locations in the global GEOS-Chem domain. The chosen points are dispersed in order to capture a variety of background conditions as well as a variety of meteorological conditions. We show more detail on the sensitivities computed at one of the 11 points. See Appendix D for the location of the points and comparison plots for the rest of the points.
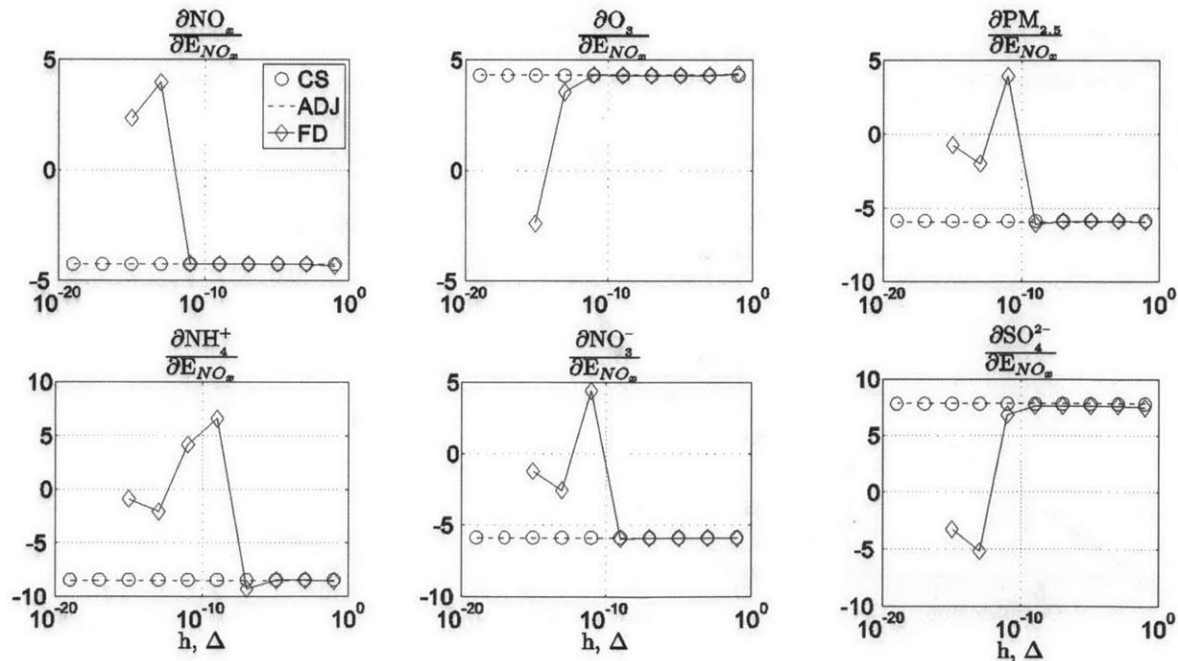


**Figure 1. Sensitivity comparisons of the CS (circles), FD (diamonds) and adjoint (ADJ, dashed line) method at a point. Units of sensitivities are ppb kg$^{-1}$ (including for PM per GEOS-Chem raw outputs without conversion to mass concentration); units of $h$ and $\Delta$ are kg s$^{-1}$.**

In Figure 1 the sensitivities are plotted on a logarithmic scale on both axes to show the behavior of the CS sensitivities and FD sensitivities over the ranges of step sizes and perturbations tested. The adjoint is plotted as a reference line as it is not dependent on any perturbation or complex-step size as the adjoint results in a single number. Figure 1 shows the CS sensitivities correspond to the adjoint sensitivities over the range of complex steps tested. The FD approach results in cancelation errors over a range where the CS method is near-exact. We note that this behavior occurs at larger perturbation in the case of $NH_4^+$ sensitivities than it does in the case of $NO_x$ sensitivities. This is because the optimal perturbation is not the same for all input-output pairs. See Appendix D for the comparison between the three sensitivity methods at the remaining ten locations.

We correlated the sensitivities obtained by the CS method and the adjoint as shown in Figure 2. It was found that the $R^2$ was in the range of 0.972 and 0.994 for all the sensitivities computed. Also, the gradients of the linear regression lines that were fitted to the data were in the range of 0.96 and 1.04.
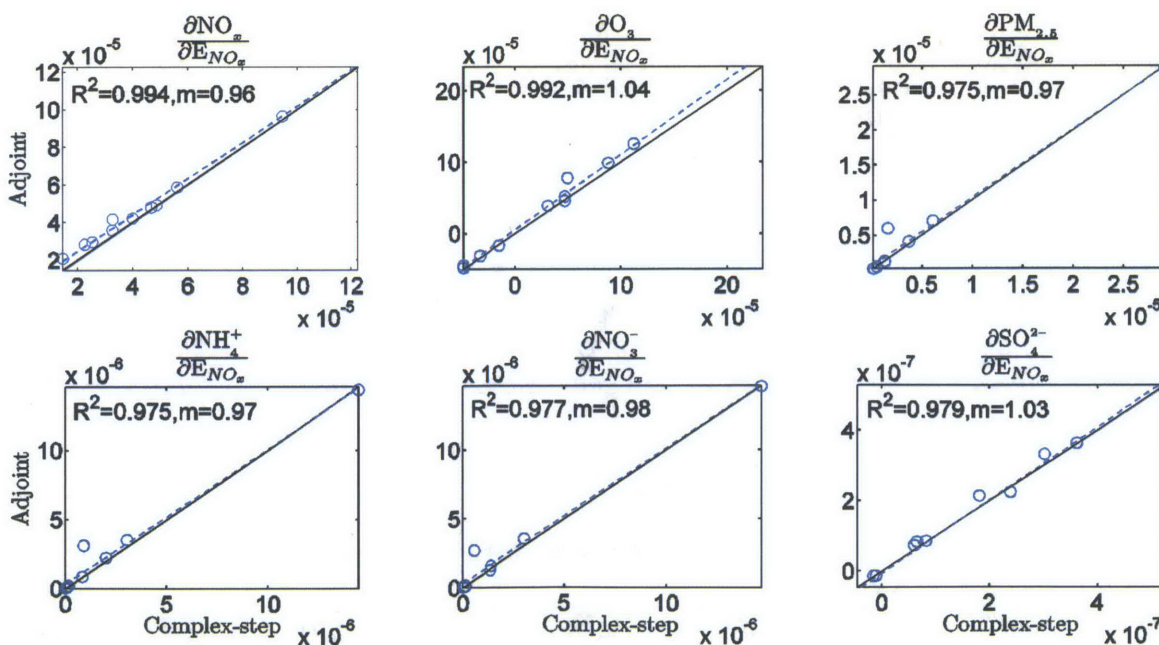


**Figure 2. Correlations of CS and adjoint sensitivity results. The solid black line represents the unity line and the dashed blue line represents the regression line fitted through the data. Units of ppb kg$^{-1}$.**

To demonstrate how the CS method overcomes cancelation errors in the FD approach for analyzing cases of small emissions perturbations, we computed the monthly average sensitivity of $O_3$ concentrations with respect to a single kilogram of surface $NO_x$ emitted at the beginning of the simulation with both the FD method and the CS method. The source of the $NO_x$ was at ground level on the East coast of the United States. The ground level sensitivities of $O_3$ are plotted in Figure 3. The FD sensitivities in Figure 3 (a) show a pattern of positive and negative sensitivities dispersed irregularly over the whole ground level domain, i.e. "noise". In contrast, the CS sensitivities show a consistent pattern of negative sensitivities with highest magnitudes in the region where the $NO_x$ was initially emitted and decreasing magnitudes over the Northern Atlantic Ocean.
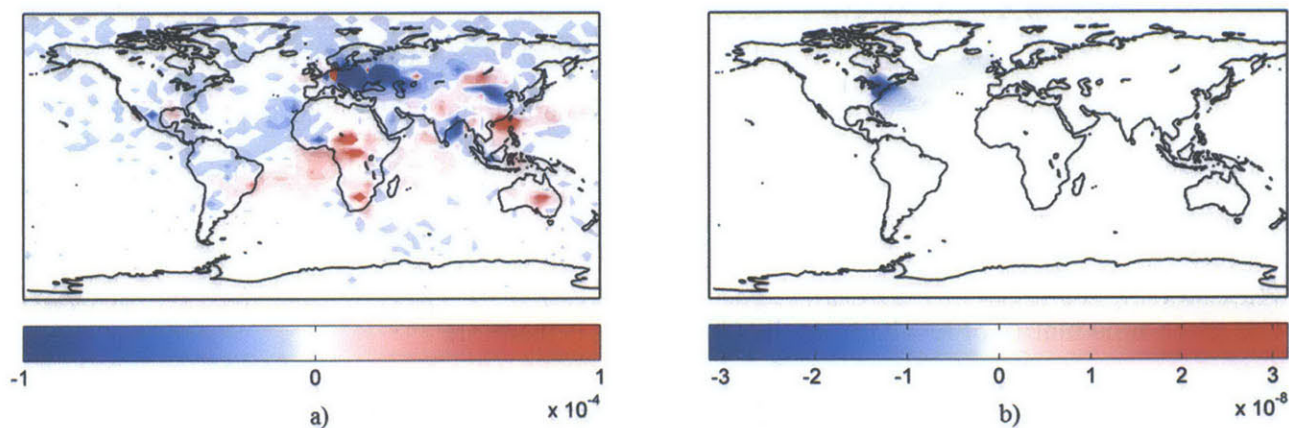


**Figure 3. Ground level average monthly sensitivities of $O_3$ to 1 kg of $NO_x$ computed by (a) the FD method and (b) the CS method. Units of ppb kg$^{-1}$.**

Also, we notice that the peak values of the CS sensitivities are roughly four orders of magnitude higher than the values of the FD sensitivities. We conclude that the irregular pattern and the higher magnitudes are a result of numerical noise and cancelation errors. This suggests that the CS method has improved the capability of the model to compute sensitivities with respect to small perturbations which was not possible before our implementation of GEOS-Chem XPLEX. Taking this together with Figure 2, we now have the complement of the adjoint – the ability to compute near-exact receptor-oriented sensitivities.

## 3.2. Second order sensitivities

We used the CS method in GEOS-Chem XPLEX in combination with the adjoint method in order to compute the annual average second order sensitivities of air quality. Specifically, we computed the average impact of ground level background emissions on the sensitivity of total $PM_{2.5}$ concentrations to the global aviation $NO_x$ emissions.

To compute these second order sensitivities with GEOS-Chem XPLEX we inputted a uniform imaginary complex step to all the aviation $NO_x$ emissions, $E_{NO_x}^{AV}\big|_{s,t} = E_{NO_x}^{AV}\big|_{s,t} + ih$. This is equivalent to saying that in all locations where aviation emits, all locations are perturbed by the same amount. (The next section provides an example of geospatially weighting the complex perturbations.) Then we defined the cost function of the adjoint as the total ground level $PM_{2.5}$ concentration over a region in North America (defined in Appendix E) and consider its sensitivity to $SO_2$ emissions (from any source).

The space-time matrix of results from the CS-Adjoint is therefore

$$\frac{\partial}{\partial(\text{aviation NO}_x \text{ emissions})}\left[\frac{\partial(\text{total ground level PM in NA})}{\partial(\text{SO}_2 \text{ emissions in any time or location})}\right].$$

The quantity in square brackets is the adjoint sensitivity, which is a four-dimensional (space and time) matrix. A particular location in this matrix quantifies the sensitivity of total ground level $PM_{2.5}$ in North America to $SO_2$ emissions at the particular location and time that the matrix location refers to. The CS-Adjoint method computes the sensitivity of the aforementioned sensitivity to, in this case, all aviation $NO_x$ emissions being perturbed by the same infinitesimal amount. This tells us how changes in aviation emissions will impact upon the effectiveness of other sector's $SO_2$ emissions at creating ground level PM. The mechanism for this in the case of aviation was described in Barrett et al. (2012) [and in other contexts by Leibensperger et al. (2011)], i.e. aviation $NO_x$ emissions increase the oxidative capacity of the atmosphere, thereby increasing the conversion of $SO_2$ emitted from other sectors to sulfate PM.

We also computed the second order sensitivities by performing the FD of two adjoint runs of the original GEOS-Chem model for comparison as in Koo et al. (2013). Computations were also

performed for the equivalent cases with ground $NH_3$ emissions instead of $SO_2$ (with results in Appendix F).

As presented in Figure 4 and Figure 5, the CS-Adjoint results are comparable in spatial distribution and order of magnitude to the FD-Adjoint results. The difference between the CS-Adjoint in GEOS-Chem XPLEX and the FD-Adjoint in the original GEOS-Chem adjoint is that the CS-Adjoint shows more pronounced features than the FD-Adjoint. The percent differences between the second order sensitivities computed by the CS-Adjoint and the FD-Adjoint ranged between 0% and 123% with an average difference of approximately 7%. This is consistent with the FD method in the adjoint introducing cancelation or truncation errors.
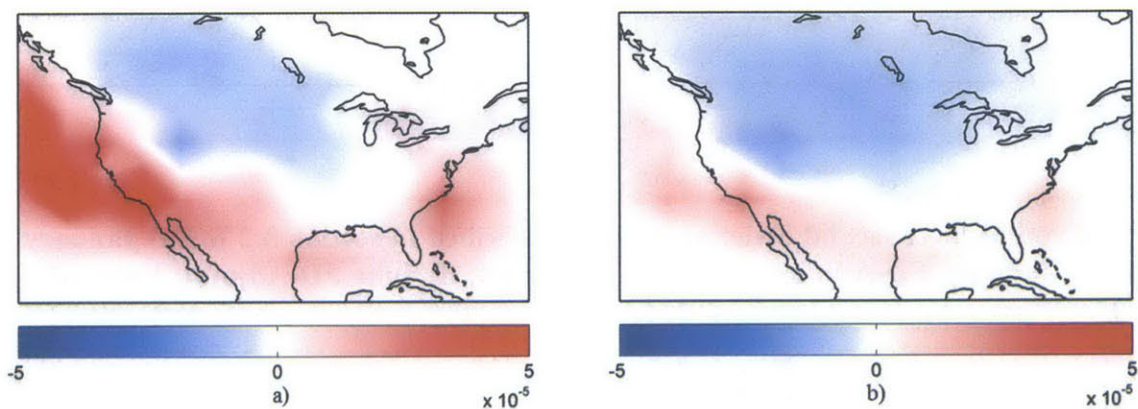


**Figure 4. Time-averaged ground-level second order sensitivity described in section 3.2 computed by a) CS-Adjoint; b) FD-Adjoint. Units of $\mu g\ m^{-3}(kg\ h^{-1})^{-2}$. A blue location means that a global increase in aviation $NO_x$ emissions will reduce the impact of $SO_2$ emissions in that location on total ground level $PM_{2.5}$ in the domain. Similarly, a red location means that the impact of $SO_2$ emissions in that location on total ground level $PM_{2.5}$ would be amplified by an increase in global aviation $NO_x$ emissions.**
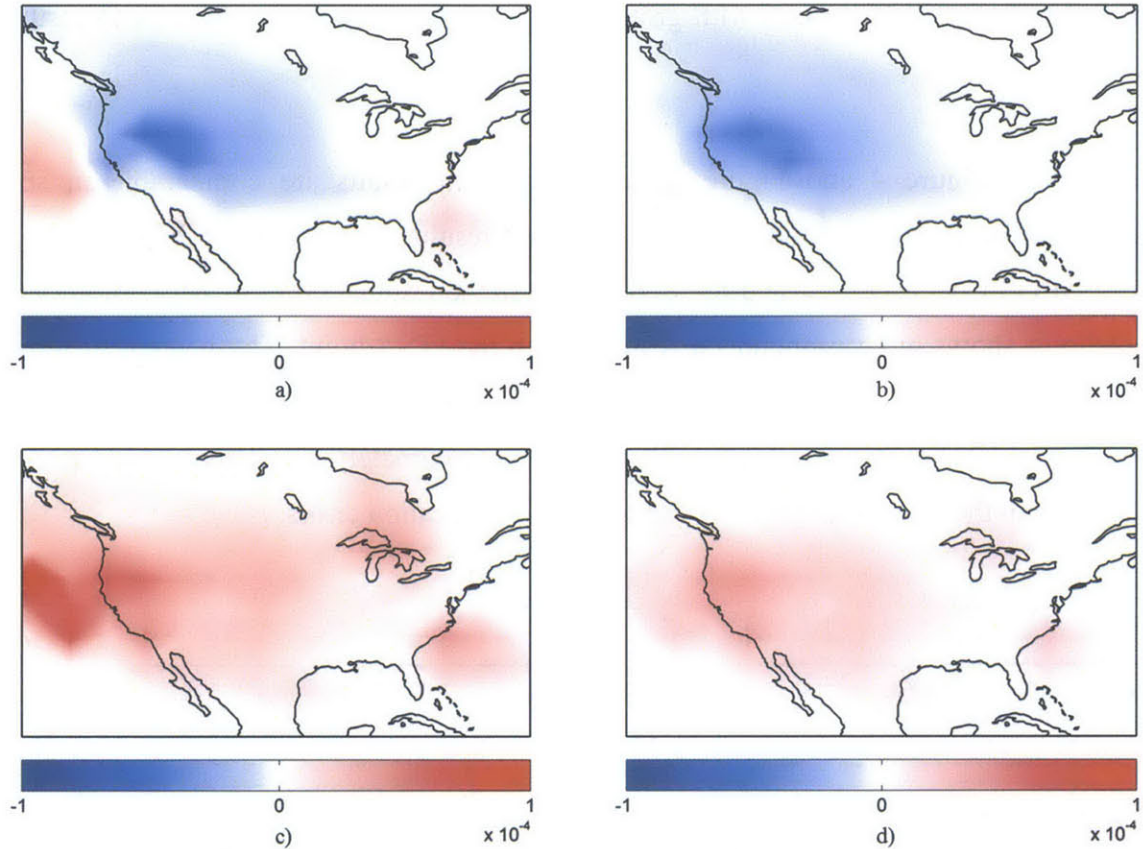
**Figure 5. Ground-level second order sensitivity described in section 3.2 for a) January CS-Adjoint; b) January FD-Adjoint; c) June CS-Adjoint; d) June FD-Adjoint. Units of μg m$^{-3}$(kg h$^{-1}$)$^{-2}$.**

We also note that, as implied by Equation (11), the following two interpretations of Figure 4 are equivalent:

1. A blue location means that a uniform increase in aviation $NO_x$ emissions will reduce the impact of $SO_2$ emissions in that location on total ground level $PM_{2.5}$ in the domain.

2. A blue location means that an increase in ground level $SO_2$ emissions at that location will reduce the impact of a uniform increase in aviation $NO_x$ emissions on aviation-attributable ground level $PM_{2.5}$ in the domain.

This is because the order of the partials in Equation (11) can be swapped.

In addition to a spatial variation of the second order sensitivities there is also a temporal variation. Figure 5 shows that in the winter aviation $NO_x$ emissions can either amplify or

suppress the sensitivity of ground level $PM_{2.5}$ to ground level $SO_2$ emissions depending on location (of the $SO_2$ emissions), while in the summer aviation $NO_x$ emissions only amplify the sensitivity. The results also show the loss of information in the FD approach.

It was found that the second order sensitivities of ammonia ($NH_3$) are mostly positive both spatially and temporally. This means that by increasing the emissions of $NH_3$ the $PM_{2.5}$ sensitivity to global aviation $NO_x$ would increase. Koo et al. (2013) performed differences of adjoint simulations with and without aviation emissions and also found that ammonia increases the PM sensitivity to aviation emissions. We found the percent difference between the second order sensitivities of $NH_3$ ground level emissions on the annual average sensitivity of total $PM_{2.5}$ with respect to global aviation $NO_x$ emissions over the NA region computed by the CS-Adjoint and the FD-Adjoint ranged between 0% and 94% with a mean percent difference of 8%. The annual second order sensitivities and monthly sensitivities are plotted in Appendix F.

## 3.3. $\Delta PM_{2.5}$ due to global aviation $NO_x$ emissions

As well as for computing sensitivities, the CS method can be used to calculate the impact of a specific emissions scenario on concentrations, and has utility where that the emissions are small relative to the background. Also the CS method (and CS-Adjoint) can be applied with weighted perturbations. In this application we give an example use of the CS sensitivity method to compute the change in total annual average $PM_{2.5}$ due to global aviation NOx emissions ($E_{NO_x}^{AV}$) over a domain in North America as defined in the SI.

We can use the sensitivities to compute concentrations in this example because we are making the assumption that the aviation $NO_x$ emissions are a slight perturbation to the overall $NO_x$ emissions and the response is in the linear regime (Barrett et al., 2010). The CS and the adjoint results are then compared to the result obtained by the difference between two simulation of the forward model with and without $E_{NO_x}^{AV}$. We ran one year simulation of the GEOS-Chem XPLEX by implementing a weighted imaginary complex step to all the aviation $NO_x$ emissions at all times ($t$) and all locations ($s$), $E_{NO_x}^{AV}\big|_{s,t} = E_{NO_x}^{AV}\big|_{s,t} + i\,h\,E_{NO_x}^{AV}\big|_{s,t}$.
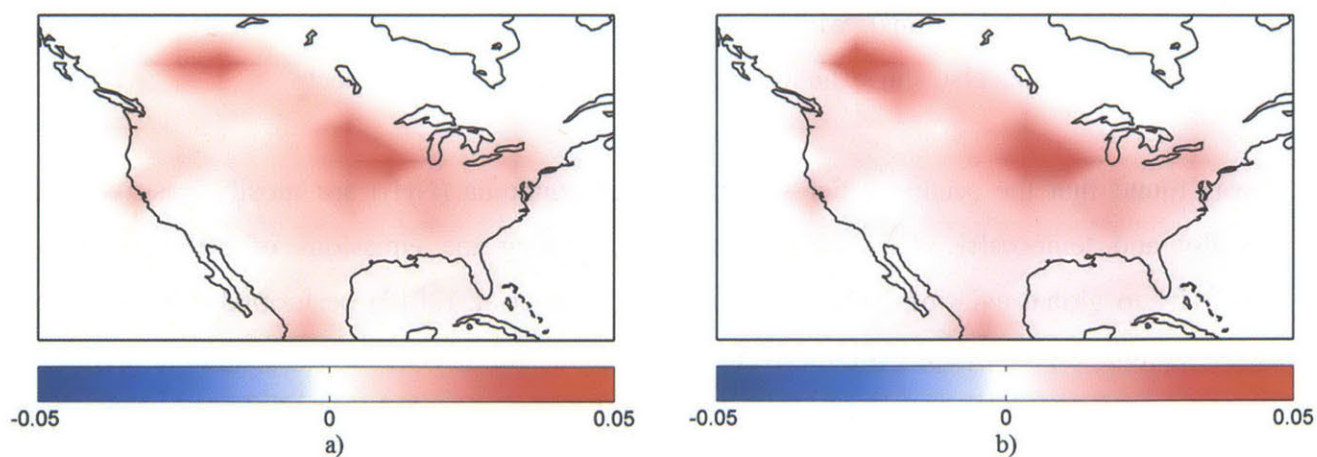
**Figure 6. Ground level annual average concentration distribution of $PM_{2.5}$ due to global aviation $NO_x$ emissions computed by a) the CS method in GEOS-Chem XPLEX and b) a difference method by subtracting two forward simulations. Units of $\mu g\ m^{-3}$.**

We found the CS method domain average perturbation was 0.0105 $\mu g\ m^{-3}$ by performing the difference between the forward simulations was 0.0111 $\mu g\ m^{-3}$. The values represent less than 0.5% of the total average $PM_{2.5}$ computed over the domain. The absolute percent difference between the CS method result and the difference result is approximately 5%. These results suggest that aviation's impacts on surface level $PM_{2.5}$ is approximately linear, but that the marginal impact of emissions beyond their current level is lower than the average impact.

# CHAPTER 4 – CONCLUSIONS

We introduce the complex step method to chemistry-transport modeling and implement it in GEOS-Chem as the GEOS-Chem XPLEX. This is the first application of the CS method to chemistry-transport modeling to our knowledge. We also introduce the idea of combining complex-step and adjoint sensitivity analysis (for the first time in any context to our knowledge) to enable the direct calculation of near-exact second order sensitivities.

We validate the complex step method against the (in principal) exact adjoint, demonstrating that the CS method yields near-exact sensitivities. The correlation coefficients between the CS and adjoint sensitivities were between 0.975 and 0.994. While GEOS-Chem previously had an exact inverse sensitivity method, the FD method incurs cancelation and truncation errors. The GEOS-Chem XPLEX can be considered the receptor-oriented complement of the source-oriented adjoint for near-exact sensitivity computation. The CS method is significantly more straightforward to implement and maintain than the DDM, which has been applied to other CTMs such as CAMx and CMAQ.

We also demonstrate that the CS method can be applied with weighted complex perturbations and can be used to compute the perturbation response of specific (relatively small) emissions for that would otherwise not be possible to compute due to cancellation errors.

Finally, we applied the CS-Adjoint method to compute second order sensitivities of global aircraft $NO_x$ emissions on ground level $PM_{2.5}$ in a region of North America to ground level emissions of $SO_2$ and $NH_3$. It was found that there is a spatial and temporal variation in the second order sensitivities in the case of $SO_2$ emissions. Increases in ground level $SO_2$ emissions at some locations in January reduce the impact of aviation $NO_x$ on ground level $PM_{2.5}$ in North America. The CS-Adjoint approach provides near-exact mixed source-receptor-oriented second order sensitivities.

The GEOS-Chem XPLEX source code is available at http://lae.mit.edu.

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# APPENDICES

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# APPENDIX A – FD Method

There are different formulations of the FD method. The two most commonly used are the forward difference (first order accurate sensitivities) and the central difference (second order accurate sensitivities). The forward difference approximation is

$$f'(x_0) \cong \frac{f(x_0+\Delta)-f(x_0)}{\Delta}, \tag{1}$$

where $x_0$ is the reference value of the input variable and $\Delta$ is the perturbation. The central difference is given by

$$f'(x_0) \cong \frac{f(x_0+\Delta)-f(x_0-\Delta)}{2\Delta}. \tag{2}$$

Relating to CTMs, $f$ is the result of the CTM (e.g. the concentration of a chemical species at a location), $x_0$ is an input to the CTM and $f'(x_0)$ is the sensitivity of the result with respect to the input.

The truncation error is associated with the non-linearity. We can show this by starting from the Taylor series expansion of a real function $f$ around a reference point $x_0$,

$$f(x) = f(x_0) + f'(x_0)(x-x_0) + \frac{1}{2!}f''(x_0)(x-x_0)^2 + \frac{1}{3!}f^{(3)}(x_0)(x-x_0)^3 + \cdots, \tag{3}$$

where $x \equiv x_0 + \Delta$. We solve for $f'(x_0)$ to obtain

$$f'(x_0) = \frac{f(x_0+\Delta)-f(x_0)}{\Delta} - \frac{1}{2!}f''(x_0)\Delta - \frac{1}{3!}f^{(3)}(x_0)\Delta^2 - \cdots = \frac{f(x_0+\Delta)-f(x_0)}{\Delta} + O(\Delta). \tag{4}$$

Notice that Equation (4) is the forward difference approximation plus the higher order terms, $O(\Delta)$, of which the largest is proportional to the perturbation, $\Delta$. The truncation error is associated to dropping these higher order terms and this is the reason why Equations (1) and (2) are only approximations of the derivatives. In order to reduce the truncation error, $\Delta$ has to be small compared to the reference variable, $x_0$. Theoretically, by reducing $\Delta$, the approximation in Equations (1) and (2) improves because the higher order terms become smaller. In practice, because of numerical noise and finite precision of the machine, reducing $\Delta$ too much causes the results of the reference and perturbed cases to become indistinguishable and introduces error. This error is also called cancelation (or subtraction) error. The tradeoff between cancelation and truncation errors means there is an optimal $\Delta$ for which the FD method yields the optimal result.

The issues are that the optimal $\Delta$ 1) is unknown (requires multiple evaluations of the CTM to find) and 2) may not be the same for every input-output pair of variables.

# APPENDIX B – Forward vs. Inverse Sensitivities

Forward (or receptor-oriented) sensitivity methods relate the inputs to the outputs. By aggregating multiple inputs (or sources) simultaneously, we obtain information on how much each output was affected by the cumulative set of inputs (i.e. retain spatial distribution of the outputs). The drawback is that we do not know how much each of the perturbed inputs affected the outputs (i.e. lose information on the spatial distribution of the inputs).

Inverse (or source-oriented) sensitivity methods relate the outputs to the inputs. Defining a cost function for the adjoint means that, rather than defining one output variables to compute the sensitivities with respect to, we combine more outputs. The cost function is usually a summation of a tracer concentration over a certain domain of interest (e.g. total ground level $PM_{2.5}$ in the United States). The benefit of doing this is that we know how much each input affects the cost function (i.e. retain spatial distribution of the inputs). The drawback is that we do not know how much each output was affected by the inputs (i.e. lose information on the spatial distribution of the output).

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# APPENDIX C – Implementation – GEOS-Chem XPLEX

In principle, the implementation of the CS method in FORTRAN is straightforward: 1) convert all the real variables to complex variables, 2) overload necessary functions and logical operators for complex variables, and 3) apply a small imaginary complex step to the desired input variable. However, due to numerical issues and the fact that it is not possible to overload intrinsic functions and logical operators that are already defined for intrinsic data types, we created a user-defined complex variable XPLEX which gives the name of the modified model – GEOS-Chem XPLEX.

The implementation of the CS method required all the variables to be changed from single to double precision in order to avoid the imaginary components becoming of the same order of magnitude as the real components and alter the underlying physics and chemistry of the original model. The original GEOS-Chem code has a mixture of floating point precision depending on the provenance of the component.

We created a module to overload all the functions and logical operators used in GEOS-Chem for the XPLEX variables. All the functions in this module were defined as for complex variables with the exception of the ABS, ATAN and ACOS functions which are based on the definitions found in the similar module, complexify.f90 (Martins et al., 2003). The logical operators are performed only on the real part of the complex variable XPLEX to keep consistency with the thread of the execution in the original code.

We created a Perl script to automatically modify the modules of GEOS-Chem to replace all the real variables definitions by XPLEX and include the necessary USE statements and IMPLICIT NONE statements where appropriate. Some manual changes had to be performed especially in the READ/WRITE statements to accommodate the XPLEX variable. This is further detailed in a technical note released with the code.

Although the implementation was not a trivial endeavor, the utilization of the code is very simple. One just needs to input a small imaginary part to the desired variables and run the code

only once to compute sensitivities. The imaginary parts of the results contain the information of the sensitivities. We also note that emissions are not the only variables that can be perturbed. Any (formerly real) variable can be perturbed, such as temperature, rate constants, humidity, etc. The result of the CS method is then the sensitivity to these changes. An example is given in Appendix F.

Also, once the code has been implemented it is easy to maintain. Any further development to the code only has to define the variables as XPLEX in order to preserve the capability of the code to compute sensitivities by the CS method, and is otherwise almost identical to conventional forward model development.

# APPENDIX D – First order sensitivity comparisons

In order to avoid potential differences in the sensitivities due to precision difference between GEOS-Chem XPLEX and the original GEOS-Chem, we converted all the variables of the original code from mixed (single and double) precision to double precision.

We implemented the CS method at each grid point location by inputting imaginary parts ranging from $10^{-1}$ to $10^{-19}$ kg s$^{-1}$ to the NO$_x$ emissions in order to observe the behavior of the results as the magnitude of the complex step changes. Because the CS sensitivities are second order accurate we implemented the central difference method in a similar fashion in the double precision version of the original code to have a second order FD approximation of the derivatives. We also computed the corresponding sensitivities with the adjoint method.
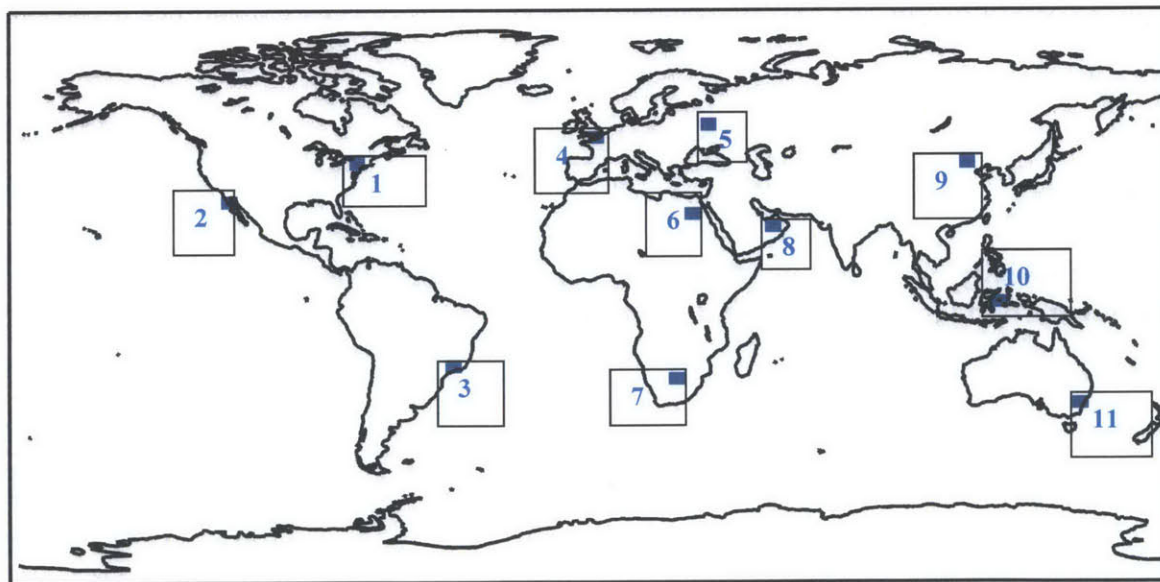


**Figure 7. Points for the sensitivity comparisons.**

In Figure 7 we show the points at which we compared the CS, FD and adjoint simulations. Sensitivity results at point labeled 1 are shown in the paper.

The greatest differences between the CS and the adjoint sensitivities were present at locations in the grid where the values of the sensitivities were relatively small or change sign. A similar behavior is noted and discussed by Henze et. al. (2007). However, at these locations we found

that the CS sensitivities and the FD sensitivities (within the range of perturbations for which the FD sensitivities were least affected by truncation or cancelation errors) were in agreement. This is shown below in Figures (8)-(17) which also present the comparisons at the remaining 10 points.
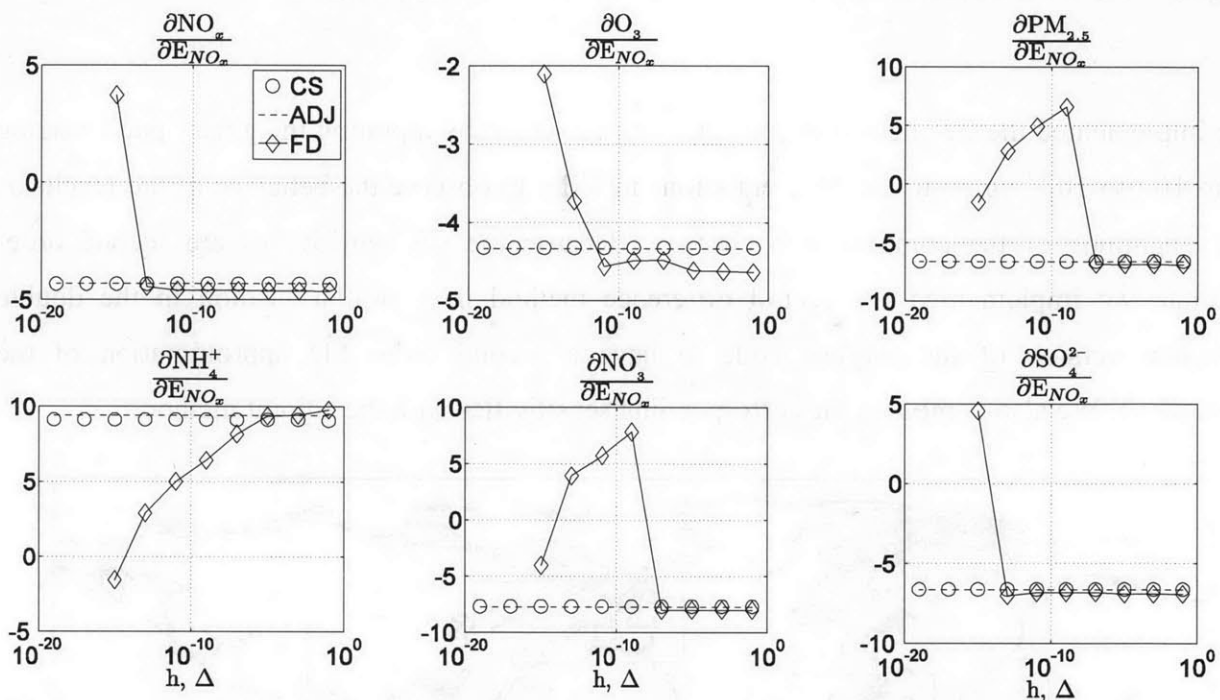


**Figure 8. Sensitivity comparisons of the CS, FD and adjoint method at point 2. Units of sensitivities are ppb kg$^{-1}$; units of $h$ and $\Delta$ are kg s$^{-1}$.**
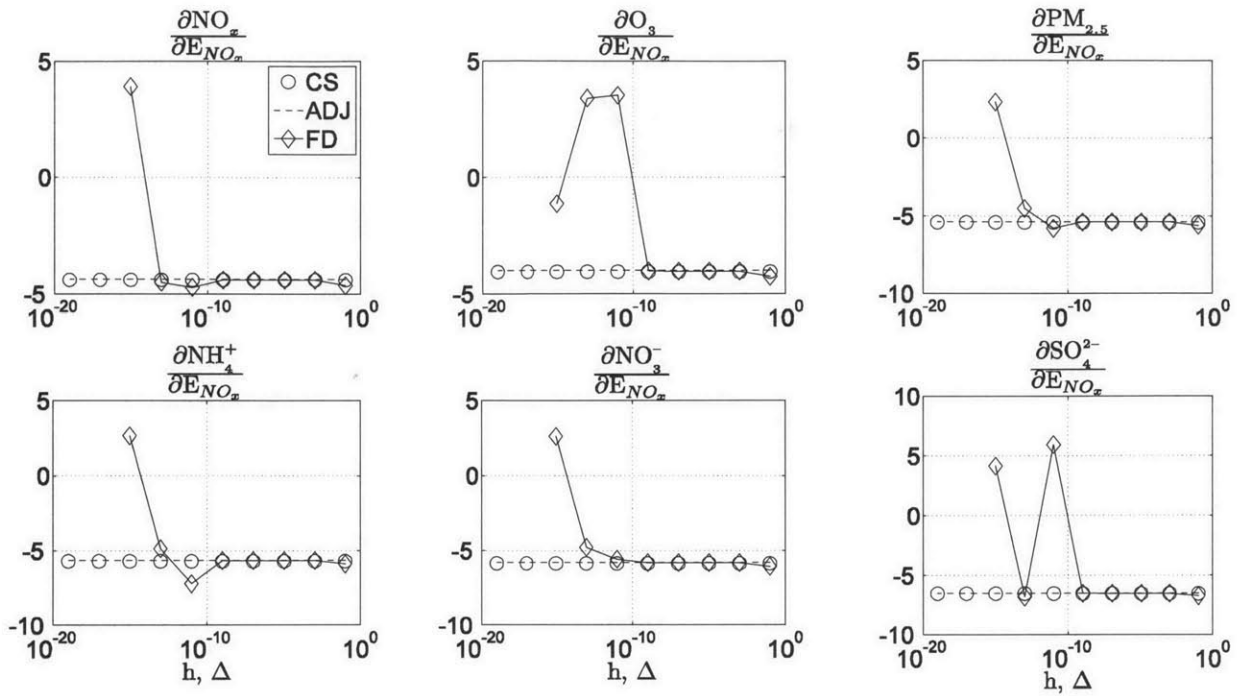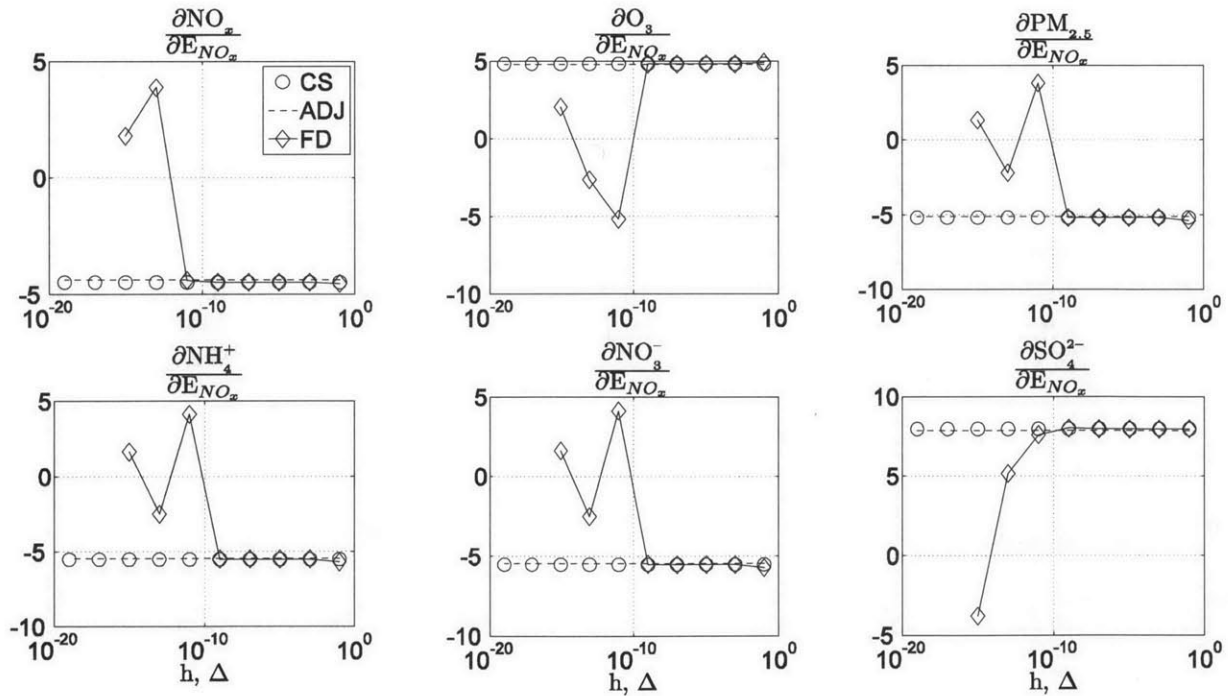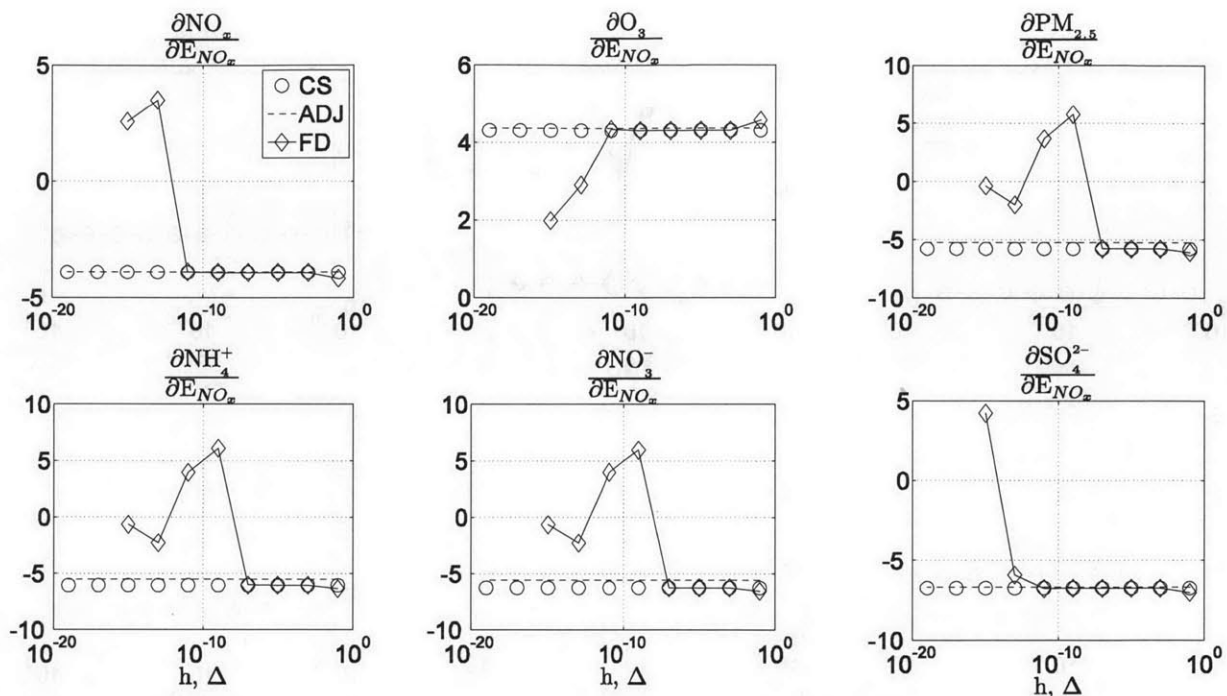
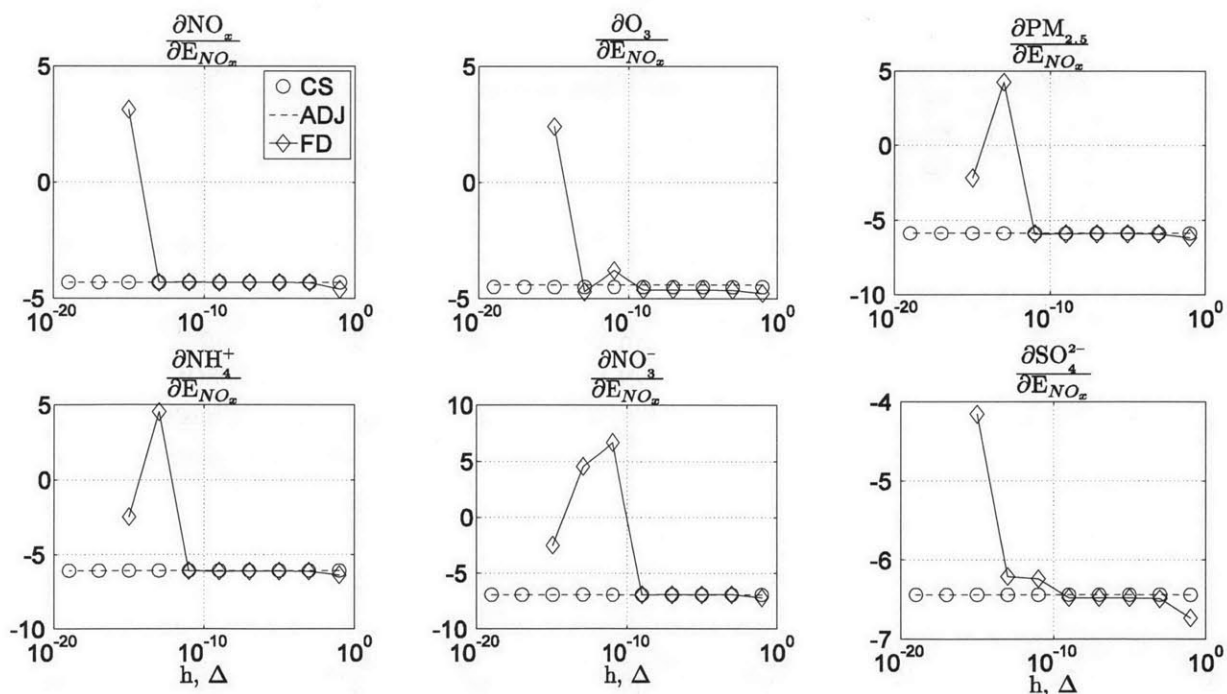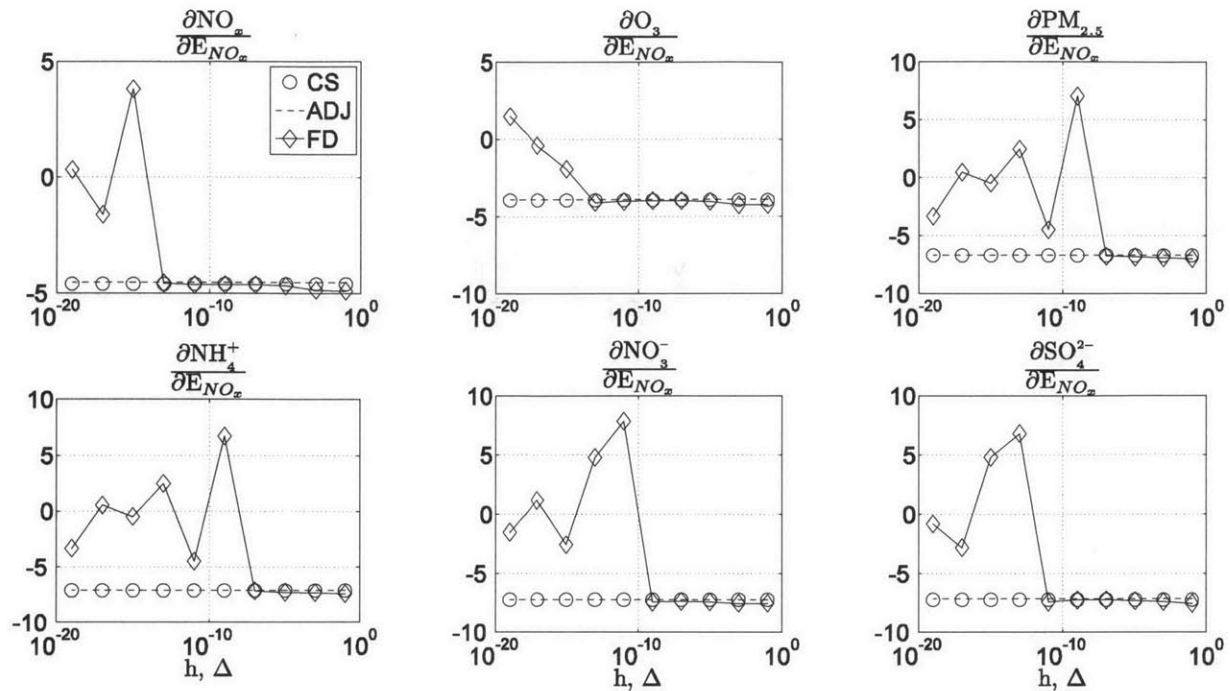**Figure 9. Sensitivity comparisons of the CS, FD and adjoint method at point 3. Units of sensitivities are ppb kg⁻¹; units of *h* and Δ are kg s⁻¹.**
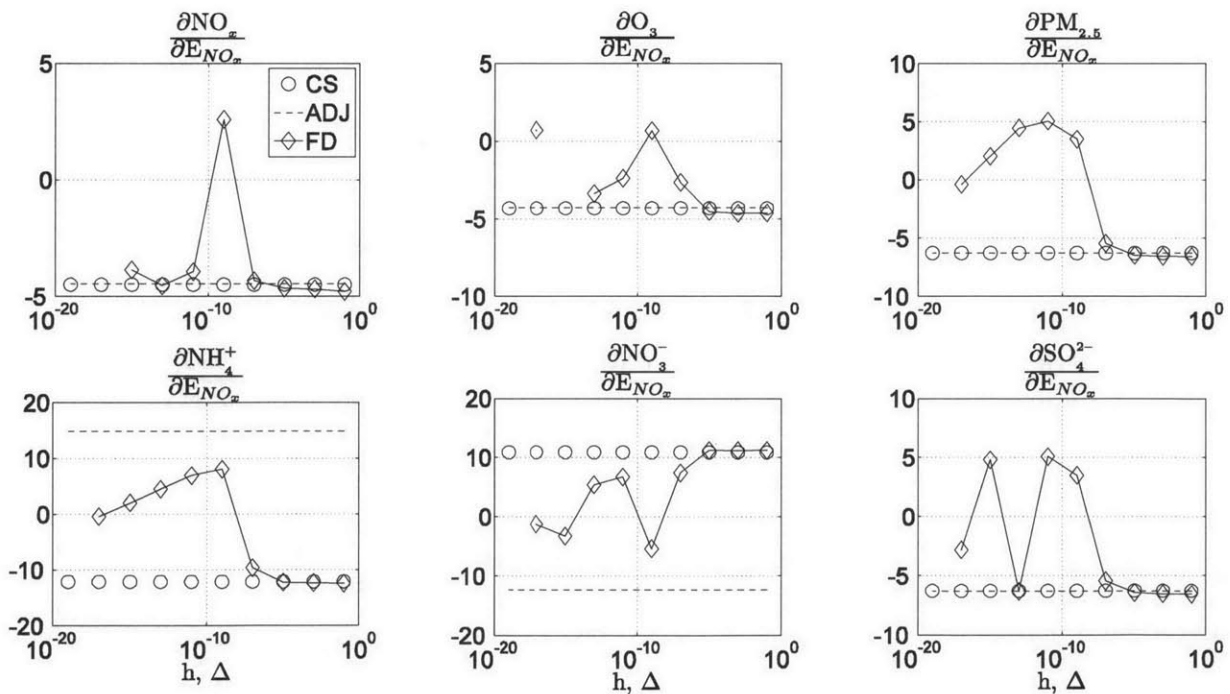


**Figure 10. Sensitivity comparisons of the CS, FD and adjoint method at point 4. Units of sensitivities are ppb kg⁻¹; units of *h* and Δ are kg s⁻¹.**

**Figure 11. Sensitivity comparisons of the CS, FD and adjoint method at point 5. Units of sensitivities are ppb kg$^{-1}$; units of $h$ and $\Delta$ are kg s$^{-1}$.**



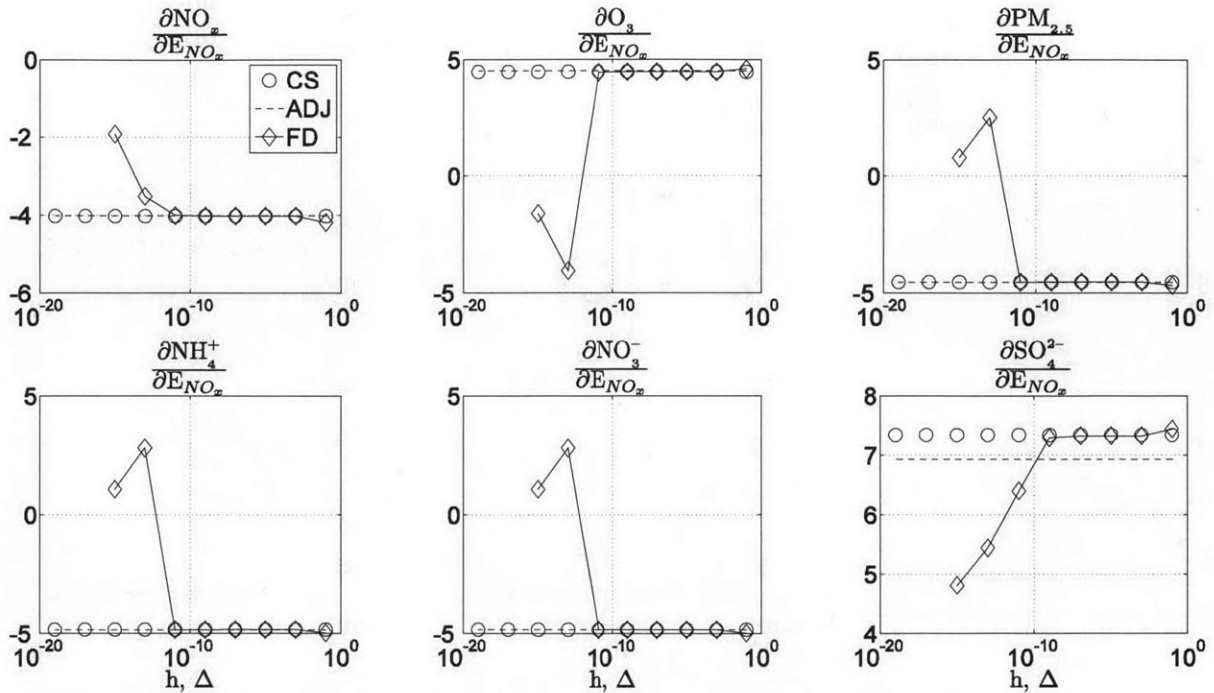**Figure 12. Sensitivity comparisons of the CS, FD and adjoint method at point 6. Units of sensitivities are ppb kg$^{-1}$; units of $h$ and $\Delta$ are kg s$^{-1}$.**

**Figure 13. Sensitivity comparisons of the CS, FD and adjoint method at point 7. Units of sensitivities are ppb kg$^{-1}$; units of $h$ and $\Delta$ are kg s$^{-1}$.**



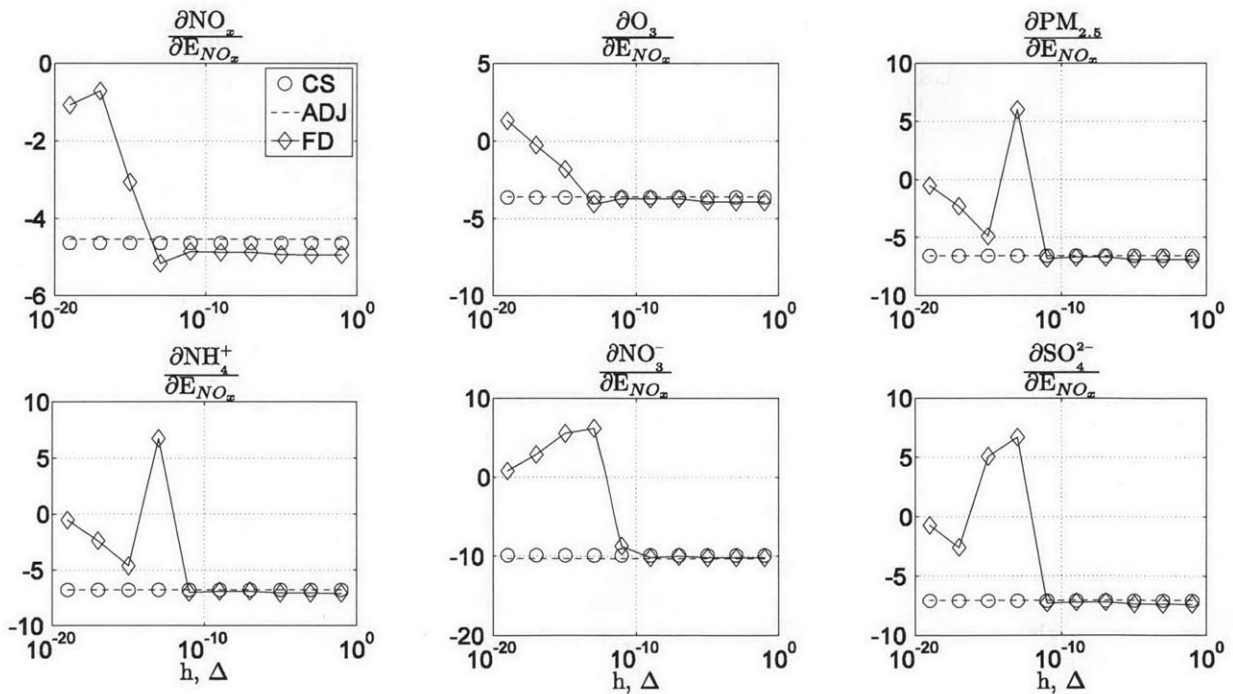**Figure 14. Sensitivity comparisons of the CS, FD and adjoint method at point 8. Units of sensitivities are ppb kg$^{-1}$; units of $h$ and $\Delta$ are kg s$^{-1}$.**

**Figure 15. Sensitivity comparisons of the CS, FD and adjoint method at point 9. Units of sensitivities are ppb kg$^{-1}$; units of $h$ and $\Delta$ are kg s$^{-1}$.**



**Figure 16. Sensitivity comparisons of the CS, FD and adjoint method at point 10. Units of sensitivities are ppb kg$^{-1}$; units of $h$ and $\Delta$ are kg s$^{-1}$.**
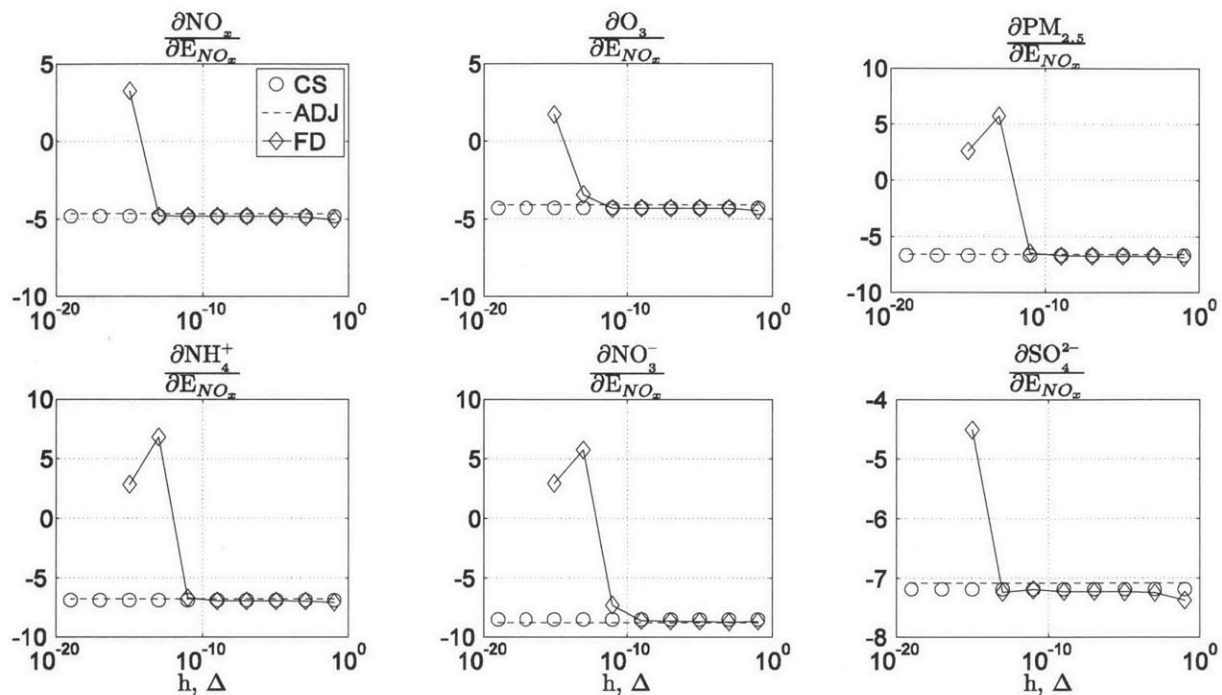
**Figure 17. Sensitivity comparisons of the CS, FD and adjoint method at point 11. Units of sensitivities are ppb kg$^{-1}$; units of $h$ and $\Delta$ are kg s$^{-1}$.**

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## APPENDIX E – North America domain for adjoint

The comparisons between the two methods (CS, adjoint) were also performed in double precision to avoid differences between the results due to precision. The complex step size for the CS method was chosen to be $h = 10^{-20}$ kg s$^{-1}$ in order to avoid coupling of the imaginary part with the real part and alter the underling physical and chemical processes. The adjoint simulations require that the cost function be defined over a spatial region before the simulation begins, shown in Figure 18.
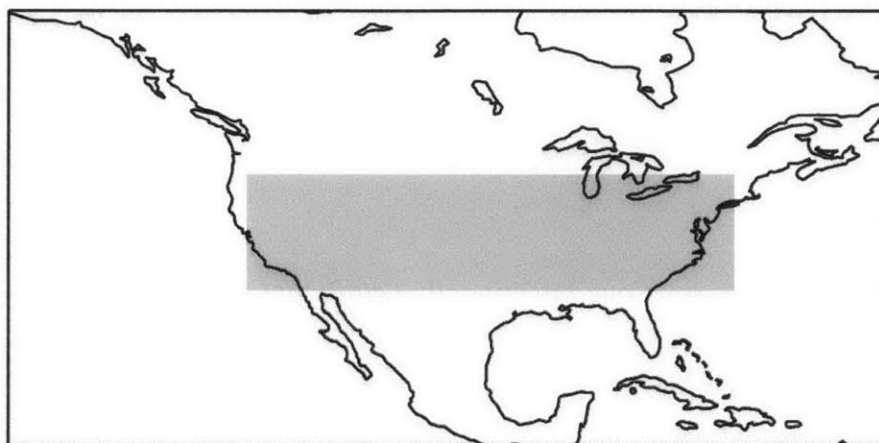


**Figure 18. The (arbitrary) North American region over which the cost function was defined for the adjoint simulations in sections 3.2. and 3.3. of the paper.**

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# APPENDIX F – Second order sensitivity

The complex step size inputted in the $NO_x$ aviation emissions for the CS method was chosen to be $h = 10^{-100}$ kg s$^{-1}$ in order to avoid coupling of the imaginary part with the real part and alter the underling physical and chemical processes. The complex step is lower than previous because the real components of the variables in the adjoint are of order $10^{-30}$ and lower. The region over which the adjoint cost function was defined is shown in Figure 18.

We present the plotted result of the CS-Adjoint method of second order sensitivities of $PM_{2.5}$ due to global aviation $NO_x$ and local $NH_3$ in comparison to the FD-Adjoint results. The perturbation for the FD-Adjoint was $\Delta = 10^{-1}$ kg s$^{-1}$, which was found to have a good balance between the truncation and the cancelation errors. As elsewhere the FD-Adjoint was implemented in double precision to avoid differences in results due to difference in precision.
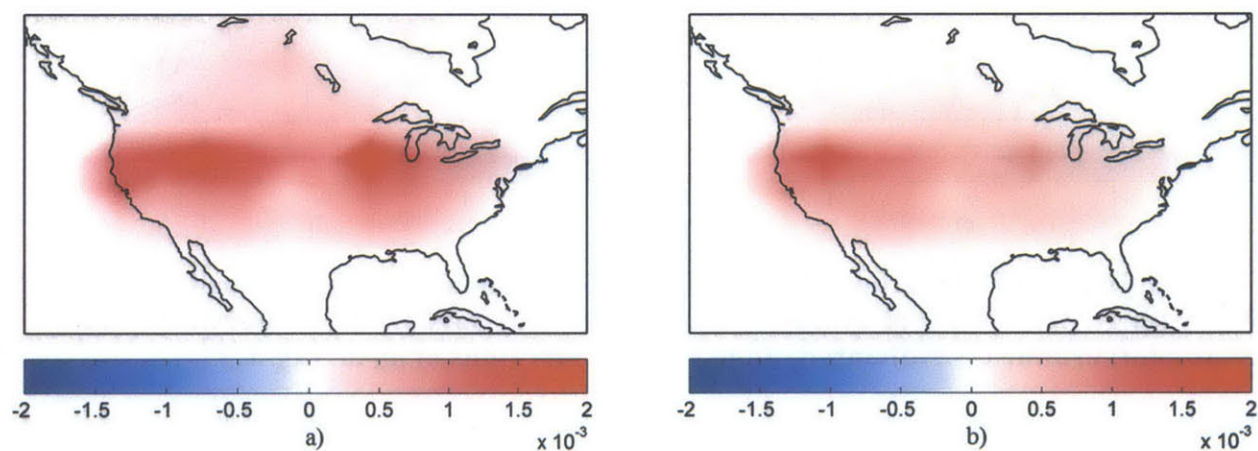


Figure 19. Impact of $NH_3$ ground level emissions on the annual average sensitivity of total $PM_{2.5}$ with respect to global aviation $NO_x$ emissions. a) CS-Adjoint; b) FD-Adjoint. Units of $\mu g\ m^{-3}(kg\ h^{-1})^{-2}$.

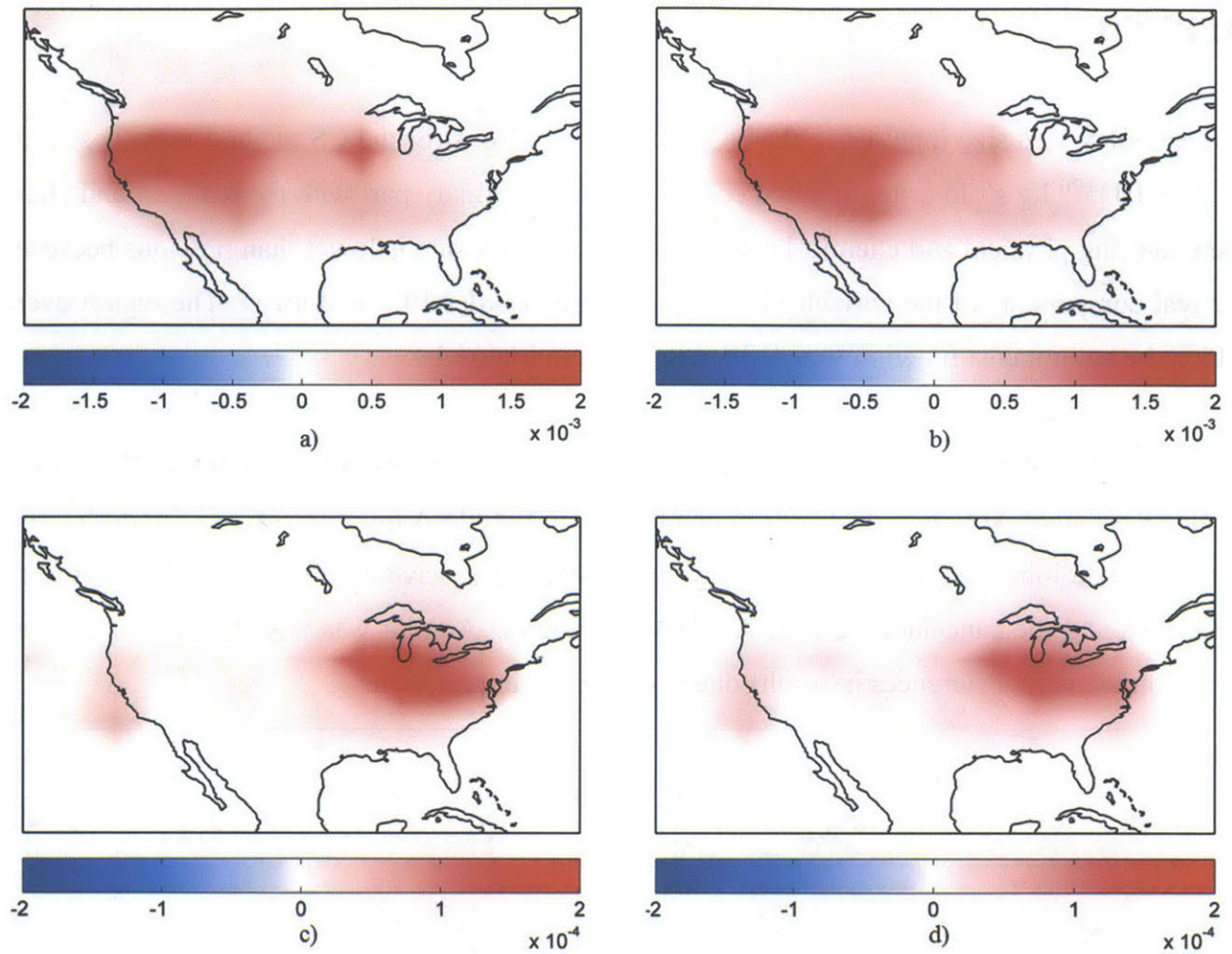Figure 20. Impact of NH₃ ground level emissions on the monthly average sensitivity of total PM₂.₅ with respect to global aviation NOₓ emissions. a) January CS-Adjoint; b) January FD-Adjoint; c) June CS-Adjoint; d) June FD-Adjoint . Units of $\mu g\ m^{-3}(kg\ h^{-1})^{-2}$.

## APPENDIX G – First order sensitivity example

Here we shown an example of applying the CS method to variables other than emissions in GEOS-Chem XPLEX. As an example, the sensitivity of ground level $PM_{2.5}$ and ozone to a uniform increase in temperature is computed

We ran a 1-year simulation of the GEOS-Chem XPLEX model (for the year 2006) with uniform imaginary complex-step $h = 10^{-20}$ inputted to the temperature field at all locations ($s$) and time steps ($t$), $T_{s,t} = T_{s,t} + ih$.

Figure 21 shows results of the CS sensitivity analysis suggests that the concentration of $PM_{2.5}$ is generally anti-correlated with temperature.
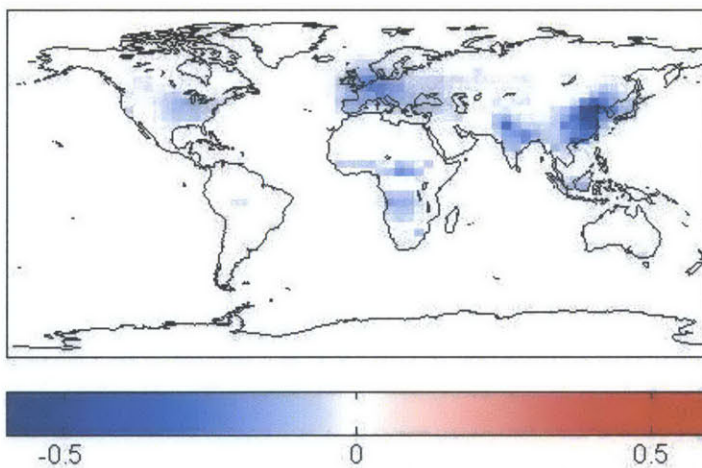


**Figure 21. Annual average ground level distribution of $PM_{2.5}$ sensitivity to global temperature field in units of $\mu g\ m^{-3}\ K^{-1}$.**

We found that nitrate has a negative sensitivity to temperature in all regions. Sulfates had a mostly positive sensitivity to temperature with the exception of Europe and East Asia. Ammonium sensitivity to temperature was mostly negative with the exception of South America.

Figure 22 shows that sensitivities of $O_3$ with respect to the temperature fields are positive over continental regions that are polluted (North America, Europe and Asia, and to a lesser extent in the southern hemisphere) and negative in regions that were clean or over water surfaces.
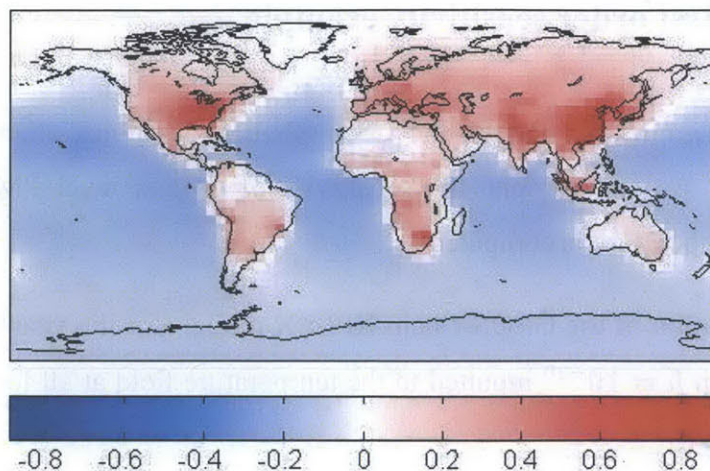
**Figure 22. Annual average ground level distribution of O₃ sensitivity to global temperature field [ppb K⁻¹].**

These results are consistent with other studies (Jacob et al., 2009; Dawson et al., 2007b; Racherla et al., 2006).

The CS method could equally be applied to weighted increases in temperature, or other variables such as rate constants, wind fields, or humidity.

**APPENDIX G References**

Dawson, J.P., Adams, P.J., Pandis, S.N., 2007a. Sensitivity of $PM_{2.5}$ to climate change in the Eastern US: a modeling case study. Atmospheric Chemistry and Physics 7, 4295-4309.

Jacob, D.J., Winner, D.A., 2009. Effect of climate change on air quality. Atmospheric Environment 43, 51-63.

Racherla, P.N., Adams, P.J., 2006. Sensitivity of global tropospheric ozone and fine particulate matter concentrations to climate change. Journal of Geophysical Research 111, D24103.