Understanding differences in upper stratospheric ozone response to changes in chlorine and temperature as computed using CCMVal-2 models

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[1] Projections of future ozone levels are made using models that couple a general circulation model with a representation of atmospheric photochemical processes, allowing interactions among photochemical processes, radiation, and dynamics. Such models are known as coupled chemistry-climate models (CCMs). Although developed from common principles and subject to the same boundary conditions, simulated ozone time series vary among models for scenarios for ozone depleting substances (ODSs) and greenhouse gases. Photochemical processes control the upper stratospheric ozone level, and there is broad agreement among CCMs in that ozone increases as ODSs decrease and temperature decreases due to greenhouse gas increase. There are quantitative differences in the ozone sensitivity to chlorine and temperature. We obtain insight into differences in sensitivity by examining the relationship between the upper stratospheric seasonal cycles of ozone and temperature as produced by fourteen CCMs. All simulations conform to expectation in that ozone is less sensitive to temperature when chlorine levels are highest because chlorine catalyzed loss is nearly independent of temperature. Analysis reveals differences in simulated temperature, ozone and reactive nitrogen that lead to differences in the relative importance of ozone loss processes and are most obvious when chlorine levels are close to background. Differences in the relative importance of loss processes underlie differences in simulated sensitivity of ozone to composition change. This suggests 1) that the multimodel mean is not a best estimate of the sensitivity of upper stratospheric ozone to changes in ODSs and temperature; and 2) that the spread of values is not an appropriate measure of uncertainty.

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1. Introduction

[2] Atmospheric models are used to interpret constituent observations and to predict the response of ozone to changes in composition, including the changes in stratospheric chlorine that have taken place due to release of man-made ozone depleting substances (ODSs). The Montreal Protocol and its amendments banned the production of many of these compounds beginning in 1996, and surface measurements of chlorofluorcarbons CFCl₃ and CF₂Cl₂ show that their atmospheric concentrations leveled off and began to decrease after the late 1990s [*Daniel and Velders et al.*, 2007]. The

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effects of ODSs are expected to be easiest to quantify in the upper stratosphere where photochemical processes control the ozone level. First efforts to identify the atmospheric response to the Montreal Protocol have focused on the upper stratosphere, and *Newchurch et al.* [2003] reported evidence that the upper stratospheric ozone had ceased to decline. Presently upper stratospheric ozone is expected to increase both because of the decline in ODSs and because greenhouse gases continue to increase, cooling the stratosphere and decreasing the rate of catalytic ozone destruction as noted in the *Scientific Assessment of Ozone Depletion: 2010 [WMO*, 2011; hereafter referred to as WMO2011]. Attribution of observed changes in ozone to changes in ODSs requires untangling the effects of ODSs from the effects of continuing increases in greenhouse gases [*Douglass and Fioletov et al.*, 2011].

[3] Projections of future ozone levels are now commonly made using models that couple a general circulation model (GCM) with a representation of atmospheric photochemical processes, allowing interactions among photochemical processes, radiation, and dynamics. Such models are known as coupled chemistry-climate models (CCMs) and were evaluated

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by the Stratospheric Processes and their Role in Climate (SPARC) -sponsored CCM validation (CCMVal) activity. Performance metrics related to model representation of processes identified in observations were agreed upon in a series of workshops. The SPARC Report on the Evaluation of Chemistry-Climate Models [SPARC CCMVal, 2010] describes in detail the successes and deficiencies of participating models. These models contributed simulations to WMO2011. Oman et al. [2010] analyzed the various projections using multiple linear regression (MLR) and reported broad agreement among models in that simulated ozone principally responds to two forcings: 1) prescribed surface mixing ratios for chlorine and bromine containing source gases that change the stratospheric amounts of chlorine and bromine; and 2) prescribed boundary conditions for greenhouse gases that result in stratospheric cooling. In spite of broad agreement, ozone sensitivity to chlorine change varies among models throughout the stratosphere. It is not surprising that model responses vary in the middle and lower stratosphere, where photochemical time scales become long and both photochemical and transport changes contribute to ozone change. However, even in the upper stratosphere where photochemical processes dominate, the computed ozone percentage changes, the year that the ozone mixing ratio returns to 1980 values, and the sensitivity of ozone to perturbations in chlorine and temperature vary among models.

[4] Inspired by the CCMVal exercises, increased attention is being given to application of performance metrics and best use of the wealth of observational information obtained from satellites, including instruments on the National Aeronautics and Space Administration (NASA) Upper Atmosphere Research Satellite (UARS) [Reber et al., 1993], European Space Agency Environmental Satellite (Envisat), the Canadian Scientific Satellite (SciSat) [Bernath et al., 2005] and the NASA satellite Aura [Schoeberl et al., 2006], in order to arrive at the best projection for twenty-first-century ozone. Waugh and Eyring [2008] assigned weights to projections of twenty-first-century total column ozone based on a set of performance metrics that quantify model representation of processes thought to be key to ozone evolution. In the Waugh and Eyring [2008] study the weighted mean was nearly the same as the unweighted mean of all of the models that participated in the exercise, in spite of obvious differences and deficiencies among models' representation of several important stratospheric processes. Strahan et al. [2011] focused on the transport evaluation of CCMVal-2 participant models, identifying four models with the most realistic transport that also performed well on the chemistry evaluation. The projections for total column ozone from these four models are more similar to each other than the ensemble of projections, and more similar than random selection of four simulations from the group of projections. The analysis by Strahan et al. [2011] identifies the models with credible transport but did not demonstrate a direct relationship between transport deficiencies and the rate of recovery for stratospheric ozone. In some models, deficiencies not directly related to transport affect simulated ozone recovery. Deficiencies that are identified in the CCMVal chemistry evaluation [SPARC CCMVal, 2010, chap. 6] include problems with partitioning among chlorine species, missing chemical reactions important to chlorine chemistry and lack of conservation for the total amount of chlorine released from

source gases whose mixing ratios are specified at the lower boundary.

[5] Similar physical concepts underlie the GCMs and photochemical representations that comprise the CCMVal-2 models. We note that the CCMVal chemistry evaluation states that all of the models contain a description of main chemical species of relevance for stratospheric ozone [SPARC CCMVal, 2010, chap. 6]. Because photochemical representations are similar, understanding why projections of ozone recovery differ is a step toward higher confidence in predictions. This paper focuses on the upper stratosphere, where the photochemical lifetimes of ozone, fluorocarbons, and other gases like N₂O are short, and the transport contribution to the ozone continuity equation is negligible. This paper relies on the well-developed conceptual model for the photochemical processes that control ozone as described below, focusing on the relationship between upper stratospheric ozone and temperature. Our focus on upper stratospheric ozone and temperature follows from previous theoretical studies and analysis of observations. Stolarski and Douglass [1985] developed a parameterization that shows how the sensitivity of ozone to temperature that is due to the temperature dependence of ozone loss varies depending on the relative contributions of recombination of atomic oxygen and ozone and the other catalytic cycles to net ozone loss. Douglass and Rood [1986] analyzed ozone and temperature observations obtained from the Limb Infrared Monitor of the Stratosphere (LIMS) experiment on Nimbus 7 [Gille and Russell, 1984], concluding that ozone would become less sensitive to temperature as chlorine increased. Chandra et al. [1995] reported a 10%–25% per decade decrease in the amplitude of the ozone seasonal cycle at 2 hPa middle latitudes in both hemispheres due to chlorine increase using ozone observations from 1979–1993. We show below although the upper stratospheric ozone sensitivity to temperature as quantified for each CCMVal-2 model decreased as anthropogenic chlorine increased and will increase as chlorine returns to unperturbed levels, there are quantitative differences in the sensitivity of simulated ozone to temperature. We investigate differences in the ozone sensitivity to temperature as obtained from the different CCMVal-2 models, focusing on their cause. Our intent is to show how this relationship and its behavior in the past and present atmosphere provide insight into the differences in predicted upper stratospheric ozone levels in the twenty-first century [Bekki and Bodeker et al., 2011].

[6] We present the conceptual model for upper stratospheric ozone in Section 2. Section 3 describes the CCMVal models (listed in Table 1) and the simulations that are analyzed using this conceptual model. Results are given in section 4, with discussion and conclusions in section 5.

2. Conceptual Model for Upper Stratospheric Ozone

[7] This section has two principle goals. The first is to illustrate the approach used in *Stolarski and Douglass* [1985] (hereafter referred to as SD1985) to show how different ozone loss processes contribute to the sensitivity of ozone to temperature and to the seasonal cycle of the zonal mean ozone. The second is to extend the work of SD1985 to show how change in the contribution of chlorine to upper stratospheric ozone loss alters the seasonal cycle.

 Table 1. CCMVal Models With a Vertical Domain Including the

 Upper Stratosphere and Also Submitted Future Simulations for

 the 2010 CCMVal Report and for WMO [2011].

Model	Reference
AMTRAC3	Austin and Wilson [2010]
CCSRNIES	Akiyoshi et al. [2009]
CMAM	Scinocca et al. [2008]; de Grandpré et al. [2000]
CNRM-ACM	Déqué [2007]; Teyssèdre et al. [2007]
GEOSCCM	Pawson et al. [2008]
LMDZrepro	Jourdain et al. [2008]
MRI	Shibata and Deushi [2008a, 2008b]
Niwa-SOCOL	Schraner et al. [2008]
SOCOL	Schraner et al. [2008]
ULAQ	Pitari et al. [2002]
UMSLIMCAT	Tian and Chipperfield [2005]; Tian et al. [2006]
UMUKCA-METO	Davies et al. [2005]; Morgenstern et al. [2009]
UMUKCA-UCAM	Davies et al. [2005]; Morgenstern et al. [2009]
WACCM	Garcia et al. [2007]

2.1. Temperature Dependence of Ozone Loss

[8] In the upper stratosphere, the time scales for formation of ozone from atomic oxygen and oxygen molecules $(O + O_2 \xrightarrow{M} O_3)$, where M is a third body) and photolysis of ozone $(O_3 + hv \rightarrow O_2 + O)$ are short compared to the time scales for reactions such as recombination of atomic oxygen and ozone $(O + O_3 \rightarrow 2O_2)$ and catalytic cycles involving nitrogen, hydrogen and chlorine radicals that have the same net effect. Bromine radicals play a minor role in the upper stratosphere and are neglected [e.g., Holloway and Wayne, 2010, Figure 9.2]. It is convenient to define odd oxygen as the sum of ozone and ground state atomic oxygen, using fast photochemical reactions to define their ratio $(O/O_3 \cong J_{O3})$ $(K_{O, O2, M}O_2M)$, and consider the production and loss to be the reactions that control their sum. Odd oxygen is produced by photolysis of molecular oxygen and destroyed by the recombination reaction mentioned above.

[9] We focus on the middle latitude upper stratosphere near 2 hPa for the following reasons: 1) the amplitude of the seasonal cycle in ozone is driven by the seasonal cycle in temperature [*Stolarski et al.*, 2012]; 2) analysis of observations showed that the amplitude of the seasonal cycle in ozone decreased between 1979 and 1993, a period of chlorine increase [*Chandra et al.*, 1995]; 3) the peak-to-peak amplitude of the middle latitude seasonal cycle in temperature in the CCMVal-2 models is about 30 K, similar to that observed; 4) photochemical time scales are short enough that transport terms can be neglected when considering perturbations of ozone and temperature from their annual zonal means; 5) ozone is nearly equal to odd oxygen. The continuity equation for odd oxygen can be written

$$\frac{\partial \gamma_{OX}}{\partial t} = P - L,\tag{1}$$

where $\gamma_{OX} = \gamma_{O3} + \gamma_O$ is the odd oxygen mixing ratio, *t* is the time, *P* is production and *L* is odd oxygen loss. Chapter 6 of the CCMVal report includes a comparison of the photolysis rates as determined by several chemistry-climate models. The values for the photolysis rate of molecular oxygen (*J*_{O2}) are not constant across the CCMVal-2 models that participated in this exercise; differences in production are likely responsible for some part of the differences in the simulated ozone mixing ratio. As will be shown below, the ozone sensitivity to temperature also varies with ozone mixing ratio. However, differences in photolysis will be insensitive to changes in composition, and it is possible to understand much of the variation in the diagnosed response of model-computed ozone to changes in chlorine and temperature by focusing on the loss terms as will be shown in section 4. Assuming small perturbations in the ozone mixing ratio (γ_{OX}) and temperature (T), assuming balance between production and loss (P \cong L), and neglecting perturbations to the production term, the continuity equation becomes

$$\frac{\partial \gamma'_{OX}}{\partial t} = -\frac{\partial L}{\partial \gamma_{OX}} \gamma'_{OX} - \frac{\partial L}{\partial T} T'$$
(2)

or

$$\frac{\partial \gamma'_{OX}}{\partial t} = -\Gamma \gamma'_{OX} - \Theta T', \qquad (3)$$

where $\Theta \equiv \partial L / \partial T$ and $\Gamma \equiv \partial L / \partial \gamma_{OX}$, following the notation of SD1985. Equation (3) reduces to $\gamma'_{OX} = -\frac{\Theta}{\Gamma}T'$ when the perturbation does not vary with time. The inverse relationship between ozone and temperature is found because loss processes for ozone are more efficient at warmer temperatures. In early observational studies such a relationship between ozone and temperature was broadly interpreted to indicate dominance of photochemical processes over transport processes [Wang et al., 1983; Nagatani and Miller, 1984]. Rood and Douglass [1985] showed that spatial perturbations in temperature produced by wave motions could lead to an inverse correlation between ozone and temperature through photochemical processes, but, depending on the horizontal gradients in odd oxygen, these wave motions could also necessitate accounting for transport terms. Here we focus on the relationship between $\gamma' = \gamma - \bar{\gamma}$ and T' = $T - \overline{T}$ where the overbar indicates annual zonal average and γ' and T are deviations of the zonal means from their annual average values.

[10] The relationship between ozone and temperature provides information about the mix of cycles contributing to ozone loss. Barnett et al. [1975] pointed out that the temperature dependence of equilibrium ozone concentration as derived from observations could be compared with that expected based on the mix of loss processes associated with the different catalytic schemes for photochemical loss that were being considered at that time. SD1985 built on the use of rate limiting steps for the catalytic cycles important to ozone destruction as discussed by Johnston and Podolske [1978] to develop a parameterization with explicit representation of catalytic loss processes. For convenience, the rate-limiting reactions for odd oxygen loss and the rate constant data for two-body reactions from Sander et al. [2011] are given in Table 2. The reaction rates are computed using the Arrhenius expression $k = A \exp(-E/RT)$. In addition to the temperature dependence of the rate limiting reaction, the photochemical reactions that control partitioning within a chemical family contribute to the total temperature dependence of each loss process as discussed in detail in SD1985. We provide the derivation of the temperature sensitivity of ozone due to the Chapman cycle at equinox as

Table 2. The Rate-Limiting Reactions for Odd Oxygen Lossand the Rate Constant Data for Two-Body Reactions From Sanderet al. [2011]

Chemical Family	Rate-Limiting Reactions	A-factor	E/R
Oxygen	$O + O_3$	8.0×10^{-12}	2060
Nitrogen	$O + NO_2$	5.0×10^{-12}	-210
Hydrogen	O + OH	1.8×10^{-11}	-180
	$O + HO_2$	3.0×10^{-11}	-200
	$O_3 + HO_2$	1.7×10^{-12}	940
	$H + O_2 + M$ (3-body reaction)		
Chlorine	O + CIO	2.8×10^{-11}	-85

an example. The 24-h average odd oxygen loss per molecule can be written

$$Loss_{OX} = 2k_{O,O3} \left(\frac{1}{2} [O]_D [O_3]_D\right) / [M].$$
(4)

[11] Here the 1/2 is the fraction of day at equinox and the 2 indicates two odd oxygen molecules lost per reaction. In this and following equations reaction rates k are subscripted by the reactants, photolysis rates are subscripted by the molecule that is being photolyzed, and the subscript D indicates the daytime average. Nighttime loss is negligible. Assuming that daytime rates of ozone photolysis and O atom recombination are in balance, the ratio $[O]_D/[O_3]_D$ can be written

$$[O]_D / [O_3]_D = 2J_{O3} / (k_{O,O2,M}[O_2][M]) \equiv R.$$
(5)

[12] The ratio is defined R for convenience. Using the definition of odd oxygen $O_x = O_3 + O$ and the rapid disappearance of atomic oxygen at night below 70 km, the expression for loss becomes

$$Loss_{OX} = k_{O,O3}[M] \frac{R}{(1+R)^2} (\gamma_{OX})^2.$$
 (6)

[13] The contribution to the temperature dependence from recombination of atomic oxygen and ozone is the partial derivative of equation (6):

$$\Theta_{OX} = \partial Loss_{OX} / \partial T = \left(\frac{2060}{T^2} + \frac{3.4}{T} - \frac{8.8R}{(1+R)T}\right) k_{O,O3} \frac{R}{(1+R)^2} \gamma_{OX}^2.$$
(7)

[14] An important aspect of equation (7) is that at 2 hPa and typical stratospheric temperatures the first two terms inside the parentheses contribute to Θ_{OX} . The first term (2060/ T^2) is the direct temperature dependence due to the rate limiting reaction and the second term (3.4/T) is the implicit temperature dependence of R. The third term is less important at this pressure because R is small compared to 1.

[15] The SD1985 approach, taken for all four loss processes, emphasizes that recombination of O and O_3 and the catalytic loss cycles associated with hydrogen, chlorine and nitrogen species all contribute to Γ , the loss frequency (inverse of the photochemical lifetime). These loss processes also make different contributions to the overall sensitivity of ozone to temperature. Following SD1985

$$Loss = Loss_{OX} + Loss_{NOX} + Loss_{HOX} + Loss_{CLX}$$
(8)

$$\Gamma = \frac{\partial Loss_{OX}}{\partial \gamma_{OX}} + \frac{\partial Loss_{NOX}}{\partial \gamma_{OX}} + \frac{\partial Loss_{HOX}}{\partial \gamma_{OX}} + \frac{\partial Loss_{CIX}}{\partial \gamma_{OX}}$$
$$= \Gamma_{OX} + \Gamma_{NOX} + \Gamma_{HOX} + \Gamma_{CIX}, \tag{9}$$

$$\Theta = \frac{\partial Loss_{OX}}{\partial T} + \frac{\partial Loss_{NOX}}{\partial T} + \frac{\partial Loss_{HOX}}{\partial T} \frac{\partial Loss_{CIX}}{\partial T}$$
$$= \Theta_{OX} + \Theta_{NOX} + \Theta_{HOX} + \Theta_{CIX}.$$
(10)

[16] At 2 hPa middle latitudes the losses due to reactions involving nitrogen, hydrogen and chlorine are comparable to each other and larger than the loss due to recombination of atomic oxygen and ozone [e.g., *Holloway and Wayne*, 2010, Figure 9.2].

[17] The ratio Θ/Γ is the sensitivity of ozone to temperature; this ratio quantifies the linear relationship between γ'_{OX} and T' and depends on the balance of loss processes. At 2 hPa, accounting for the explicit and implicit contributions to $\partial Loss_{OX}/\partial T$, the reaction $O + O_3$ makes the largest contribution to the $\partial Loss_{OX}/\partial T$. As shown in SD1985, implicit terms that arise from the temperature dependence of the ratio of atomic oxygen to ozone and that of reactions that control partitioning among family members like nitric oxide (NO) and nitrogen dioxide (NO_2) make the largest contributions to $\partial Loss_{NOx}/\partial T$ and $\partial Loss_{HOx}/\partial T$. The catalytic cycle involving chlorine makes the smallest contribution to Θ due to weak temperature dependence of the rate limiting reaction and of the reactions that control partitioning among chlorine radicals in the upper stratosphere. For each loss process the explicit dependence on the odd oxygen mixing ratio γ_{ox} makes the largest contribution to the partial derivatives of the loss terms with respect γ_{ox} as given in (9).

[18] This approach shows that a model with higher ozone levels will be more sensitive to temperature and have a larger amplitude seasonal cycle than a model with lower ozone and the same amplitude seasonal cycle in temperature because $O + O_3 \rightarrow 2O_2$ will be more important in (8) and the contribution of $\partial Loss_{OX}/\partial T$ to $\partial Loss/\partial T$ is proportional to γ_{OX}^2 as shown in (7) [SD1985]. The greater sensitivity follows directly from higher ozone levels regardless of the cause, which could be greater production, cooler temperature leading to less total loss, or smaller contributions from other catalytic cycles due to lower mixing ratios for nitrogen, hydrogen or chlorine radicals.

[19] A similar approach can be taken to understand the sensitivity of ozone to chlorine change and why it may vary among models that include the same set of photochemical reactions. Transport of source gases including chlorofluor-carbons, nitrous oxide and methane, destruction of the source gases to produce radicals, and processes that control the amount of water vapor entering the stratosphere contribute to the mix of species in the upper stratosphere middle latitudes. Differences in this mix of species or differences in the background temperature contribute to differences in the computed

ozone mixing ratio. The ozone response to composition change such as the increase and decrease of anthropogenic chlorine will depend on the change in the balance of loss processes relative to the balance of processes in the unperturbed (base) state. Note that for the upper stratosphere ozone production is nearly equal to loss, so the net loss is similar in both the perturbed and base states. An increase in the chlorine contribution to loss changes partitioning among short-lived species and causes ozone and atomic oxygen to decrease such that the net loss is nearly unchanged. The fractional contributions of other loss processes to the balance of loss processes affect ozone sensitivity to chlorine change. For example, for models that produce the same upper stratospheric temperature, a simulation in which the nitrogen loss cycle is more important will be less sensitive to chlorine change than a simulation in which the nitrogen loss cycle is less important. We do not consider changes in photolysis of molecular oxygen due to change in overhead column ozone because such effects are minimal for small changes in composition.

[20] These concepts have been applied broadly. Observational and theoretical studies discuss the dependence of the modeled response on the simulated mix of loss processes [e.g., Douglass et al., 1985; Douglass and Rood, 1986; Froidevaux et al., 1989; Smith, 1995]. Such a linear relationship has been used in simulations to study the response of ozone to temperature variations due to planetary waves [e.g., Hartmann and Garcia, 1979; Randel, 1993; McCormack et al., 2006]. Hood and Douglass [1988] applied the same formalism to the ozone and temperature responses to shortterm variation in solar ultraviolet radiation. Chandra et al. [1993] compared the seasonal variation of ozone as observed by Solar Backscatter Ultraviolet radiometers with that simulated using a two-dimensional model with specified temperatures, noting that the observations and model were in better agreement if the chlorine catalyzed ozone loss was less important. At that time this work supported the conjecture that products of the reaction ClO + OH included HCl + O_2 in addition to $Cl + HO_2$. The HCl product channel reduces *ClO* relative to total inorganic chlorine (Cl_y) in the upper stratosphere, thereby reducing the importance of chlorine-catalyzed loss and increasing the sensitivity of ozone to the seasonal cycle in temperature. DeMore et al. [1994] pointed out that although uncertainties in all studies at that time allowed for the zero yield of HCl, none of the experiments could exclude the possibility of an atmospherically significant HCl yield. Laboratory experiments resolved the question by directly measuring the production of HCl [Lipson et al., 1999] and provide the branching ratio for this experiment that is used in current models [Sander et al., 2011].

2.2. Consequence of Chlorine Change for the Temperature Dependence of Ozone Loss

[21] The relationship between ozone and temperature can also be used to show how the mix of loss processes changes due to composition change. *Douglass and Rood* [1986] used 1979 data from the Limb Infrared Monitor of the Stratosphere (LIMS) to derive photochemical information from the spatial perturbations in ozone and temperature, suggesting that the ozone sensitivity to temperature would decrease as chlorine increased in importance. *Chandra et al.* [1995] show that at 2 hPa middle latitudes the observed seasonal amplitude of ozone decreased as chlorine increased. *Stolarski et al.* [2012] argue that observed changes in the sensitivity of ozone to temperature as chlorine decreases are useful in attribution studies to separate two mechanisms that are expected to increase upper stratospheric ozone: anthropogenic chlorine decrease and reduced loss as a result of cooling due to greenhouse gas increase on ozone.

[22] We extend the SD1985 formalism to derive an expression that shows how the sensitivity of ozone to temperature will change due to changes in anthropogenic chlorine, ozone and increases in greenhouses gases that cool the stratosphere. It is conceptually straightforward but algebraically complex to compute the dependence of Γ and Θ on changes in ozone, temperature and chlorine (γ_{OX} , T and γ_{Cl}) by differentiating the expressions for Γ and Θ found in SD1985. The contribution of Θ_{CIX} to Θ is small compared to contributions from other loss terms because chlorine catalyzed loss is nearly independent of temperature, thus the derivative of Θ with respect to γ_{Cl} is zero and only the derivatives with respect to γ_{OX} and T contribute. For Γ all three derivatives must be considered. Because we are focused on the upper stratosphere near 2 hPa where the effects of chlorine change are significant and the seasonal cycle of ozone is driven by the seasonal cycle in temperature, we keep only the leading terms that contribute to Γ and Θ , ignoring terms that couple loss cycles through interference reactions that are important in the middle and lower stratosphere. After differentiating and rearranging, we obtain the following expressions for the logarithmic derivative of Θ due to changes in temperature and odd oxygen mixing ratio:

$$\frac{\Delta\Theta}{\Theta} = \left\{ \frac{\Theta_{OX}}{\Theta} \left(\frac{2060}{T} - 4120 \right) + 2.4 \frac{\Theta_{NOX}}{\Theta} \right\} \frac{\Delta T}{T} + \left\{ \frac{2\Theta_{OX} + \Theta_{NOX} + \Theta_{HOX}}{\Theta} \right\} \frac{\Delta\gamma_{OX}}{\gamma_{OX}}.$$
 (11)

[23] It is straightforward to show the first term on the right, the contribution due to the fractional change in temperature, is small compared with the second term, the contribution due to the fractional change in odd oxygen mixing ratio that is primarily due to chlorine change. Noting that $\Theta \approx \Theta_{OX} + \Theta_{NOX} + \Theta_{HOX}$, equation (11) is approximated

$$\frac{\Delta\Theta}{\Theta} \cong \left\{ 1 + \frac{\Theta_{OX}}{\Theta} \right\} \frac{\Delta\gamma_{OX}}{\gamma_{OX}}.$$
(12)

[24] The implicit dependence of hydrogen catalytic loss cycles on the odd oxygen mixing ratio described in detail in SD1985 complicates the expression that is obtained by differentiating the expressions for Γ . However, for the limited altitude domain considered here the direct dependence on the odd oxygen mixing ratio is most important for all of the loss processes, and the expression for the logarithmic derivative of Γ is approximated

$$\frac{\Delta\Gamma}{\Gamma} \cong \left\{ \left(1 + \frac{\Gamma_{OX}}{\Gamma} \right) \frac{\Delta\gamma_{OX}}{\gamma_{OX}} + \frac{\Gamma_{CL}}{\Gamma} \frac{\Delta\gamma_{CL}}{\gamma_{CL}} \right\}.$$
 (13)

[25] The ratio Γ_{OX}/Γ appears in the term in parenthesis because the $Loss_{OX}$ depends on the square of the odd oxygen mixing ratio. We combine equations (12) and (13) to obtain a remarkably simple expression for the logarithmic derivative of Θ/Γ :

$$\frac{\Delta(\Theta/\Gamma)}{\Theta/\Gamma} \cong \left[\frac{\Theta_{OX}}{\Theta} - \frac{\Gamma_{OX}}{\Gamma}\right] \frac{\Delta\gamma_{OX}}{\gamma_{OX}} - \frac{\Gamma_{Cl}}{\Gamma} \frac{\Delta\gamma_{Cl}}{\gamma}.$$
 (14)

[26] For convenience in the remainder of the paper we define the ozone sensitivity to temperature as $S = -\Theta/\Gamma$ and $\frac{\Delta(\Theta/\Gamma)}{\Theta/\Gamma} = \frac{\Delta S}{S}$. The first term on the right in (14) depends on the contribution of $O + O_3 \rightarrow 2O_2$ to the net ozone loss compared with other cycles. The contributions of Θ_{OX} to temperature sensitivity and Γ_{OX} to loss frequency (inverse lifetime) are greater when this process is more important to net loss and vice versa. At 2 hPa the quantity in brackets is always positive and less than 1 since $O + O_3$ is more important to the temperature sensitivity than to inverse lifetime. The absolute contribution of the second term is the same sign as the first term, since the sign of $\frac{\Delta \gamma_{OX}}{\gamma_{OX}}$ is opposite to the sign of $\frac{\Delta \gamma_{CI}}{\gamma_{CI}}$. The above analysis shows that *S* is expected to vary with chlorine change. Furthermore, for a given model i, the fractional change in the ozone sensitivity to temperature $\Delta S_i/S_i$ depends on the importance of odd oxygen loss relative to the other loss processes (first term in (14)) and on the importance of chlorine loss to the total loss (second term in (14)). Note that (14) was derived for small perturbations, and the perturbation to chlorine from the early 1960s to the late 1990s is not small. We evaluate these terms in Section 4, focusing on periods during which inorganic chlorine varies within 12.5% of a base level of 2 ppbv (1.75-2.25 ppbv).

3. Models and Data

3.1. CCMVal Models

[27] Morgenstern et al. [2010] present a detailed overview of the models that participated in the CCMVal-2 assessment. These models contributed simulations that are evaluated in the CCMVal report [SPARC CCMVal, 2010] and which are used in chapters 2 and 3 of WMO2011: Stratospheric ozone and surface ultraviolet radiation [Douglass and Fioletov et al., 2011], and Future ozone and its impact on surface UV [Bekki and Bodeker et al., 2011]. Eighteen groups contributed simulations to CCMVal-2, but for this analysis we include only the fourteen models that contributed a future scenario simulation whose vertical domain includes the upper stratosphere. These models are listed in Table 1. The future scenario (referred to as REF-B2) uses the A1B greenhouse gas scenario from the Intergovernmental Panel on Climate Change [2000] and the revised A1 halogen scenario from WMO [2007] and SPARC CCMVal [2010]. Most models have simulations that cover 1960–2099 with 10-year model spin-up prior to 1960. The Unified Model/United Kingdom Chemistry Aerosol Community Model - Met Office (UMUKCA-METO) is an exception in that their future simulation ends in 2083. Morgenstern et al. [2010] and Oman et al. [2010] provide details about the scenarios and the other inputs to these simulations.

3.2. Data

[28] The primary intent of this paper is to demonstrate that many of the differences in simulated upper stratospheric ozone can be interpreted and understood. We make no attempt to identify 'best' simulations that agree with one or more sets of observations. However, it is useful to include some observations that show the seasonal cycles in upper stratosphere ozone and temperature in order to establish a context for discussion. Data shown here are from two sources, the Microwave Limb Sounder (MLS) on the Aura satellite [*Waters et al.*, 2006], and from the Halogen Occultation Experiment (HALOE) on the Upper Atmosphere Research Satellite (UARS) [*Russell et al.*, 1993].

[29] MLS began measurements in August 2004 and continues to measure profiles of a suite of constituents important to the stratosphere. Here we consider only ozone and temperature. According to the data quality document [*Livesey et al.*, 2011], MLS V3.3 ozone accuracy at 2 hPa is 5%. The accuracy of the temperature profiles is estimated to be a few degrees. For our comparisons we use the MLS annual mean \pm 2 K. As will be shown below the maximum difference among simulated values for the annual mean temperature during the MLS era is about 25 K, much larger than any realistic estimate of accuracy derived from comparisons with other temperature estimates.

[30] HALOE measured profiles of a suite of constituents of stratospheric importance from late 1991 until late 2005 using solar occultation. We use sunset HALOE profiles of nitric oxide (*NO*) and nitrogen dioxide (*NO*₂) to estimate the total reactive nitrogen (*NO*_Y) at 2 hPa for middle latitudes. *Gordley et al.* [1996] discuss validation of these constituents. Because *NO*_Y varies temporally and because HALOE sampling is not uniform, we obtain an estimate for annually averaged *NO*_Y from HALOE but consider simulated values within 1–2 parts per billion of the HALOE estimate to be equally possible.

4. Results

4.1. Simulated Ozone Sensitivity to Changes in Chlorine and Temperature

[31] In the midlatitude upper stratosphere, the annual means of zonal mean ozone and temperature vary markedly among the CCMVal models. These mean values exhibit similar temporal behavior to each other for 1960–2100, but significant biases among the models persist throughout the integration. Time series of annual mean ozone and temperature that are typical for the upper stratosphere are shown in Figure 1 for 50°N, 2 hPa. In 1960, stratospheric chlorine was close to its natural level, and simulated ozone varies among models both due to differences in the photolysis of molecular oxygen that controls odd oxygen production and due to differences in loss (i.e., differences in levels of reactive odd nitrogen and hydrogen that affect catalytic loss cycles directly and also differences in temperature that affect loss through the temperature dependence of photochemical reactions). The black crosses on each panel show the MLS 2005-2009 mean values interpolated to 2 hPa. The horizontal extent of the crosses are the four years that are used to obtain the mean value. The vertical extent is the estimate of MLS accuracy.



Figure 1. Time series for annual zonal mean (a) ozone mixing ratio and (b) temperature at 50°N 2 hPa from the CCMVal models listed in Table 1. In both panels the large cross indicates the four-year mean obtained from MLS observations.

[32] Chapter 3 of *SPARC CCMVal* [2010] discusses temperature biases and their possible relationship to biases in ozone and water vapor, concluding that deficiencies in the radiation codes are the main driver of temperature differences. For the CCMs used here, higher ozone levels are associated with lower temperatures, consistent with the conclusion that the temperature biases indicate differences in the radiative part of the CCMs. The range of temperature and ozone values obtained from the CCMVal-2 models for identical boundary conditions provides an opportunity to test the conceptual model described in the first half of section 2. Figure 1 shows that the CCM with the lowest temperatures in the upper stratosphere produces the highest ozone values and that the CCMs with the warmest temperatures tend to produce lower ozone values.

[33] We test the conceptual model by calculating the differences of each model from the 1960 multimodel mean, $\Delta T = T_i - \overline{T}^{MM}$ and $\Delta \gamma = \gamma_i - \overline{\gamma}^{MM}$ where the subscript *i* represents a single model, and overbar with superscript MM indicates the multimodel mean. These differences are anticorrelated, with r² of -0.74, suggesting that the temperature

differences are responsible for part of the spread in the simulated ozone values. To test if this interpretation quantitatively follows the conceptual model, we obtain values for the sensitivity of ozone to temperature $(S_i = -(\Theta/\Gamma)_i)$ for each model using linear regression to relate the seasonal cycles in ozone and temperature. This approach yields a measure of the ratio Θ/Γ but these parameters cannot be obtained independently in this manner. We use these coefficients to estimate how much of the difference from the multimodel mean is explained by the simulated sensitivity to temperature and the temperature difference relative to the multimodel mean. The ozone differences from the multimodel mean expected from temperature differences $(S_i \Delta T)$ are compared with the ozone differences from the multimodel mean ($\Delta \gamma_{OX}$) in Figure 2. This comparison shows that much of the variation in ozone among the CCMVal-2 models is a result of the differences in temperature. The results in Figure 2 are similar whether using values for S_i that are obtained from the ozone and temperature seasonal cycles or by obtaining the ozone sensitivity to chlorine and to temperature simultaneously by applying multiple linear



Figure 2. (left) The 1960 50°N 2 hPa ozone difference from the multimodel mean ($\gamma_{O3} - \gamma_{O3}^{MM}$, y axis) is approximated for each model by its sensitivity of ozone to temperature multiplied by the temperature difference from the multimodel mean ($\partial\Gamma_{O3}/\partial T * (T - T^{MM})$, x axis). In both panels points for each model are colored according to the annually averaged local NO_Y mixing ratio. HALOE indicates $\sim 12 \pm 1-2$ ppbv for annual zonal mean for NO_Y at 50°N, 2 hPa (all shades of green for this color scale). (right) Simulated values for 2006 annual mean temperature and ozone at the same location also show the association of cooler temperature with higher ozone and vice versa. The large cross indicates annual mean ozone and temperature calculated from MLS observations for 2005–2010; the size of the cross indicates estimated accuracies.

regression (MLR) to the entire time series as done by *Oman et al.* [2010]. The disadvantage of using MLR is that this approach cannot separate the dependence of the ozone sensitivity to temperature on chlorine level.

[34] The spread in computed ozone values in 1960 is greater than 2 ppmv; the multimodel mean and standard deviation are 5.51 and 0.55 ppmv respectively. The standard deviation in ozone values after accounting for the temperature difference is reduced to 0.34 ppmv. The individual model sensitivity to temperature times the difference in each model temperature from the multimodel mean accounts for about half of the spread in 1960 ozone values. The largest differences from multimodel mean ozone are nearly equal to those expected from the temperature difference and derived sensitivity of ozone to temperature. The correlation between $\Delta \gamma_{OX}$ and $S_i \Delta T$ is greater than the correlation between $\Delta \gamma_{OX}$ and ΔT , supporting the conclusion that differences in the mix of loss processes contribute to the spread in ozone values shown in Figure 1. We illustrate the difference in loss processes by coloring the points in Figure 2a according to the local mixing ratio for total reactive nitrogen (NO_Y) . The points with low values of NO_Y tend to appear on the high side of the 1:1 line, thus larger ozone anomalies are consistent with lower temperatures, and less loss due to the nitrogen loss cycle. The converse is also true. The mixing ratio for water also varies among models, contributing to different levels of hydrogen radicals, but the hydrogen loss cycles are less important than the nitrogen loss cycle at this altitude (SD1985).

[35] It is useful here to notice how well the various models reproduce observed values for ozone, temperature, and NO_{Y} . Figure 2b is a scatterplot for 2006 simulated temperature versus ozone mixing ratios for 50°N at 2 hPa. The cross indicates values for these quantities computed from measurements obtained within 2 degrees latitude by the Aura MLS. Several thousand profiles contribute to the mean, thus the standard error of the mean is miniscule. The height and width of the cross reflect the estimates of accuracy as discussed above. Figure 2b also supports the statements above that the simulated ozone levels are higher for lower temperatures and vice versa. Even in 2006, when the upper stratospheric ozone is less sensitive to temperature due to the importance of the chlorine catalyzed loss cycle, the models with lower temperatures tend to have higher ozone and vice versa

[36] Although *NOy* varies temporally in all of the models, the effect of the temporal increase in the boundary condition for nitrous oxide (N_2O) , the source of nitrogen radicals) is opposed by the effect of cooling temperatures [Rosenfield and Douglass, 1998], and the differences among models in upper stratospheric NO_{Y} are much larger than the trend computed in any model. Since $NO_Y \cong NO + NO_2$ at this pressure, we obtain an estimate for annual mean NO_{Y} from the multiannual time series of sunset observations obtained by the UARS HALOE [Reber et al., 1993]. HALOE is an occultation instrument and measures 13-15 profiles per day at each of two latitudes. Middle latitude NO_Y varies seasonally, and HALOE sampling is not uniform. The data indicate $\sim 12 \pm 1-2$ ppbv for annual zonal mean for NO_y at 50°N, 2 hPa. In Figure 2a, low NO_Y likely accounts for the somewhat larger difference from multimodel mean O3 than explained by the cooler than multimodel mean temperature for the two models with the largest positive O_3 differences. The model with the largest positive difference from the multimodel mean temperature is consistent with ~ -1 ppmv difference in O_3 . The NO_Y from this model is generally consistent with HALOE. A cluster of models with very small temperature differences from the multimodel mean have NO_Y values that are above, below and consistent with the HALOE estimate.

[37] Observed annual mean values for ozone, temperature and NO_Y are included as a point of reference, and generally illustrate how the computed ozone and its sensitivity to temperature conform to expectations that follow from the conceptual model described above. These comparisons also attest to the difficulty in producing simultaneous agreement with observations for all of these quantities. Figure 2b shows that most simulations are warmer and have lower ozone than observed by MLS. Two models have mean ozone approximately equal to the MLS mean; for one model temperature and NO_Y are also comparable to observed values but the other model is cold compared with MLS and NO_Y is too low compared HALOE.

[38] Note that biases among temperature time series (Figure 1b) are similar to each other throughout the integrations, and the biases among simulated ozone time series vary with time (Figure 1a). This shows that the simulated radiative response of temperature to the change in greenhouse gases is more similar among the models than the simulated photochemical response of ozone. In most of the simulations the rate of change of temperature with time decreases around 2000, when chlorine stops increasing. This change in slope, discussed by Stolarski et al. [2010], occurs because greenhouse gas increase and ozone change due to anthropogenic chlorine both affect temperature. Prior to the late 1990s, anthropogenic chlorine is increasing and ozone is decreasing, thus greenhouse gas increase and chlorine increase both act to decrease temperature. Once anthropogenic chlorine begins to decrease ozone decreases and these the changes in anthropogenic chlorine and greenhouse gases oppose each other.

[39] The differences among ozone profiles are much smaller in 2000 than they were in 1960 when chlorine levels in the stratosphere were not greatly elevated compared with the natural background. As discussed in section 2, chlorine catalyzed ozone loss in the upper stratosphere is nearly independent of temperature [SD1985], thus because the wide range of temperatures produced by the various models is responsible for much of the range in simulated ozone values, the balance of ozone loss processes and the ozone level are more similar among the models when the chlorine term is most important. After 2000 the time series of simulated ozone diverge as chlorine decreases. We compute the standard deviation of the annual zonal means from the group of models for each year to show quantitatively that the simulations are more similar when chlorine is elevated. Figure 3 shows this standard deviation at 50°N 2 hPa as a function of chlorine amount from one of the models. Although there are differences among models in the chlorine amount at 2 hPa, the time dependence follows the boundary conditions and the conclusion drawn from this figure is the same using chlorine amount from any model. The standard deviation for maximum chlorine is reduced by nearly 50% compared to its value for 1960 chlorine. This near linear



Figure 3. The standard deviation of annual mean ozone (σ) at 50°N 2 hPa as computed from the CCMVal simulations varies nearly linearly with upper stratospheric chlorine level and is minimal when the chlorine level is highest.

dependence of the standard deviation of ozone from the CCMVal models on chlorine amount is found throughout the upper stratosphere.

[40] Given the differences in ozone, temperature and the mix of loss processes, it is not surprising that the sensitivity of ozone to temperature $(\partial \gamma_{O3}/\partial T)$ and its sensitivity to inorganic chlorine $(\partial \gamma_{O3}/\partial \gamma_{Cl})$, both obtained through application of MLR to the ozone time series, vary among the models. The ozone sensitivity to chlorine and temperature are shown as functions of 1960 ozone in Figure 4a and b respectively. The ozone sensitivity to chlorine is nearly linearly related to the 1960 ozone level (Figure 4a), with one obvious outlier. In all panels of Figure 4 the sensitivity indicated by a star (*) is the MRI model that omitted $ClO + OH \rightarrow HCl + O_2$ [see *SPARC CCMVal*, 2010, chap. 6]. This

difference in chemical mechanism shifts the partitioning of inorganic chlorine toward *ClO*, increasing the sensitivity of ozone to chlorine since *ClO* + *O* is the rate-limiting step for chlorine-catalyzed catalytic ozone destruction. Eliminating the MRI model just for this calculation, the correlation coefficient between 1960 ozone and sensitivity to γ_{Cl} is 0.9; the dashed line in Figure 4a is the linear fit.

[41] Figure 4a shows that the sensitivity of ozone to γ_{Cl} is correlated with the unperturbed ozone level, implying dependence on net production and on the balance among loss processes other than chlorine. For simulations with the same chemical mechanism, it does not matter exactly what combination of temperature, level of nitrogen or hydrogen species, or photolysis of molecular oxygen leads to higher or lower ozone levels. The simulations with lower ozone in



Figure 4. (a) Sensitivity of ozone (O_3) to chlorine change at 50°N 2 hPa obtained from multiple linear regression (MLR) as a function of 1960 ozone mixing ratio. Colors indicate NO_Y levels. Star is the MRI model that is more sensitive to chlorine because of a missing reaction. Solid line is a linear fit excluding the MRI model. (b) Sensitivity of ozone to temperature obtained from the MLR as a function of 1960 ozone mixing ratio. Simulations with higher initial ozone are generally more sensitive to temperature than those with lower ozone levels. (c) Sensitivity of ozone to temperature obtained from 2007 seasonal cycle as a function of the 2007 ozone mixing ratio. The large cross shows values obtained from MLS observations assuming 5% error in the ozone mixing ratio and 10% error in the ozone sensitivity to temperature. See text for discussion.



Figure 5. (a) Time series for *S* (sensitivity of ozone to temperature) at 2 hPa 50°N as determined for each model from the seasonal cycles in ozone and temperature; (b) Same time series for *S* as in Figure 5a but divided by the 100-year mean for each simulation.

1960 are associated with greater contributions to loss from cycles other than $O + O_3$, thus addition of chlorine makes a smaller relative increase in loss and the simulation is less sensitive to γ_{Cl} . Conversely, the simulations with higher ozone in 1960 have less loss due to cycles other than $O + O_3$, addition of chlorine is of greater relative importance, and the sensitivity to γ_{Cl} is greater.

[42] The ozone sensitivity to temperature also depends on the ozone amount (Figure 4b), although with much more scatter than the ozone sensitivity to γ_{Cl} . Simulations with higher ozone levels are more sensitive to temperature because the odd oxygen loss cycle is the most temperature dependent. The ozone sensitivity to temperature shown in Figure 4b also depends on the relative importance of the catalytic cycles involving nitrogen and hydrogen species, because the catalytic cycle involving nitrogen species is more temperature dependent than the cycles involving hydrogen species at this altitude [SD1985].

[43] Figure 4c shows the ozone sensitivity to temperature as obtained from the seasonal cycles as a function of 2007 ozone. As will be discussed in more detail below, in all of the simulations ozone is less sensitive to temperature in 2007 than in 1960 due to the increased importance of chlorinecatalyzed loss. A black cross indicates values of ozone and the sensitivity of ozone to temperature obtained from the seasonal cycle as observed by MLS; the size of the cross corresponds to 5% errors in ozone and 10% errors in the sensitivity of ozone to temperature. Simulated ozone levels and sensitivity of ozone to temperature are always less than the mean values obtained from MLS, although a few models produce values within the error limits.

4.2. Sensitivity of the Seasonal Cycle of Ozone to Chlorine Level

[44] Chandra et al. [1995] discuss the variation of the seasonal cycle of ozone due to change in the mix of loss processes. Clearly as γ_{Cl} increases and ozone decreases due to chlorine-catalyzed loss, the importance of the most temperature dependent of the loss processes $O + O_3$ decreases. At the same time, the importance of the least temperature dependent of the loss processes ClO + O increases. We

compute the sensitivity of ozone to temperature $S = -\Theta/\Gamma$ each year for each of the CCMVal models using linear regression to relate the seasonal cycles of ozone and temperature.

[45] A time series for *S* (the ozone sensitivity to temperature) is obtained for each model; these are shown in Figure 5a and all conform to expectation. For each model, *S* decreases beween 1960 and 2000. During this time period γ_{Cl} increases, chlorine catalyzed ozone loss becomes more important, and ozone decreases. After 2000 *S* increases as γ_{Cl} decreases toward its natural level. The values of *S* for each model vary due to differences in ozone, temperature, and the relative importance of the catalytic cycles that contribute to ozone destruction. The model for which ozone becomes least sensitive to temperature, the MRI model (indicated by the green dashed line in Figure 5a), is the most sensitive to chlorine due to an error in the photochemical scheme.

[46] Figure 5b shows the time series from 5(a) normalized by their respective 100 year means (i.e., S/\bar{S} , where the overbar indicates the 100 year mean). This normalization emphasizes the relative changes in the annual cycle amplitude that are due to composition change. The models' normalized time series are remarkably similar to each other. Even the relative behavior of S/\bar{S} from MRI conforms, following the conceptual model presented in section 2, in spite of the missing reaction in the photochemical scheme that leads to higher values for the ClO mixing ratio relative to γ_{Cl} and greater importance for chlorine catalyzed loss as discussed above. The rate-limiting steps of the catalytic loss cycles, and their magnitudes relative to each other, control the time dependence of S/\bar{S} without regard to why one or another loss cycle is more or less important. Note that although there are differences among models that affect both their absolute level of γ_{Cl} and partitioning among the chlorine containing species, the overall time dependence of chlorine and the relative changes in chlorine containing species are specified by the boundary conditions. The time dependence of S/\bar{S} conforms across the models because the efficiency of the chlorine catalyzed loss is proportional to the



Figure 6. The logarithmic derivative of *S* divided by the logarithmic derivative of the chlorine mixing ratio as a function of local 1960 NO_Y mixing ratio at 50°N 2 hPa.

ClO level and the fractional changes in *ClO* are mainly controlled by the boundary conditions.

[47] The dependence of S/\overline{S} on chlorine amount can be used to obtain a final test of the conceptual model described in section 2. *Stolarski et al.* [2012] show that S/\overline{S} is nearly constant for a simulation that considers climate change without chlorine change; this result follows from (14) because the chlorine term is zero and the two contributions to the ozone term oppose each other. We neglect the ozone term (first term on the right-hand side of (14)) and rearrange to obtain the following difference equation:

$$\left(\frac{\Delta S}{S}\right) \left/ \left(\frac{\Delta \gamma_{Cl}}{\gamma_{Cl}}\right) \approx \frac{\Gamma_{Cl}}{\Gamma}.$$
(15)

[48] The left side of (15) is ratio of the logarithmic derivative of the sensitivity of ozone to temperature to the logarithmic derivative of inorganic chlorine. We use the time series for S obtained from the seasonal cycles in ozone and temperature to estimate $\Delta S/S$ for each model. Equation (15) shows that this ratio is a measure of the importance of chlorine-catalyzed loss to relative to the total ozone loss. We evaluate the left side of equation (15) for the chlorine change from 1.75 ppbv to 2.25 ppbv as obtained from each of the CCMVal-2 models, using parts of each time series where γ_{Cl} increases and decreases. Figure 6 shows values for the left side of (15) as a function of simulated NO_Y . The contribution of chlorine to total ozone loss as inferred from the left side of (15) is greater for low NO_Y , less for higher NO_Y . This result follows directly from the conceptual model and shows that the chlorine catalyzed loss produces a larger change in ozone annual cycle in simulations with lower NO_{ν} and vice versa. As discussed above, other factors contribute to the balance of loss processes, and lead to scatter.

4.3. Summary of Results

[49] Overall, this analysis relates the differences in response of the CCMVal models to changes in anthropogenic chlorine and greenhouse gases to differences in the simulated unperturbed state using the conceptual model presented in section 2. This conclusion follows from the key results of this section.

[50] 1. Differences in simulated temperature account for much of the difference in the simulated ozone levels shown in Figure 1. At low chlorine (1960), the simulated differences account for about half of the differences in ozone levels.

[51] 2. Simulated ozone is more sensitive to changes in chlorine if $O + O_3$ plays a more important role in the balance of loss processes in 1960 when chlorine levels are low. The converse is also true.

[52] 3. Simulated ozone is more sensitive to temperature change when $O + O_3$ plays a more important role because this is the most temperature dependent loss processes. Again, the converse is true.

[53] 4. Although the magnitude of the change varies among models, the amplitude of the seasonal cycle in ozone varies with chlorine amount, decreasing as chlorine increases and increasing as chlorine decreases. This evolution is similar for all models because all models represent the same odd oxygen loss processes and the boundary conditions control the temporal dependence of upper stratospheric chlorine.

[54] 5. The magnitude of the relative change in ozone sensitivity to temperature divided by the relative change in chlorine (the left side of equation (15) above) varies among models, showing that the contribution of chlorine to ozone loss varies among models. The contribution of chlorine to ozone loss is lowest in models with high NO_Y and vice versa.

[55] The differences in computed temperature, ozone and odd nitrogen are consistent with differences in the balance of loss processes that control ozone in the upper stratosphere. Analysis of the simulated time series shows that differences in the balance of loss processes are responsible for the variations in the models' ozone sensitivity to chlorine change and temperature change that are obtained by analysis of the simulated time series.

5. Discussion and Conclusions

[56] This analysis shows that temporal behavior of ozone as simulated by CCMVal models conforms to the same conceptual model. Much of the spread in the ozone values shown in Figures 1 and 2 is explained by the spread in temperatures. We use the same conceptual model to show that differences in sensitivity of ozone to temperature and chlorine are due to differences in the balance of loss processes. In all models the amplitude of the ozone seasonal cycle decreases as chlorine increases and vice versa. The simulated changes in the amplitude of the ozone seasonal cycle are expected from the conceptual model and also derived from observations. The change in ozone sensitivity to temperature as a result of chlorine change is larger for models with less NO_Y .

[57] This analysis reinforces statements that have been made often over the past decades – simulated responses to perturbations in anthropogenic chlorine or temperature depend on the simulated balance of loss processes in the unperturbed atmosphere. The ozone sensitivity to changes in chlorine and temperature as computed from simulations provided by the CCMVal-2 models varies among models. We focus on computed ozone levels in 1960, when chlorine loading is perturbed by only a few tenths of a ppbv above background. Both the spread in 1960 values and the sensitivity of ozone to temperature as revealed by the seasonal cycle show that there are differences in the simulated balance of loss processes. This analysis shows that quantitative simulation of upper stratospheric ozone evolution as chlorofluorcarbons vary requires accurate simulation of ozone, temperature and reactive nitrogen prior to the introduction of the anthropogenic compounds. The analysis also shows that the range of ozone values produced by the CCMVal-2 models will converge if the range of simulated temperatures is reduced by improvements to the radiation schemes [see *SPARC CCMVal*, 2010, chap. 3].

[58] Although we focused on a single latitude and pressure surface, the results are general in that the sensitivities of ozone to chlorine and temperature change computed at this level correlate with the response at other locations and to the integrated response for the upper stratosphere. For example the correlation coefficient between the sensitivities to γ_{Cl} at 50° N 2 hPa and the sensitivity of the partial ozone column for 20 – 0.1 hPa averaged between 60°S and 60°N computed using multiple linear regression is 0.85.

[59] Most of the simulations do not produce values of ozone, temperature and NO_{V} within the uncertainty range of the observations of all three. This analysis highlights the importance of verifying that a model produces appropriate upper stratospheric temperature and balance of loss processes if attempting to use a simulation along with observations to untangle the dependence of observed ozone changes on changes in chlorine and temperature. Such an effort can only be successful if simulated values for all three fall within boundaries dictated by observations. If these conditions are met, the approach can be useful in attribution studies. For example, Stolarski et al. [2012] use the same conceptual model to argue that a signature of the change in importance of chlorine to ozone loss can be obtained from the sensitivity of ozone to temperature as determined by analysis of their seasonal cycles.

[60] For the upper stratosphere, this analysis demonstrates the weakness of using a multimodel mean to obtain a 'best estimate' for future ozone levels. The different responses from these simulations are expected given differences in temperature, NO_{Y} and ozone when chlorine levels are near background, and averaging over such responses blurs the understanding of the differences in sensitivity to chlorine that arise from the wide range of annual mean values for ozone, temperature and NO_v (Figures 1 and 2). For the simulations shown here, the model that uses the accepted chemical mechanism and is most sensitive to chlorine is also the coldest and has unrealistically low NO_{Y} . Understanding of the upper stratospheric sensitivity to chlorine change and confidence in prediction are enhanced by analysis that reveals the cause of differences in sensitivity to chlorine. The multimodel mean masks the differences. Furthermore, it is clear from this analysis that the range of simulated responses is related to differences in composition and climate that can be fairly judged to be realistic or not using measurements. It is therefore not appropriate to interpret this sort of range in sensitivity as a measure of uncertainty.

[61] The key result of this work is that it is possible to apply the conceptual model to interpret the differences in the CCMVal model projections for upper stratospheric ozone. The analysis of *Oman et al.* [2010] shows variations in the projected level of ozone and in the sensitivity of ozone to chlorine change and temperature change derived from multiple linear regression. This analysis takes an additional step, building on the foundation of ozone photochemistry developed over decades, to show that the differences in the ozone sensitivity to chlorine and temperature arise because of differences in the balance of loss processes. Identifying the processes that control the differences among simulations of present-day ozone is a necessary step toward understanding the differences in ozone projections. Improved prediction and confidence therein follow.

[62] The upper stratosphere is the focus of this initial effort because of the simplicity of the conceptual model. *Strahan et al.* [2011] show that the transport diagnostics can be used to separate predictions for total ozone. Further work is needed to apply the methodology of the present work to obtain a quantitative explanation of both the photochemical and transport changes that lead to variance in the projections of lower stratospheric ozone and the ozone column.

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References

- Akiyoshi, H., L. B. Zhou, Y. Yamashita, K. Sakamoto, M. Yoshiki, T. Nagashima, M. Takahashi, J. Kurokawa, M. Takigawa, and T. Imamura (2009), A CCM simulation of the breakup of the Antarctic polar vortex in the years 1980–2004 under the CCMVal scenarios, *J. Geophys. Res.*, 114, D03103, doi:10.1029/2007JD009261.
- Austin, J., and R. J. Wilson (2010), Sensitivity of polar ozone to sea surface temperatures and halogen amounts, J. Geophys. Res., 115, D18308, doi:10.1029/2009JD013292.
- Barnett, J. J., J. T. Houghton, and J. A. Pyle (1975), The temperature dependence of the ozone concentration near the stratopause, *Q. J. R. Meteorol. Soc.*, 101, 245–257, doi:10.1002/qj.49710142808.
- Bekki, S., G. Bodeker, et al. (2011), Future ozone and its impact on surface UV, in *Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project–Report 52*, pp. 3.1–3.60, World Meteorol. Organ., Geneva, Switzerland.
- Bernath, P. F., et al. (2005), Atmospheric Chemistry Experiment (ACE): Mission overview, *Geophys. Res. Lett.*, 32, L15S01, doi:10.1029/ 2005GL022386.
- Chandra, S., C. H. Jackman, A. R. Douglass, E. L. Fleming, and D. B. Considine (1993), Chlorine catalyzed destruction of ozone: Implications for ozone variability in the upper stratosphere, *Geophys. Res. Lett.*, 20(5), 351–354, doi:10.1029/93GL00212.
- Chandra, S., C. H. Jackman, and E. L. Fleming (1995), Recent trends in ozone in the upper stratosphere: Implications for chlorine chemistry, *Geophys. Res. Lett.*, 22(7), 843–846, doi:10.1029/94GL03395.
- Daniel, J. S., G. J. M. Velders, et al. (2007), Halocarbon scenarios, ozone depletion potentials, and global warming potentials, in *Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project–Report 50*, pp. 8.1–8.39, World Meteorol. Organ., Geneva, Switzerland.
- Davies, T., M. J. P. Cullen, A. J. Malcolm, M. H. Mawson, A. Staniforth, A. A. White, and N. Wood (2005), A new dynamical core for the Met Office's global and regional modelling of the atmosphere, Q. J. R. Meteorol. Soc., 131, 1759–1782, doi:10.1256/qj.04.101.
- de Grandpré, J., S. R. Beagley, V. I. Fonichev, E. Griffioen, J. C. McConnell, A. S. Medvedev, and T. G. Shepherd (2000), Ozone climatology using interactive chemistry: Results from the Canadian Middle Atmosphere Model, J. Geophys. Res., 105(D21), 26,475–26,491, doi:10.1029/2000JD900427.
- DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina (1994), Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation 11, JPL Publ. 94–26, Jet Propulsion Lab., Pasadena, Calif., http://jpldataeval.jpl.nasa.gov.
- Déqué, M. (2007), Frequency of precipitation and temperature extremes over France in an anthropogenic scenario: Model results and statistical

correction according to observed values, *Global Planet. Change*, 57, 16–26, doi:10.1016/j.gloplacha.2006.11.030.

- Douglass, A. R., and R. B. Rood (1986), Derivation of photochemical information near 1 mbar from ozone and temperature data, J. Geophys. Res., 91, 13,153–13,156, doi:10.1029/JD091iD12p13153.
- Douglass, A. R., R. B. Rood, and R. S. Stolarski (1985), Interpretation of ozone temperature correlations: 2. Analysis of SBUV ozone data, J. Geophys. Res., 90, 10,693–10,708, doi:10.1029/JD090iD06p10693.
- Douglass, A. R., V. E. Fioletov, et al. (2011), Stratospheric ozone and surface ultraviolet radiation, in *Scientific Assessment of Ozone Depletion:* 2010, Global Ozone Research and Monitoring Project–Report 52, pp. 2.1–2.76, World Meteorol. Organ., Geneva, Switzerland.
- Froidevaux, L., M. Allen, S. Berman, and A. Daughton (1989), The mean ozone profile and its temperature sensitivity in the upper stratosphere and lower mesosphere–an analysis of LIMS observations, *J. Geophys. Res.*, 94, 6389–6417, doi:10.1029/JD094iD05p06389.
- Garcia, R. R., D. Marsh, D. E. Kinnison, B. Boville, and F. Sassi (2007), Simulations of secular trends in the middle atmosphere, 1950–2003, *J. Geophys. Res.*, 112, D09301, doi:10.1029/2006JD007485.
- Gille, J. C., and J. M. Russell III (1984), The Limb Infrared Monitor of the Stratosphere: Experiment description, performance, and results, *J. Geophys. Res.*, 89(D4), 5125–5140, doi:10.1029/JD089iD04p05125.
- Gordley, L. L., et al. (1996), Validation of nitric oxide and nitrogen dioxide measurements made by the halogen occultation experiment for UARS platform, J. Geophys. Res., 101, 10,241–10,266, doi:10.1029/ 95JD02143.
- Hartmann, D. L., and R. R. Garcia (1979), Mechanistic model of ozone transport by planetary waves, *J. Atmos. Sci.*, *36*, 350–364, doi:10.1175/1520-0469(1979)036<0350:AMMOOT>2.0.CO;2.
- Holloway, A. M., and R. P. Wayne (2010), *Atmospheric Chemistry*, The Royal Society of Chemistry, Cambridge, UK.
- Hood, L. L., and A. R. Douglass (1988), Stratospheric responses to solar ultraviolet variations–comparisons with photochemical models, *J. Geophys. Res.*, 93, 3905–3911, doi:10.1029/JD093iD04p03905.
- Intergovernmental Panel on Climate Change (2000), Special Report on Emissions Scenarios: A Special Report of Working Group III of the Intergovernmental Panel on Climate Change, 599 pp., Cambridge Univ. Press, Cambridge, U. K.
- Johnston, H. S., and J. Podolske (1978), Interpretations of stratospheric photochemistry, *Rev. Geophys.*, 16, 491–520, doi:10.1029/ RG016i004p00491.
- Jourdain, L., S. Bekki, F. Lott, and F. Lefevre (2008), The coupled chemistry-climate model LMDZ-REPROBUS: Description and evaluation of a transient simulation of the period 1980–1999, *Ann. Geophys.*, *26*, 1391–1413, doi:10.5194/angeo-26-1391-2008.
- Lipson, J. B., T. W. Beiderhase, L. T. Molina, M. J. Molina, and M. Olzmann (1999), Production of HCl in the OH + ClO reaction: Laboratory measurements and statistical rate theory calculations, *J. Phys. Chem. A*, 103, 6540–6551, doi:10.1021/jp9847787.
- Livesey, J., et al. (2011), Earth Observing System Aura Microwave Limb Sounder, version 3.3, Level 2 data quality and description document, *JPL D-33509*, Jet Propulsion Lab., Pasadena, Calif., http://mls.jpl.nasa. gov/.
- McCormack, J. P., S. D. Eckermann, D. E. Siskind, and T. J. McGee (2006), CHEM2D-OPP: A new linearized gas-phase ozone photochemistry parameterization for high-altitude NEP and climate models, *Atmos. Chem. Phys.*, *6*, 4943–4972, doi:10.5194/acp-6-4943-2006.
- Morgenstern, O., P. Braesicke, F. M. O'Connor, A. C. Bushell, C. E. Johnson, S. M. Osprey, and J. A. Pyle (2009), Evaluation of the new UKCA climate-composition model Part 1: The stratosphere, *Geosci. Model Dev.*, 2, 43–57, doi:10.5194/gmd-2-43-2009.
- Morgenstern, O., et al. (2010), Review of the formulation of present generation stratospheric chemistry-climate models and associated external forcings. J. Geophys. Res., 115, D00M02, doi:10.1029/2009JD013728.
- forcings, J. Geophys. Res., 115, D00M02, doi:10.1029/2009JD013728. Nagatani, R. M., and A. J. Miller (1984), Stratospheric ozone changes during the first year of SBUV Observations, J. Geophys. Res., 89, 5191–5198, doi:10.1029/JD089iD04p05191.
- Newchurch, M. J., E.-S. Yang, D. M. Cunnold, G. C. Reinsel, J. M. Zawodny, and J. M. Russell III (2003), Evidence for slowdown in stratospheric ozone loss: First stage of ozone recovery, *J. Geophys. Res.*, 108(D16), 4507, doi:10.1029/2003JD003471.
- Oman, L. D., et al. (2010), Multimodel assessment of the factors driving stratospheric ozone evolution over the 21st century, *J. Geophys. Res.*, *115*, D24306, doi:10.1029/2010JD014362.
- Pawson, S., R. S. Stolarski, A. R. Douglass, P. A. Newman, J. E. Nielsen, S. M. Frith, and M. L. Gupta (2008), Goddard Earth Observing System chemistry-climate model simulations of stratospheric ozone-temperature between 1950 and 2005, *J. Geophys. Res.*, 113, D12103, doi:10.1029/ 2007JD009511.

- Pitari, G., E. Mancini, V. Rizi, and D. T. Shindell (2002), Impact of future climate and emission changes on stratospheric aerosols and ozone, *J. Atmos. Sci.*, 59, 414–440, doi:10.1175/1520-0469(2002)059<0414: IOFCAE>2.0.CO;2.
- Randel, W. J. (1993), Global variations of zonal mean ozone during stratospheric warming events, J. Atmos. Sci., 50, 3308–3321, doi:10.1175/ 1520-0469(1993)050<3308:GVOZMO>2.0.CO;2.
- Reber, C. A., C. E. Trevathan, R. J. McNeal, and M. R. Luther (1993), The Upper Atmosphere Research Satellite (UARS) mission, J. Geophys. Res., 98, 10,643–10,647, doi:10.1029/92JD02828.
- Rood, R. B., and A. R. Douglass (1985), Interpretation of ozone temperature correlations: 1. Theory, J. Geophys. Res., 90, 5733–5743, doi:10.1029/ JD090iD03p05733.
- Rosenfield, J. E., and A. R. Douglass (1998), Doubled CO₂ effects on NO_y in a coupled 2D model, *Geophys. Res. Lett.*, 25(23), 4381–4384, doi:10.1029/1998GL900147.
- Russell, J. M., et al. (1993), The Halogen Occultation Experiment, J. Geophys. Res., 98(D6), 10,777–10,797, doi:10.1029/93JD00799.
- Sander, S. P., et al. (2011), Chemical kinetics and photochemical data for use in atmospheric studies, Evaluation 17, JPL Publ. 10–6, Jet Propulsion Lab., Pasadena, Calif., http://jpldataeval.jpl.nasa.gov.
- Schoeberl, M. R., et al. (2006), Overview of the EOS Aura mission, *IEEE Trans. Geosci. Remote Sens.*, 44, 1066–1074, doi:10.1109/TGRS.2005. 861950.
- Schraner, M., et al. (2008), Technical Note: Chemistry-climate model SOCOL: Version 2.0 with improved transport and chemistry/microphysics schemes, *Atmos. Chem. Phys.*, 8, 5957–5974, doi:10.5194/acp-8-5957-2008.
- Scinocca, J. F., N. A. McFarlane, M. Lazare, J. Li, and D. Plummer (2008), Technical note: The CCCma third generation AGCM and its extension into the middle atmosphere, *Atmos. Chem. Phys.*, 8, 7055–7074, doi:10.5194/acp-8-7055-2008.
- Shibata, K., and M. Deushi (2008a), Long-term variations and trends in the simulation of the middle atmosphere 1980–2004 by the chemistry climate model of the Meteorological Research Institute, *Ann. Geophys.*, 26, 1299–1326, doi:10.5194/angeo-26-1299-2008.
- Shibata, K., and M. Deushi (2008b), Simulation of the stratospheric circulation and ozone during the recent past (1980–2004) with the MRI chemistry-climate model, *Rep. 14*, 154 pp., Cent for Gobal Environ. Res., Natl. Inst. for Environ. Studies, Tsukuba, Japan.
- Smith, A. K. (1995), Numerical simulation of global variations of temperature, ozone and trace species in the stratosphere, J. Geophys. Res., 100, 1253–1269, doi:10.1029/94JD02395.
- SPARC CCMVal (2010), SPARC report on the evaluation of chemistry-climate models, edited by V. Eyring, T. G. Shepherd, and D. W. Waugh, *SPARC Rep. 5*, Toronto, Ont., Canada. [Available at http://www.atmosp. physics.utoronto.ca/SPARC.]
- Stolarski, R. S., and A. R. Douglass (1985), Parameterization of the photochemistry of stratospheric ozone including catalytic loss processes, *J. Geophys. Res.*, 90, 10,709–10,718, doi:10.1029/JD090iD06p10709.
- Stolarski, R. S., A. R. Douglass, P. A. Newman, S. Pawson, and M. R. Schoeberl (2010), Relative contribution of greenhouse gases and ozone-depleting substances to temperature trends in the stratosphere: A chemistry-climate model study, J. Clim., 23, 28–42, doi:10.1175/ 2009JCLI2955.1.
- Stolarski, R. S., A. R. Douglass, E. E. Remsberg, N. J. Livesey, and J. C. Gille (2012), Ozone temperature correlations in the upper stratosphere as a measure of chlorine content, *J. Geophys. Res.*, 117, D10305, doi:10.1029/2012JD017456.
- Strahan, S. E., et al. (2011), Using transport diagnostics to understand chemistry climate model ozone simulations, J. Geophys. Res., 116, D17302, doi:10.1029/2010JD015360.
- Teyssèdre, H., et al. (2007), A new tropospheric and stratospheric Chemistry and Transport Model MOCAGE–Climat for multi-year studies: Evaluation of the present-day climatology and sensitivity to surface processes, *Atmos. Chem. Phys.*, 7, 5815–5860, doi:10.5194/acp-7-5815-2007.
- Tian, W., and M. P. Chipperfield (2005), A new coupled chemistry-climate of the stratosphere: The importance of coupling for future O3-climate predictions, Q. J. R. Meteorol. Soc., 131, 281–303, doi:10.1256/qj.04.05.
- Tian, W., M. P. Chipperfield, L. J. Gray, and J. M. Zawodny (2006), Quasibiennial oscillation and tracer distributions in a coupled chemistryclimate model, J. Geophys. Res., 111, D20301, doi:10.1029/2005JD006871.
- Wang, P.-H., M. P. McCormick, and W. P. Chu (1983), A study on the planetary wave transport of ozone during the late February 1979 stratospheric warming using the SAGE ozone observation and meteorological information, J. Atmos. Sci., 40, 2419–2431, doi:10.1175/1520-0469 (1983)040<2419:ASOTPW>2.0.CO;2.

- Waters, J. W., et al. (2006), The Earth Observing System Microwave Limb Sounder (EOS MLS) on the Aura Satellite, *IEEE Trans. Geosci. Remote* Sens., 44, 1075–1092, doi:10.1109/TGRS.2006.873771.
- Waugh, D. W., and V. Eyring (2008), Quantitative performance metrics for stratospheric-resolving chemistry-climate models, *Atmos. Chem. Phys.*, *8*, 5699–5713, doi:10.5194/acp-8-5699-2008.
- World Meteorological Organization (WMO) (2007), Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project-Report 50, 572 pp., World Meteorol. Organ., Geneva, Switzerland.
- World Meteorological Organization (WMO) (2011), Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project–Report 52, 516 pp., World Meteorol. Organ., Geneva, Switzerland.