THE STATUS OF NUMERICAL MODELING OF HALOCARBON IMPACTS ON STRATOSPHERIC OZONE

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INTRODUCTION

Numerical models of the chemistry and physics of the global atmosphere have played a key role in the scientific understanding of past, current and potential future effects of human-related emissions of halocarbons, including Halons, other brominated compounds and various replacement compounds on stratospheric ozone and climate change. As a result, these models have led directly to the Montreal Protocol and other national and international policy decisions regarding halocarbon controls due to their effects on stratospheric ozone.

The purpose of this paper is to provide a perspective on atmospheric models, the role they have played in studies of the effects of Halons and other halocarbons on ozone, and to discuss what role models will likely play in future studies of stratospheric ozone

THE COMPLEXITY OF STRATOSPHERIC OZONE

It is important to recognize that the stratospheric ozone layer is a naturally occurring phenomenon that has great benefits to life on Earth. In fact, the formation of the ozone layer is generally believed to have played an important role in the development of life here on Earth. The accumulation of oxygen molecules in the atmosphere allowed for the production of ozone. Gradually the increasing levels of ozone led to the formation of the stratosphere, a region of the upper atmosphere where temperature increases with altitude largely as a result of the absorption of solar radiation by ozone. The resulting screening of lethal levels of solar ultraviolet radiation by the ozone layer is thought to have been important in allowing life to migrate from the oceans onto land. A decrease in the amount of stratospheric ozone can thus increase the amount of harmful levels of ultraviolet radiation.

The distribution of ozone also has important implications for the Earth's climate system, not only because ozone absorbs solar radiation but also because it is a greenhouse gas that helps warm the Earth by absorbing some of the infrared radiation emitted from the Earth's surface, preventing it from going directly to space. Ozone is particularly effective as a greenhouse or heat-trapping gas at lower elevations (Figure 1). Thus, changes in both ozone distribution as well as overall amounts can also affect climate.

Ozone, O_3, is composed of three oxygen atoms and exists in gaseous form at atmospheric pressures and temperatures. Approximately 90 % of the atmospheric ozone is in the stratosphere. Most of the remaining ozone is in the troposphere, the lower region of the atmosphere extending from the Earth's surface up to roughly 10 km at midlatitudes and 16 km in the tropics. Figure 1 shows a typical vertical ozone distribution for mid-latitudes. At these latitudes, the peak concentrations of ozone occur at altitudes between 20 and 30 km. At high latitudes, the peak occurs at lower altitudes, largely as the result of atmospheric transport processes and the lower height of the tropopause (the transition region between the troposphere and stratosphere).

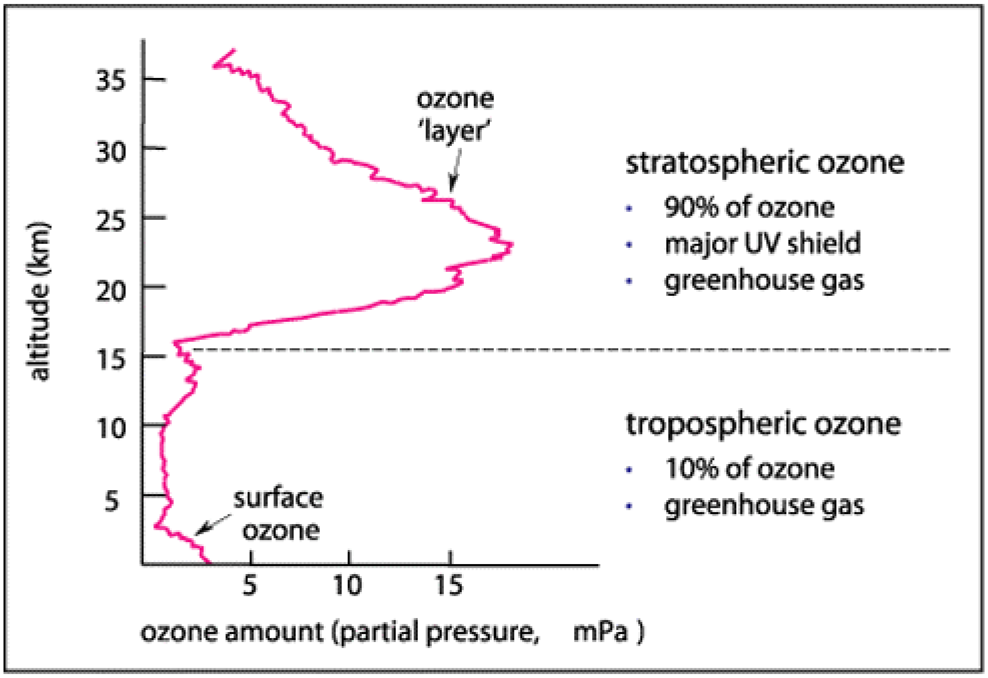


Figure 1. Typical vertical distribution of stratospheric ozone for mid-latitudes

The processes affecting the distribution of ozone are extremely complex, involving nonlinear chemical and photochemical processes and the combined effects of winds, waves (e.g., planetary waves, gravity waves), convection and other transport processes. Although the primary production of ozone occurs in the tropics and primarily above 30 km altitude, the largest concentrations of ozone occur at lower altitudes, and at higher latitudes. The minimum in total ozone actually occurs in the tropics, while the maximum amounts in total ozone occur in late winter and early spring in both hemispheres. The ozone peak is closer to the pole in the Northern Hemisphere than the peak in the Southern Hemisphere, largely due to the differences in winds and other processes affecting the transport of ozone between the two hemispheres. Variations in total ozone with longitude are generally small in comparison with variations with latitude; however, recent decreases in ozone during the Northern Hemisphere winter and early spring associated with ozone "hole" type processes have occurred at specific longitudes where the polar winter vortex was occurring in that hemisphere.

Because of the complexity of the processes affecting ozone, it is not possible to understand past and potential future changes in ozone through atmospheric observations or through a simple analytic solution of the continuity equation used to represent all of the processes affecting ozone. As a result, numerical models of the various processes affecting ozone have been developed to gain a better understanding of the changes occurring to ozone and of all of the factors affecting ozone. These models integrate our understanding of the past and current distributions of ozone and help us to understand how ozone might change in the future.

Changes in ozone can occur as a result of both natural and human-related causes. For example, natural variations in the solar flux [1] affect the production of stratospheric ozone. Variations in the solar flux during the 11-year solar cycle result in changes in total ozone of about 1.5 percent [2, 3]. Sulfuric aerosols from volcanic eruptions that are blown high into the atmosphere, such as that of Mt. Pinatubo in June 1991, can result in changes to the distribution of ozone for several years after the eruption [3-5]. These changes in ozone result from a complex set of photochemical, radiative, and transport interactions involving the radiative absorption and scattering by the aerosols and the changes in atmospheric chemistry that occur from the aerosols acting as sites for heterogeneous reactions with atmospheric gases. Human related emissions of chlorine-containing and bromine-containing halocarbons such as chlorofluorocarbons (CFCs), carbon tetrachloride (CCl_4), methyl chloroform (CH_3CCl_3) and Halons are now recognized as being largely responsible for the significant decreases in stratospheric ozone over the last few decades [3-5]. Emissions from these and other halocarbons are also likely to have a significant influence on future levels of ozone. There are also concerns about the impacts of emissions from current and projected fleets of commercial aircraft on both tropospheric and stratospheric ozone [6].

Greenhouse gases that cause climate change like carbon dioxide (CO_2) also affect stratospheric ozone; increasing concentrations of CO_2 radiatively cool the stratosphere, with resulting effects on the catalytic loss mechanisms controlling stratospheric ozone [7]. Increasing concentrations of methane (CH_4) and nitrous oxide (N_2O) are not only important as greenhouse gases, but also have direct effects on the amounts of hydrogen oxides and nitrogen oxides in the stratosphere and their corresponding catalytic mechanisms that affect ozone. Climate change in the troposphere can affect stratospheric ozone as a result of changing wind patterns in the stratosphere and the effects on transport of ozone, water vapor and other gases across the tropopause.

The recognition of possible threats to ozone has required ways of understanding and predicting the extent of possible changes to global ozone. Laboratory and direct atmospheric observations can provide important data towards understanding of the atmospheric processes affecting ozone; however, the chemical and physical processes determining the ozone distribution are much too complex for these measurements to provide adequate information alone towards predicting future changes to ozone. Numerical models of the global atmospheric chemistry and physics provide an important means to synthesize the laboratory and atmospheric observations, thus allowing for more complete study of these complex processes and the response of ozone to changes in these processes. Such models have been the primary tools for studies aimed at projecting possible changes to ozone. However, these models are only representative of the processes as they are understood and are, therefore, subject to uncertainties in their representation of the real atmosphere.

The distribution of ozone in the global atmosphere depends on a number of factors. These include: the chemistry and photochemistry leading to the production and destruction of ozone; the temperature, which affects ozone directly through effects on chemical rates of reaction and indirectly through effects on winds and clouds; and the winds and other processes leading to its transport within the atmosphere. As a result, the formidable task of predicting ozone requires that models consider the coupling of and interactions between the many chemical and physical processes affecting ozone and other relevant atmospheric constituents. The models used must also be applicable on a variety of spatial and temporal scales.

A HISTORICAL PERSPECTIVE ON ATMOSPHERIC MODELS

All models of atmospheric chemistry are based on the numerical solution of the continuity equation that represents all relevant chemical and photochemical reactions and the effects of relevant physical processes on all atmospheric gases and particles of interest. Most models are based on the Eulerian approach where the atmosphere is divided into a series of boxes that exchange mass to resolve spatial structure. A few are based on the Lagrangian approach where puffs of air are followed directly as they travel through the atmosphere. Both past and existing models of global atmospheric ozone and associated processes have used various simplifications of the processes involved in order to make the problems to be addressed more computationally tractable. For example, many of the models have used observed temperature distributions and fixed wind circulations. Reduced spatial dimensionality (i.e., longitudinal and latitudinal averaging) has historically been used to reduce computational complexity.

Most of the original studies of the chlorofluorocarbons and other halocarbon effects on ozone were done with, by today's standards, relatively crude one-dimensional (1-D). Although these models are not used much any longer, they were extensively used in studies of ozone in the 1970s and early 1980s, including most of the early analyses of the effects of CFCs and other halocarbons [8, 9]. These models were designed to represent the vertical distribution of relevant atmospheric constituents. Transport of these species is represented by vertical eddy diffusion, while chemistry is treated as completely as possible. These models required relatively little computer time and provided surprisingly reasonable representation (given the assumptions made) of the mid-latitude distributions of the species evaluated. The Ozone Depletion Potential concept was originally developed using a 1-D model [10]. However, as more powerful computers became available, the crudeness of their representation of atmospheric processes in 1-D models eventually led to the development to higher dimensional models.

In the late 1980s, as computing capabilities continued to improve, two-dimensional (latitude, altitude) models became the tools of choice for studies of stratospheric ozone because of their representation of latitudinal and seasonal variations. Two-dimensional models provide important information on variations with latitude as well as altitude, while also including full seasonal variations (not included in 1-D models). The effects of zonally averaged winds are included in the evaluation of species transport; eddy diffusion is generally used to represent the effects of wave activity and subgrid scale transport. A complete representation of chemical and photochemical processes can be included.

The vast majority of the analyses of halocarbon effects on ozone over the last 15+ years, including new evaluations of ODPs, have been based on results from two-dimensional models. These models are still useful and have the advantage of being much more computationally efficient than three-dimensional models, but they also have several significant deficiencies that can be particularly important in analyses of the potential impacts of halocarbon emissions. For example, for emissions of short-lived halocarbons (residence time less than a year), where tropospheric chemistry will be extremely important and the halocarbon gas would not be expected to have well-mixed distributions in the troposphere, two-dimensional models cannot adequately account for the strong spatial variations in tropospheric chemistry and associated constituents. The 2-D models just have no way of accounting fully for the short-lifetime chemistry of tropospheric constituents affected by strong variations in emissions from land- and ocean-related sources. These models also have major deficiencies in representing the polar winter vortex and thus ozone "hole" processes. However, the 2-D models have been redesigned in the last few years to much better represent the observed strong observational-based variations in the "age of air" with latitude and altitude in the stratosphere, thus improving their capabilities for determining halocarbon effects on ozone.

Although three-dimensional (3-D) chemical-transport models have existed since the early 1970s, models representing the full three-dimensional behavior of the coupled troposphere and stratosphere have only recently been developed. Earlier models either represented either stratospheric processes or tropospheric processes but not both. Three-dimensional models are extremely computationally intensive but are the preferred tools for global atmospheric studies of the troposphere and stratosphere. However, the 3-D models are not yet necessarily better in representing stratospheric ozone effects than 2-D models. There is a large additional computational burden imposed by incorporating chemistry into a Global Climate Model (GCM) that solves the complete set of equations of momentum, energy, thermodynamic, and mass continuity. As a result, several different approaches are used; these models are now designed so that they can be fully coupled with climate models or can be run with fixed meteorological fields from climate models or from assimilations of observed datasets. The models with fixed meteorological fields, because of reduced computational requirements, are used in most research studies at this point.

THE EVALUATION OF MODELS

For the predictions from models to be relevant, the capabilities and limitations of the models need to be well understood. There are several approaches used to test the quality of atmospheric models: (a) comparison with atmospheric observations, if possible, under the conditions (temporally, spatially) that the measurements were made; (b) comparison of model-predicted responses to natural- or human-induced perturbations to ozone; (c) comparison with the predictions of other suitable models; and (d) analysis of uncertainties in the treatment of chemistry, physics, and other model parameters. All of these approaches are used in evaluating models, although each of them has limitations due to insufficient data for a complete analysis. As part of the assessments of stratospheric ozone, a number of modeling groups have been brought together to apply these tests to a set of global atmospheric models used to study human effects on ozone [11].

An important test of the accuracy of the numerical models used for prognostic purposes is their comparison with detailed atmospheric observations**.** Over the last twenty-five years, an extensive amount of data from ground-, balloon-, aircraft-, and satellite-based instruments have become available for study of the stratosphere. Model-derived atmospheric distributions of relevant constituents are then compared with the measurements they are attempting to simulate. A variety of comparisons are used in order to test various aspects of the capabilities of the model, such as the chemically or dynamically driven relationship between different gases or the derivation of diurnal variations in a given gas.

Adequate representation of the present-day atmosphere is a necessary but insufficient condition for testing the accuracy of these models as predictive tools. It is also important to compare the changes in atmospheric parameters such as species distributions with existing measurements following an existing natural or anthropogenic perturbation to ozone. Unfortunately, there are only a few such events that can help define the accuracy of models.

One example is the comparison of model results with the observed change in ozone over recent decades. Figure 2 shows the excellent comparison found when results from the current version of the UIUC 2-D model are compared with observations of total ozone columns from the Solar Backscatter Ultraviolet (SBUV) satellite instrument. The effects of the Quasi-Biennial Oscillation (QBO), a wave-driven variation in ozone with a cycle of roughly two years, was eliminated from the data because the model does not represent QBO effects.

In addition to the changing emissions of halocarbons and the corresponding changes in chlorine and bromine amounts in the stratosphere, there are many possible factors that could determine the state of future ozone levels in the global atmosphere. Models are being used to evaluate the possible importance of potential perturbations to ozone. After sufficient testing and evaluating of a model to gain confidence in its capabilities and to have understanding of its limitations and associated uncertainties, one also gains some sense of confidence in the use of models to predict future conditions. However, forecasts of future changes in ozone from human-related emissions depend on the projections made in all of the constituents and other factors that influence ozone. Thus, projections of changes in ozone into the near future, perhaps over the next few years, can be made with reasonable accuracy, but projections are increasingly uncertain as the time extends farther into the future. These uncertainties derive both from those in the model itself and from limitations in the ability to project emissions from future human activities (and uncertainties in projected changes in nature, such as in the solar flux).

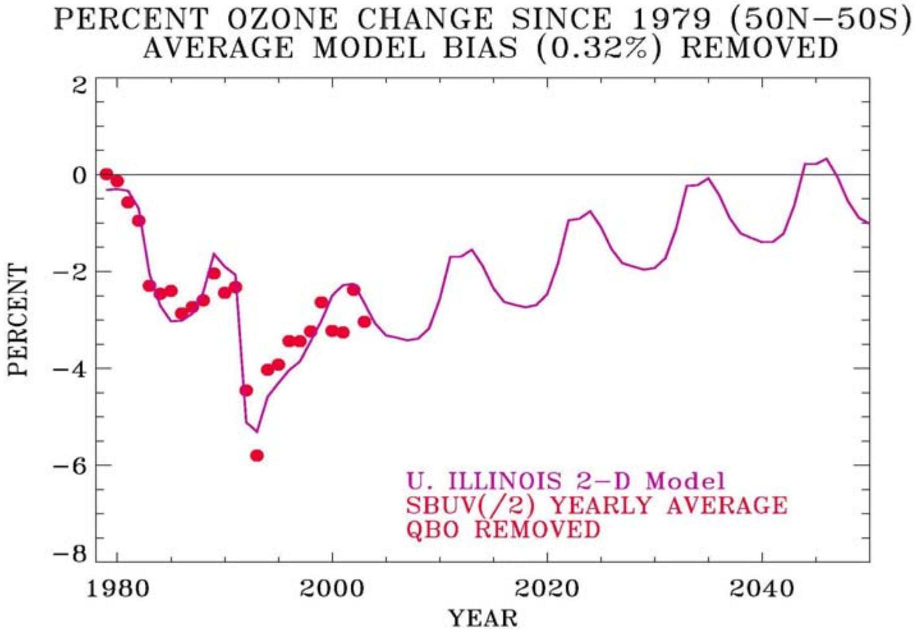


Figure 2. Comparison of total ozone derived changes in total ozone between 50 degrees North and 50 degrees South derived from the UIUC 2-D model (solid line) compared with annually averaged satellite data from the Solar Backscatter Ultraviolet (SBUV) spectrometer (solid circles). Model includes effects of changing emissions of halocarbons and other gases, solar flux variations, aerosols from volcanic eruptions and observed changes in stratospheric temperatures. Model projections into the future follow the expected emissions changes following the Montreal Protocol for halocarbons and a mid-level (A2) scenario from IPCC [7] for other gases. The effect of solar variations based on the last 11-year solar cycle is repeated in the future years.

USING MODELS TO RELATE SCIENCE TO POLICY

Chlorine, bromine and iodine atoms react extremely efficiently with ozone in catalytic processes. Thus, chlorine, bromine, or iodine released in or transported to the stratosphere can destroy thousands of ozone molecules. The concept of Ozone Depletion Potentials (ODPs) [10, 3, 4, 12] arose as a means of determining the relative ability of a chemical to destroy ozone. Thus a key screening approach relative to stratospheric ozone is to ask whether the chemical being considered contains chlorine, bromine, or iodine. If it does, then the ODP needs to be determined.

The concept of ODPs provides a relative cumulative measure of the expected effects on ozone of the emissions of a gas relative to CFC-11, one of the gases of most concern to ozone change. The ODP of a gas is defined as the integrated change in total ozone per unit mass emission of the gas, relative to the change in total ozone per unit mass emission of CFC-11. Alternatively, the ODP can be derived by using a constant emission calculated to steady state relative to the same for CFC-11. Numerically, the two approaches are equivalent. As a relative measure, ODPs are subject to fewer uncertainties than estimates of the absolute percentage of ozone depletion caused by different gases. ODPs are an integral part of national and international considerations on ozone-protection policy, including the Montreal Protocol and its Amendments and the U.S. Clean Air Act. ODPs provide an important and relatively straightforward way of analyzing the potential for a new chemical to affect ozone relative to CFCs, Halons, and other replacement compounds.

ODPs are currently determined by two different means: calculations from models, primarily from models of the global atmosphere, historically primarily from zonally averaged two-dimensional models, and the semi-empirical approach [12, 13]. The two approaches give very similar results. In the model derivation of ODPs, the compounds are assumed to enter the atmosphere at ground level, and are then transported in the atmosphere by dynamical processes and react by a variety of pathways, depending on their molecular structure and associated reactivity. The compounds may undergo photolytic breakdown by UV or near-UV light, react with OH in the troposphere and stratosphere, or react with atomic oxygen. Products resulting from these reactions, such as atomic chlorine and bromine, can react in the modeled atmosphere, which in turn may affect the calculated distribution of ozone. A major uncertainty in the models is the amount of tropospheric hydroxyl, OH. Since few reliable measurements of OH are available, the global distribution has not been directly measured. As a result, given the importance of the atmospheric lifetime in determining the ODP for a substance, those gases where reaction with tropospheric OH is the primary loss mechanism, as it is for many of the replacement compounds, a scaling to the partial lifetime based on atmospheric observations of methyl chloroform (CH_3CCl_3) is used due to its reaction with tropospheric OH.

Table 1 shows a sample list of derived Ozone Depletion Potentials for several compounds, emphasizing some of the compounds containing bromine. By definition, the ODP for CFC-11 is 1.0. The calculated ODPs for other chlorofluorocarbons (CFCs) being banned are all greater than 0.4. The Clean Air Act currently calls for policy actions on compounds whose ODPs are greater than 0.2. The ODPs for halons are all extremely large, much greater than 1.0, reflecting the high reactivity of bromine with ozone. Except for extremely short-lived compounds, the ODPs of brominated compounds generally tend to all have ODPs higher than 0.1. The ODPs for the hydrogenated CFCs (HCFCs) being used or considered as replacements are generally quite small relative to CFCs. The effect on ozone from a unit mass emission of one of these HCFCs would correspondingly be less than a hundredth of the effect on ozone than the CFC or Halon they would replace. ODPs for all the halocarbons not containing chlorine, bromine or iodine, e.g., the HFCs, PFCs, and for sulfur hexafluoride are near zero, owing to the low reactivity of their dissociation products with ozone.

The ODP of methyl bromide (CH_3Br) has changed over the last 15 years as understanding improved of the surface removal processes for CH_3Br. In addition to its reaction with atmospheric OH, methyl bromide has removal through fluxes into the oceans, soils and to a lesser degree into plants. As understanding of these processes improved, the atmospheric lifetime of CH_3Br became smaller with a corresponding effect on the ODP. However, the current ODP of 0.38 has not changed in the last two ozone assessments [4, 12] even though understanding of the removal processes continued to improve. Although there could continue to be further refinements in the surface losses, it is unlikely that there will continue to be significant changes in the ODP for CH_3Br.

The definition of ODPs has been revised for extremely short-lived compounds [14, 12], those compounds with atmospheric lifetimes less than one year. The new ODP definition for these compounds account for the variation that can occur in the ODP as a function of where and when the compound is used and emitted. The most important factor is likely to be the latitude of the emissions because gases emitted at higher latitudes take longer to reach the stratosphere than gases emitted in the tropics (as a result of the solar-driven atmospheric circulation patterns). The only short-lived compound currently evaluated is 1-propyl bromide, and only a range of estimated ODPs are available for it. Future evaluations of ODPs for short-lived gases need to be based on three-dimensional models representing the full chemistry and physics processes affecting the gases and their reaction products in the troposphere and stratosphere.

Table 1 also shows sample results for the Global Warming Potentials of the selected compounds. Global Warming Potentials (GWPs) provide a means for comparing the relative effects on climate expected from various greenhouse gases [12, 7]. The concept of Global Warming Potentials (GWPs) is used to estimate the relative impact of emission of a fixed amount of one greenhouse gas compared to another for globally averaged radiative forcing of the climate system over a specified time scale. Greenhouse gases in the atmosphere absorb infrared radiation emitted by the Earth that would otherwise escape to space. This trapped radiation warms the atmosphere, creating a positive forcing on climate, called radiative forcing, which in turn warms the Earth's surface. The concept of radiative forcing provides an estimate of the potential effect on climate from greenhouse gases. For the given concentration of a gas, the radiative forcing depends primarily on the infrared absorption capabilities of the gas. GWPs are expressed as the time-integrated radiative forcing from the instantaneous release of a kilogram of a gas expressed relative to that of a kilogram of the reference gas, carbon dioxide. Numerical models are used to determine the atmospheric lifetimes and radiative forcing for the various compounds. GWPs are a better measure of the relative climatic impacts than radiative forcing alone as they also account for the atmospheric lifetime, and thus the change in concentration for a given emission, of the gases. GWPs have been evaluated for a number of replacement compounds and have been reported in the international IPCC and WMO assessments. The GWP concept is also being used in policymaking considerations associated with concerns about global warming from greenhouse gases, generally with a 100-year integration time. In relationship to halocarbons and halocarbon replacements, policymakers are most concerned about GWPs that are quite large such as those for the CFCs (note however, that although CO_2 has a GWP of 1 by definition, it is still the greenhouse gas of most concern to current concerns about climate change).

THE FUTURE OF MODELING STRATOSPHERIC OZONE

Three-dimensional models, in principle, should give the most realistic simulation of the atmosphere. With further advancements in the science representation in these models and with enhanced computer resources, three-dimensional models should become the tool of choice for future studies of stratospheric ozone processes within the next few years. Before that happens, there are a few key areas of uncertainties that still need to be resolved for these models. One of the key uncertainties is their representation of chemical and transport processes in the region of the tropopause, the transition region between the troposphere and stratosphere. Extensive analyses are ongoing to study this region and the processes that affect the transport of gases and particles across the tropopause.

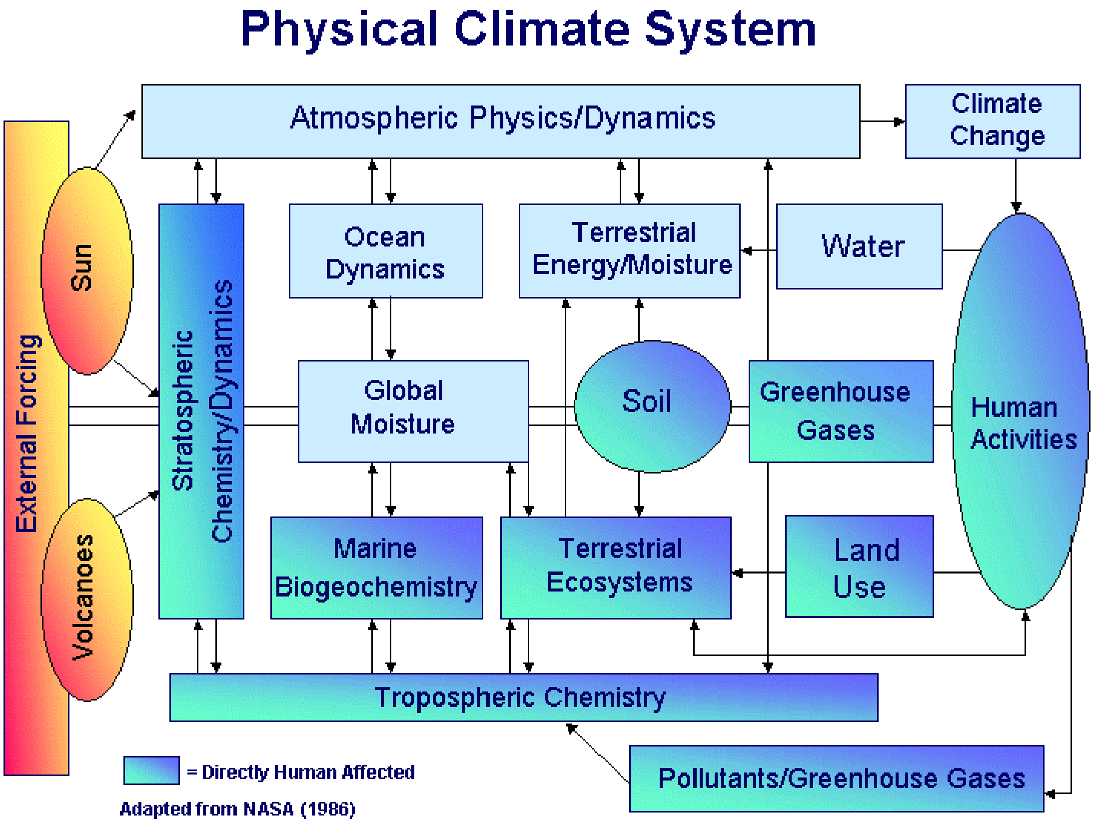
Future studies of the stratosphere are also likely to involve a much fuller representation of the interactive coupling between the biosphere, the troposphere and the stratosphere, As mentioned earlier, changes in climate could have important implications to the future levels of stratospheric ozone. Figure 3 gives a simple diagram of some of the interactions occurring within the Earth's climate system that may be important to studying future changes in ozone.

Table 1. ODPs and GWPs (100 year integration) for sample halocarbons. Atmospheric lifetimes correspond to best available modeling studies. There are differences between the WMO [12] and IPCC [7] assessment values for GWPs due to further refinement in radiative forcing and atmospheric lifetimes for some compounds.

Chemical Name	Atmos. Lifetime, (years)	ODP [12]	GWP [12]	GWP [7]
CFC-12 Dichlorofluoromethane	100	1.0	10720	10600
Halon-1211 (CF_2ClBr) Bromochlorofluoromethane	16	6.0	1860	1300
Halon-1301 (CF_3Br) Bromotrifluoromethane	65	12	7030	6900
Halon-2402 ($C_2F_4Br_2$) Dibromotetrafluoroethane	20	<8.6	1620	
CH_3Br Methyl bromide	0.7	0.38	5	5
$CHFBr_2$ Dibromofluoromethane	7.0	1.0		
CHF_2Br (HBFC-12B1) Bromodifluoromethane		0.74	470	
CH_2FBr Bromofluoromethane		0.73		
CH_2BrCl Chlorobromomethane	0.37	0.12		

Although still under major development and currently extremely computationally intensive, models of the entire Earth system that incorporate these interactions and feedbacks will likely become favored tools for studies of atmospheric chemistry as this decade progresses. Models such as the Whole Atmosphere Community Climate Model (WACCM) being developed at the National Center for Atmospheric Research that incorporate interactively all of the important physics and chemistry of the troposphere, stratosphere and higher altitudes, but that do not incorporate all of the land, ocean, and ecosystem interactions, will in the interim improve our understanding of how stratospheric ozone may change this century as a result of climate change and the other factors influencing its distribution.

With the exception of zero-dimensional models and their trajectory model counterparts, other modeling approaches (e.g., 2-D models) will likely not be used in research by the end of this decade. Zero-dimensional or box models will continue to be used in studies of atmospheric ozone, but primarily as diagnostic tools in initial evaluation of changes in chemistry from laboratory studies and in understanding of atmospheric processes related to specific atmospheric measurements.



Adapted from NASA (1986)

Figure 3. A simplistic representation of the full complexity required in a model of the Earth's climate system that consider the implications of atmospheric chemistry processes in the troposphere and stratosphere.

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