

4929 **Chapter 4. How Do Climate Change and Stratospheric**
4930 **Ozone Loss Interact?**
4931

4932 **Convening Lead Author:** D. W. Fahey, NOAA

4933

4934 **Lead Authors:** A. R. Douglass, NASA; V. Ramaswamy, NOAA; and A.M. Schmoltnier,

4935 NSF

4936

4937 **KEY ISSUES**

4938 Stratospheric ozone abundances are dependent on a balance of chemical processes that
4939 both produce and destroy ozone and dynamical processes that transport ozone throughout
4940 the stratosphere. The chemical processes depend on atmospheric temperatures and the
4941 abundances of ozone-depleting substances and other trace gases, such as water vapor and
4942 nitric oxides. Transport depends on heating in the atmosphere, which also depends on the
4943 distribution and abundance of trace gases, such as carbon dioxide, ozone-depleting
4944 substances, and ozone. Atmospheric temperature, transport, and trace gas amounts, for
4945 example, are all aspects of Earth's climate. As these and other climate parameters change
4946 as result of human activities and natural variability, ozone abundances will decrease or
4947 increase in response in a manner that depends on a variety of factors.

4948

4949 This complex coupling of ozone and climate parameters is not fully defined at present
4950 and has significant uncertainties associated with known key aspects. Chemistry climate
4951 models (CCMs) of the atmosphere are in development and use by researchers aiming to

4952 reduce the uncertainty in the ozone-climate interaction and to explore other aspects of the
4953 interrelationship. Key questions related to the coupling of ozone and climate are:

- 4954 • How do ozone-depleting substances and ozone depletion contribute to the
4955 radiative forcing (RF) of climate?
- 4956 • How do long-term changes in greenhouse gases affect stratospheric ozone?
- 4957 • How have stratospheric temperatures changed in recent decades and what is the
4958 cause of these changes?
- 4959 • Is stratospheric water vapor changing in a way that influences ozone abundances?
- 4960 • How do ozone changes influence the climate of the stratosphere and troposphere?
- 4961 • Will volcanic eruptions influence future ozone amounts?

4962

4963 **KEY FINDINGS**

4964 *Linking of ozone and climate change*

- 4965 • Ozone and climate change are linked because ozone-depleting substances (ODSs)
4966 are also greenhouse gases, which contribute to radiative forcing. The ODS
4967 contribution to global radiative forcing between 1750 and 2005 is approximately
4968 20% ($0.34 \text{ W per m}^{-2}$) of that from carbon dioxide, the largest anthropogenic
4969 contribution. The ODS contribution is expected to decline in coming decades as
4970 ODS emissions and their atmospheric abundances continue to decline in the
4971 atmosphere.
- 4972 • Each ODS contributes to ozone depletion and climate warming with different
4973 levels of effectiveness as represented, for example, by the ozone depletion
4974 potentials (ODP) and global warming potentials (GWP), respectively. For the

- 4975 principal ODSs, these values vary over orders of magnitude for equal mass of
4976 emissions.
- 4977 • The abundance of stratospheric ozone is dependent on a balance of production
4978 and loss processes. These processes are dependent on several features of the
4979 atmosphere: namely, its chemical composition, air motions, radiation, and
4980 temperatures. Climate change will lead to changes in these features, which in turn
4981 will affect ozone abundances. Feedback from climate change has the potential to
4982 increase or decrease ozone abundances depending on the region and extent of
4983 climate change.
 - 4984 • Chemical ozone depletion also contributes to climate change by modifying
4985 atmospheric radiative properties. Feedback from ozone losses can alter
4986 atmospheric temperatures and atmospheric transport. Ozone depletion can affect
4987 the climate of both the troposphere and stratosphere.

4988

4989 ***Impact of climate change on ozone***

- 4990 • The complexity of the interactions of ozone changes with climate parameters
4991 requires that coupled models of Earth's atmospheric chemistry and climate
4992 processes (called chemistry climate models, CCMs) be used to predict future
4993 ozone amounts. In addition, CCMs are needed to evaluate the sensitivity of ozone
4994 to climate parameters and the response of climate to ozone changes.
- 4995 • Stratospheric temperatures have decreased in the observational records that begin
4996 in the 1960s. This is attributed to ozone depletion, increased carbon dioxide, and
4997 changes in water vapor.

- 4998 • Stratospheric temperatures influence ozone amounts through chemical and
4999 transport processes. Future increases in CO₂ will continue to contribute to global
5000 stratospheric cooling. The photochemical loss of ozone is slowed in some regions
5001 when temperatures decrease with the result that ozone recovery may be
5002 accelerated.
- 5003 • Human activities are expected to increase the future abundances of greenhouse
5004 gases that influence stratospheric ozone amounts, principally, carbon dioxide
5005 (CO₂), methane (CH₄) and nitrous oxide (N₂O).
- 5006 • Stratospheric water vapor has increased in recent decades but since 2001 has been
5007 decreasing in the lower stratosphere. The oxidation of methane emissions is an
5008 important contribution to increasing water vapor trends. Tropical tropopause
5009 temperatures modulate dehydration of air entering the stratosphere, and recent
5010 decreases in water vapor are well correlated with negative tropical tropopause
5011 anomalies. Future trends are uncertain because stratospheric water vapor responds
5012 to both atmospheric methane emissions and the temperature of the tropical
5013 tropopause. Stratospheric water vapor influences stratospheric ozone through
5014 reactive hydrogen chemistry and polar stratospheric cloud formation.
- 5015 • CCM simulations predict that the atmospheric circulation between the
5016 stratosphere and troposphere will increase in a changing climate in the coming
5017 decades. If this occurs, the increased circulation will increase the stratospheric
5018 flux of ozone to the troposphere.

5019

5020 ***Impact of changes in stratospheric ozone on climate change***

- 5021 • Depletion of stratospheric ozone since about 1980 has caused a *negative* radiative
5022 forcing of climate change (~ 0.05 W per m^2) because ozone is a greenhouse gas.
5023 The short-wave cooling of the lower stratosphere has in turn led to a long-wave
5024 cooling of the upper troposphere. Increases in ozone from pollution chemistry
5025 have increased average tropospheric ozone, causing a *positive* radiative forcing
5026 (~ 0.35 W per m^2).
- 5027 • Ozone depletion causes changes to the temperature and circulation of the
5028 stratosphere and troposphere. Meteorological analyses indicate that stratospheric
5029 ozone depletion over Antarctica has caused strengthened circumpolar flow
5030 throughout the troposphere over Antarctica and caused surface temperature
5031 changes.

5032

5033 *Importance of volcanic eruptions*

- 5034 • If explosive volcanic eruptions occur again in the coming decades, they will
5035 decrease stratospheric ozone levels for several years as a result of the
5036 heterogeneous reactions occurring on volcanic sulfate aerosols. These reactions
5037 enhance halogen loss processes by reducing the abundance of key reactive
5038 nitrogen compounds. For a given size eruption, the resulting effect on ozone will
5039 decrease as halogen amounts decrease in the coming decades.
- 5040 • Explosive volcanic eruptions are expected to cause major temperature and
5041 circulation changes in the stratosphere as have occurred after past eruptions.
5042 These changes are a feedback response to the large increases in sulfate aerosol
5043 amounts in the stratosphere following such eruptions. The increases result in only

5044 a short-term shift in stratospheric climate because natural processes remove the
5045 additional sulfate aerosols within 2-3 years after the eruption.

5046

5047 **4.1 INTRODUCTION**

5048 Ozone occurs naturally in the atmosphere as a result of photochemical processes. In the
5049 stratosphere ozone is beneficial to life on Earth because it absorbs ultraviolet radiation
5050 from the sun. Ultraviolet light absorption heats the stratosphere. Ozone is also a
5051 greenhouse gas that helps trap terrestrial infrared radiation, which leads to heating of the
5052 troposphere and stratosphere. In the natural atmosphere, ozone's warming of the planet
5053 makes it the third most important greenhouse gas after water vapor and carbon dioxide
5054 (Kiehl and Trenberth, 1997). As a consequence, changes in ozone amounts have the
5055 potential to change climate parameters in the stratosphere and troposphere.

5056 Anthropogenic pollution has led to increased ozone production and abundances in the
5057 troposphere, particularly near Earth's surface. In contrast, emissions of ozone-depleting
5058 substances (ODSs) in recent decades have led to significant depletion of global
5059 stratospheric ozone with particularly high losses in polar regions. The Montreal Protocol
5060 has been established to protect the ozone layer by reducing the global production and
5061 consumption of ODSs.

5062

5063 The complex interrelationship between ozone and climate change is illustrated in Figure
5064 4.1. Multiple radiative, chemical, and dynamical processes control ozone amounts and
5065 their distribution in the troposphere and stratosphere. Production and loss cycles of ozone
5066 involve many chemical species, as well as aerosols, and are influenced by atmospheric

5067 parameters such as solar insolation and temperature. Natural and anthropogenic processes
 5068 on Earth's surface influence ozone through changes caused in atmospheric composition
 5069 and climate parameters. The chemical loss rate of ozone leads to an atmospheric lifetime
 5070 that is relatively short compared to carbon dioxide, for example. As a result, the
 5071 distribution of ozone is non-uniform in the atmosphere and dynamical processes such as
 5072 planetary waves and the Brewer-Dobson circulation have important roles in establishing
 5073 the distribution.

5074

5075

5076

5077

5078

5079

5080

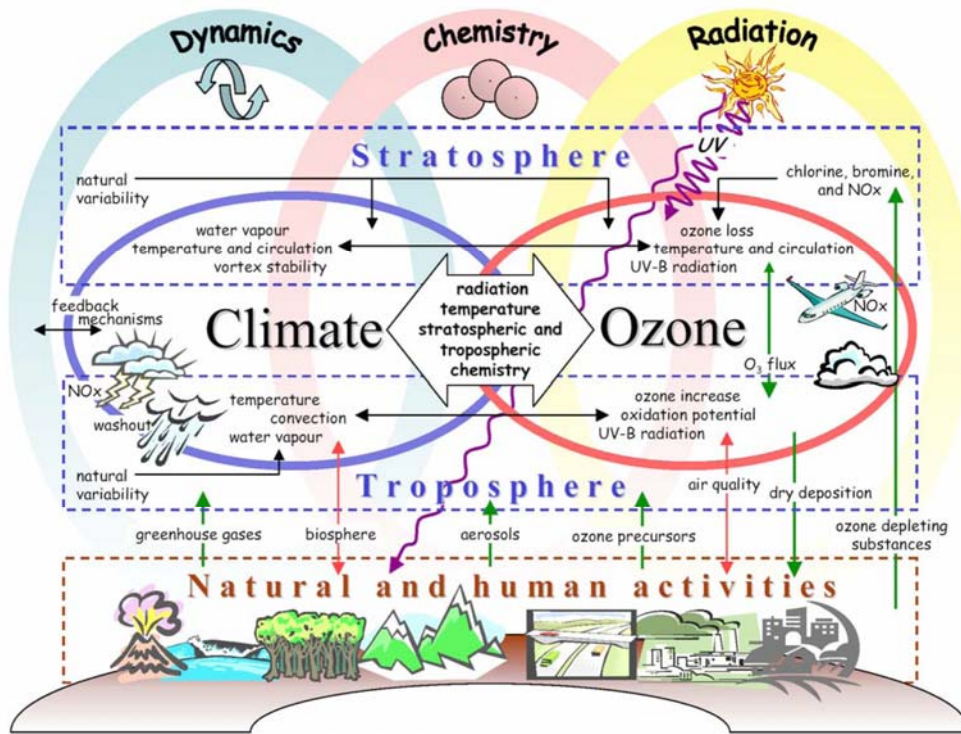
5081

5082

5083

5084

5085



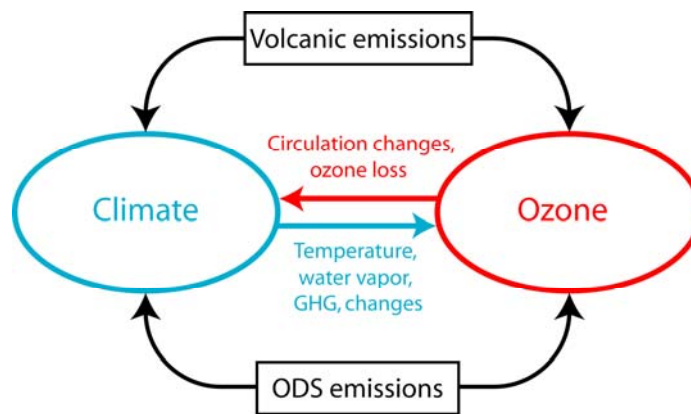
5086 **Figure 4.1** Schematic depiction of the processes that link climate change and ozone abundances (Isaksen,
 5087 I.S.A., 2003).

5088

5089

5090 The ODSs that destroy ozone are also greenhouse gases. Thus, the radiative effect of
 5091 accumulated ODS emissions is partially offset by the subsequent reduction in global

5092 ozone amounts. Systematic and long-term ozone depletion can change atmospheric
 5093 circulation patterns and contribute to climate change. Furthermore, changes in climate
 5094 can potentially alter ozone amounts. Changes in temperature, amounts of trace gases such
 5095 as methane, nitrous oxide, and water vapor, and atmospheric circulation can all
 5096 potentially lead to ozone changes in the stratosphere and troposphere. Finally, large
 5097 volcanic emissions can alter both ozone and climate for temporary periods of several
 5098 years. This chapter assesses these interconnections, schematically shown in Figure 4.2,
 5099 by outlining what is known about ODS and volcanic emissions and the processes through
 5100 which ozone influences climate and through which climate change will influence ozone
 5101 amounts. Further detail on the coupling of climate and ozone changes can be found in
 5102 recent scientific assessments (IPCC/TEAP, 2005; WMO, 2007).



5103
 5104
 5105
 5106
 5107
 5108

5109 **Figure 4.2** Schematic of specific processes that interconnect and influence atmospheric ozone amounts
 5110 and climate parameters and that are addressed in this assessment.
 5111

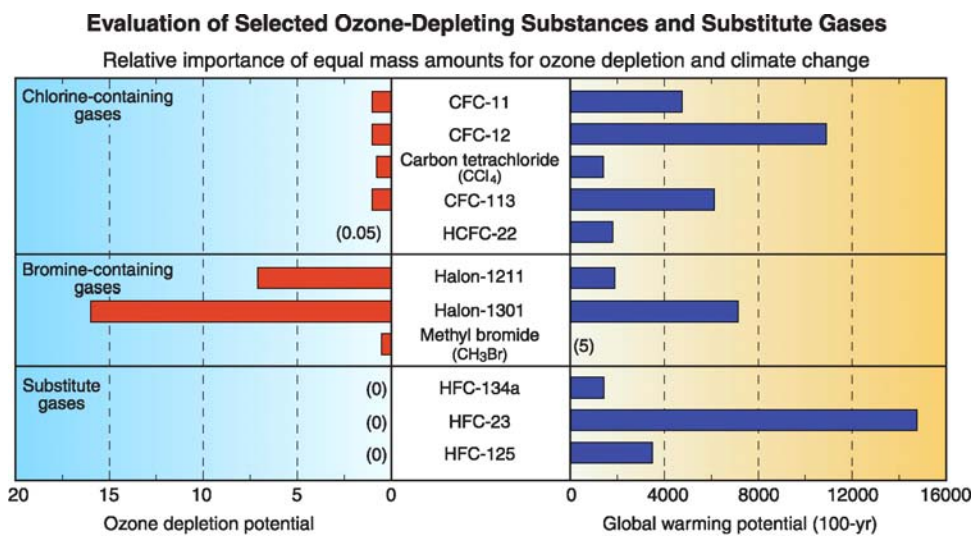
5112

5113 **4.2 RADIATIVE FORCING OF CLIMATE BY OZONE-DEPLETING** 5114 **SUBSTANCES AND OZONE CHANGES**

5115 **4.2.1 Radiative Forcing by Ozone-Depleting Substances**

5116 The accumulation of ozone-depleting substances in the atmosphere has contributed to the

5117 radiative forcing of climate because all ODSs are greenhouse gases. The ODS
 5118 efficiencies as ozone-depleting substances (*i.e.*, ODPs) and as greenhouse gases (*i.e.*,
 5119 GWPs) are contrasted in Figure 4.3. A large range is found in both metrics for the
 5120 principal gases. The continuous measurements of ODS abundances in the atmosphere
 5121 over the last 2-3 decades allow an accurate evaluation of their contributions to ozone
 5122 depletion and climate change. Projections of emissions allow the future contribution of
 5123 ODSs to be estimated. Time series of ODP-weighted and GWP-weighted ODS emissions
 5124 in Figure 4.4 show that both weighted emissions grew substantially in recent decades but
 5125 peaked in the late 1990s (Velders *et al.*, 2007). The decline is in response to the
 5126 provisions of the Montreal Protocol, which requires a staged phase-out of all principal
 5127 ODS use in developed and developing nations. The RF contribution from ODSs likely
 5128 would have been approximately twice as large in 2010 in the absence of the Montreal
 5129 Protocol or other regulation (Velders *et al.*, 2007).
 5130



5131

Figure 4.3 Comparison of the ozone depletion potentials (ODPs) and global warming potentials (GWPs) for principal ozone-depleting substances (ODSs) and HFCs. The contributions of emissions to ozone depletion and climate change increase with the ODP and GWP values, respectively. HFCs are ODS substitute gases which do not destroy ozone (*i.e.*, ODP = 0). The comparison is for emissions of equal mass. The GWPs are evaluated for a 100-yr period after emission. The ODPs of CFC-11 and CFC-12, and the GWP of CO₂ are defined to have values of 1.0 (WMO, 2007)

5132
5133

5134 ***** BEGIN BOX *****

5135 **BOX 4.1: The Ozone Depletion Potential and Global Warming Potential¹**

5136

5137 *Ozone Depletion Potential.* Ozone-depleting substances are compared in their effectiveness to destroy
5138 stratospheric ozone using the “Ozone Depletion Potential” (ODP), as shown in Figure 4.3. A gas with a
5139 larger ODP has a greater potential to destroy ozone over its lifetime in the atmosphere. The ODP is
5140 calculated on a “per mass” basis for each gas relative to CFC-11, which has an ODP defined to be 1.
5141 Halon-1211 and halon-1301 have ODPs significantly larger than CFC-11 and most other emitted gases,
5142 because bromine is much more effective overall (about 60 times) on a per-atom basis than chlorine in
5143 chemical reactions that destroy ozone in the stratosphere. The gases with small ODP values generally have
5144 short atmospheric lifetimes or fewer chlorine and bromine atoms. The production and consumption of all
5145 principal halogen source gases by humans are regulated under the provisions of the Montreal Protocol.

5146

5147 *Global Warming Potential.* The climate impact of a given mass of a halocarbon emitted to the atmosphere
5148 depends on its radiative properties and atmospheric lifetime. The two can be combined to compute the
5149 global warming potential (GWP), which is a proxy for the climate effect of a gas relative to the emission of
5150 a pulse of an equal mass of CO₂. Multiplying emissions of a gas by its GWP gives the CO₂-equivalent
5151 emission of that gas over a given time horizon. A value of 100 yrs is often chosen as a reference time
5152 horizon for intercomparisons of GWPs.

5153

5154 GWPs are most useful as relative measures of the climate response due to direct radiative forcing of well-
5155 mixed greenhouse gases whose atmospheric lifetimes are controlled by similar processes, which includes
5156 most of the halocarbons.

5157

5158 ¹Excerpted from WMO (2007) and IPCC/TEAP (2005).

5159

5160 ***** END BOX 4.1 *****

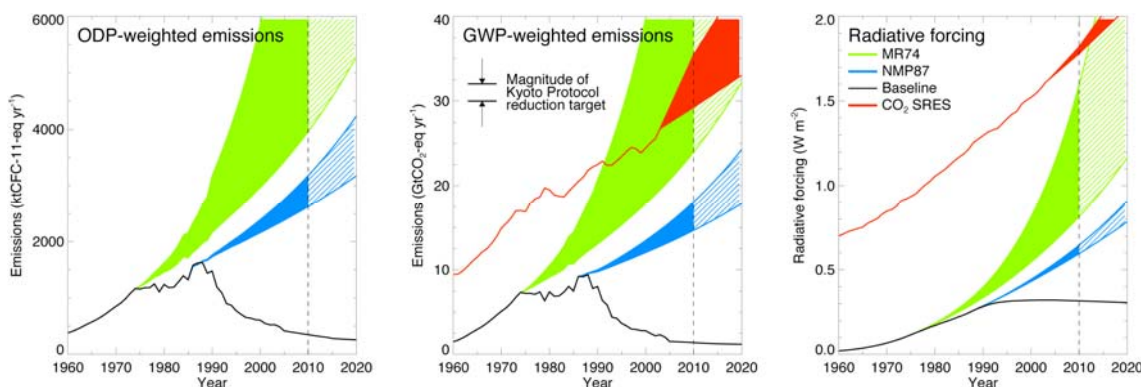
5161

5162 The radiative forcing of individual ODSs varies because of differences in emissions,
5163 lifetimes, and GWPs. The RF values attributable to individual ODSs for the period 1970-
5164 2000 are shown in Table 4.1 along with values for CO₂ and CH₄. CFCs as a group form
5165 the largest contribution to RF amongst all ODSs. A comparison of the RF from
5166 halocarbon gases as a group with values associated with other aspects of natural and
5167 anthropogenic climate forcing is shown in Figure 4.5. Halocarbon gases represent 13% of
5168 the RF from all long-lived greenhouse gases and 21% of the total anthropogenic RF.

5169

5170 ODSs account for 94% (0.32 W per m^2) of the halocarbon term in Figure 4.5. The
 5171 balance (6%) is due to the accumulation of hydrofluorocarbon (HFC) emissions, which
 5172 are included in the Kyoto Protocol (UNFCCC, 1997). Emissions of HFCs are increasing
 5173 because they are ODS substitute gases. HFCs do not deplete ozone ($\text{ODP} = 0$) but can
 5174 have substantial GWPs (Figure 4.3).

5175



5176

5177 **Figure 4.4** ODP-weighted emissions (left panel), GWP-weighted emissions (100-yr) (middle panel), and
 5178 radiative forcing (right panel) for ODS and CO_2 scenarios for 1960–2020. Four scenarios are used: the
 5179 baseline which represents ODS observations to date and projections for the future; the emissions that
 5180 plausibly would have occurred in absence of the Molina and Roland warning that ODSs deplete ozone
 5181 (MR74), the emissions that plausibly would have occurred in absence of the implementation of the
 5182 Montreal Protocol (NMP87), and the IPCC SRES scenario for CO_2 emissions beyond 2003 (see legend).
 5183 ODS emissions are normalized by their direct GWPs to form units of “equivalent $\text{GtCO}_2 \text{ yr}^{-1}$ ”. The shaded
 5184 regions reflect uncertainties in the MR74 and NMP87 scenarios in projecting ODS growth rates. The
 5185 striped shaded regions indicate larger scenario uncertainties past 2010. The CO_2 emissions for 1960–2003
 5186 are from global fossil fuel and cement production. All RF values represent net changes from the start of the
 5187 industrial era (1750) to present. The reduction target of the first commitment period of the Kyoto Protocol
 5188 is shown in the middle panel for reference. (Velders *et al.*, 2007)
 5189

5190

5191

5192

5193 **Table 4.1 Radiative Forcing of CO₂, CH₄ and principal ODSs**

5194

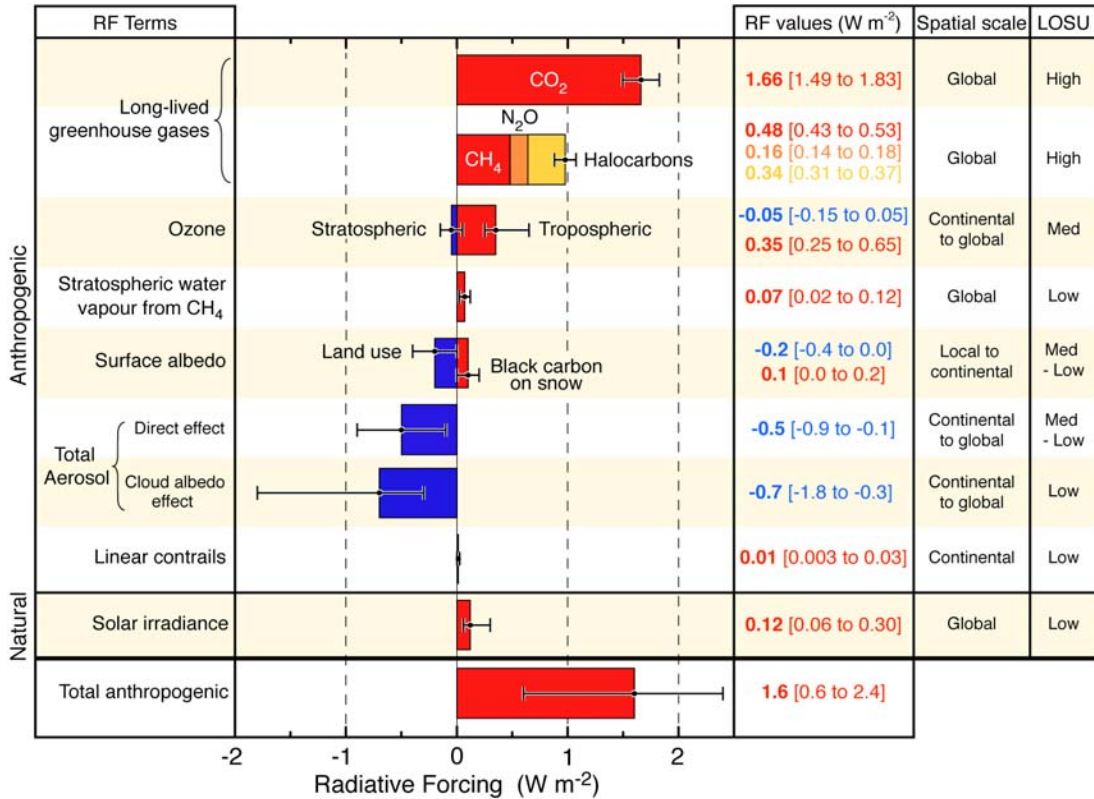
Gas	Radiative forcing (W per m ⁻²)
CO ₂	0.67
CH ₄	0.13
N ₂ O	0.068
CFC-11	0.053
CFC-12	0.136
CFC-113	0.023
CFC-114	0.003
CFC-115	0.002
HCFC-22	0.0263
HCFC-141b	0.0018
HCFC-142b	0.0024
Halon-1211	0.0012
Halon-1301	0.0009
CCl ₄	0.0029

5195 For accumulated emissions in the period 1970-2000. (Adapted from IPCC/TEAP, 2005).

5196

5197 A comprehensive evaluation of the protection of climate afforded by reductions in ODS
5198 emissions must take into account two compensating factors or offsets (Velders *et al.*,
5199 2007). As ODS emissions are reduced, global stratospheric ozone are restored from their
5200 depleted state. Since ozone is a greenhouse gas, ozone RF increases as ozone levels are
5201 restored, thereby offsetting the reductions in RF from ODS reductions. The second offset
5202 is the increase in emissions of HFCs, all potent greenhouse gases, which is intrinsically
5203 tied to ODS reductions because HFCs are key substitute gases for ODSs. Thus, the net
5204 gain from reducing the RF contribution of ODSs must include negative offsets due to the
5205 reversal of some ozone depletion and increased abundances of other greenhouse gases. In
5206 2010, these factors offset about 25% of the RF decrease attributable to reductions of

5207



5208 **Figure 4.5** Radiative forcing values for the principal contributions to climate change from anthropogenic
 5209 activities and natural processes. Each numerical value listed and indicated with a bar is a global mean value
 5210 representing the change between preindustrial times (ca, 1750) and the present (2005). The error bars
 5211 indicate the uncertainty ranges. The spatial scale and level of scientific understanding (LOSU) is also
 5212 indicated for each value. (IPCC, 2007)
 5213

5214 ODSs under the Montreal Protocol since 1990 (Velders *et al.*, 2007). As ODS
 5215 abundances continue to decline in the atmosphere after 2010, the relative size of the
 5216 ozone offset is likely to remain unchanged while the HFC offset might increase
 5217 depending on growth in production and use of HFCs, which are not regulated by the
 5218 Montreal Protocol.

5219

5220 **4.2.2 Radiative Forcing From Ozone Changes**

5221 Stratospheric ozone depletion and increases in tropospheric ozone both contribute to the
 5222 RF of climate. The response of surface climate to ozone changes is complex, in general,

5223 because of the balance between short-wave and long-wave radiative effects. For example,
5224 when ozone is increased in the troposphere or lower stratosphere, surface temperatures
5225 tend to increase due to increased long-wave forcing (Forster and Shine, 1997;
5226 IPCC/TEAP, 2005). Overall, surface temperatures are most sensitive to changes in ozone
5227 concentrations near the tropopause.

5228

5229 Stratospheric ozone depletion has occurred primarily at extratropical latitudes with
5230 substantially larger changes in the Southern Hemisphere. Southern Hemisphere ozone
5231 values over the period 2000-2003 are on average 6% below pre-1980 values, while
5232 Northern Hemisphere values are 3% lower. The net RF change from these observed
5233 depletions has been assessed by the IPCC to be near -0.05 W per m^2 (Figure 4.5) (IPCC,
5234 2007; Hansen *et al.*, 2005). The instantaneous response to ozone depletion in the lower
5235 stratosphere is a positive forcing because solar flux significantly increases below the
5236 tropopause and downwelling longwave radiation decreases slightly. In addition, less solar
5237 and longwave radiation is absorbed in the lower stratosphere when ozone amounts are
5238 reduced, thereby cooling the region and further reducing the downwelling longwave flux
5239 from ozone and other gases. When all effects and feedbacks are taken into account, ozone
5240 depletion causes a net reduction in RF at the tropopause and a cooling effect on the
5241 atmosphere.

5242

5243 With an uncertainty of $\pm 0.1 \text{ W per m}^2$, the IPCC best estimate of the RF from
5244 stratospheric ozone lies between -0.15 and $+0.05 \text{ W per m}^2$ (IPCC, 2007). The possibility
5245 of a positive RF reflects that stratospheric ozone may have increased in some regions

5246 since preindustrial times, despite losses related to ODSs. The RF value is particularly
5247 sensitive to ozone changes in the tropical lower stratosphere, which are small compared
5248 to changes at high latitudes. Observational and modeling studies indicate how Northern
5249 Hemisphere ozone amounts are also influenced by changes in atmospheric dynamics,
5250 such as changes in tropopause heights (Pyle *et al.*, 2005), in addition to increased
5251 amounts of ODSs. The model results show large differences in how ozone column
5252 amounts have responded at mid latitudes to changes in ODSs and other parameters, such
5253 as circulation (Gauss *et al.*, 2006).

5254

5255 Tropospheric ozone since preindustrial times has increased as a result of increased
5256 emissions of anthropogenic pollutants, primarily nitrogen oxides, carbon monoxide, and
5257 organic compounds, including methane. Photochemical and radiative transfer models are
5258 used to calculate ozone changes and the associated RF, respectively. The changes include
5259 the net transport of ozone from the stratosphere to the troposphere, which can be altered
5260 by climate change and stratospheric ozone depletion. The tropospheric ozone RF (0.35 W
5261 per m²) from human activities is larger than the stratospheric ozone term and associated
5262 with large uncertainties (Figure 4.5).

5263

5264 **4.3 THE RESPONSE OF OZONE TO CLIMATE CHANGE PARAMETERS**

5265 Ozone responds to climate change parameters in a variety of ways because ozone is
5266 photochemically produced and destroyed in the atmosphere and thus dependent on the
5267 abundance of other gases emitted by natural and anthropogenic processes. The
5268 complexity of the interaction of ozone with climate change parameters (Figure 4.1)

5269 requires the use of chemistry climate models (CCMs) to diagnose the sensitivity of ozone
5270 to climate change parameters and to predict future ozone amounts in a changing climate.

5271

5272 **BOX 4.2: Model Used To Study Climate Processes¹**

5273

5274 **Atmospheric General Circulation Model (AGCM):** A three-dimensional model of large-scale (spatial
5275 resolution of a few hundred km) physical, radiative, and dynamical processes in the atmosphere over years
5276 and decades. An AGCM is used to study changes in natural variability of the atmosphere and for
5277 investigations of climate effects of radiatively active trace gases (greenhouse gases) and aerosols (natural
5278 and anthropogenic), along with their interactions and feedbacks. Usually, AGCM calculations employ
5279 prescribed concentrations of radiatively active gases, *e.g.*, carbon dioxide (CO₂), methane (CH₄), nitrous
5280 oxide (N₂O), chlorofluorocarbons (CFCs), and ozone (O₃). Changes of water vapor (H₂O) concentrations
5281 due to the hydrological cycle are directly simulated by an AGCM. Sea surface temperatures (SSTs) are
5282 prescribed. An AGCM coupled to an ocean model, commonly referred to as an AOGCM or a climate
5283 model, is used for investigation of climate change. More recently, climate models may also include other
5284 feedback processes (*e.g.*, carbon cycle, interaction with the biosphere).

5285

5286 **Chemistry-Climate Model (CCM):** An AGCM that is interactively coupled to a detailed chemistry module.
5287 In a CCM, the simulated concentrations of the radiatively active gases are used in the calculations of net
5288 heating rates. Changes in the abundance of these gases due to chemistry and advection influence heating
5289 rates and, consequently, variables describing atmospheric dynamics such as temperature and wind. This
5290 gives rise to a dynamical-chemical coupling in which the chemistry influences the dynamics (via radiative
5291 heating) and vice versa (via temperature and advection). Not all CCMs have full coupling for all chemical
5292 constituents; some radiatively active gases are specified in either the climate or chemistry modules. Ozone
5293 is always fully coupled, as it represents the overwhelmingly dominant radiative-chemical feedback in the
5294 stratosphere.

5295

5296 ¹Excerpted from WMO (2007).

5297

5298 **END BOX 4.2**

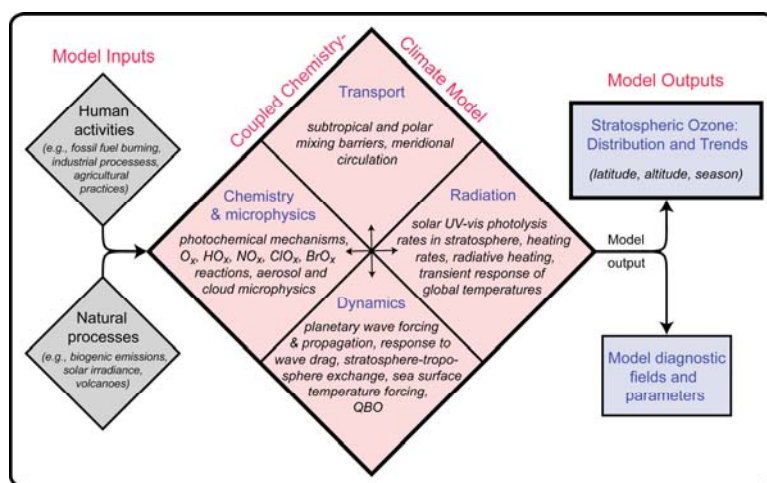
5299

5300 **4.3.1 Calculating the Response of Ozone to Climate Change Parameters with CCMs**

5301 The approach to CCM use is schematically shown in Figure 4.6. Transport, radiation,
5302 dynamics, and chemistry and microphysics are the four principal aspects of a CCM. A
5303 CCM requires as input specific knowledge of natural process and their trends, such as in
5304 emissions, solar irradiance, and volcanic eruptions; and of human activities and their
5305 trends, primarily for emissions. These inputs define and constrain the current and future
5306 state of climate parameters. The CCM output includes a wide array of parameters and
5307 diagnostics in addition to ozone that can be compared to observations and other models.

5308

5309



5310 **Figure 4.6** The processes in a Chemistry Climate Model (CCM) are represented by four basic groups:
 5311 transport, dynamics, radiation, and stratospheric chemistry & microphysics. Significant interactions occur
 5312 between aspects within each group. The CCM requires inputs describing human activities and natural
 5313 processes. The CCM provides as output projections of future ozone abundances and their distribution along
 5314 with a large variety of other parameters and diagnostics. See Box 4.2. (Eyring *et al.*, 2005).
 5315

5316 CCMs are complex because simulating the atmosphere requires interdependence and
 5317 interaction between the core aspects of the model. Important examples include the
 5318 coupling between transport and radiation. Transport depends in part on atmospheric
 5319 temperature gradients that are established by the distribution of radiative heating.
 5320 Radiative heating is determined, in part, by long-lived greenhouse gases and ozone.
 5321 Photochemical reaction rates also depend on ambient temperatures. Thus, the
 5322 photochemical balance controlling the abundances of ozone and other species depends
 5323 substantially on the atmospheric abundances of greenhouse gases. Sea surface
 5324 temperatures, land-sea temperature differences and other factors influence wave
 5325 propagation into the stratosphere, thereby affecting meridional transport rates. These
 5326 couplings are discussed in more detail in WMO (2007) and Eyring *et al.* (2005).

5327

5328 The validation of CCM output for ozone and other parameters has become a focus topic
5329 because of the heightened need to project future ozone abundances with reliable
5330 uncertainty estimates (Eyring *et al.*, 2005; 2006). Reasonable agreement is found between
5331 many CCMs and global ozone trends, but for polar ozone trends the CCMs show a large
5332 spread in results. Uncertainties in CCM results reflect limitations in our understanding of
5333 how to represent atmospheric processes and their feedbacks in model simulations and,
5334 therefore, limit the precision and accuracy of our projections of future ozone amounts and
5335 the influence of climate change.

5336

5337 **4.3.2 Stratospheric Temperature Changes**

5338 Stratospheric temperatures have decreased over the last 3 to 4 decades. Observations
5339 from satellites beginning in 1979 and radiosonde observations from about 1960 both
5340 reveal the cooling. The trend is about -0.5K/decade in the lower stratosphere and about 1
5341 – 2K/decade in the middle stratosphere (~25-30 km). The latitude dependence of the
5342 temperature trends is not fully consistent across the various datasets, especially in the
5343 tropics, and remains a topic of research (WMO, 2007). The time series of temperatures
5344 reveals a non-monotonic decrease in the lower stratospheric temperatures (Figure 4.7).
5345 Volcanic aerosols formed in the aftermath of explosive volcanic eruptions led to a
5346 warming of the stratosphere for a few years following an eruption. Both the El Chichón
5347 and Mt. Pinatubo (1991) volcanic eruptions increased stratospheric aerosol amounts
5348 (McCormick *et al.*, 1995; Pawson *et al.*, 1998). The temperature trend decreases after
5349 1995 after the gradual decay of volcanic aerosol amounts removed a large fraction from

5350 the stratosphere (IPCC, 2007). In the evolution of the global lower stratospheric
 5351 temperature, a sharp increase lasting for ~2 years is found immediately following the El
 5352 Chichón (1982) eruption and is followed by a period of quasi-steady temperatures that
 5353 are lower than the pre-eruption value. After the eruption of Mt. Pinatubo (1991),
 5354 temperatures again increased sharply and were followed by a steady period in which the
 5355 temperatures became lower than before this eruption. There is a slightly reduced cooling
 5356 towards the end of 1990s and beginning of 2000s (Mears *et al.*, 2003).

5357

5358

5359

5360

5361

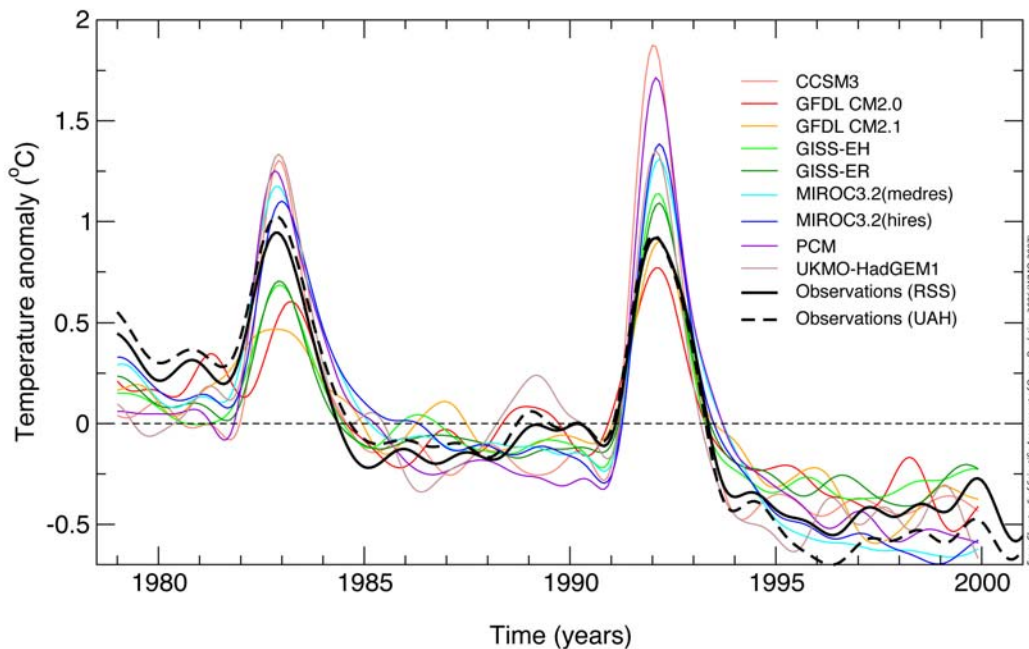
5362

5363

5364

5365

5366



5367

5368

5369

5370

Figure 4.7 Temperature anomalies in the lower stratosphere as calculated by an ensemble of climate models. Results are compared with observations derived from satellite datasets. Further details are in Section 4.3.2. (From Santer *et al.*, 2006 and (WMO, 2007: Figure 5-3)

5371

5372

5373

5374

Climate model simulations also show that the combined influences of the agents that are known to “drive” the climate system offer a reasonable quantitative explanation of the observed non-monotonic decrease of the temperatures in the global lower stratosphere (Seidel and Lanzante, 2004; Dameris *et al.*, 2005; Ramaswamy *et al.*, 2006). The global

5375 stratospheric temperature trends over the past 2-3 decades are attributed in modeling
5376 studies to a combination of increases in greenhouse gases and water vapor, and decreases
5377 in ozone (Ramaswamy and Schwarzkopf, 2002; Schwarzkopf and Ramaswamy, 2002;
5378 Langematz *et al.*, 2003; Shine *et al.*, 2003; Santer *et al.*, 2006). The above studies
5379 indicate that attribution of the cooling trend is possible on the global-annual and zonal-
5380 annual scales, and for the springtime Antarctic, but smaller spatial scales and seasonal
5381 behavior pose problems in attribution owing to the dynamical variability present. The
5382 results from an ensemble of climate models are shown in Figure 4.7 for stratospheric
5383 temperature anomalies calculated as global and monthly means (Santer *et al.*, 2006). In
5384 addition to stratospheric ozone depletion, the models all include climate forcings from
5385 changes in WMGHGs sulfate aerosol, volcanic aerosol, and solar irradiance. The
5386 temperature anomalies are differences from a 1979-1999 reference period. The models in
5387 general account for the long-term decrease in stratospheric temperatures and the short-
5388 term increases caused by two large volcanic eruptions.

5389

5390 The effects on climate of a wide range of forcings have been examined by Hansen *et al.*
5391 (2005), which shows that different forcings produce different response patterns in the
5392 vertical temperature profile. Results from climate model simulations as outlined in CCSP
5393 (2006) show:

- 5394 • increases in greenhouse gases warm the troposphere and cool the stratosphere
- 5395 • volcanic aerosols warm the stratosphere and cool the troposphere
- 5396 • increase in solar forcing warms most of the atmosphere
- 5397 • increases in tropospheric ozone warm the troposphere

5398 • decreases in stratospheric ozone cool the stratosphere

5399 • sulfate aerosols cool the troposphere and slightly warm the stratosphere.

5400 The projections for the 21st century by coupled atmosphere-ocean general-circulation

5401 models (AOGCMs) using IPCC emissions scenarios show that average global

5402 temperatures continue to decrease in the stratosphere and increase in the troposphere

5403 (Figure 4.8). This result is primarily a consequence of increases in well-mixed

5404 greenhouse gases (WMGHGs) (mainly CO₂). Changes in the thermal gradients in the

5405 stratosphere and troposphere, initiated by greenhouse gas and aerosol changes, could

5406 additionally alter stratosphere-troposphere interactions and the state of the stratosphere.

5407 Changes of water vapor in the stratosphere arising from tropospheric warming, possible

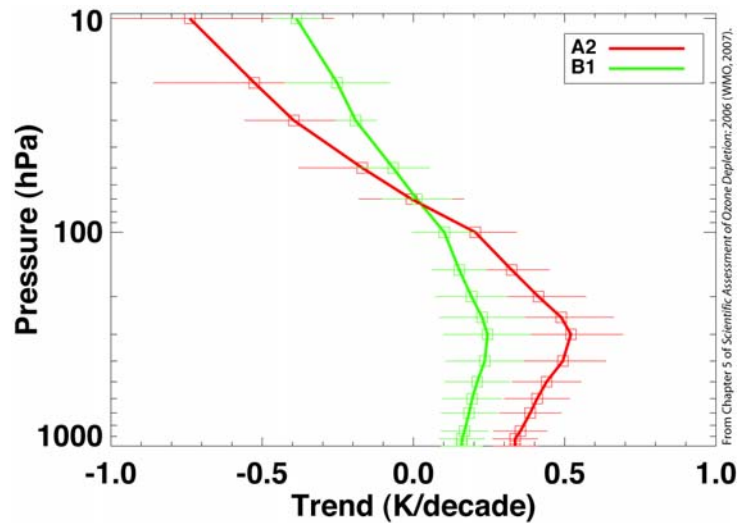
5408 changes in convective activity and transport of water to the stratosphere, also can affect

5409 the stratospheric thermal state. Increased frequency of explosive volcanic events and ones

5410 much more intense than the Mt. Pinatubo eruption, should they occur, can be expected to

5411 substantially alter the climate and chemistry of the stratosphere for a few years through

5412 the particulates produced and impacts on atmospheric circulation.



5413

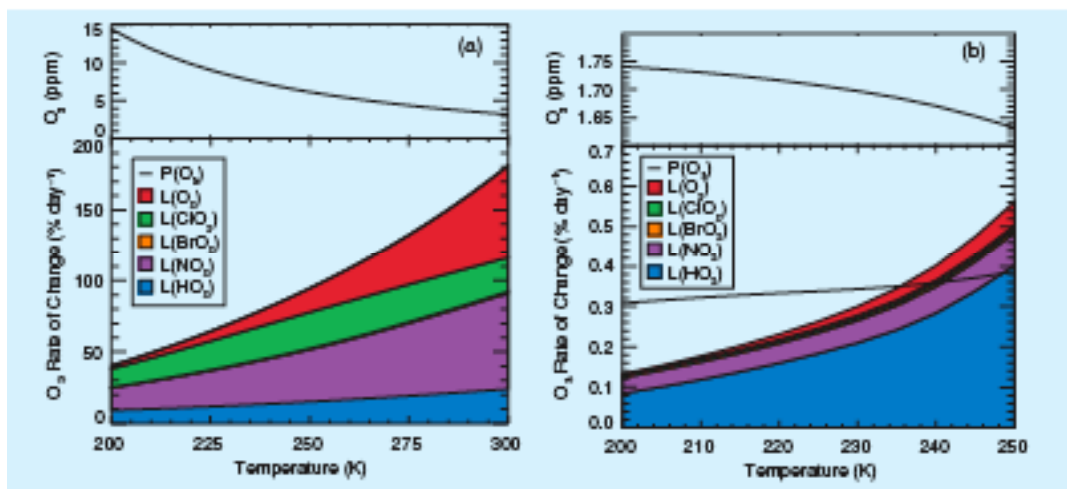
5414 **Figure 4.8** Temperature trends in the troposphere and stratosphere calculated as global and annual means
 5415 for the 21st century using atmosphere-ocean GCMs (with no ozone chemistry) (AOGCMs). The
 5416 calculations were made for two IPCC emission scenarios: A2 (high) and B1 (low). The symbols indicate
 5417 the average trend computed for all models, while the thin horizontal lines indicate the range. (WMO,
 5418 2007).
 5419

5420 4.3.2.1 Response of ozone to stratospheric temperature changes

5421 With the coupling of ozone with climate parameters as outlined above, the effect of
 5422 temperature changes on ozone is difficult to isolate. However, model simulations reveal
 5423 some strong tendencies arising due to temperature changes. In the upper stratosphere,
 5424 ozone amounts are controlled primarily by photochemical processes rather than transport
 5425 and these processes are considered well understood. When temperatures decrease, ozone
 5426 loss slows in the dominant photochemical cycles (NO_x , ClO_x , and HO_x) (Figure 4.9).
 5427 For example, 15-20% ozone increases were calculated in the upper stratosphere for a
 5428 climate with doubled CO_2 concentrations (Jonsson *et al.*, 2004). In the lower
 5429 stratosphere, lower temperatures also decrease the destruction rate; but, production and
 5430 destruction rates are lower than in the upper stratosphere and transport plays a more

5431 important role. As a result, temperature changes have less influence on steady state ozone
 5432 values in the lower stratosphere than in the upper stratosphere.

5433



5434

5435 **Figure 4.9** Comparison of ozone production and loss rates as a function of stratospheric temperature for
 5436 40-km altitude (left panel) and 20-km altitude (right panel) conditions at 45°N at equinox (end of March).
 5437 The colored regions indicate the contribution from the principal loss cycles of ozone: odd-oxygen (O_x),
 5438 reactive chlorine (ClO_x), reactive bromine (BrO_x), reactive nitrogen (NO_x), and reactive hydrogen (HO_x).
 5439 The fractional contribution of each cycle varies with temperature differently in the two regions. The top
 5440 trace in each panel is the ozone value at the end of 20-day runs of a chemical box model starting from
 5441 climatological values for ozone, other constituents, and temperature (250K at 40 km; 215K at 20 km). At
 5442 40 km, the production rate coincides with the sum of loss rates because ozone is in photochemical balance
 5443 at all temperatures shown. At 20 km, ozone production can be higher or lower than total loss depending on
 5444 temperature because transport plays a more important role. The changes in ozone after 20-day runs are
 5445 much smaller at 20 km than at 40 km, confirming that small temperature changes in the upper stratosphere
 5446 will significantly alter ozone abundances. (IPCC/TEAP, 2005)
 5447

5448 In the polar lower stratosphere, the reduction in photochemical loss with lower
 5449 temperatures can be completely offset by increased activation of reactive chlorine and
 5450 bromine, which increases ozone loss. Lower temperatures promote the formation of polar
 5451 stratospheric clouds (PSCs), which facilitate heterogeneous reactions that form reactive
 5452 halogens from reservoir gases. In the Arctic region, increased reactive halogens have the
 5453 largest effect in controlling the ozone response to lower temperatures. For Northern

5454 Hemisphere winters from 1993 to present, a strong linear relationship is found between
5455 winter/early spring ozone depletion and the volume of air containing PSCs during the
5456 winter. The ODS abundances are nearly constant during this time period (Rex *et al.*,
5457 2004). Arctic ozone depletion might increase if further reductions occur in Arctic
5458 stratospheric temperatures because temperature decreases can lead to increases in the
5459 duration and frequency of PSCs (Douglass *et al.*, 2006).

5460

5461 In the Antarctic lower stratosphere, winter temperatures are well below the thresholds for
5462 heterogeneous conversion of halogen reservoirs for much longer periods and for much
5463 larger fractions of the polar vortex than found in the Arctic. Antarctic ozone depletion is
5464 currently much more extensive and complete, and decreasing temperatures would have
5465 less of an effect (Tilmes *et al.*, 2006). Under current conditions, seasonal Antarctic ozone
5466 depletion is more sensitive to reductions in ODS amounts than to small decreases in
5467 temperature (See Chapter 3) (Newman *et al.*, 2004). As ODS abundances decrease in the
5468 coming decades, polar ozone destruction due to reactions with halogen species ultimately
5469 will decrease in both hemispheres regardless of changes in the frequency and duration of
5470 PSCs.

5471

5472 **4.3.3 Stratospheric Water Vapor Changes**

5473 The amounts of atmospheric water vapor, the most important and abundant greenhouse
5474 gas, serve as a feedback in the climate system. Change in the global distribution of water
5475 vapor is one of the important responses to the anthropogenic climate forcings
5476 summarized in Figure 4.5. Water vapor enters the stratosphere primarily through the

5477 tropical tropopause. The water vapor abundance is reduced in dehydration processes
5478 involving low tropical tropopause temperatures and the formation and sedimentation of
5479 ice particles. Methane, released in the troposphere and oxidized in the stratosphere, is the
5480 underlying cause of the water-vapor component of anthropogenic radiative forcing as
5481 summarized in Figure 4.5.

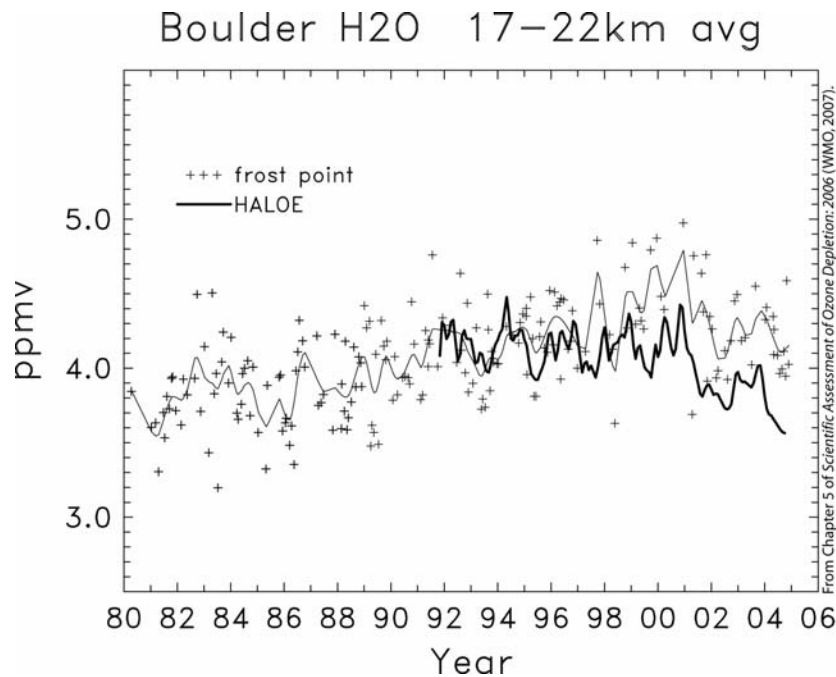
5482

5483 Stratospheric water vapor has been measured by a wide variety of instruments and
5484 platforms, including balloons, aircraft, and satellites. The longest time series of
5485 continuous measurements is from small-balloon observations beginning in 1980. These
5486 measurements show that water vapor has increased at all levels between 15 and 26 km.
5487 At 17-22 km altitude, the increase can be expressed as a trend of ~5-10% per decade
5488 (Figure 4.10) (Oltmans *et al.*, 2000; Rosenlof *et al.*, 2001). Other stratospheric
5489 observations up to 30-35 km also show increasing trends, but over shorter time periods
5490 and with a high degree of variability (SPARC, 2000; Rosenlof *et al.*, 2001). Part of the
5491 long-term increase in water vapor is attributable to increases in methane abundances due
5492 to anthropogenic emissions. Methane, which has increased by about 0.55 ppmv since the
5493 1950s, is oxidized in the stratosphere producing two water molecules for each molecule
5494 of methane. The methane water vapor source in the stratosphere increases radiative
5495 forcing from water vapor by an estimated 0.1 W per m⁻² (Myhre *et al.*, 2007). The
5496 implications of this indirect effect are not clear for the interpretation of water vapor and
5497 temperature trends in the stratosphere.

5498

5499 Since about 2000 the water vapor in key balloon and satellite observations in the mid to

5500 lower stratosphere has shown significant decreases (Randel *et al.*, 2004). As a possible
 5501 explanation, an analysis of the tropical tropopause temperatures for 1992-2005 shows that
 5502 satellite water vapor amounts are consistent with interannual changes in the cold point
 5503 temperatures and with the occasions of anomalously low tropopause temperatures
 5504 (Randel *et al.*, 2004; 2006). Tropopause temperatures modulate the dehydration of air
 5505 entering the lower stratosphere from the troposphere. In contrast, the earlier, longer water
 5506 record from balloon measurements is not fully consistent with the record of tropopause
 5507 temperatures (Seidel *et al.*, 2001). In general, the attribution of the causes of observed
 5508 water vapor changes and trends in the stratosphere is incomplete, suggesting that
 5509 projections of future amounts are uncertain.



5510

5511 **Figure 4.10** Time series of stratospheric water vapor mixing ratios (ppm, parts per million by volume) for
 5512 the period 1980 to 2005. The measurements were made with a balloon-borne frost point hygrometer over
 5513 Boulder, Colorado (40°N, 105°W). The data points are averages over 17-22 km altitudes. The thin line is a
 5514 smoothed fit to the measurements. HALOE satellite observations for 1992-2005 are shown with the heavy
 5515 line for the same altitude near Boulder (latitude 35°N-45°N, longitude 80°W-130°W). Preliminary
 5516 revisions to the frost-point data reveal a slightly smaller trend (Scherer *et al.*, 2007). Updated from Randel

5517 *et al.* (2004). (WMO, 2007)
5518

5519 **4.3.3.1 Response of Ozone to Stratospheric Water Vapor Changes**

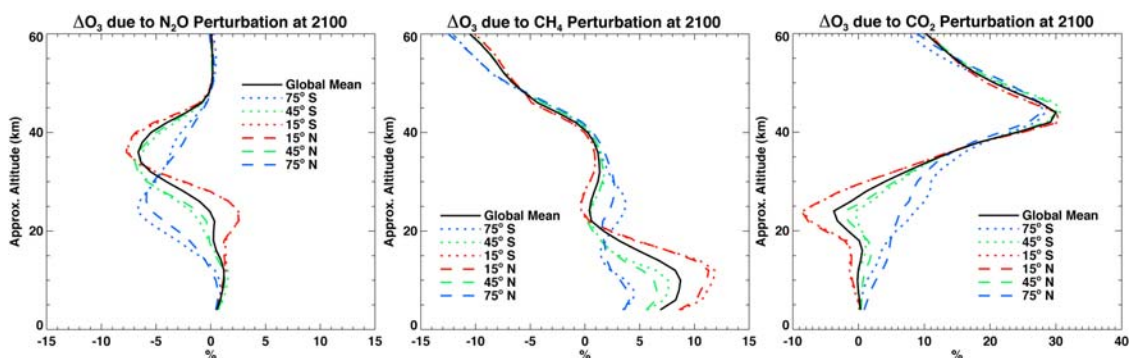
5520 Increases in stratospheric water lead to increases in reactive hydrogen species (HO_x),
5521 which catalyze the chemical destruction of ozone (Wennberg *et al.*, 1994; Brasseur and
5522 Solomon, 1986). Ozone destruction is chemically buffered with a combination of loss
5523 cycles so that the response to increased HO_x is generally not linear and varies with
5524 location in the stratosphere (Figure 4.9). Model simulations show that a 1%/year, long-
5525 term trend in water vapor would increase ozone loss due to increases in HO_x and delay
5526 the recovery of the ozone layer (Dvortsov and Solomon, 2001). Increased water vapor
5527 also increases the temperature threshold for PSC formation in both polar regions because
5528 PSC are formed, in part, from water-vapor condensation. A higher threshold increases
5529 heterogeneous conversion of chlorine and extends the time period over which PSCs can
5530 form in the winter season (Stenke and Grewe, 2005). Both effects lead to increased ozone
5531 destruction in polar regions at constant ODS amounts. However, the sensitivity of ozone
5532 to PSCs will decrease as ODS amounts decrease, because less chlorine and bromine will
5533 be available to participate in ozone destruction reactions.

5534

5535 **4.3.4 Changes in Ozone from Increases in Long-Lived Gases in the Stratosphere**

5536 The atmospheric concentrations of the three long-lived greenhouse gases, CO₂, CH₄, and
5537 N₂O, have increased significantly due to human activities since 1750 and are expected to
5538 continue increasing in the 21st century (IPCC, 2007). These continuing increases have
5539 consequences for ozone amounts and, hence, also indirectly influence climate through the
5540 changes they produce in ozone (Portmann and Solomon, 2007). Calculations with a two-

5541 dimensional, chemical-radiative-dynamical model illustrate the sensitivity of ozone to
 5542 each of these gases (Figure 4.11). CO₂ increases, as discussed above, reduce
 5543 stratospheric temperatures and ozone loss rates, and consequently, increase ozone
 5544 amounts in the mid to upper stratosphere. The increased ozone in the upper stratosphere
 5545 can lead to reduced ozone in the lower stratosphere because of the reduced penetration of
 5546 solar UV into the lower stratosphere. Increases in N₂O lead to increases in the NO_x
 5547 catalytic loss cycle for ozone in the mid to upper stratosphere, because N₂O decomposes
 5548 to form NO_x in the stratosphere. The effect of increased NO_x is less in the lower
 5549 stratosphere, because the NO_x loss cycle plays a less prominent role, competing with the
 5550 HO_x and ClO_x catalytic loss cycles (Wennberg *et al.*, 1994). Finally, the oxidation of
 5551 CH₄ increases H₂O and ozone losses in the HO_x catalytic cycle in the upper stratosphere
 5552 and lower mesosphere. In the troposphere, ozone is increased because oxidation of CH₄
 5553 catalyzed by NO_x produces ozone.
 5554



5555

5556 **Figure 4.11** Comparison of perturbations to ozone amounts for changes in three principal greenhouse
 5557 gases: CO₂, N₂O, and CH₄, as a function of altitude in the troposphere, stratosphere, and mesosphere. The
 5558 changes are computed for six 30°-wide latitude bands with the NOCAR 2-D model and expressed as the
 5559 percent change from 2000 to 2100. The global mean change is shown with the black line in each panel.
 5560 The halogen changes follow the WMO (2003) scenario and greenhouse gas increases follow the IPCC A2

5561 scenario. The latter is high compared to other scenarios but was chosen to maximize the ozone response in
5562 the model. (Portmann and Solomon, 2007)
5563

5564 **4.3.4.1 Changes in Ozone from Stratospheric Circulation Changes**

5565 The net mass exchange between the troposphere and stratosphere is associated with the
5566 large-scale Brewer-Dobson circulation (Holton *et al.*, 1995) with a net upward flux in the
5567 tropics balanced by a net downward flux in the extratropics. Model studies indicate that
5568 climate change will impact the mass exchange rates across the tropopause. For a doubled
5569 CO₂ concentration, all 14 climate-change model simulations analyzed by Butchart *et al.*
5570 (2006) showed an increase in the annual mean troposphere-to-stratosphere exchange rate,
5571 with a mean trend of about 2% per decade. Consequences of such an increase include
5572 shorter lifetimes and more rapid removal from the atmosphere for long-lived gases,
5573 including CFCs, CH₄ and N₂O (Butchart and Scaife, 2001) and increased mass flux of
5574 ozone from the stratosphere to the troposphere at mid and high latitudes. A model
5575 simulation by Zeng and Pyle (2003) shows that a strengthened Brewer Dobson
5576 circulation would increase the flux of ozone to the troposphere. A larger flux results from
5577 increased transport across the tropopause and enhanced ozone amounts in the extra-
5578 tropical lower stratosphere. The enhanced ozone results from the strengthened circulation
5579 and decreases in ODSs and temperatures.

5580

5581 **4.4 THE EFFECT OF OZONE CHANGES ON CLIMATE PARAMETERS**

5582 Ozone and climate change are highly coupled as illustrated in Figures 4.1 and 4.2. The
5583 response of ozone to changes in stratospheric temperature and water vapor is discussed in
5584 Section 4.3 above. In this section, changes in atmospheric temperatures and circulation
5585 are described as examples of the feedback responses in the climate system to ozone

5586 depletion.

5587

5588 **4.4.1 Response of Stratospheric and Tropospheric Temperatures to Ozone Depletion**

5589 Temperatures have decreased throughout the stratosphere in recent decades as described

5590 above in Section 4.3.2. Furthermore, model simulations show that a combination of

5591 increases in greenhouse gases and water vapor and decreases in ozone can account for

5592 observed temperature changes. A more detailed examination of the ozone feedback on

5593 temperature was carried out with the SKYHI GCM for ozone decreases observed in the

5594 period 1979-1997 (Ramaswamy and Schwarzkopf, 2002). The results in Figure 4.12

5595 indicate that in the lower to middle stratosphere (5 – 100 hPa) ozone changes create a

5596 larger decrease in temperature than increases in WMOGHGs. In this case, these include

5597 CO₂, CH₄, N₂O, CFC11, CFC-12, CFC-113 and HCFC-22. However, above about 5 hPa

5598 (~38 km) changes in both ozone and WMOGHGs contribute significantly to temperature

5599 decreases. Thus, depletion in stratospheric ozone plays a significant role throughout the

5600 stratosphere in creating a reduction in stratospheric temperatures in GCM simulations.

5601

5602 The feedback on temperature for stratospheric ozone depletion extends into the upper

5603 troposphere. The Reading Narrow Band Model was used to calculate temperature

5604 changes for observed ozone depletion with the assumption of fixed dynamical heating

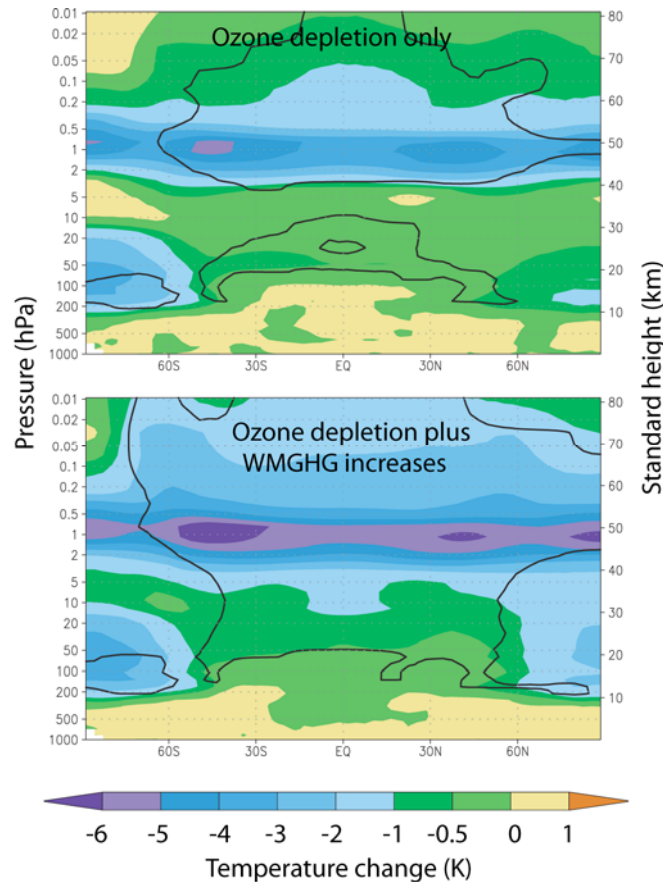
5605 (Forster *et al.*, 2007). Model cooling occurs in the 30 - 70 hPa (25-13 km) region due to

5606 ozone depletion. Short-wave absorption and upwelling long-wave radiation are both

5607 reduced and contribute comparably to the cooling in this region. The missing ozone also

5608 causes a decrease in the down-welling long-wave radiation that causes reduced

5609 temperatures at altitudes below the ozone depletion region (100-150 hPa, 21-14 km). This
 5610 feedback response or coupling of temperatures in different altitude regions is found at all
 5611 latitudes in the model and may be a cause of upper tropospheric temperature trends.
 5612



5613 **Figure 4.12** GCM feedback response of stratospheric temperatures to ozone depletion as observed
 5614 between 1979 and 1997. Upper panel: ozone changes alone. Lower panel: ozone changes plus increases in
 5615 WMGHGs over the same period. Solid lines enclose regions of statistical significance. (Adapted from
 5616 Ramaswamy *et al.*, 2002)
 5617

5618 4.4.2 Response of Surface Temperatures to Antarctic Ozone Depletion

5619 The largest depletion in stratospheric ozone is found over Antarctic in late winter/early
 5620 spring. Studies of Antarctic ozone depletion have revealed strong evidence for feedbacks
 5621 on the temperatures and circulation of the Antarctic troposphere (Gillett and Thompson,
 5622 2003; Thompson and Solomon, 2002). Severe ozone depletion strengthens the

5623 circumpolar winds of the Antarctic winter vortex in many model simulations. Recent
5624 observations show that strengthened circumpolar winds extend to the surface, especially
5625 in the summer months, with changes in geopotential heights serving as a proxy. A model
5626 with high vertical resolution was used to show anomalies in geopotential height in the
5627 troposphere could be well simulated in intensity and seasonality (Gillet and Thompson,
5628 2003). Changes in surface circulation also lead to cooling over most of the Antarctic
5629 continent and modest warming of the Antarctic Peninsula. Figure 4.13 shows model
5630 results compared to observed changes in 500-hPa geopotential height over a 22-year
5631 period and in surface temperature over a 32-year period (1969 to 2000), both averaged
5632 over December to May. The observed and simulated patterns in geopotential height and
5633 surface temperature show strong similarities, reinforcing the conclusion that stratospheric
5634 circulation influences tropospheric circulation patterns and, hence, that intense
5635 stratospheric ozone depletion can effect changes in surface climate parameters.

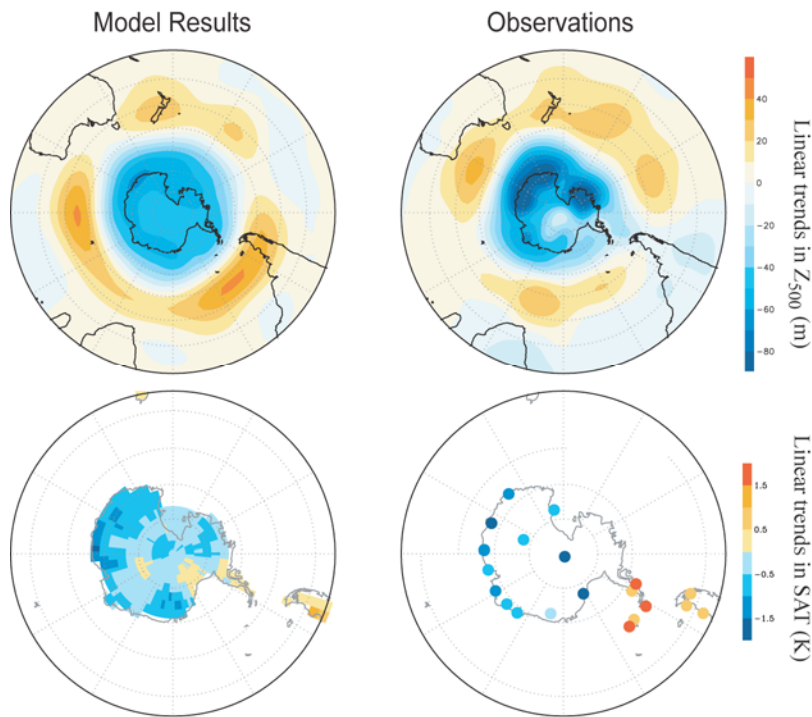
5636

5637 **4.5 IMPORTANCE OF VOLCANOES**

5638 **4.5.1 The Effect of Volcanic Aerosol on Ozone**

5639 Large volcanic eruptions are those that inject significant quantities of SO₂ into the
5640 stratosphere. SO₂ is subsequently oxidized to sulfuric acid, which condenses onto
5641 preexisting aerosols, causing significant increases in aerosol surface area and volume in
5642 the lower stratosphere. As a consequence, heterogeneous reactions occurring on these
5643 surfaces gain prominence in the chemical production and loss balance of ozone, leading
5644 to decreased ozone amounts (WMO, 2007: Figures 3-26). These reactions convert
5645 nitrogen oxides (NO_x) to a more stable form, nitric acid (HNO₃). In the lower

5646 stratosphere, reduced NO_x increases the role that reactive halogen compounds (ClO_x)
 5647 play in destroying ozone. Analysis following the most recent large volcanic eruption, that
 5648 of Mt. Pinatubo in 1991, shows that ozone amounts reached record lows and that halogen
 5649 reactions, aided by temperature variability could explain the observed losses (Solomon *et*
 5650 *al.*, 1998; Tie and Brasseur, 1995).
 5651



5652

5653 **Figure 4.13** Comparison of model results (left column) with observations (right column) for changes in
 5654 500-hPa geopotential height (m) (upper row) and near-surface temperature (K) (lower row) in the Southern
 5655 Hemisphere in response to stratospheric ozone depletion between 1979 and 1997. (Adapted from Gillett
 5656 and Thompson, 2003)
 5657

5658 As ODS amounts decrease to pre-1980 levels in the coming decades, the sensitivity of
 5659 ozone to depletion caused by volcanic aerosol reactions will also decrease. Global ozone
 5660 levels decreased by about 2% following the 1991 Mt. Pinatubo eruption. Sedimentation
 5661 and transport removal of volcanic aerosol occurs over a 2- to 3-year period following an

5662 eruption, so the effects are short lived compared to ODS atmospheric lifetimes which are
5663 45-100 yrs for principal species (*e.g.*, CFC-11 and CFC-12). Thus, expectations for the
5664 long-term recovery of ozone are not significantly affected by episodic volcanic eruptions.

5665

5666 The plumes of large volcanic eruptions contain significant amounts of HCl that are
5667 removed in the troposphere by uptake and sedimentation of liquid aerosols formed
5668 (Tabazadeh and Turco, 1993). However, some eruptions inject non-negligible amounts of
5669 HCl into the stratosphere, adding to inorganic chlorine. For example, temporary increases
5670 in HCl column amounts of up to 40% were observed after the Mt. Pinatubo eruption
5671 (Coffey, 1996). Overall, the frequency of explosive volcanic eruptions has been low in
5672 the past two decades, thereby precluding significant volcanic enhancements in global
5673 stratospheric chlorine.

5674

5675 Volcanic aerosols have a direct radiative impact that increases stratospheric temperatures
5676 while decreasing the surface temperatures. Volcanic aerosols scatter incoming solar
5677 radiation and absorb solar infrared radiation, heating the lower stratosphere. The
5678 tropospheric cooling that results can be expected to change the tropospheric circulation,
5679 as well as the interaction between the stratosphere and the troposphere. Lower
5680 stratospheric temperatures, for example, following the eruptions of El Chichón and Mt.
5681 Pinatubo, were observed to increase by about 1K near 20 km altitude (Figure 4.7). The
5682 loss of ozone following an eruption also adds to the temperature perturbation. Lower
5683 stratospheric temperatures influence water vapor amounts through dehydration of air
5684 parcels entering the stratosphere from the troposphere and influence ozone amounts

5685 through the sensitivity of ozone chemical reaction rates. Climate-chemistry model
5686 simulations of the temperature perturbations after the eruptions of El Chichón and Mt.
5687 Pinatubo often show larger increases than observed (Figure 4.7). The elevated
5688 temperatures are evident for several years and are followed by an overall slow cooling.
5689 The strength of the volcanic signal varies substantially between the different CCM and
5690 climate models (see also Eyring *et al.*, 2006).

5691

5692 Volcanic eruptions are not predictable but expected to be a feature of the future
5693 atmosphere. A large volcanic eruption is likely to occur in the next 30 years based on the
5694 historical record (Roscoe, 2001). Infrequent large volcanic eruptions would affect ozone
5695 with timescales as observed for previous large eruptions. A period of frequent large
5696 eruptions in the next century could enhance ozone depletion from ODSs for many years
5697 but the enhancement would lessen as global ODS abundances decline in the coming
5698 decades. Whenever the stratosphere is cleansed of volcanic aerosol, ozone abundances
5699 are expected to recover fully from volcanic effects.

5700

5701 **4.6 SUMMARY**

5702 Stratospheric ozone and climate change are linked through a variety of processes.
5703 Radiative forcing of climate occurs from the depletion of stratospheric ozone, as well as
5704 the increases in ozone-depleting substances. Global ozone depletion is a principal cause
5705 of decreasing temperature trends in the stratosphere and upper troposphere. Severe ozone
5706 depletion over Antarctica has changed the circulation over the continent in both the
5707 stratosphere and troposphere and altered surface temperatures. Other important

5708 components of anthropogenic climate change arise from emissions of long-lived
5709 greenhouse gases, such as carbon dioxide. Observed and anticipated changes in climate
5710 parameters include decreases in stratospheric temperatures and increases in stratospheric
5711 water vapor, carbon dioxide, methane, and nitrous oxide. Lower stratospheric
5712 temperatures reduce ozone loss rates in the mid to upper stratosphere, thereby aiding the
5713 recovery from ozone depletion. Enhanced water vapor alters ozone destruction rates in
5714 reactive hydrogen photochemistry and can increase the frequency and extent of polar
5715 stratospheric clouds, which aid ozone destruction. These varied composition changes
5716 contribute to circulation changes in the stratosphere and between the stratosphere and
5717 troposphere that can cause significant changes in the ozone distribution. The increases in
5718 stratospheric aerosols that follow explosive volcanic eruptions create several-year
5719 changes in climate parameters in the stratosphere and troposphere and increase ozone
5720 depletion.

5721

5722 The complexity of the interactions between ozone and climate involving changes in
5723 atmospheric composition pose a challenge to our understanding of basic stratospheric and
5724 tropospheric processes. Tools of the complexity of Chemistry Climate Models (CCMs)
5725 are required to combine stratospheric transport, dynamics, radiation, and chemistry and
5726 microphysics to analyze past ozone amounts and project future amounts. CCMs guided
5727 by atmospheric observations will help define the sensitivity of ozone to future climate
5728 changes and reduce the uncertainties in our understanding of ozone and climate
5729 interactions. As ozone depletion slows and ozone amounts recover from ODSs in the
5730 coming decades, changes in climate parameters will increase in importance in influencing

5731 stratospheric ozone amounts.

5732

5733 **4.6.1 Relevance for the United States**

5734 Human activities have led to changes in ozone abundances and climate parameters.

5735 Ozone depletion is attributed primarily to the accumulation of ozone-depleting substances

5736 and climate change is attributed to increases in long-lived greenhouse gases and surface

5737 albedo changes (Figure 4.5). Ozone is further influenced by changes in climate

5738 parameters such as stratospheric temperatures and composition, and atmospheric

5739 circulation. Since activities in the United States have caused significant emissions of

5740 greenhouse gases and ozone-depleting substances, the changes in ozone and climate

5741 attributable to human activities are, in part, attributable to the United States.

5742

5743 Decisions initiated or supported by United States policymakers have great potential to

5744 influence ozone and climate in the future. Important decisions could be taken on the

5745 following topics or issues:

5746

- 5747 • *Increased stringency of Montreal Protocol regulations.* The Montreal Protocol
5748 regulates production and consumption of ODSs in developed and developing
5749 nations. Stratospheric ODS amounts will decline to pre-1980 values around the
5750 middle of this century based on current regulations. More stringent regulations
5751 could accelerate this decline. For example, recent unratified regulation, supported
5752 by the United States, accelerates HCFC production in developed and developing
5753 nations.

- 5754 • *Increased destruction or capture of ODS banks.* Banks of ODS compounds
5755 represent large sources of future ODS emissions (see Chapters 2 and 5).
- 5756 • *Increased climate protection under the Montreal Protocol.* ODSs compounds are
5757 also greenhouse gases. Reducing ODS production and consumption under the
5758 Montreal Protocol has led to significant reductions in ODS atmospheric
5759 abundances and their associated radiative forcing of climate. Further reductions in
5760 ODS production, as well as emissions, will further protect climate. The
5761 accelerated HCFC phase-out under the Montreal Protocol represents a large
5762 potential benefit to climate. In addition, promotion of low-GWP compounds as
5763 replacement for ODSs in widespread applications can help minimize the climate
5764 consequences of new and existing Montreal Protocol regulations.
- 5765 • *Reductions in the future growth rates of methane and nitrous oxide emissions.*
5766 Ozone and climate are strongly influence by methane and nitrous oxide emissions.
5767 These emissions affect the photochemical production and loss of ozone in both
5768 the troposphere and stratosphere. Both gases are greenhouse gases that have
5769 increased significantly due to human activities.
- 5770

5771 **CHAPTER 4 REFERENCES**

- 5772 **Brasseur, G.** and S. Solomon, 1986: *Aeronomy of the Middle Atmosphere*, D. Reidel
5773 Publishing Co, Dordrecht, Holland.
5774
- 5775 **Butchart, N.,** A. A. Scaife, M. Bourqui, J. de Grandpré, S. H. E. Hare, J. Kettleborough,
5776 U. Langematz, E. Manzini, F. Sassi, K. Shibata, D. Shindell and M. Sigmund,
5777 2006: Simulations of anthropogenic change in the strength of the Brewer-Dobson
5778 circulation, *Climate Dynamics*, **27** (7-8), 727-741, doi:10.1007/s00382-006-0162-
5779 4.
5780
- 5781 **Butchart, N.** and A. A. Scaife, 2001: Removal of chlorofluorocarbons by increased mass
5782 exchange between the stratosphere and the troposphere in a changing climate.
5783 *Nature*, **410** (6830), 799-802.
5784
- 5785 **CCSP**, Temperature trends in the lower atmosphere: Steps for understanding and
5786 reconciling differences, 2006: T. Karl *et al.*, editors, A report by the Climate
5787 Change Science Program and the Subcommittee on Global Change Research,
5788 Washington, DC.
5789
- 5790 **Coffey, M. T.**, 1996: Observations of the impact of volcanic activity on stratospheric
5791 chemistry, *Journal of Geophysical Research*, **101**(D3), 6767-6780,
5792 doi:10.1029/95JD03763.
5793
- 5794 **Dameris, M.,** V. Grewe, M. Ponater, R. Deckert, V. Eyring, F. Mager, S. Matthes, C.
5795 Schnadt, A. Stenke, B. Steil, C. Bruhl, M.A. Giorgetta, 2005: Long-term changes
5796 and variability in a transient simulation with a chemistry-climate model
5797 employing realistic forcing. *Atmospheric Chemistry and Physics*, **5**, 2121-2145.
5798
- 5799 **Douglass, A. R.,** R. S. Stolarski, S. E. Strahan, and B. C. Polansky, 2006: Sensitivity of
5800 Arctic ozone loss to polar stratospheric cloud volume and chlorine and bromine
5801 loading in a chemistry and transport model. *Geophysical Research Letters*, **33**,
5802 L17809, doi:10.1029/2006GL026492.
5803
- 5804 **Dvortsov, V.L.,** and S. Solomon, 2001: Response of the stratospheric temperatures and
5805 ozone to past and future increases in stratospheric humidity. *Journal of*
5806 *Geophysical Research*, **106** (D7), 7505-7514.
5807
- 5808 **Eyring, V.,** N. R. P. Harris, M. Rex, T. G. Shepherd, D. W. Fahey, G. T. Amanatidis, J.
5809 Austin, M. P. Chipperfield, M. Dameris, P. M. De F. Forster, A. Gettleman, H. F.
5810 Graf, T. Nagashima, P. A. Newman, S. Pawson, M. J. Prather, J. A. Pyle, R. J.
5811 Salawitch, B. D. Santer, D. W. Waugh, 2005: A strategy for process-oriented
5812 validation of coupled-chemistry-climate models. *Bulletin of the American*
5813 *Meteorological Society*, **85**, 1117-1133, doi:10.1175/BAMS-86-8-1117.
5814

- 5815 **Eyring** V., N. Butchart, D. W. Waugh, H. Akiyoshi, J. Austin, S. Bekki, G. E. Bodeker,
5816 B. A. Boville, C. Brühl, M. P. Chipperfield, E. Cordero, M. Dameris, M. Deushi,
5817 V. E. Fioletov, S. M. Frith, R. R. Garcia, A. Gettelman, M. A. Giorgetta, V.
5818 Grewe, L. Jourdain, D. E. Kinnison, E. Mancini, E. Manzini, M. Marchand, D. R.
5819 Marsh, T. Nagashima, P. A. Newman, J. E. Nielsen, S. Pawson, G. Pitari, D. A.
5820 Plummer, E. Rozanov, M. Schraner, T. G. Shepherd, K. Shibata, R. S. Stolarski,
5821 H. Struthers, W. Tian, and M. Yoshiki, 2006: Assessment of temperature, trace
5822 species, and ozone in chemistry-climate model simulations of the recent past.
5823 *Journal of Geophysical Research*, **111**, D22308, doi:10.1029/2006JD007327.
5824
- 5825 **Forster**, P. M. D. F. and K. P. Shine, 1997: Radiative forcing and temperature trends
5826 from stratospheric ozone changes. *Journal of Geophysical Research*, **102**, 10841-
5827 10855.
5828
- 5829 **Forster**, P. M., G. Bodeker, R. Schofield, S. Solomon, D. Thompson 2007: Effects of
5830 ozone cooling in the tropical lower stratosphere and upper troposphere.
5831 *Geophysical Research Letters*, **34**, L23813, doi:10.1029/2007GL031994.
5832
- 5833 **Gauss**, M., *et al.*, 2006: Radiative forcing since preindustrial times due to ozone changes
5834 in the troposphere and the lower stratosphere. *Atmospheric Chemistry and*
5835 *Physics*, **6**, 575–599.
5836
- 5837 **Gillett**, N. P. and D. W. J. Thompson, 2003: Simulation of recent Southern Hemisphere
5838 climate change. *Science*, **302**, 273-275.
5839
- 5840 **Hansen**, J., *et al.*, 2005: Efficacy of climate forcings. *Journal of Geophysical Research*,
5841 **110**, D18104, doi:10.1029/2005JD005776.
5842
- 5843 **Holton**, J. R., P. H. Haynes, M. E. McIntyre, A. R. Douglass, R. B. Rood, and L. Pfister,
5844 1995: Stratosphere-troposphere exchange. *Reviews of Geophysics*, **33** (4), 403-
5845 440.
5846
- 5847 **IPCC**, 2007: Summary for Policymakers. In: *Climate Change 2007: The Physical*
5848 *Science Basis. Contribution of Working Group I to the Fourth Assessment Report*
5849 *of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M.
5850 Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)].
5851 Cambridge University Press, Cambridge, United Kingdom and New York, NY,
5852 USA.
5853
- 5854 **IPCC/TEAP**, 2005: Special Report: Safeguarding the ozone layer and the global climate
5855 system: Issues related to hydrofluorocarbons and perfluorocarbons,
5856 *Intergovernmental Panel on Climate Change*, Cambridge University Press,
5857 Cambridge, United Kingdom and New York, NY, USA.
5858
- 5859 **Isaksen**, I.S.A., (Editor) EC Air Pollution Report No. 81: Ozone-Climate Interactions,
5860 2003.

- 5861
5862 **Jonsson, A.I., J. de Grandpré, V.I. Fomichev, J.C. McConnell, and S.R. Beagley, 2004:**
5863 Doubled CO₂- induced cooling in the middle atmosphere: Photochemical analysis
5864 of the ozone radiative feedback. *Journal of Geophysical Research*, **109**, D24103,
5865 doi:10.1029/2004JD005093.
5866
- 5867 **Kiehl, J. T. and K. E. Trenberth, 1997:** Earth's annual global mean energy budget.
5868 *Bulletin of the American Meteorological Society*, **78**, 197-208.
5869
- 5870 **Langematz, U., M. Kunze, K. Krüger, K. Labitzke, and G.L. Roff, 2003:** Thermal and
5871 dynamical changes of the stratosphere since 1979 and their link to ozone and CO₂
5872 changes. *Journal of Geophysical Research*, **108** (D1), 4027, doi:
5873 10.1029/2002JD002069.
5874
- 5875 **McCormick, M. P., L. W. Thomason, and C. R. Trepte, 1995:** Atmospheric effects of the
5876 Mount Pinatubo eruption. *Nature*, **373**, 399-404.
5877
- 5878 **Mears, C., M. Schabel, and F. Wentz, 2003:** A reanalysis of the MSU channel 2
5879 tropospheric temperature record. *Journal of Climate*, **16**, 3650.
5880
- 5881 **Myhre, G., J. S. Nilsen, L. Gulstad, K. P. Shine, B. Rognerud, I. S. A. Isaksen, 2007:**
5882 Radiative forcing due to stratospheric water vapour from CH₄ oxidation.
5883 *Geophysical Research Letters*, **34**, L01807, doi:10.1029/2006GL027472.
5884
- 5885 **Newman, P.A., S.R. Kawa, and E.R. Nash, 2004:** On the size of the Antarctic ozone
5886 hole. *Geophysical Research Letters*, **31**, L21104, doi: 10.1029/2004GL020596.
5887
- 5888 **Oltmans, S.J., H. Vömel, D.J. Hofmann, K.H. Rosenlof, and D. Kley, 2000:** The increase
5889 in stratospheric water vapor from balloonborne frostpoint hygrometer
5890 measurements at Washington D.C., and Boulder, Colorado. *Geophysical*
5891 *Research Letters*, **27** (21), 3453-3456.
5892
- 5893 **Pawson, S., K. Labitzke, and S. Leder, 1998:** Stepwise changes in stratospheric
5894 temperature. *Geophysical Research Letters*, **25** (12), 2157-2160.
5895
- 5896 **Portmann, R. W. and S. Solomon, 2007:** Indirect radiative forcing of the ozone layer
5897 during the 21st century. *Geophysical Research Letters*, **34**, L02813,
5898 doi:10.1029/2006GL028252.
5899
- 5900 **Pyle, J., et al., 2005:** Ozone and climate: a review of interconnections. In: *Special Report*
5901 *on Safeguarding the Ozone Layer and Global Climate System: Issues Related to*
5902 *Hydrofluorocarbons and Perfluorocarbons* [Metz., B., et al. (eds.)]. Cambridge
5903 University Press, Cambridge, United Kingdom and New York, NY, USA, pp. 83–
5904 132.
5905

- 5906 **Ramaswamy, V.**, and M. D. Schwarzkopf, 2002: Effects of ozone and well-mixed gases
5907 on annual-mean stratospheric temperature trends. *Geophysical Research Letters*,
5908 **29** (22), 2064, doi:10.1029/2002GL015141.
5909
- 5910 **Ramaswamy, V.**, M. D. Schwarzkopf, W. J. Randel, B. D. Santer, B. J. Soden, and G. L.
5911 Stenchikov, 2006: Anthropogenic and natural influences in the evolution of lower
5912 stratospheric cooling. *Science*, **311**, 1138-1141.
5913
- 5914 **Randel, W.J.**, F. Wu, S.J. Oltmans, K. Rosenlof, and G.E. Nedoluha, 2004: Interannual
5915 changes of stratospheric water vapor and correlations with tropical tropopause
5916 temperatures. *Journal of Atmospheric Science*, **61** (17), 2133-2148.
5917
- 5918 **Randel, W.J.**, F. Wu, H. Vömel, G. E. Nedoluha, P. Forster, 2006: Decreases in
5919 stratospheric water vapor after 2001: Links to changes in the tropical tropopause
5920 and the Brewer-Dobson circulation. *Journal of Geophysical Research*, **112**,
5921 10.1029/2006JD007339.
5922
- 5923 **Rex, M.**, R.J. Salawitch, P. von der Gathen, N.R.P. Harris, M.P. Chipperfield, and B.
5924 Naujokat, 2004: Arctic ozone loss and climate change. *Geophysical Research*
5925 *Letters*, **31**, L04116, doi: 10.1029/2003GL018844.
5926
- 5927 **Roscoe, H.K.**, 2001: The risk of large volcanic eruptions and the impact of this risk on
5928 future ozone depletion. *Natural Hazards*, **23** (2-3), 231-246.
5929
- 5930 **Rosenlof, K.H.**, S.J. Oltmans, D. Kley, J.M. Russell III, E.-W Chiou, W.P. Chu, D.G.
5931 Johnson, K.K. Kelly, H.A. Michelsen, G.E. Nedoluha, E.E. Remsburg, G.C.
5932 Toon, and M.P. McCormick, 2001: Stratospheric water vapor increases over the
5933 past half-century. *Geophysical Research Letters*, **28** (7), 1195-1198.
5934
- 5935 **Santer, B.D.**, J.E. Penner, and P.W. Thorne, How well can the observed vertical
5936 temperature changes been reconciled with our understanding of the causes of
5937 these changes?, in *Temperature Trends in the Lower Atmosphere: Steps for*
5938 *Understanding and Reconciling Differences*, A Report by the U.S. Climate
5939 Change Science Program and the Subcommittee on Global Change Research,
5940 edited by T.R. Karl, S.J. Hassol, C.D. Miller, and W.L. Murray, 89-118, NOAA,
5941 National Climatic Data Center, Asheville, North Carolina, USA, 2006.
5942
- 5943 **Scherer, M.**, H. Vömel, S. Fueglistaler, S. J. Oltmans, J. Staehlin, 2007: Trends and
5944 variability of midlatitude stratospheric water vapour deduced from the re-
5945 evaluated Boulder balloon series and HALOE. *Atmospheric Chemistry and*
5946 *Physics Discussions*, **7**, 14511–14542.
5947
- 5948 **Schwarzkopf, M. D.**, and V. Ramaswamy, 2002: Effects of Changes in well-mixed gases
5949 and ozone on stratospheric seasonal temperatures. *Geophysical Research Letters*,
5950 **29** (24), 2184, doi:10.1029/2002GL015759.
5951

- 5952 **Seidel**, D. J., R. J. Ross, J. K. Angell, and G.C. Reid, 2001: Climatological characteristics
5953 of the tropical tropopause as revealed by radiosondes. *Journal of Geophysical*
5954 *Research*, **106** (D8), 7857-7878.
5955
- 5956 **Seidel**, D. J., and J. R. Lanzante, 2004: An assessment of three alternatives to linear
5957 trends for characterizing global atmospheric temperature changes. *Journal of*
5958 *Geophysical Research*, **109**, D14108, doi: 10.1029/2003- JD004414.
5959
- 5960 **Shine**, K. P., M. S. Bourqui, P. M. F. Forster, S. H. E. Hare, U. Langematz, P. Braesicke,
5961 V. Grewe, M. Ponater, C. Schnadt, C. A. Smith, J. D. Haigh, J. Austin, N.
5962 Butchart, D. T. Shindell, W. J. Randel, T. Nagashima, R. W. Portmann, S.
5963 Solomon, D. J. Seidel, J. Lanzante, S. Klein, V. Ramaswamy, and M. D.
5964 Schwarzkopf, 2003: A comparison of model-simulated trends in stratospheric
5965 temperatures. *Quarterly Journal of the Royal Meteorological Society*, **129** (590),
5966 1565-1588.
5967
- 5968 **Solomon**, S., R. Portmann, R. Garcia, W. Randel, F. Wu, R. Nagatani, J. Gleason, L.
5969 Thomason, L. Poole, and M. McCormick, 1998: Ozone Depletion at Mid-
5970 Latitudes: Coupling of Volcanic Aerosols and Temperature Variability to
5971 Anthropogenic Chlorine. *Geophysical Research Letters*, **25**(11), 1871-1874.
5972
- 5973 **SPARC**, 2000: *SPARC assessment of upper tropospheric and stratospheric water*
5974 *vapour*, Edited by D. Kley, J. M. Russell III, C. Phillips, Stratospheric Processes
5975 and their role in climate, SPARC Report No. 2.
5976
- 5977 **Stenke**, A., and V. Grewe, 2005: Simulation of stratospheric water vapor trends: impact
5978 on stratospheric ozone chemistry. *Atmospheric Chemistry and Physics*, **5**, 1257-
5979 1272.
5980
- 5981 **Tabazadeh**, A. and R. P. Turco, 1993: Stratospheric Chlorine Injection by Volcanic
5982 Eruptions: HCl Scavenging and Implications for Ozone. *Science*, **260** (5111),
5983 1082–1086, doi:10.1126/science.260.5111.1082.
5984
- 5985 **Thompson**, D. W. J., and S. Solomon, 2002: Interpretation of recent Southern
5986 Hemisphere climate change. *Science*, **296**, 895-899.
5987
- 5988 **Tie**, X., and G. Brasseur, 1995: The Response of Stratospheric Ozone to Volcanic
5989 Eruptions: Sensitivity to Atmospheric Chlorine Loading. *Geophysical Research*
5990 *Letters*, **22**(22), 3035-3038.
5991
- 5992 **Tilmes**, S., R. Muller, A. Engel, M. Rex, and J. Russell III, 2006: Chemical ozone loss in
5993 the Arctic and Antarctic stratosphere between 1992 and 2005. *Geophysical*
5994 *Research Letters*, **33** , L20812, doi:10.1029/2006GL026925.
5995
- 5996 **UNFCC**, 1997: United Nations Framework Convention on Climate Change, *Kyoto*
5997 *Protocol to the United Nations Framework Convention on Climate Change*.

5998

5999 **Velders, G. J. M., S. O. Andersen, J. S. Daniel, D. W. Fahey, M. McFarland, 2007:** The
6000 importance of the Montreal Protocol in protecting climate. *Proceedings of the*
6001 *National Academy of Sciences*, **104**, 4814-4819.

6002

6003 **Wennberg, P. O., R. C. Cohen, R. M. Stimpfle, J. P. Koplow, J. G. Anderson, R. J.**
6004 **Salawitch, D. W. Fahey, E. L. Woodbridge, E. R. Keim, R. S. Gao, C. R.**
6005 **Webster, R. D. May, D. W. Toohey, L. M. Avallone, M. H. Proffitt, M.**
6006 **Loewenstein, J. R. Podolske, K.R. Chan, and S. C. Wofsy, 1994:** Removal of
6007 stratospheric O₃ by radicals: *In situ* measurements of OH, H₂O, NO, NO₂, ClO,
6008 and BrO, *Science*, **266** (5184), 398-404.

6009

6010 **WMO (World Meteorological Organization), 2003:** *Scientific Assessment of Ozone*
6011 *Depletion: 2002*, Global Ozone Research and Monitoring Project – Report No.
6012 47, 498 pp., Geneva, Switzerland.

6013

6014 **WMO (World Meteorological Organization), 2007:** *Scientific Assessment of Ozone*
6015 *Depletion: 2006*, Global Ozone Research and Monitoring Project – Report No.
6016 50, 572 pp., Geneva, Switzerland.

6017

6018 **Zeng, G., and J. A. Pyle, 2003:** Changes in tropospheric ozone between 2000 and 2100
6019 modeled in a chemistry-climate model. *Geophysical Research Letters*, **30** (7),
6020 1392, doi:10.1029/2002GL016708.

6021

6022

6023

6024

6025

6026

6027

6028

6029

6030

6031

6032