



Atmospheric chemistry-climate feedbacks

Frank Raes,^{1,2} Hong Liao,³ Wei-Ting Chen,^{2,4} and John H. Seinfeld²

Received 29 September 2009; revised 2 February 2010; accepted 24 February 2010; published 26 June 2010.

[1] We extend the theory of climate feedbacks to include atmospheric chemistry. A change in temperature caused by a radiative forcing will include, in general, a contribution from the chemical change that is fed back into the climate system; likewise, the change in atmospheric burdens caused by a chemical forcing will include a contribution from the associated climate change that is fed back into the chemical system. The theory includes two feedback gains, G_{che} and G_{cli} . G_{che} is defined as the ratio of the change in equilibrium global mean temperature owing to long-lived greenhouse gas radiative forcing, under full climate-chemistry coupling, to that in the absence of coupling. G_{cli} is defined as the ratio of the change in equilibrium mean aerosol or gas-phase burdens owing to chemical forcing under full coupling, to that in the absence of coupling. We employ a climate-atmospheric chemistry model based on the Goddard Institute for Space Studies (GISS) GCM II⁷, including tropospheric gas-phase chemistry, sulfate, nitrate, ammonium, black carbon, and organic carbon. While the model describes many essential couplings between climate and atmospheric chemistry, not all couplings are accounted for, such as indirect aerosol forcing and the role of natural dust and sea salt aerosols. Guided by the feedback theory, we perform perturbation experiments to quantify G_{che} and G_{cli} . We find that G_{che} for surface air temperature is essentially equal to 1.00 on a planetary scale. Regionally, G_{che} is estimated to be 0.80–1.30. The gains are small compared to those of the physical feedbacks in the climate system (e.g., water vapor, and cloud feedbacks). These values for G_{che} are robust for the specific model used, but may change when using more comprehensive climate-atmospheric chemistry models. Our perturbation experiments do not allow one to obtain robust values for G_{cli} . Globally averaged, the values range from 0.99 to 1.28, depending on the chemical species, while, in areas of high pollution, G_{cli} can be up to 1.15 for ozone, and as large as 1.40 for total aerosol. These preliminary values indicate a significant role of climate feedbacks in the atmospheric chemistry system.

Citation: Raes, F., H. Liao, W.-T. Chen, and J. H. Seinfeld (2010), Atmospheric chemistry-climate feedbacks, *J. Geophys. Res.*, 115, D12121, doi:10.1029/2009JD013300.

1. Introduction

[2] Attributing and predicting climate change requires linking perturbations in the Earth's radiation balance to changes in temperature and other climate variables. Radiative perturbations, also called radiative "forcings" under certain conditions, can be caused by many factors [Forster *et al.*, 2007]. Here, we are concerned with changes in the concentrations

of long-lived and short-lived greenhouse gases and aerosols. Their role in radiative forcing has been recently reviewed by Isaksen *et al.* [2009]. The response of the global mean temperature to radiative forcings is embodied in the climate sensitivity [Knutti and Hegerl, 2008]. It is composed of changes in the blackbody radiation of the Earth and physical feedbacks involving water vapor, clouds and ice/snow effects [Hansen *et al.*, 1984; Bony *et al.*, 2006, equation (24)]. Initially, climate analyses were performed using general circulation models (GCM) including only the radiative effects of long-lived greenhouse gases (LLGHGs). Later, the effects of short-lived greenhouse gases (SLGHGs: e.g., ozone) and aerosols were included, based on prescribed fields or on fields calculated from fixed emissions. While the latter studies quantified the radiative forcings by SLGHGs and aerosols (dashed arrow in Figure 1), they initially did not consider the effects of a changing climate on the emissions and other formation and removal processes of SLGHGs and aerosols (dotted arrow in Figure 1).

¹Joint Research Centre, European Commission, Ispra, Italy.

²Department of Chemical Engineering and Department of Environmental Science and Engineering, California Institute of Technology, Pasadena, California, USA.

³State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China.

⁴Now at Jet Propulsion Laboratory, Pasadena, California, USA.

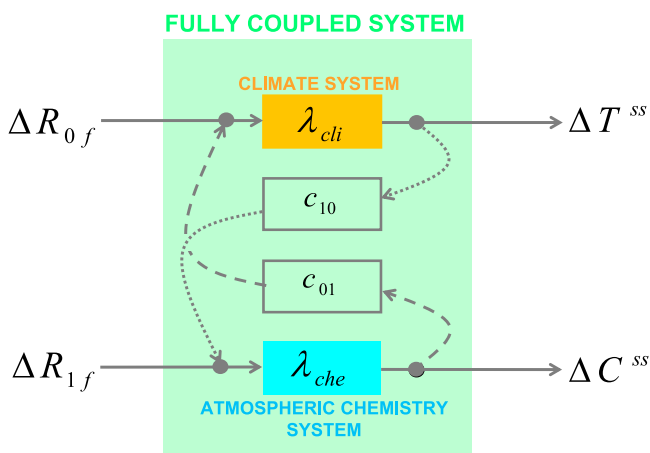


Figure 1. Box diagram of the fully coupled climate-atmospheric chemistry system, where λ_{cli} and λ_{che} are the climate and atmospheric chemistry sensitivities, respectively, c_{10} is a coupling factor used in describing the effect of climate on atmospheric chemistry, and c_{01} is a coupling factor describing the effect of atmospheric chemistry on climate. We are interested in how radiative and chemical perturbations/forcings, ΔR_{0f} and ΔR_{1f} , affect steady state climate and atmospheric chemistry, ΔT^{ss} and ΔC^{ss} .

[3] Atmospheric chemistry developed initially in parallel with climate science, with its early applications to air pollution. Following the thinking in climate sciences, we will consider perturbations in the formation, transformation, and removal of atmospheric species, and describe the response of the chemical composition of the atmosphere to such perturbations through an atmospheric chemistry sensitivity. This sensitivity includes chemical feedbacks, such as those in the CH_4 , CO , OH system [Isaksen and Hov, 1987]. Because of the many interacting atmospheric species, the atmospheric chemistry sensitivity is not a single value. This sensitivity should, in fact, be expressed in terms of the Jacobian matrix of the atmospheric chemistry system [Prather, 1994], through which the change of the concentration of a single species can be calculated as a function of the rates of change (including, e.g., emission changes) of all other species. Atmospheric chemistry and air pollution studies are typically performed with atmospheric chemical transport models (CTMs), with prescribed climate. For example, in studies that evaluate the effect of reducing emissions of air pollutants over, say, the next 30 years, a constant climate is typically assumed. Isaksen *et al.* [2009] reviewed studies of the effect of air pollution emission changes in a future climate as compared to that at present (dotted arrow in Figure 1); however, in those studies, the effects of the changing atmospheric composition on the climate itself are usually not considered (dashed arrow in Figure 1).

[4] Climate models have become increasingly sophisticated, although not yet comprehensive in allowing for complete two-way coupling between climate and chemical processes. The review by Isaksen *et al.* [2009], dealing with climate-chemistry interactions, largely divides the work into, on one hand, the impacts of changes in atmospheric

composition on climate, and, on the other hand, impacts of climate change on atmospheric composition. Many of the studies reviewed note the existence of feedbacks but, in fact, refer only to a one-way coupling between climate and atmospheric chemistry, or vice versa. Two recent papers more systematically address the feedback effects resulting from two-way coupling. Liao *et al.* [2009] approach the climate-atmospheric chemistry system by studying the production, transformation, and removal of tropospheric ozone and aerosols fully coupled to the evolving climate. GCM simulations with and without full coupling show significant differences in the predicted levels of equilibrium global mean temperature and global and regional levels of ozone and aerosols. Their study did not include aerosol-cloud interactions: the aerosol indirect effect. Unger *et al.* [2009] looked, in particular, at the effect of coupling of ozone and aerosols with cloud microphysical processes. They also found significant effects of full coupling on levels of air pollutants.

[5] The above mentioned review and studies, while giving an exhaustive overview of processes that couple climate with atmospheric chemistry, indicate that atmospheric chemistry research would benefit from a consistent framework for discussing, quantifying and comparing feedbacks in the climate-atmospheric chemistry system. We propose a framework based on Figure 1. Although we deal essentially with one feedback loop within the fully coupled system, we can, and will, throughout this paper, maintain two points of view. The first is that of the climatologist, who is interested in how the presence of chemically active species in the atmosphere leads to feedbacks in the climate system, in the same way as, for example, water vapor leads to feedbacks and enhances climate sensitivity. As such we will speak about the atmospheric chemistry feedback in the climate system. The second view is that of the atmospheric chemist, who is interested how climate leads to feedbacks in the atmospheric chemistry system that affect the relationship between emissions and burdens of chemical components, or, generally speaking, the atmospheric chemistry sensitivity. We will speak about the climate feedback in the atmospheric chemistry system. Together these constitute the atmospheric chemistry-climate feedbacks referred to in the title of this paper.

[6] The working of feedbacks in the coupled climate-atmospheric chemistry system can be illustrated with a concrete example. Consider a scenario in which both climate and atmospheric chemistry are at steady state and global SO_2 emissions were to be suddenly reduced. Reduction in SO_2 emissions leads immediately to a reduction in the formation of airborne sulfate aerosol. A global reduction in sulfate aerosol leads to a decrease in the negative radiative forcing associated with sulfate aerosol. As the Earth warms in response to the aerosol perturbation, the hydrological cycle adjusts such that the removal of sulfate aerosol by precipitation is, say, increased. At this point the feedback loop is closed. The additional decrease in sulfate aerosol, beyond that resulting from the original SO_2 reduction, further warms the system, and so on, until a new steady state is achieved. The eventual new steady state results from the two-way coupling between climate and atmospheric chemistry. The atmospheric chemistry sensitivity, linking the SO_2 emission reduction to a change in sulfate burden,

as well as the climate sensitivity, linking the sulfate forcing to a temperature change, are each changed by the feedback within the fully coupled system. The question is: by how much?

[7] Hence, at a general level, we seek to evaluate the extent to which the presence of chemically active species in the atmosphere leads to feedbacks in the climate system. At the same time, we will evaluate how climate processes lead to feedbacks in the atmospheric chemistry system. At a more practical level, we want know what degree of sophistication is needed to perform integrated climate change and air pollution analysis. Ideally, the best tool is a fully coupled climate-atmospheric chemistry model, with comprehensive treatment of all important climate and chemical processes. However, even the most comprehensive current coupled models require the maximum computing capacity available in, for example, a typical research or meteorological center. They are therefore not practical for evaluating multiple scenarios needed in the analysis of combined climate change and air pollution mitigation options. Before making the case that fully coupled models are indeed necessary, it is of interest to evaluate the importance of coupling, i.e., to quantify the strength of the atmospheric chemistry-climate feedbacks.

[8] In this work, we use Figure 1 as a framework to study more systematically the full coupling between climate and atmospheric chemistry and the resulting feedbacks. In doing so, we use the traditional analysis of climate sensitivity and feedbacks [e.g., Hansen *et al.*, 1984; Bony *et al.*, 2006; Schwartz, 2007; Roe and Baker, 2007; Roe, 2009] and extend it to include atmospheric chemistry sensitivity and feedbacks. In section 2, we describe this framework theoretically, and in section 3, guided by the framework, we perform a number of perturbation experiments with a fully coupled climate-atmospheric chemistry GCM. This allows us to study the effect of full coupling on both global climate and levels of air pollutants. In section 4, we focus on the climate system, quantify the atmospheric chemistry feedback and compare it with the known physical feedbacks due to changing water vapor, lapse rate, albedo, and clouds.

2. Coupling the Climate and Atmospheric Chemistry Systems: Theoretical Framework

[9] In order to illustrate the coupling between climate and atmospheric chemistry, it is sufficient to describe the coupled system in terms of the Earth's global mean temperature, T , and the concentration of a single generic chemical component, C .

[10] The basic dynamic equation for T follows from the overall planetary energy balance,

$$c \frac{dT}{dt} = \frac{S_0}{4} (1 - A(T, C)) - \varepsilon(T, C) \sigma T^4, \quad (1)$$

where c is the effective heat capacity of the atmosphere-ocean system, and cdT is the change in the heat content of the system arising from an imbalance between incoming and outgoing radiation. S_0 is the solar constant and σ the Stefan-Boltzmann constant. $A(T, C)$ is the planetary albedo, determined partly by cloudiness, aerosols, and the presence

of snow and ice, each of which depends in a complex manner on T and C . $\varepsilon(T, C)$ is the planetary longwave emissivity, which depends on the level of LLGHGs in the atmosphere, including water vapor and SLGHGs, such as tropospheric ozone, which themselves depend on T and C .

[11] The dynamic equation for C follows from the global material balance of a species,

$$\frac{dC}{dt} = E(T, C) - D(T, C) + RX(T, C). \quad (2)$$

$E(T, C)$ and $D(T, C)$ are the emission and physical removal rates, respectively, of the chemical component. The latter includes dry and wet deposition rates, which are dependent on the concentration of the species and on climatic conditions. Emissions of one species could, in principle, depend on the concentration of other chemical components. $RX(T, C)$ describes the net rate of chemical production of the species.

[12] At this stage we have introduced two ways to describe the coupling between climate and atmospheric chemistry: the set of coupled differential equations (1) and (2), for T and C , respectively, and the "box diagram" in Figure 1, with its sensitivity parameters λ and coupling factors c . It is useful to show how these two descriptions relate to one another, as it will help us in the discussion of feedbacks.

2.1. Perturbation Analysis

[13] We can express equations (1) and (2) in terms of radiative and chemical imbalances as follows,

$$c \frac{dT}{dt} = R_0(T, C) = \text{the radiative imbalance (W m}^{-2}\text{)} \quad (3a)$$

$$\frac{dC}{dt} = R_1(T, C) = \text{the chemical imbalance } (\mu\text{g m}^{-3} \text{ s}^{-1}\text{)}. \quad (3b)$$

Starting from a steady state, $R_i(T^{ss}, C^{ss}) = 0$ ($i = 0, 1$), and applying sustained perturbations, ΔR_{0f} and ΔR_{1f} (i.e., radiative and chemical forcings, respectively), the climate-atmospheric chemistry system will act to restore radiative and chemical equilibrium. It will relax to a new steady state at which incoming and outgoing energy fluxes and sources and sinks of chemical species are again in balance: $R_i(T^{ss} + \Delta T^{ss}, C^{ss} + \Delta C^{ss}) = 0$ ($i = 0, 1$). At any moment during the relaxation, the change of the imbalances can be written as follows:

$$\delta R_i = \left. \frac{\partial R_i}{\partial T} \right|_C \delta T + \left. \frac{\partial R_i}{\partial C} \right|_T \delta C \quad i = 0, 1. \quad (4)$$

Integrating between the start of the perturbation (when $R_i = \Delta R_{if}$) and reaching the new steady state (when $R_i = 0$) yields

$$\int_{\Delta R_{if}}^0 \delta R_i = \int_{T^{ss}}^{T^{ss} + \Delta T^{ss}} \left. \frac{\partial R_i}{\partial T} \right|_C \delta T + \int_{C^{ss}}^{C^{ss} + \Delta C^{ss}} \left. \frac{\partial R_i}{\partial C} \right|_T \delta C \quad i = 0, 1. \quad (5)$$

Assuming linear behavior in the vicinity of the steady states, it follows that

$$\Delta R_{if} = - \left. \frac{\partial R_i}{\partial T} \right|_C \Delta T^{ss} - \left. \frac{\partial R_i}{\partial C} \right|_T \Delta C^{ss} \quad i = 0, 1 \quad (6)$$

or, in matrix form,

$$\begin{bmatrix} \Delta R_{0f} \\ \Delta R_{1f} \end{bmatrix} = - \begin{bmatrix} \left. \frac{\partial R_0}{\partial T} \right|_C & \left. \frac{\partial R_0}{\partial C} \right|_T \\ \left. \frac{\partial R_1}{\partial T} \right|_C & \left. \frac{\partial R_1}{\partial C} \right|_T \end{bmatrix} \begin{bmatrix} \Delta T^{ss} \\ \Delta C^{ss} \end{bmatrix} = -\mathbf{J} \begin{bmatrix} \Delta T^{ss} \\ \Delta C^{ss} \end{bmatrix}. \quad (7)$$

\mathbf{J} , the Jacobian of the coupled system described by equations (1) and (2), contains the complete sensitivity information. The result as expressed in equation (7) is a standard one in systems and control theory [Athans and Falb, 1966].

2.2. Feedback Analysis

[14] Figure 1 is a “box diagram,” used in traditional feedback analysis. It shows (see Appendix A) that the change in temperature, caused by a radiative forcing ΔR_{0f} , will be a result from that forcing, plus a contribution from the chemical change that also results and that is fed back into the climate system. Hence,

$$\Delta T^{ss} = \lambda_{cli}(\Delta R_{0f} + c_{01}\Delta C^{ss}), \quad (8a)$$

where λ_{cli} is the sensitivity parameter of the climate system, and c_{01} is the factor that represents one-way coupling of chemical change with climate. Similarly, for the change in the concentration of a chemical compound, caused by a chemical forcing ΔR_{1f} we can write

$$\Delta C^{ss} = \lambda_{che}(\Delta R_{1f} + c_{10}\Delta T^{ss}), \quad (8b)$$

where λ_{che} is the sensitivity parameter of the atmospheric chemistry system, and c_{10} is the factor that represents one-way coupling of climate change on atmospheric chemistry.

[15] Solving (8a) and (8b) for ΔR_{0f} and ΔR_{1f} , and writing in matrix notation yields

$$\begin{bmatrix} \Delta R_{0f} \\ \Delta R_{1f} \end{bmatrix} = \begin{bmatrix} \lambda_{cli}^{-1} & -c_{01} \\ -c_{10} & \lambda_{che}^{-1} \end{bmatrix} \begin{bmatrix} \Delta T^{ss} \\ \Delta C^{ss} \end{bmatrix}. \quad (9)$$

Comparing (7) with (9) gives an immediate interpretation of the elements in the Jacobian, of which we will make use later.

[16] Inverting equation (9) yields

$$\begin{bmatrix} \Delta T^{ss} \\ \Delta C^{ss} \end{bmatrix} = \frac{\lambda_{cli}\lambda_{che}}{1 - \lambda_{cli}\lambda_{che}c_{01}c_{10}} \begin{bmatrix} \lambda_{che}^{-1} & c_{01} \\ c_{10} & \lambda_{cli}^{-1} \end{bmatrix} \begin{bmatrix} \Delta R_{0f} \\ \Delta R_{1f} \end{bmatrix}. \quad (10)$$

2.3. Assessing the Atmospheric Chemistry Feedback in the Climate System

[17] From equation (10) it follows that

$$\Delta T^{ss} = \frac{\lambda_{cli}}{1 - \lambda_{cli}\lambda_{che}c_{01}c_{10}} (\Delta R_{0f} + \lambda_{che}c_{01}\Delta R_{1f}). \quad (11)$$

This shows that in the fully, i.e., two-way, coupled climate-atmospheric chemistry system, the global mean temperature is, in principle, sensitive to both radiative and chemical forcings. The effects of both forcings are additive, but that holds only as long as it is justified to assume linear behavior (see equations (6) and (8)), which must be checked subsequently.

[18] If there is no full coupling between climate and chemistry ($c_{01} = 0$ or $c_{10} = 0$ or $c_{01} = c_{10} = 0$), equation (11) becomes

$$\Delta T_{un}^{ss} = \lambda_{cli}(\Delta R_{0f} + \lambda_{che}c_{01}\Delta R_{1f}). \quad (12)$$

Comparing (11) and (12) shows how, because of full coupling with atmospheric chemistry, the climate sensitivity parameter changes,

$$\lambda_{cli} \xrightarrow{\text{coupling}} \lambda = \frac{\lambda_{cli}}{1 - \lambda_{cli}\lambda_{che}c_{01}c_{10}}, \quad (13)$$

where λ is the climate sensitivity parameter of the coupled system. According to the feedback analysis (see equation (A4)), $\lambda_{che}c_{01}c_{10}$ has the significance of a feedback parameter, and can be termed the atmospheric chemistry feedback parameter, c_{che} ,

$$c_{che} = \lambda_{che}c_{01}c_{10}. \quad (14)$$

In fact, if we are interested only in radiative perturbations ($\Delta R_{1f} = 0$), but still want to describe the feedback due to atmospheric chemistry, Figure 1 can be simplified into Figure 2.

[19] Following equation (A5), the gain G_{che} of the system, i.e., the ratio of output of the coupled system to the output of the uncoupled system, can be calculated as the ratio of equations (11) and (12),

$$G_{che} = \frac{\Delta T^{ss}}{\Delta T_{un}^{ss}} = \frac{1}{1 - \lambda_{cli}c_{che}}. \quad (15)$$

If $c_{che} < 0$, then $G_{che} < 1$ and atmospheric chemistry will dampen the climate sensitivity; if $c_{che} > 0$, then $G_{che} > 1$ and it will amplify the climate sensitivity.

[20] As shown in equation (14), the atmospheric chemistry feedback is composed of three factors, and using the comparison of the matrices in (7) and (9), it can be written more explicitly as

$$c_{che} = \lambda_{che}c_{01}c_{10} = - \left[\left. \frac{\partial R_1}{\partial C} \right|_T \right]^{-1} \left. \frac{\partial R_0}{\partial C} \right|_T \left. \frac{\partial R_1}{\partial T} \right|_C \quad (\text{W m}^{-2}/\text{K}). \quad (16)$$

Each of the three factors can determine the sign and the magnitude of the atmospheric chemistry feedback. What this means can be illustrated by considering a simple system, consisting of nonreactive black carbon (BC) aerosols only. In this case, equation (2) becomes

$$\frac{dC}{dt} = E - \beta(T)C = R_1(T), \quad (17)$$

where C is the global burden of BC, E its global emissions rate, and $\beta(T)$ its globally average removal rate. The latter is taken to be proportional to the precipitation rate P , which is known to be dependent on the global mean temperature T : $\beta(T) = \alpha P(T)$.

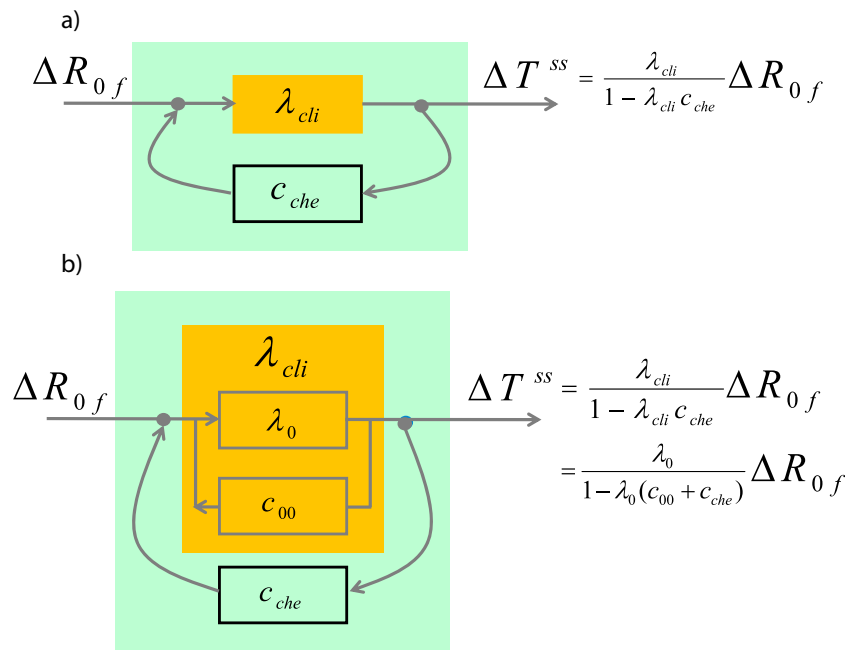


Figure 2. (a) Reduced version of Figure 1. The atmospheric chemistry feedback, i.e., the coupling through c_{10} , λ_{che} , and c_{01} , is captured by a single feedback parameter, c_{che} . (b) Expansion of Figure 2a in which the climate sensitivity parameter λ_{cli} is decomposed into the Earth's blackbody sensitivity parameter, λ_0 , and the physical feedback parameter, c_{00} .

[21] The first and third factors on the LHS of equation (16) can be obtained by differentiating equation (17). Hence

$$c_{che} = -\frac{1}{P} \frac{\partial P}{\partial T} \bigg|_c C \frac{\partial R_0}{\partial C} \bigg|_T = -hr. \quad (18)$$

The first factor on the RHS of equation (18) is the hydrological sensitivity, h , defined as the fractional change in global mean precipitation per unit of increase of global mean temperature. The second factor can be called the radiative forcing sensitivity, r , defined as the change in global radiative forcing per fractional change in the burden of the forcing agent. The latter can be calculated from the radiative forcing of BC between pre-industrial and present day, which is 0.60 W m^{-2} in the model used here, and from the consideration that this forcing is caused by about 90% of the present burden of BC [Chung and Seinfeld, 2005]. Hence $r = 0.60/0.90 = 0.66 \text{ W m}^{-2}$. The sign of h depends critically on how the increase in global mean temperature occurs. If it is due to an increase in LLGHG, it is about $0.02/\text{K}$; if it is the result of an increase in LLGHG and aerosols combined, it can be $-0.02/\text{K}$, depending on the aerosol mixture and assumed scenario for the aerosol increase [Feichter et al., 2004]. Remembering that we are assessing the atmospheric chemistry feedback that possibly affects the warming initially caused by a change in LLGHGs, we take $h = 0.02/\text{K}$, and hence, $c_{che} = -0.013 \text{ W m}^{-2}/\text{K}$. The negative sign means that the presence of BC aerosols in the climate system results in a damping of the climate sensitivity; an increase in T will lead to an increase in precipitation and therefore increased removal of BC, and since BC is a warming agent, its removal will lead to a cooling, and a damping of the initial warming. The value of c_{che} in this example is, however, quite small

and, as we will see in section 4, essentially negligible compared to the values of the physical feedback parameters in the climate system. This is despite the fact that BC aerosols exert a strong positive radiative forcing. However, in the overall feedback loop, the contribution of radiative forcing is diminished by the low hydrological sensitivity. In other words, the fact that a chemical component exerts a strong radiative forcing is clearly a necessary, but not a sufficient, condition for it to lead to a nonnegligible feedback in the climate system.

[22] The simple calculation above for black carbon cannot be easily repeated for the mixture of reactive chemical components in the atmosphere, the burdens of which are interdependent in a complex manner and can lead, for example, to either a positive or negative hydrological sensitivity. Instead, we will perform perturbation experiments with a fully coupled climate-atmospheric chemistry model, as described in section 3. These experiments will lead to an overall gain, G_{che} , which describes the feedback produced by all interacting chemical components in the climate system. From G_{che} the chemical feedback parameter, c_{che} , can be obtained, using equation (15), assuming that λ_{cli} is known.

2.4. Assessing the Climate Feedback in the Atmospheric Chemistry System

[23] From equation (10) it also follows that

$$\Delta C^{ss} = \frac{\lambda_{che}}{1 - \lambda_{che} \lambda_{cli} c_{01} c_{10}} (\Delta R_{1f} + \lambda_{cli} c_{10} \Delta R_{0f}). \quad (19)$$

Further developing this equation, in the same way as we did for ΔT^{ss} above, is of limited use, because it is difficult to select a generic chemical component from the

Table 1a. Climate Variables, Considered in the Present Study, That Influence Emissions, Chemical Reactions, Transport, and Deposition of Gas-Phase Species and Aerosols

Climate Variables	Atmospheric Chemistry Processes
Temperature, precipitation	NO _x emissions (soil)
Frequency of convective events	NO _x emissions (lightning)
Temperature, solar radiation	biogenic hydrocarbon emissions
Surface wind, temperature	dimethyl sulfide (DMS) emissions
Wind	sea salt emissions
Wind, precipitation	mineral dust emissions
Temperature, water vapor	chemical reaction rates
Temperature, relative humidity	aerosol-gas-phase equilibrium
Cloud amount, cloud water content	in-cloud aerosol formation
Winds, atmospheric stability	transport of chemical species
Atmospheric stability, clouds, precipitation	deposition (wet and dry)

many that are present in the atmosphere. A vector/matrix analysis could be carried out to describe the effect of climate feedback on the chemical components, but it is not necessary to present that here.

[24] Perturbation experiments with the full climate-atmospheric chemistry model will yield, for each of the chemical components i , a gain,

$$G_{cli,i} = \frac{\Delta C_i^{SS}}{\Delta C_{i,un}^{SS}}, \quad (20)$$

where ΔC_i^{SS} is the change in the concentration of component i due to a forcing in the fully coupled climate-chemistry system, and $\Delta C_{i,un}^{SS}$ is the corresponding change in the uncoupled system. These gains will give insight into the importance of climate as a feedback within the atmospheric chemistry system.

3. Quantifying Atmospheric Chemistry and Climate Feedbacks

[25] Given the complexity of the coupled climate-atmospheric chemistry system, one cannot estimate a priori in many cases even the sign of the atmospheric chemistry and climate feedbacks. This can only be done through simulations with a fully coupled climate-atmospheric chemistry model. While many processes in such a model are known to be nonlinear, the structure of the linear feedback theory is used here as a guide for a series of perturbation experiments that are required to compare the magnitude and sign of the various feedbacks within a consistent conceptual framework. In particular, the experiments allow the quantification of the gains, G_{che} and $G_{cli,i}$ and their related feedback parameters.

[26] It should be clear that the values for the gains and feedback parameters are descriptors of the particular climate-atmospheric chemistry used in the experiments, in the same way as the climate sensitivity is a descriptor of a particular climate model. The robustness of the values for the gains and feedback factors obtained from the perturbation experiments will need to be discussed, especially when deviations from the linear theory do occur.

3.1. Model Description: CACTUS Unified Model

[27] The Unified Model developed in the National Aeronautics and Space Administration (NASA) project, Chem-

istry, Aerosols, and Climate: Tropospheric Unified Simulation (CACTUS), simulates the fully coupled interactions of chemistry, aerosol, and climate based on the 4° latitude by 5° longitude, nine-layer Goddard Institute for Space Studies (GISS) GCM II', as described in detail in previous studies [Liao *et al.*, 2003, 2004; Liao and Seinfeld, 2005; Liao *et al.*, 2006, 2009].

[28] The model includes a detailed simulation of tropospheric O₃-NO_x-hydrocarbon chemistry, as well as sulfate, nitrate, ammonium, black carbon (BC), primary organic aerosols (POA), secondary organic aerosols (SOA), sea salt, and mineral dust. Two-way coupling between aerosols and gas-phase chemistry provides consistent chemical fields for aerosol dynamics and aerosol mass, for heterogeneous processes and calculations of gas-phase photolysis rates. Additional information on the treatment of atmospheric chemistry is given in Appendix B. Table 1a list the climate variables in the model that influence emissions, chemical reactions, transport, and deposition of gas-phase species and aerosols, whereas Table 1b lists the atmospheric chemistry variables in the model that influence climate. Hence, in the fully coupled mode, the climate responds to radiative perturbations associated with the varying concentrations of LLGHGs, aerosols and O₃. Only the direct radiative effect of aerosols, through scattering and absorption of radiation, is considered here. The aerosol indirect effect is not considered; clouds do, however, respond to changes in climate variables driven by LLGHGs, tropospheric ozone, and direct aerosol forcing. Consideration of the aerosol indirect radiative effect in climate-chemistry feedbacks should be the subject of future work. For aerosol and gas-phase species, the removal and transport processes, the thermodynamic partitioning, and reaction rates of the temperature-sensitive reactions are calculated simultaneously based on relevant climate variables such as temperature, precipitation, and wind fields. Coupling between climate and the chemistry fields can be turned on and off, depending on the need of the experiments.

[29] In the GCM the atmosphere is coupled to a "Q-flux" ocean [Hansen *et al.*, 1984], in which the monthly horizontal heat transport fluxes are held constant as in work by Mickleby *et al.* [2004], while changes in the sea surface temperature and sea ice are calculated based on energy exchange with the atmosphere, ocean heat transport, and the ocean mixed layer heat capacity [Hansen *et al.*, 1984]. In the atmosphere nine vertical layers in a σ -coordinate system extend from the surface to 10 mbar. The dynamical time step in the GCM is 1 h, while the chemistry subroutines are called every 4 h. The GISS GCM-II' has been used extensively to probe the climate response to perturbations in LLGHG concentrations, solar luminosity, and tropospheric O₃ and aerosol burdens [e.g., Grenfell *et al.*, 2001; Rind

Table 1b. Atmospheric Chemistry Variables, Considered in the Present Study, That Influence Climate

Atmospheric Chemistry Variable	Climate Processes
Concentration of tropospheric ozone	radiative effect
Concentration of all aerosol species, except sea salt and mineral dust	direct radiative effect only (assuming internal mixing of aerosol components)

Table 2. Global and Annual Mean 2000 and 2100 GHG Concentrations and Anthropogenic Species Emissions Based on IPCC Scenario SRES A2^a

Species	Present Day (Year 2000)	Year 2100 (IPCC SRES A2)
CO ₂ (ppmv)	367	836
CH ₄ (ppbv)	1760	3731
N ₂ O (ppbv)	316	447
CFC-11 (pptv)	246	45
CFC-12 (pptv)	535	222
NO _x (Tg N yr ⁻¹)	32	109.7
CO (Tg CO yr ⁻¹)	1030	2498
Ethane (Tg C yr ⁻¹)	8.6	100.1
Propane (Tg C yr ⁻¹)	6.7	28.1
≥C ₄ alkanes (Tg C yr ⁻¹)	30.1	60.5
≥C ₃ alkenes (Tg C yr ⁻¹)	22	41
Acetone (Tg C yr ⁻¹)	9	9
SO ₂ (Tg S yr ⁻¹)	71.3	62.6
NH ₃ (Tg N yr ⁻¹)	46.9	102.6
POA (Tg OM yr ⁻¹)	82.2	189.5
BC (Tg C yr ⁻¹)	12.2	28.8

^aIntergovernmental Panel on Climate Change [2000] and Liao *et al.* [2006].

et al., 2001; Shindell *et al.*, 2001; Menon, 2004; Mickley *et al.*, 2004; Chung and Seinfeld, 2005; Chen *et al.*, 2007].

3.2. Perturbation Experiments: Setup

[30] The sensitivity of climate models can be studied using future scenarios, which prescribe changes in concentrations for LLGHGs and in emissions of air pollutants

and their precursors [Soden and Held, 2006; Kloster *et al.*, 2010]. We follow this approach. Therefore, the radiative forcing applied in the experiments results from changing the LLGHG concentrations from 2000 to 2100 values, as prescribed by the IPCC SRES A2 scenario. Similarly, in order to force the system chemically, we change the emissions of air pollutants and their precursors from 2000 values to 2100 values (See Table 2 and Appendix B for further details on how 2100 emissions are calculated).

[31] In the chemical forcing experiments, all emissions are changed in concert, and the eventual changes in temperature and concentrations are the end result of a wide range of climatic and chemical processes, which act to enhance or oppose each other. For instance, in the A2 scenario, SO₂ emissions decrease, which contributes to a warming, because of a reduction in sulfate aerosols. At the same time, NH₃ emissions increase, which leads to cooling, as more gas-phase nitric acid is incorporated into the aerosol phase as nitrate. Therefore, the resulting overall warming is expected to be smaller than when SO₂ and NH₃ emissions are perturbed individually. This is to say that in our study, the values for the gains and feedback parameters obtained from the chemical perturbation experiments depend on the particular scenario assumed for the perturbation. Therefore, results based on chemical forcing experiments should be viewed as preliminary.

[32] The numerical experiments are summarized in Table 3. They consist of seven pairs of model runs, some of which were carried out in previous studies [Liao *et al.*, 2006; Chen *et al.*, 2007; Liao *et al.*, 2009]. Five new runs (B₂, C₁, C₂,

Table 3. Description of the Model Experiments and Their Outcome

Experiments	Outcome	Gains
A ^a A ₁ : 2000 aerosol and gas-phase concentrations kept fixed; 2000 GHG concentrations A ₂ : 2000 aerosol and gas-phase concentrations kept fixed; 2100 GHG concentrations	$\Delta T_{r,am}^{ss}$: change in equilibrium global mean temperature owing to GHG radiative forcing, without allowing climate to affect air pollutant concentrations. (uncoupled)	$G_{che} = \frac{\Delta T_r^{ss}}{\Delta T_{r,am}^{ss}}$
B ^a B ₁ : 2000 aerosol and gas-phase precursor emissions; 2000 GHG concentrations B ₂ : 2000 aerosol and gas-phase precursor emissions; 2100 GHG concentrations at year 2100 level	ΔT_r^{ss} and ΔC_r^{ss} : changes in equilibrium global mean temperature and in levels of air pollutants, owing to GHG radiative forcing, allowing for full climate-chemistry coupling	$G_{che} = \frac{\Delta T_r^{ss}}{\Delta T_{r,am}^{ss}}$
C ^a C ₁ : 2000 aerosol and gas-phase precursor emissions; 2000 climate kept fixed C ₂ : 2100 aerosol and gas-phase precursor emissions; 2000 climate kept fixed	$\Delta C_{c,am}^{ss}$: change in equilibrium global air pollutant concentrations owing to a chemical forcing, without allowing atmospheric chemistry to affect climate. (uncoupled)	$G_{i,cli} = \frac{\Delta C_r^{ss}}{\Delta C_{c,am}^{ss}}$
D ^a D ₁ : 2000 aerosol and gas-phase precursor emissions; 2000 GHG concentrations D ₂ : 2100 aerosol and gas-phase precursor emissions; 2000 GHG concentrations	ΔT_c^{ss} and ΔC_c^{ss} : changes in equilibrium global mean temperature and in levels of air pollutants owing to the chemical forcing, allowing for full climate-chemistry coupling	$G_{i,cli} = \frac{\Delta C_r^{ss}}{\Delta C_{c,am}^{ss}}$
E ^a E ₁ : 2000 aerosol and gas phase precursor emissions; 2000 GHG concentrations E ₂ : 2100 aerosol and gas phase precursor emissions; 2100 GHG concentrations	ΔT_{r+c}^{ss} and ΔC_{r+c}^{ss} : changes in equilibrium global mean temperature and air pollutant concentrations owing to a simultaneous radiative and chemical forcing, allowing for full climate-chemistry coupling	Comparing, e.g., ΔT_{r+c}^{ss} with $\Delta T_r^{ss} + \Delta T_c^{ss}$ allows quantifying the linearity of the system
F ^b F ₁ : 2100 aerosol and gas-phase concentrations kept fixed; 2000 GHG concentrations F ₂ : 2100 aerosol and gas-phase concentrations kept fixed; 2100 GHG concentrations	$\Delta T_{r,am}^{ss}$: change in equilibrium global mean temperature owing to a radiative forcing, without allowing climate to affect air pollutant concentrations (uncoupled)	$G_{che} = \frac{\Delta T_r^{ss}}{\Delta T_{r,am}^{ss}}$
G ^b G ₁ : 2100 aerosol and gas-phase precursor emissions; 2000 GHG concentrations G ₂ : 2100 aerosol and gas-phase precursor emissions; 2100 GHG concentrations	ΔT_r^{ss} and ΔC_r^{ss} : changes in equilibrium global mean temperature and in levels of air pollutants owing to a radiative forcing, allowing for full climate-chemistry coupling	$G_{che} = \frac{\Delta T_r^{ss}}{\Delta T_{r,am}^{ss}}$

^aReference year for atmospheric chemical composition: 2000. Note: B₁ = D₁ = E₁.

^bReference year for atmospheric chemical composition: 2100. Note: G₂ = E₂.

Table 4. Results of the Perturbation Experiments

	ΔA_s	ΔB_s	ΔC_s	ΔD_s	ΔE_s	ΔF_s	ΔG_s	$G_{che,2000-2100}^a$	$G_{cli,i}^b$	L_{irr}^c (%)
Radiative Forcing, $W\ m^{-2}$	6.63 GHG	6.63 GHG		0.72 $O_3 + 0.23\ AER = 0.95$	0.72 $O_3 + 0.23\ AER + 6.63\ GHG = 7.58$	6.63 GHG	6.63 GHG			0
$\Delta T, K$	5.32	5.28		0.48	0.48	5.93	5.46	0.99–1.02		3
$\Delta precip, mm\ d^{-1}$	0.34	0.34		–0.02	–0.02	0.33	0.35	1.02–1.05		3
$\Delta O_3, Tg\ (%)$		–39.3 (–12)	190 (59)	187 (59)	115 (36)		–72.8 (–14)	0.99	0.99	–29
$\Delta H_2O_2, Tg\ (%)$		1.05 (28)	4.47 (119)	4.91 (129)	6.96 (183)		2.05 (24)	1.10	1.10	14
$\Delta SO_2, Tg\ (%)$		–0.14 (–13)	–0.51 (–47)	–0.49 (–47)	–0.45 (–42)		0.04 (8)	0.96	0.96	–40
$\Delta sulfate, Tg\ (%)$		–0.25 (–12)	–0.11 (–5)	–0.09 (–4)	–0.19 (–9)		–0.10 (–5)	0.82	0.82	–79
$\Delta nitrate, Tg\ (%)$		–0.20 (–48)	1.63 (382)	1.69 (399)	0.74 (175)		–0.95 (–45)	1.04	1.04	–101
$\Delta NH_4, Tg\ (%)$		–0.15 (–25)	0.52 (92)	0.55 (93)	0.23 (39)		–0.32 (–28)	1.06	1.06	–74
$\Delta BC, Tg\ (%)$		–0.02 (–10)	0.30 (134)	0.34 (144)	0.27 (116)		–0.07 (–12)	1.13	1.13	–19
$\Delta POA, Tg\ (%)$		–0.09 (–7)	1.66 (134)	1.86 (143)	1.64 (126)		–0.22 (–7)	1.12	1.12	–8
$\Delta SOA, Tg\ (%)$		0.002 (1)	0.18 (52)	0.23 (63)	0.24 (67)		0.01 (2)	1.28	1.28	+3
$\Delta total\ AER, Tg\ (%)$		–0.70 (–14)	4.18 (87)	4.57 (91)	2.93 (59)		–1.64 (–17)	1.09	1.09	–32

^aCalculated as $\Delta B/\Delta A$ and $\Delta G/\Delta F$ for 2000 and 2100 chemistry, respectively.

^bCalculated as $\Delta D/\Delta C$.

^cLinearity (or additivity) calculated as $100 \times (\Delta E - (\Delta B + \Delta D))/\Delta E$. Zero means perfect linearity.

D_2 , and F_1) were performed to complete the present study. All experiments were run for a sufficiently long time, ranging from 35 to 80 years, to establish a steady state in climate and atmospheric chemistry. Each of the pairs allows one to calculate a particular forcing and its effect on climate and chemical burdens. This is done with climate and chemistry uncoupled (pairs A, C and F), and with climate and chemistry fully coupled (pairs B, D, E and G). By combining results from the coupled and uncoupled runs, values for G_{che} and $G_{cli,i}$ are obtained (see Table 3). For the A–E runs summarized in Table 3, the reference case, which is subsequently perturbed, has 2000 GHG levels and chemical composition. For the F and G runs in Table 3 the reference case has 2000 GHG levels but a 2100 chemical composition. In this way the effect of the atmospheric chemical state on the atmospheric chemistry feedback can be evaluated.

3.3. Perturbation Experiments: Results

[33] Results of the perturbation experiments are summarized in Table 4.

3.3.1. Effect of Atmospheric Chemistry Feedback on Climate (Temperature and Precipitation) Sensitivity

[34] In experiments A and B, the radiative forcing at the top of the atmosphere, as a result of perturbing the concentrations of LLGHGs, is $6.63\ W\ m^{-2}$. The steady state temperature and precipitation increase by $5.32\ K$ and $0.336\ mm\ d^{-1}$ in experiment A, and by $5.28\ K$ and $0.342\ mm\ d^{-1}$ in experiment B. As a result of the latter increases, the burdens of chemical species also undergo significant changes in experiment B, for example, -12% for ozone, -48% for nitrate aerosols -10% for black carbon and -14% for total aerosols (i.e., the sum of all individual aerosol species). With a positive hydrological sensitivity, a decrease in scattering aerosols amplifies the climate sensitivity, while a decrease in ozone and black carbon dampens it (see illustrative example above). Apparently, the latter effect dominates, as the gain G_{che} for temperature, derived from experiments A and B is $5.28/5.32 = 0.99$, i.e., a small damping of the climate (= temperature) sensitivity. The gain G_{che} for precipitation, $0.342/0.336 = 1.02$, indicates a small amplification of the precipitation sensitivity. The latter can be explained by the fact that the initial reduction in aerosol burdens owing to an increase in precipitation allows for more radiation reaching the surface, more evaporation, and a further increase in precipitation. The strength of these feedbacks appears to be dependent on the chemical state of the atmosphere; this is shown by experiments F and G, in which the chemical composition of the atmosphere is that of 2100. The temperature and precipitation sensitivities now increase by factors 1.02 and 1.05, respectively. The values of these gains are very small, indicating that atmospheric chemistry, as treated here, does not lead to important feedbacks in the climate system at the planetary scale. We will discuss this further in section 4.

[35] So far we have calculated the gain G_{che} from the globally averaged values of surface temperature and precipitation. We can also use values in each surface grid point of the model and study the geographical distribution of G_{che} . This is done in Figure 3 for the gain for temperature. It shows that, locally, this gain can be significant: as low as 0.8 and as high as 1.3. As can be expected, G_{che} depends on the

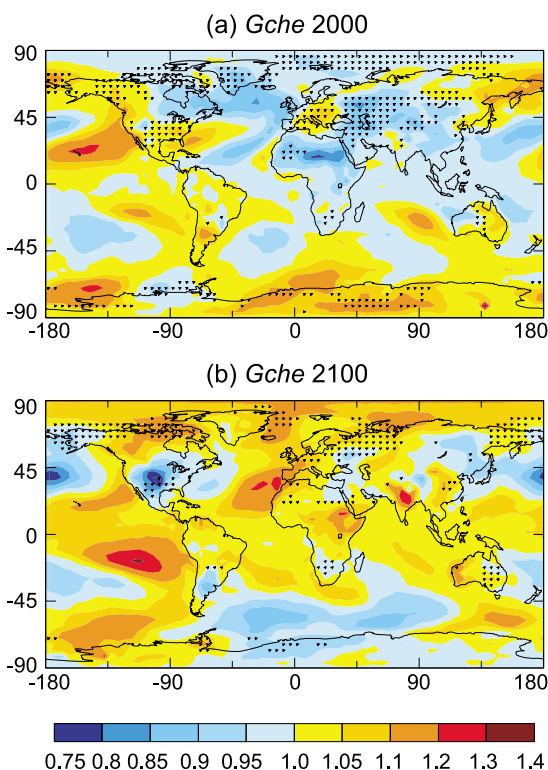


Figure 3. The gain G_{che} in surface temperature, caused by atmospheric chemistry feedback, in an atmosphere with (a) year 2000 chemical composition and (b) 2100 chemical composition. Dotted areas indicate that local values of $\Delta B - \Delta A$ and of $\Delta G - \Delta F$, in Figures 3a and 3b, respectively, are significantly different from zero at the 95% level.

chemical composition of the atmosphere. It might be of interest to point out that many areas where atmospheric chemistry has a damping effect in the 2000 atmosphere turn into areas in which atmospheric chemistry has an amplifying effect in the 2100 atmosphere. Their geographical pattern does not correlate with those of the air pollution fields nor with that of warming. This shows that the atmospheric chemistry feedback is not necessarily related to polluted atmospheres, and that climate sensitivity is rather governed by the physical feedbacks, such as, e.g., the snow/ice feedback, operating in the high latitudes.

[36] In experiments C and D a chemical forcing is imposed by changing emissions of air pollutants and their precursors. This generally leads to large changes in the burdens of the chemical components, for example, up to an increase of 400% in nitrate burdens, reflecting the large increases in NO_x and NH_3 emissions in the A2 scenario (see Table 2). These changes in the burdens also result in a top of the atmosphere radiative forcing. This forcing can be calculated from experiment C, where climate is kept fixed, and amounts to 0.95 W m^{-2} ; 0.72 W m^{-2} due to the change in ozone burden plus 0.23 W m^{-2} due to the change in aerosol burden. This forcing is effective in experiment D where it leads to an increase of temperature of 0.48 K and a decrease of precipitation, -0.019 mm d^{-1} . The warming is again explained by the dominance of ozone and BC,

whereas the drying is explained by a reduction of incoming radiation, hence a reduction in evaporation at the surface due to the increased aerosol burden.

[37] Experiment E evaluates the effects of the radiative and chemical forcings combined. In a purely linear system, these effects on climate are expected to be equal to the sum of the effects of the individual forcings, obtained in experiments B and D (see equation (11)). The *Lin* column in Table 4 shows that the temperature increase owing to increasing LLGHGs and air pollutants simultaneously is within 3% of the sum of the temperature increases obtained by increasing LLGHGs and air pollutants separately. The same conclusion holds for precipitation change. A similar conclusion was reached by Kirkevåg *et al.* [2008] and Kloster *et al.* [2010]. Feichter *et al.* [2004], on the other hand, found significant deviations from additivity. We will refrain from making numerical comparisons with these or other studies, because the air pollutants considered as well as their interactions with the climate system are different. To explain the differences would require a detailed intercomparison study, which is beyond the scope of the present study.

[38] The fact that additivity holds in the present experiments is an indication that the imposed perturbations do not lead the modeled temperature and precipitation out of the linear range. The changes in temperature and precipitation, at most 5.93 K and 0.35 mm d^{-1} , are indeed small compared to the unperturbed values of 287.4 K and 3.19 mm d^{-1} , respectively. In addition, the values for G_{che} are obtained by radiative forcing experiments alone, hence we are not concerned about the issues existing with chemical forcings mentioned earlier. We conclude that the values for G_{che} are robust, but valid only for the particular climate-atmospheric chemistry model used.

3.3.2. Effects of Climate Feedback on Atmospheric Chemistry Sensitivity

[39] Changing the emissions of air pollutants and their precursors in experiment C leads to a change in the steady state global burdens. As pointed out earlier, these changes are large, for example, up to +59% in ozone burdens, +382% in nitrate aerosol, +134% in BC and +87% in total aerosol. The same change of emissions in experiment D, in which full coupling between atmospheric chemistry and climate occurs, leads to different changes: +59%, +399%, +144% and +91% for ozone, nitrate aerosol, BC and total aerosol burdens, respectively. These changes show that climate does feed back on the atmospheric chemistry sensitivity, or, more simply, on the relationship between emissions and burdens.

[40] In the case of ozone, the global gain G_{cli} is 0.99, but with local values that are significant and up to 1.15, especially in the Northern Hemisphere, and down to 0.8 in some areas over the remote oceans (see Figure 4a). The positive feedback values can be explained by the positive effect of chemical forcing on temperature ($+0.48 \text{ K}$), which over the continents of the Northern Hemisphere has a positive impact on ozone production, by, for example, more active NO_x chemistry and increased biogenic ozone precursors. Over the oceans the higher water vapor, resulting from the slight warming, dominates and contributes to ozone destruction.

[41] For aerosols, the climate feedback is generally positive; $G_{cli,i} > 1$. As pointed out by Liao *et al.* [2009], this is

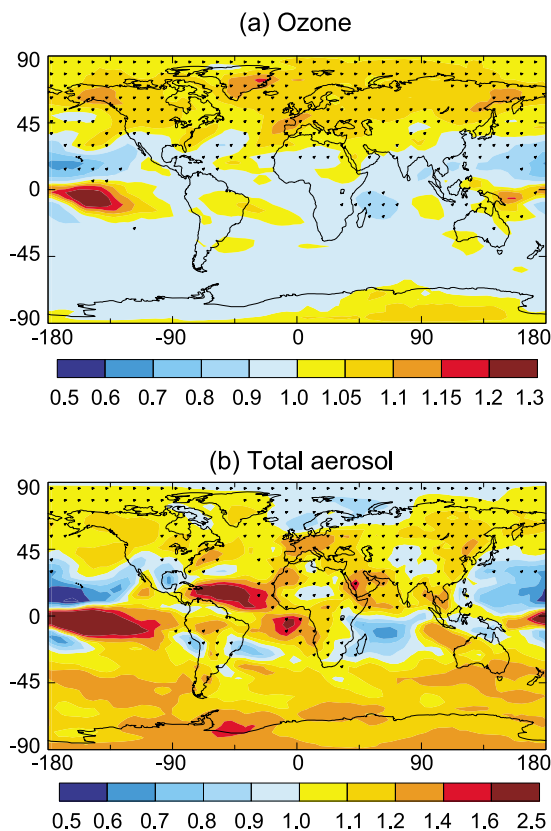


Figure 4. The gain G_{cli} in column burdens of (a) tropospheric ozone and (b) total aerosol, caused by climate feedbacks. Dotted areas indicate that local values of $\Delta D - \Delta C$, for ozone and total aerosol, are significantly different from zero at the 95% level.

mainly through a reduction in precipitation (-0.019 mm d^{-1} in our experiments) and a reduction in convection (not evaluated here), which leads to higher steady state burdens in experiment D compared to experiment C. SO_2 and sulfate aerosols seem to be an exception ($G_{cli} = 0.92$ and 0.82 , respectively), but this is only an artifact of the reduction of SO_2 emissions in the A2 scenario and the way G_{cli} is defined. The fact is that the reduction in precipitation leads to smaller reductions in SO_2 and sulfate than would be expected from the SO_2 emission reduction only. In practical terms, the climate feedback works against sulfur emission controls. For BC and POA, the gain is larger than 1.10 and reaches 1.23 for SOA. This points, for most individual aerosol components, to a significant effect of climate feedback on the atmospheric chemistry sensitivity. The geographical distribution of G_{cli} for the total aerosol column burden is shown in Figure 4b. As expected, fields of significant positive feedback exist over populated and biomass burning areas, with values of G_{cli} up to 1.4.

[42] It is of interest to examine also the linearity of the changes in burdens with respect to radiative and chemical forcings (see equation (16)). The last column of Table 4 shows that adding the changes in burdens obtained by applying radiative and chemical forcing experiments separately (experiments B and D), can lead to large overprediction or underpredictions compared to the results of applying these

forcings simultaneously (experiment E). These deviations are generally larger than the 3% found in calculating temperature and precipitation. In the case of ozone, adding the burden changes separately would lead to an overprediction of 29%. This is explained by the fact that in experiment E, ozone chemistry is occurring at a temperature that is 5.93 K higher than the unperturbed run, compared to only 0.48 K higher in experiment D. At this higher temperature, global ozone destruction through higher water vapor concentrations seems to be more important than global ozone production by more active NO_x chemistry and higher biogenic emissions. In the case of nitrate and ammonium, the overpredictions are 101% and 74%, respectively. This can again be explained by the much larger temperature increase in experiment E and the temperature dependence of the ammonium/nitrate-ammonia/nitric acid equilibrium, which leads to less ammonium nitrate in experiment E.

[43] The fact that additivity does not hold in these experiments is an indication that the imposed perturbations do lead to modeled chemical burdens that are out of the linear range. In addition, we need to recognize the problem that the calculated gains are dependent on the particular IPCC A2 scenario from which the perturbations were derived. The values for the gains $G_{cli,i}$ in Table 4 and Figure 4 should be considered as preliminary and give an indication of the strength of climate feedback in the atmospheric chemistry of individual species. In future experiments, it will be worthwhile to perturb systematically the emissions of individual chemical compounds or groups of components, for example, emitted by a single economic sector, to come to robust values of $G_{cli,i}$.

4. Comparison of Atmospheric Chemistry Feedback With Known Physical Feedbacks in the Climate System

[44] The atmospheric chemistry feedback parameter, $c_{che} = \lambda_{che} c_{01} c_{10}$, derived in section 2.3, equation (14), can be compared directly with the parameters of the physical feedbacks. This can be understood by making the physical feedbacks explicit in the analysis. Figure 2a can be transformed into Figure 2b, in which λ_0 is the sensitivity parameter of a new reference system, with respect to which the physical feedbacks, c_{00} , as well as the atmospheric chemistry feedback, c_{che} , can be assessed. The climate sensitivity parameter, λ_{cli} , appearing in Figures 1 and 2a, can thus be written as

$$\lambda_{cli} = \frac{\lambda_0}{1 - \lambda_0 c_{00}} \text{ or } \lambda_{cli}^{-1} = \lambda_0^{-1} - c_{00}. \quad (21)$$

Introducing this in the expression for the climate sensitivity parameter of the coupled climate-atmospheric chemistry system, λ (see equation (13)), yields

$$\lambda = \frac{\lambda_{cli}}{1 - \lambda_{cli} c_{che}} = \frac{\lambda_0}{1 - \lambda_0 (c_{00} + c_{che})} \text{ or } \lambda^{-1} = \lambda_0^{-1} - c_{00} - c_{che}. \quad (22)$$

Equation (22) shows how the physical and chemical feedback parameters are additive and can be quantitatively compared.

Table 5. Climate Feedback Parameters and Gains

	c_i (W m ⁻² /K)	$G_i = \frac{1}{1-\lambda_0 c_i}$	Reference
Water vapor	1.80 ± 0.18	2.27	<i>Randall et al.</i> [2007]
Lapse rate	-0.84 ± 0.26	0.80	<i>Randall et al.</i> [2007]
Clouds	0.69 ± 0.38	1.28	<i>Randall et al.</i> [2007]
Surface albedo	0.26 ± 0.08	1.09	<i>Randall et al.</i> [2007]
Atmospheric chemistry (2000)	-0.013	1.00	this work
Atmospheric chemistry (2100)	0.025	1.01	this work

[45] The physical significance of λ_0 and c_{00} is straightforward. Comparison of (7) and (9) shows that

$$\lambda_{cli}^{-1} = -\left. \frac{\partial R_0}{\partial T} \right|_c. \quad (23)$$

Differentiating equation (1) with respect to T yields

$$\lambda_{cli}^{-1} = 4\sigma\varepsilon T^3 + \frac{S_0}{4} \left. \frac{\partial A}{\partial T} \right|_c + \sigma T^{ss^4} \left. \frac{\partial \varepsilon}{\partial T} \right|_c, \quad (24)$$

and from a comparison with equation (21) we can write

$$\lambda_0^{-1} = 4\sigma\varepsilon T^3 \quad (25)$$

$$c_{00} = -\frac{S_0}{4} \left. \frac{\partial A}{\partial T} \right|_c - \sigma T^{ss^4} \left. \frac{\partial \varepsilon}{\partial T} \right|_c. \quad (26)$$

Equation (25) shows that the new reference system for a joint analysis of physical and chemical feedbacks is the Earth acting as a blackbody, for which $\lambda_0 = 0.31$ K/W m⁻² [e.g., *Soden and Held*, 2006]. Equation (26) shows that c_{00} can be decomposed into various contributions. The first term on the RHS of (26) describes feedbacks related to changes in the planetary albedo with temperature, such as cloud and snow/ice feedbacks. The second term describes feedbacks related to changes in the emissivity with temperature, such as water vapor and atmospheric lapse rate feedback. The feedback parameters of each of these processes are continuously being refined by the climate modeling community. Most probable values are given by *Randall et al.* [2007] (see Table 5), and their summation leads to a value for c_{00} of 1.91 W m⁻²/K. (Note that with the latter value for c_{00} and $\lambda_0 = 0.31$ K/W m⁻², it follows from (21) that $\lambda_{cli} = 0.78$ K/W m⁻². That is practically equal to the climate sensitivity of the particular climate model used in our study, GISS GCM II', $\lambda_{cli} = 0.80$ K/W m⁻².)

[46] Finally, using equation (15), the atmospheric chemistry feedback parameter c_{che} can be calculated from the values for G_{che} obtained in the perturbation analyses and $\lambda_{cli} = 0.80$ K/W m⁻². This results in a value of -0.013 W m⁻²/K under the present-day chemical composition of the atmosphere, and 0.025 W m⁻²/K under a 2100 chemical composition. The gains G_{che} obtained in the perturbation analyses are those with respect to a reference system including the physical feedbacks. In order to calculate the gains with respect to the Earth as a blackbody, and be able to compare them with the gains of the physical feedbacks, we can use the values just obtained for c_{che} and plug them in equation (15) using $\lambda_0 = 0.31$ K/W m⁻², instead of $\lambda_{cli} = 0.80$ K/W m⁻². The result, shown in Table 5, is a gain of 0.996 under present-day chemical composition and 1.008

under 2100 chemical composition. Hence, a change in atmospheric chemical composition according to the A2 scenario might turn the atmospheric chemistry feedback from slightly negative to slightly positive.

[47] Table 5 shows how the values for the atmospheric chemistry feedback parameter and the corresponding gain are quite small compared to the parameters and gains of the known physical feedbacks: for example, atmospheric chemistry gains of 0.996 and 1.008, compared to gains of 2.26, 0.80, 1.28 and 1.09, for the water vapor, lapse rate, cloud and surface albedo feedback, respectively. While atmospheric chemistry is found to lead only to a minor feedback in the globally averaged climate system, chemical feedbacks on climate can be important regionally, owing to the unique features of ozone and aerosols in the climate system.

5. Summary and Conclusions

[48] We have developed a framework to analyze and quantify atmospheric chemistry-climate feedbacks. We do so by extending the familiar feedback analysis used in climate studies to include atmospheric chemistry.

[49] Feedbacks exist only when there is a full, i.e., two-way, coupling between climate and atmospheric chemistry; i.e., when a feedback loop is created (see Figure 1). Atmospheric chemistry creates a feedback in the climate system, and by the same token, climate creates a feedback in the atmospheric chemistry system.

[50] The analysis of the coupled climate-atmospheric chemistry system shows how each of these feedbacks consists of three factors. For instance, the atmospheric chemistry feedback in the climate system is determined by: (1) the change in chemical imbalance, per unit of temperature change (c_{10} in Figure 1); (2) the atmospheric chemistry sensitivity, λ_{che} ; and (3) the radiative imbalance per unit of chemical burden (c_{01}). Hence, the fact that a change in the global burden of a chemical compound leads to a large radiative imbalance (forcing) is a necessary, but not a sufficient, condition for a strong feedback of atmospheric chemistry on climate. For aerosols in particular, the hydrological sensitivity, i.e., the fractional change in precipitation per degree K warming, seems to play an important role in determining both the magnitude and sign of the atmospheric chemistry feedback. In the case of a positive hydrological sensitivity, absorbing aerosols like black carbon will dampen the climate (temperature) sensitivity, while scattering species like sulfate and nitrate aerosols will amplify the climate sensitivity. In the case of a negative hydrological sensitivity, the roles of absorbing and scattering aerosols will reverse.

[51] We use the framework to define a number of perturbation experiments with the CACTUS model, which simulates many, but not all, of the interactions of chemistry,

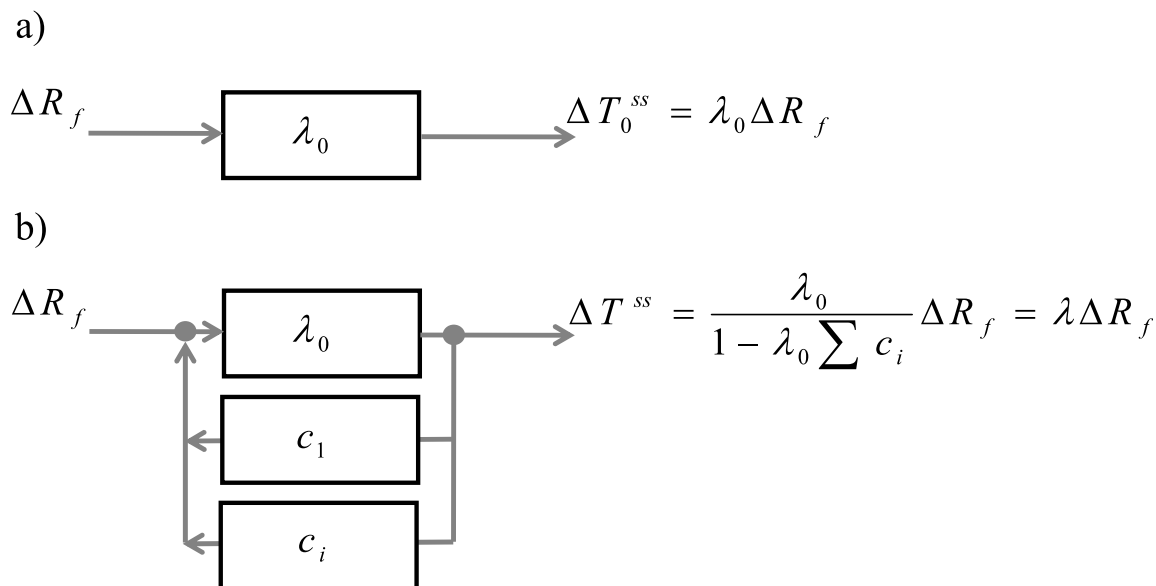


Figure A1. (a) Reference “open loop” system, that transforms a permanent perturbation (or forcing) of the input, ΔR_f , into a steady state change in the output, ΔT_0^{ss} . In climate science, the reference system is the Earth acting as a blackbody without feedbacks. (b) The “closed loop” system, including feedbacks. Fractions of the output, $c_1 \Delta T^{ss}$ and $c_i \Delta T^{ss}$, are fed back and added to the input ΔR_f .

aerosol, and climate within the GISS GCM II’ climate model. Radiative perturbations allow one to quantify the effect of atmospheric chemistry on climate sensitivity and to calculate an atmospheric chemistry feedback parameter that can be directly compared with the corresponding parameters of known physical feedbacks: the water vapor, cloud, lapse rate and surface albedo feedbacks. Chemical perturbations allow one to quantify the effect of climate on atmospheric chemistry sensitivity. The following conclusions can be drawn from these experiments.

[52] Within the context of our particular climate-atmospheric chemistry model (CACTUS), atmospheric chemistry has only a small effect on the climate sensitivity on a planetary scale. In the presence of the physical feedbacks, the climate sensitivity would be reduced by a factor of 0.99 and enhanced by a factor of 1.02, in an atmosphere with a 2000 and 2100, respectively, chemical composition. Locally, however, damping can be by as much as a factor 0.80 and amplification by as much as a factor 1.30. These values seem to be robust descriptors of the CACTUS model.

[53] Mainly because of the way the chemical perturbations were prescribed, it has not been possible to assess in a robust way the effect of climate on atmospheric chemistry sensitivity, for example, on the relationship between emissions and atmospheric burdens. The values obtained by experiments are indicative only of a significant climate feedback in the atmospheric chemistry system. In the case of aerosols, the global atmospheric burden of an individual species can be up to about 30% higher than expected from the emissions in a fixed climate; that is, the gain is about 1.3. For the total aerosol, the gain is about 1.1, globally, while, locally, it varies between about 0.8 and 1.4, over areas with strong air pollution. In the case of ozone, the gain is 0.99 globally, but up to 1.15 in the Northern Hemisphere, and down to 0.80 over the remote oceans. These results show the utility of a fully coupled model to describe the chemical

composition of an atmosphere. They show, in particular, that air pollution studies, considering changes in air pollutant emissions, must account for the fact that the resulting burdens can be significantly impacted by climate feedbacks. This confirms the conclusion, also arrived at by others [Feichter *et al.*, 2004; Liao *et al.*, 2009] that ongoing climate change might render air pollution control less effective.

[54] We stress once again that the quantitative results of our study should be viewed as preliminary for two reasons. The CACTUS model does not include all possible processes that could contribute to creating feedbacks. First and foremost, it does not consider the indirect radiative effects of aerosols through their effect on clouds and precipitation. It also does not consider the climate effect of changes in levels of sea salt and mineral dust through direct and indirect radiative effects, and we have not considered the longer-term climate feedback associated with methane perturbations. More comprehensive climate-atmospheric chemistry models will lead to different gains and feedback factors. Second, the results regarding climate feedbacks in the atmospheric chemistry system are expected to be dependent on the particular scenario used in performing the perturbations experiments in our study. Systematic perturbations by small changes in the emissions of one species or one group of species at a time are in order.

[55] The theoretical framework developed and applied here allows one to unravel various aspects of atmospheric chemistry-climate feedbacks and address them in a consistent way.

Appendix A: Block Diagram Analysis of Climate Feedbacks

[56] We follow the notation and much of the terminology of Roe [2009]. Consider, as a reference, the open loop system in Figure A1a. The system behaves in such a way

that a sustained perturbation of the input, ΔR_f , leads to a change in the output ΔT_0^{ss} . The equilibrium sensitivity parameter λ_0 of this system is defined by

$$\Delta T_0^{ss} \equiv \lambda_0 \Delta R_f. \quad (\text{A1})$$

We now consider the presence of a number of feedbacks as depicted in Figure A1b.

[57] The system relaxes to a new steady state at which

$$\Delta T^{ss} = \lambda_0 (\Delta R_f + \sum_i c_i \Delta T^{ss}). \quad (\text{A2})$$

The coefficients c_i are called the feedback parameters. The customary and inherent assumption is that feedbacks are linearly proportional to the system output, and that they are independent of one another. Solving (A2) for ΔT^{ss} gives

$$\Delta T^{ss} = \frac{\lambda_0}{1 - \lambda_0 \sum_i c_i} \Delta R_f. \quad (\text{A3})$$

Comparing equations (A1) and (A3) shows how, because of the feedback coupling, the sensitivity parameter has changed

$$\lambda_0 \xrightarrow{\text{coupling}} \lambda = \frac{\lambda_0}{1 - \lambda_0 \sum_i c_i} \quad \text{or} \quad \lambda_0^{-1} \rightarrow \lambda^{-1} = \lambda_0^{-1} - \sum_i c_i. \quad (\text{A4})$$

The second form of the equation highlights the additivity of the feedback parameters. In climate studies, λ_0^{-1} is often also called a feedback parameter.

[58] Another descriptor that follows from the feedback analysis is the gain G of the system, defined as the ratio of the output in the closed loop system, ΔT^{ss} , to the output in the reference system, ΔT_0^{ss} . By dividing (A3) by (A1), we obtain

$$G = \frac{\Delta T^{ss}}{\Delta T_0^{ss}} = \frac{\lambda}{\lambda_0} = \frac{1}{1 - \lambda_0 \sum_i c_i}. \quad (\text{A5})$$

The gain G results from the effect of all feedbacks acting in concert. The gain G_i for an individual feedback process is

$$G_i = \frac{1}{1 - \lambda_0 c_i}. \quad (\text{A6})$$

Appendix B: Treatment of Atmospheric Chemistry in the CACTUS Unified Model

[59] The gas-phase atmospheric chemical mechanism includes 225 chemical species and 346 reactions for simulating gas-phase species and aerosols. The partitioning of ammonia and nitrate between gas and aerosol phases is determined by the online thermodynamic equilibrium model ISORROPIA [Nenes *et al.*, 1998], and the formation of secondary organic aerosol from monoterpenes is based on equilibrium partitioning and experimentally determined yield factors [Chung and Seinfeld, 2002]. Note that the simulation of secondary organic aerosol does not include isoprene or more recent laboratory yields. Heterogeneous reactions considered in the model include those of N_2O_5 ,

NO_3 , NO_2 , and HO_2 on wet aerosols, the uptake coefficients are taken to depend on atmospheric temperature and relative humidity, as described by Liao and Seinfeld [2005]. Upper boundary layer conditions for O_3 and NO_x are applied at the tropopause (about 150 hPa) to represent transport across the tropopause, as described by Wang *et al.* [1998].

[60] The direct radiative effect of O_3 as well as that of internally mixed aerosols including sulfate, nitrate, ammonium, black carbon, and organic carbon is fed back into the GISS GCM-II'. Aerosol optical properties (extinction cross section, single-scattering albedo, and asymmetry factor) are calculated by Mie theory with a look-up table based on wavelength-dependent refractive indices and aerosol size distributions. Assumptions and parameters used for the calculations of aerosol optical properties are given by Liao *et al.* [2004]. Water uptake by sulfate/nitrate/ammonium aerosols is determined by the aerosol thermodynamic equilibrium module, ISORROPIA [Nenes *et al.*, 1998]. Water uptake by organic carbon aerosol follows the treatment of Chung and Seinfeld [2002]. The refractive index of internally mixed aerosols is calculated by volume-weighting of the refractive index of each aerosol species and water. It should be noted that the actual (unknown) mixing state of aerosols in the atmosphere depends on the aging and coagulation of aerosol particles, and to some extent internal and external mixtures coexist. In our work the refractive index of the internal mixture is calculated by volume weighting as in most previous studies, but such a linear combination may represent an oversimplification. Present-day global optical depths and single-scattering albedos predicted by this model have been evaluated by comparison with measurements from Liao *et al.* [2004].

[61] Biomass burning emissions are, in part, anthropogenic and, in part, natural. We assume in this study that biomass burning emissions remain unchanged in 2000 and 2100; the effect of climate change on the occurrence and intensity of wildfires is therefore not considered. The seasonal and geographical distributions of BC and POA emissions in year 2100 are obtained by scaling year 2000 monthly values, grid by grid, using projected changes in IPCC SRES A2 CO emissions. Climate-sensitive natural emissions, including lightning NO_x , NO_x from soil, biogenic hydrocarbons, sea salt, desert dust and dimethyl sulfide (DMS), are calculated as described by Liao *et al.* [2006]. Ozone and all aerosols, except sea salt and desert dust, affect the radiative balance in the model. Global and annual GHG concentrations and species emissions, for the years 2000 and 2100 are given in Table 2.

[62] **Acknowledgments.** This work was supported by the U.S. Environmental Protection Agency STAR Program (grant RD-83337001). Hong Liao acknowledges support from the National Science Foundation of China (grant 40775083). Frank Raes acknowledges support by the JRC Director General Sabbatical Programme.

References

- Athans, M., and P. L. Falb (1966), *Optimal Control*, McGraw-Hill, New York.
- Bony, S., *et al.* (2006), How well do we understand and evaluate climate change feedback processes?, *J. Clim.*, 19, 3445–3482, doi:10.1175/JCLI3819.1.
- Chen, W. T., H. Liao, and J. H. Seinfeld (2007), Future climate impacts of direct radiative forcing of anthropogenic aerosols, tropospheric ozone,

- and long-lived greenhouse gases, *J. Geophys. Res.*, *112*, D14209, doi:10.1029/2006JD008051.
- Chung, S. H., and J. H. Seinfeld (2002), Global distribution and climate forcing of carbonaceous aerosols, *J. Geophys. Res.*, *107*(D19), 4407, doi:10.1029/2001JD001397.
- Chung, S. H., and J. H. Seinfeld (2005), Climate response of direct radiative forcing of anthropogenic black carbon, *J. Geophys. Res.*, *110*, D11102, doi:10.1029/2004JD005441.
- Feichter, J., E. Roeckner, U. Lohmann, and B. Liepert (2004), Nonlinear aspects of the climate response to greenhouse gas and aerosol forcing, *J. Clim.*, *17*, 2384–2398, doi:10.1175/1520-0442(2004)017<2384:NAOTCR>2.0.CO;2.
- Forster, P., et al. (2007), Changes in atmospheric constituents and in radiative forcing, in *Climate Change 2007. The Physical Science Basis. Working Group I Contribution to the Fourth Assessment Report of the IPCC*, pp. 129–234, Cambridge Univ. Press, Cambridge, U. K.
- Grenfell, J. L., D. T. Shindell, D. Koch, and D. Rind (2001), Chemistry-climate interactions in the Goddard Institute for Space Studies general circulation model: 2. New insights into modeling the pre-industrial atmosphere, *J. Geophys. Res.*, *106*(D24), 33,435–33,451, doi:10.1029/2000JD000090.
- Hansen, J., A. Lacis, D. Rind, G. Russell, P. Stone, I. Fung, R. Ruedy, and J. Lerner (1984), Climate sensitivity: Analysis of feedback mechanisms, in *Climate Processes and Climate Sensitivity*, *Geophys. Monogr. Ser.*, vol. 29, edited by J. E. Hansen and T. Takahashi, pp. 130–163, AGU, Washington, D. C.
- Intergovernmental Panel on Climate Change (2000), *Emissions Scenarios. A Special Report of Working Group III of the Intergovernmental Panel on Climate Change*, edited by N. Nakicenovic et al., 599 pp., Cambridge Univ. Press, New York.
- Isaksen, I. S. A., and O. Hov (1987), Calculations of trends in the tropospheric concentrations of O₃, OH, and CH₄, *Tellus, Ser. B*, *39*, 271–285, doi:10.1111/j.1600-0889.1987.tb00099.x.
- Isaksen, I. S. A., et al. (2009), Atmospheric composition change: Climate-chemistry interaction, *Atmos. Environ.*, *43*, 5138–5192, doi:10.1016/j.atmosenv.2009.08.003.
- Kirkevåg, A., T. Iversen, J. E. Kristjansson, O. Seland, and J. B. Debernard (2008), On the additivity of climate response to anthropogenic aerosols and CO₂, and the enhancement of future global warming by carbonaceous aerosols, *Tellus, Ser. A*, *60*, 513–527.
- Kloster, S., F. Dentener, J. Feichter, F. Raes, U. Lohmann, E. Roeckner, and I. Fisher-Bruns (2010), A GCM study of future climate response to air pollution reductions, *Clim. Dyn.*, in press, doi:10.1007/s00382-009-0573-0.
- Knutti, R., and G. C. Hegerl (2008), The equilibrium sensitivity of the Earth's temperature to radiation changes, *Nat. Geosci.*, *1*, 735–743, doi:10.1038/ngeo337.
- Liao, H., and J. H. Seinfeld (2005), Global impacts of gas-phase chemistry-aerosol interactions on direct radiative forcing by anthropogenic aerosols and ozone, *J. Geophys. Res.*, *110*, D18208, doi:10.1029/2005JD005907.
- Liao, H., P. J. Adams, J. H. Seinfeld, L. J. Mickley, and D. J. Jacob (2003), Interactions between tropospheric chemistry and aerosols in a unified GCM simulation, *J. Geophys. Res.*, *108*(D1), 4001, doi:10.1029/2001JD001260.
- Liao, H., J. H. Seinfeld, P. J. Adams, and L. J. Mickley (2004), Global radiative forcing of coupled tropospheric ozone and aerosols in a unified general circulation model, *J. Geophys. Res.*, *109*, D16207, doi:10.1029/2003JD004456.
- Liao, H., W. T. Chen, and J. H. Seinfeld (2006), Role of climate change in global predictions of future tropospheric ozone and aerosols, *J. Geophys. Res.*, *111*, D12304, doi:10.1029/2005JD006852.
- Liao, H., Y. Zhang, W.-T. Chen, F. Raes, and J. H. Seinfeld (2009), Effect of chemistry-aerosol-climate coupling on predictions of future climate and future levels of tropospheric ozone and aerosols, *J. Geophys. Res.*, *114*, D10306, doi:10.1029/2008JD010984.
- Menon, S. (2004), Current uncertainties in assessing aerosol effects on climate, *Annu. Rev. Environ. Resour.*, *29*, 1–30, doi:10.1146/annurev.energy.29.063003.132549.
- Mickley, L. J., D. J. Jacob, B. D. Field, and D. Rind (2004), Climate response to the increase in tropospheric ozone since preindustrial times: A comparison between ozone and equivalent CO₂ forcings, *J. Geophys. Res.*, *109*, D05106, doi:10.1029/2003JD003653.
- Nenes, A., C. Pilinis, and S. N. Pandis (1998), ISORROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols, *Aquat. Geochem.*, *4*, 123–152, doi:10.1023/A:1009604003981.
- Prather, M. J. (1994), Lifetimes and eigenstates in atmospheric chemistry, *Geophys. Res. Lett.*, *21*, 801–804, doi:10.1029/94GL00840.
- Randall, D. A., et al. (2007), Climate models and their evaluation, in *Climate Change 2007. The Physical Science Basis. Working Group I Contribution to the Fourth Assessment Report of the IPCC*, pp. 590–662, Cambridge Univ. Press, Cambridge, U. K.
- Rind, D., J. Lerner, and C. McLinden (2001), Changes of tracer distribution in the doubled CO₂ climate, *J. Geophys. Res.*, *106*(D22), 28,061–28,079, doi:10.1029/2001JD000439.
- Roe, G. H. (2009), Feedbacks, timescales, and seeing red, *Annu. Rev. Earth Planet. Sci.*, *37*, 93–115, doi:10.1146/annurev.earth.061008.134734.
- Roe, G. H., and M. Baker (2007), Why is climate sensitivity so unpredictable?, *Science*, *318*, 629–632, doi:10.1126/science.1144735.
- Schwartz, S. E. (2007), Heat capacity, time constant, and sensitivity of the Earth's climate system, *J. Geophys. Res.*, *112*, D24S05, doi:10.1029/2007JD008746.
- Shindell, D. T., J. L. Grenfell, D. Rind, V. Grewe, and C. Price (2001), Chemistry-climate interactions in the Goddard Institute for Space Studies general circulation model: 1. Tropospheric chemistry model description and evaluation, *J. Geophys. Res.*, *106*(D8), 8047–8075, doi:10.1029/2000JD900704.
- Soden, B. J., and I. M. Held (2006), An assessment of climate feedbacks in coupled ocean-atmosphere models, *J. Clim.*, *19*, 3354–3360, doi:10.1175/JCLI3799.1.
- Unger, N., S. Menon, D. M. Koch, and D. T. Shindell (2009), Impacts of aerosol-cloud interactions on past and future changes in tropospheric composition, *Atmos. Chem. Phys.*, *9*, 4115–4129, doi:10.5194/acp-9-4115-2009.
- Wang, Y., D. J. Jacob, and J. A. Logan (1998), Global simulation of tropospheric O₃-NO_x-hydrocarbon chemistry: 1. Model formulation, *J. Geophys. Res.*, *103*(D9), 10,713–10,725, doi:10.1029/98JD00158.

W.-T. Chen, Jet Propulsion Laboratory, Pasadena, 4800 Oak Grove Dr., Pasadena, CA 91109, USA.

H. Liao, State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China.

F. Raes, Joint Research Centre, European Commission, I-21020 Ispra, Italy.

J. H. Seinfeld, Department of Chemical Engineering, California Institute of Technology, 1200 E. California Blvd., Mail Code 210-41, Pasadena, CA 91125, USA. (seinfeld@caltech.edu)