CHAPTER 1

Introduction

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Summary

- The lifetimes of chemical species are used to predict their future abundances, to perform emission estimates, and to calculate the ozone-depletion potentials (ODPs) and global warming potentials (GWPs). It is therefore very important to have the best possible estimates of lifetimes of ozone depleting substances (ODSs), replacement compounds, and climate forcing gases to guide policy making of these substances.

- Twenty-seven chemical species are evaluated in this report. These substances were chosen because they are either ODSs, are being used as replacements for ODSs, or are major climate-forcing gases. No comprehensive evaluation of lifetimes of these substances has been performed since the mid-1990s. Important progress in modeling and observations along with unresolved science challenges necessitate revisions to current lifetime estimates.

Chapter 1: An Introduction to the Lifetimes of Stratospheric Ozone-Depleting Substances, Their Replacements, and Related Species

For a long-lived halocarbon source gas (atmospheric lifetime > 0.5 years), knowing the time evolution of surface concentrations is the first step in obtaining estimates for its contribution to both ozone depletion and radiative forcing. This behavior can be approximated by a simple integral (see Equation 1.4) if an appropriate constant lifetime is specified. Unfortunately, the lifetime of a chemical species in the atmosphere is not an observable quantity. Slightly different values for the lifetime are derived using different methods that, to varying degrees, make use of the following information:

- Physical and chemical properties of the species
- Chemical and radiative environment of the atmosphere
- Spatial and temporal distribution of the species in the atmosphere
- Spatial and temporal information of the species' emissions
- Transport pathways in the atmosphere

Different values for the lifetime of an ozone depleting substance (ODS) are being used to predict its future abundances from given emissions, to derive estimates for emissions based on observed abundance, and to calculate the ozone-depletion potentials (ODPs) and global warming potentials (GWPs). Thus, changes in the recommended value have implications for estimates of the timing for ozone recovery as the concentrations of the controlled ODSs fall below the threshold for ozone depletion. This will also have an indirect effect on the radiative forcing. It is therefore very important to have the best possible estimates of ODS lifetimes to guide policy making on these substances.

Comprehensive atmospheric chemistry/transport models provide a self-consistent framework for calculating lifetimes, but the accuracy of lifetimes calculated with models depends on their ability to represent the atmosphere. While models have significantly improved since the last lifetime evaluation (Kaye *et al.,* 1994), estimates of CFC and other species' lifetimes still include significant uncertainties resulting from model representations of chemistry, radiation, and transport. Accurate determination of lifetimes using observations (i.e., concentration measurements) requires knowledge of the atmospheric burden, its rate of change, and quantification of past emissions. There is insufficient information to determine lifetimes (particularly steady-state lifetimes, see Chapter 2) solely from observations.

Theoretical concepts as well as numerical results derived from modeling studies are needed to bridge the gap. The quality of information on the burdens, the emissions, and the loss rate is limited and so all have associated uncertainties which limit the accuracy of the derived lifetime estimates. Therefore, evaluating the various sources of uncertainty is a central part of this report.

In the past several years it has become evident that recommended lifetimes of some ODSs do not agree with lifetimes deduced from sophisticated models or lead to inferred emissions (from observed atmospheric burden) that do not agree with independent bottom-up emission estimates. For example, in the 2010 Ozone Assessment Report (Montzka and Reimann, 2011) an inconsistency was noted in the global budget of carbon tetrachloride (CCl_4). Resolving the inconsistency will require a combination of identifying missing sources and/or assuming a longer lifetime for CCl_4. The other example has to do with the lifetime of CFC-11. Modeling studies (e.g., Douglass *et al.* 2008) indicated that the global CFC-11 lifetime was possibly longer than the value of 45 years, which has been used since the 1998 Ozone Assessment Report (WMO, 1999). This is of particular importance since CFC-11 is the reference species in defining ODPs, and its lifetime is used as a reference to obtain lifetimes of other ODSs (see Chapter 4).

This report is the first comprehensive attempt in over a decade to assess the impact of new developments in existing methods and models for the evaluation of atmospheric lifetimes. This lifetime evaluation report aims not only to provide new estimates of lifetimes but also to deliver an in-depth analysis of their uncertainties.

This report is limited to analyzing and estimating atmospheric lifetimes and their uncertainties for substances with atmospheric lifetimes greater than 6 months. Very short-lived substances (VSLSs) are not included in this report since the concept of a single atmospheric lifetime cannot be used to relate VSLS emissions to observed concentrations (see e.g., Montzka and Reimann, 2011 and references therein). This report also does not include estimates of either ODPs or GWPs. Although a substance's ODP and GWP are approximately proportional to its lifetime, there are a number of theoretical considerations that cause empirical estimates to differ from model-estimated values. This report also does not include analysis of emissions or how uncertainty in the emissions affects the budget uncertainties. All of these limitations are mainly a result of the desire to constrain the scope of the report. Finally, carbon dioxide (CO_2) is not considered in this report because its atmospheric lifetime is ultimately defined by the exchange with the ocean and land surfaces.

Table 1.1 lists the 27 species evaluated in this report. Also given are the previously recommended lifetimes, the 2008 atmospheric mixing ratios, and the basis for their inclusion in this report. The species marked in bold indicate the high priority for model simulations performed for this report. The reasons for a special focus on these species are:

- CFC-11 and CFC-12 are major ODSs with long data records for surface concentrations and historical emission rates.
- There is a need to reconcile the lifetime of carbon tetrachloride (CCl_4), which is in conflict with the observed trends of surface mixing ratios and reported emissions (Montzka and Reimann, 2011).
- The model calculated methyl chloroform (CH_3CCl_3) lifetime has served as a proxy for model calculated tropospheric OH abundance (Prinn *et al.,* 1987). Subsequently, this OH value is used to estimate the lifetimes of substances that are primarily removed in the

troposphere (Table 1.1) from their reaction rate constants with OH. Observations of methyl chloroform surface concentration in the next decade should provide further validation of its lifetime since banking is not an issue for its applications.
- HCFC-22 is the ODS replacement with the highest current emissions.
- Methane (CH_4) and nitrous oxide (N_2O) are not only greenhouse gases but they are also critical for stratospheric ozone chemistry because of their roles as sources gases of odd hydrogen and odd nitrogen radicals. Their lifetimes and distributions are important diagnostics of model performance. Furthermore, the CH_4 chemistry is needed for proper simulations of tropospheric OH radicals.
- HCFCs and HFCs are included because they are replacement compounds for many ODS uses and have relatively high GWP values.
- Halons are evaluated because of their contribution to stratospheric ozone depletion.

Lifetime and Atmospheric Burden

A full description of the different definitions of lifetime, and the relationship among lifetime, emission and burden are provided in Chapter 2 of this report. Specifically, the formalism explains how a given lifetime value can be used to predict burdens from emissions, and how the observed burden and emission history can be used to derive a value for the lifetime. The atmospheric lifetime of a molecule can be simply thought of as the time it remains in the atmosphere. As noted above, its magnitude depends on the properties of the molecule, the properties of the atmosphere, and where and when the molecule is emitted. This means that a molecule does not have a unique lifetime and that the lifetime is time-dependent. Calculation of the lifetimes relies on the basic equation that relates the time evolution of the atmospheric burden $B(t)$ of an atmospheric constituent to its sources $S(t)$ (emissions or *in situ* production) and its removal processes $R(t)$:

$$\frac{\partial B(t)}{\partial t} = S(t) - R(t) \qquad (1.1)$$

The 2nd term on the right (R) represents the removal rate of the molecule and is related to the local concentration $n(x,y,z,t)$ of the species and the local removal frequency $L(x,y,z,t)$ (with $R(t)=\int Ln\,dV$, where the volume integral $dV=dxdydz$ is over the whole atmosphere).

Equation (1.1) is not very useful in practice because we often do not have sufficient information to solve for $n(x,y,z,t)$ and $L(x,y,z,t)$ explicitly. It is desirable to have alternative methods to calculate burdens from emissions. If we define the global atmospheric lifetime $\tau(t)$ as

$$\tau(t) = \frac{B(t)}{R(t)} \qquad (1.2)$$

Equation (1.1) becomes:

$$\frac{\partial B}{\partial t} = S(t) - \frac{B(t)}{\tau(t)} \qquad (1.3)$$

Table 1.1. The list of 27 species evaluated in this report, with previous lifetimes and 2008 mixing ratios (WMO, 2011). Bold fonts represent high priority species.

Name	Formula	Lifetimes from WMO (2011) [a]	Mixing Ratio in 2008 [b]	Remarks [c]
Primarily stratospheric removal				
CFC-11	CCl_3F	45 yr	244.1 ppt	Long-lived ODS, reference for ODP, chlorine source gas
CFC-12	CCl_2F_2	100 yr	536.5 ppt	Long-lived ODS, chlorine source gas
CFC-113	CCl_2FCClF_2	85 yr	76.9 ppt	Long-lived ODS, chlorine source gas
CFC-114	$CClF_2CClF_2$	190 yr	16.4 ppt	Long-lived ODS, chlorine source gas
CFC-115	$CClF_2CF_3$	1020 yr	8.4 ppt	Long-lived ODS, chlorine source gas
CCl₄	CCl_4	35 yr [d]	89.8 ppt	Long-lived ODS, chlorine source gas
Nitrous oxide	N_2O	114 yr [e]	321.6 ppb	Natural and anthropogenic sources Greenhouse gas, odd-nitrogen source gas
Halon-1211	$CBrClF_2$	16 yr [f]	4.2 ppt	Long-lived ODS, bromine source gas
Halon-1301	$CBrF_3$	65 yr	3.2 ppt	Long-lived ODS, bromine source gas
Halon-2402	$CBrF_2CBrF_2$	20 yr [f]	0.5 ppt	Long-lived ODS, bromine source gas
Nitrogen trifluoride	NF_3	500 yr	0.45 ppt [g]	Greenhouse gas
Primarily tropospheric removal				
Methane	CH_4	8.7yr/12.0 yr [e,h]	1781.3 ppb	Natural and anthropogenic sources Greenhouse gas, odd-hydrogen source in the atmosphere
Methyl chloroform	CH_3CCl_3	5 yr	10.9 ppt	Long-lived ODS, chlorine source gas
Methyl chloride	CH_3Cl	1.5 yr [i]	546.0 ppt	Mainly natural sources, chlorine source gas
Methyl bromide	CH_3Br	1.9 yr [i]	7.4 ppt	Natural and anthropogenic sources, bromine source gas
HCFC-22	$CHClF_2$	11.9 yr	191.5 ppt	CFC replacement, chlorine source gas
HCFC-141b	CH_3CCl_2F	9.2 yr	19.4 ppt	CFC replacement, chlorine source gas
HCFC-142b	CH_3CClF_2	17.2 yr	18.7 ppt	CFC replacement, chlorine source gas
HFC-23	CHF_3	222 yr	21.8 ppt	Mainly a by-product in HCFC-22 production
HFC-32	CH_2F_2	5.2 yr	2.7 ppt	ODS replacement
HFC-125	CHF_2CF_3	28.2 yr	6.1 ppt	ODS replacement
HFC-134a	CH_2FCF_3	13.4 yr	47.9 ppt	ODS replacement
HFC-143a	CH_3CF_3	47.1 yr	8.5 ppt	ODS replacement
HFC-152a	CH_3CHF_2	1.5 yr	5.9 ppt	ODS replacement
HFC-227ea	CF_3CHFCF_3	38.9 yr	0.45 ppt[j]	ODS replacement
HFC-245fa	$CHF_2CH_2CF_3$	7.7 yr	1.0 ppt	ODS replacement
Halon-1202	CF_2Br_2	2.9 yr [k]	0.03 ppt [l]	Long-lived ODS, bromine source gas

[a] Previous atmospheric lifetimes are from WMO (2011), unless indicated otherwise.

[b] Mixing ratios in 2008 are an average of NOAA and AGAGE measurements from Table 1-1 of WMO (2011), if not indicated otherwise.

[c] Unless indicated otherwise, sources of the substances in this table are exclusively anthropogenic. Chlorine/bromine/odd-nitrogen source gas signifies inorganic chlorine/bromine/odd-nitrogen source gas to the stratosphere. All long-lived ODSs and replacements (i.e., HCFCs, HFCs) are greenhouse gases.

[d] This lifetime does only include the stratospheric sink and not sinks in the ocean, and the soil.

[e] Lifetime from IPCC (2007).

[f] The stratospheric and tropospheric removal rates (both by photolysis) are comparable for the species.

[g] Global mean mixing ratio in 2008 from Weiss *et al.* (2008).

[h] Total lifetime/pulse decay lifetime from IPCC (2007).

[i] This lifetime only includes tropospheric sinks. In addition, there is a small stratospheric sink (WMO, 2003)
[j] Global mean mixing ratio in 2008 from Vollmer *et al.* (2011).
[k] This lifetime is due primarily to tropospheric photolysis, with a smaller contribution associated with the stratospheric photolysis (WMO, 2011).
[l] University of East Anglia flask measurements

If we further assume that τ(t) is constant in time (a major assumption) and roughly independent of emission patterns, Equation (1.3) can be expressed in integral form as:

$$B(t) = B(0)e^{-t/\tau} + e^{-t/\tau}\int_0^t S(t')e^{t'/\tau}dt' \qquad (1.4)$$

Equation (1.4) provides an efficient way to compute burdens for different emission scenarios.

There are several options for computing τ. Chapter 2 defines and discusses different methods for calculating lifetimes. The steady-state global atmospheric lifetime can be calculated for a specific emission pattern as calculated by an atmospheric model (Chapter 5) using the available kinetic data for the reaction rate constants (Chapter 3). Alternatively, observations can be combined with a model to derive an instantaneous lifetime (see Chapter 4).

Historical Perspective

Historically the first estimates of CFC lifetimes were based solely upon atmospheric observations and a simple global 1-box model. Lovelock *et al.* (1973) measured the surface concentration of CFC-11 in 1971-72, showing that it had accumulated, consistent with the time-integrated global production and very slow loss processes. They estimated that the lifetime was greater than 10 years. However, this estimate was poorly constrained because emissions were not well known, and there was no knowledge of the mechanism for possible sinks.

Molina and Rowland (1974) sparked great interest in the atmospheric lifetimes of CFC-11 and CFC-12 by suggesting that the chlorine released from these molecules could deplete the stratospheric ozone layer. Specifically, they used the measured absorption spectra of CFC-11 and CFC-12 to calculate the photochemical loss from a one-dimensional (1-D) diffusion model of the atmosphere and estimated that the atmospheric lifetimes of CFC-11 and CFC-12 fell in the range of 40-150 years. Rowland and Molina (1975) followed by looking at a series of 1-D models to estimate lifetimes of 29-85 years for CFC-11 and 53-205 years for CFC-12. NAS (1976) provided a detailed discussion of the lifetime, and, based upon the photolysis rates, estimated the lifetimes of CFC-11 and 12 to be 54 and 80 years, respectively. Further evolutions of the ground-based observation network and models are summarized in Boxes 1.1 and 1.2. Discussions of how measured concentrations of the species in the stratosphere are used to derive lifetime values are found in Chapter 4.

Figure 1.1 shows how estimates for the atmospheric lifetimes of CFC-11 and CFC-12 have changed over the past four decades. The results illustrate how knowledge from laboratory measurements, atmospheric observations, and models evolved and provided improved information. The two dozen lifetimes estimates for CFC-11 and CFC-12 shown in Figure 1.1 were calculated using various methods yet have consistent results: the means and one standard deviation are 58±10 and 116±24 years, respectively.

Atmospheric Lifetimes for CFC-11 and CFC-12
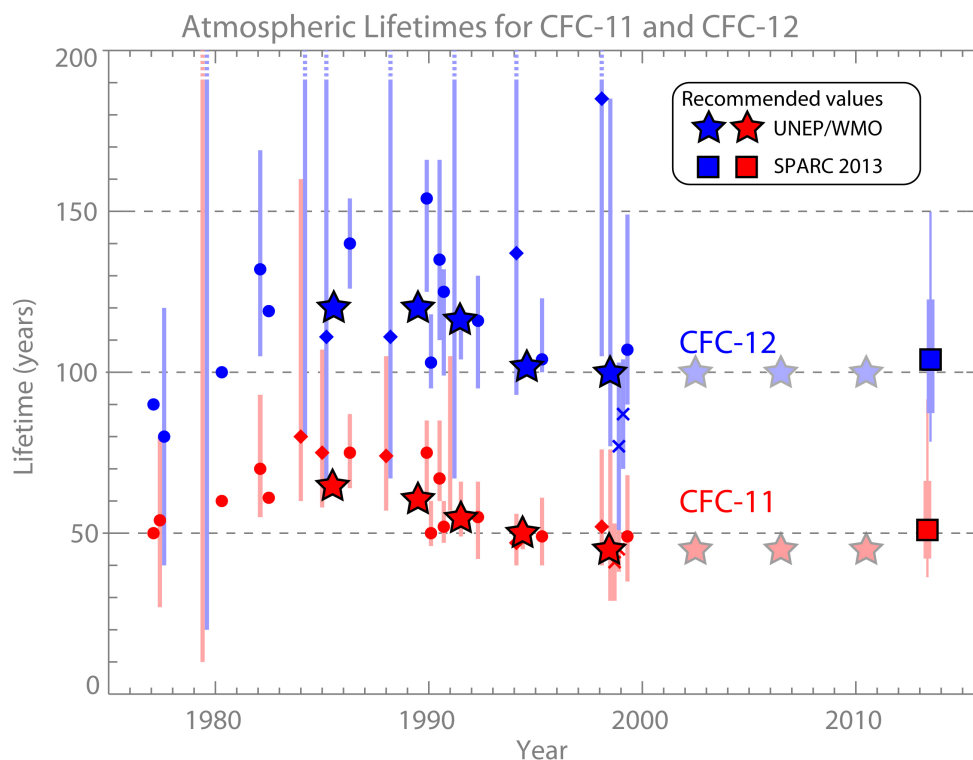
- Model-calculated values and model range (primarily 1-D models prior to 1988, and 2-D models from 1988 to 1998).
- Values derived from NOAA and AGAGE observed surface concentrations and uncertainties.
- Values from the Volk *et al.* (1997) method using aircraft observations as cited in WMO (1999).
- Values reported in assessment reports - lighter colors in 2002, 2006, and 2010 reflect that these values have not been adjusted since WMO (1999).

Figure 1.1. Lifetime estimates from various reports between 1976 and 2010 for CFC-11 (red) and CFC-12 (blue). Uncertainty estimates (or ranges) are shown as vertical bars (lifetimes without vertical bars did not include uncertainty estimates; Watson *et al.* (1984) included only a range of lifetimes for CFC-12). Some reports included multiple estimates for lifetimes using different methods. 2010 (WMO, 2011); 2006 (WMO, 2007); 2002 (WMO, 2003); 1998 (WMO, 1999; Volk *et al.,* 1997); 1994a (WMO, 1995); 1994b (Kaye *et al.,* 1994); 1991 (WMO, 1992); 1989 (WMO, 1989); 1988 (WMO, 1988); 1985a (WMO, 1985); 1985b (WMO, 1985); 1984 (Watson *et al.,* 1984); 1981 (WMO, 1981); 1979 (Hudson and Reed, 1979); 1976 (NAS, 1976).

Box 1.1. Development of Ground-Based Observation Networks

During the period 1974-1978 sporadic ground-based measurements of CFCs around the globe were accumulating from various researchers. Cunnold *et al.* (1978) identified the problems associated with estimating lifetimes based upon atmospheric observations: uncertainties in emissions, uncertainties in measurements of mixing ratios, and atmospheric variability. They provided the theoretical basis to establish a set of measurement stations that became the Atmospheric Lifetime Experiment (ALE), which was founded in 1978. The major goal of ALE was to measure the trends of the surface concentrations of long-lived atmospheric species with common calibrations to define their atmospheric lifetimes. Cunnold *et al.* (1983) used the observations from ALE to estimate the lifetime of CFC-11 as 83 years. Since then, ALE has evolved to the Advanced Global Atmospheric Gases Experiment (AGAGE, see Prinn *et al.,* 2000). In parallel to AGAGE, the Global Monitoring Division of the National Oceanic and Atmospheric Administration (NOAA, USA) established and maintains a network that provides measurements of halocarbons and other trace gases at a variety of stations worldwide. It has been operating since 1977 (http://www.esrl.noaa.gov/gmd/hats/). These two networks are regularly inter-calibrated and provide mixing ratios from globally representative ground-based stations as input into models (e.g., for deriving lifetimes of long-lived atmospheric species). See additional details in Chapter 4.

Several Ozone Assessment Reports attempted to provide reference lifetimes or best values for the steady-state lifetimes. These are denoted by the stars (★) in Figure 1.1. However, it should be noted that not every report placed the same emphasis on the evaluation of the uncertainties in the quantities used for the lifetime estimates. The most comprehensive lifetime assessment was made in the 1994 NASA 'Report on Concentrations, Lifetimes, and Trends of CFCs, Halons, and Related Species' (Kaye *et al.,* 1994). In that report, lifetimes for numerous ODSs were estimated based on both observations and available models. The report concluded that significant differences in model photolysis rates and transport led to a considerable range in lifetime estimates, and that the available observations were not sufficient to constrain the uncertainty in the model estimates. The calculated 2-D model lifetimes for CFC-11, for example, ranged from 40 to 61 years. The reported estimate inferred from atmospheric observations and a 2-D model with parameterized transport was 42 years (+7, -5, with 68% confidence). Later, Chapter 1 of the 1998 WMO Ozone Assessment (Prinn and Zander, 1999) refined the values with best estimates of 45 years and 100 years for the lifetimes of CFC-11 and CFC-12, respectively. WMO (1999) used these results to present a more integrated approach compared to some previous WMO reports. There has been no attempt to assess lifetimes since, and the same reference values (shown as faded stars) were adopted in subsequent reports (WMO, 2003; 2007; 2011).

Report Outline

This report has an introduction (this chapter) and a summary section (Chapter 6). The body of the report is composed of four chapters. This report recognizes that it is not possible to use observations exclusively to define values for the lifetimes. A theoretical framework is always needed to provide missing information and to derive estimates for the steady-state lifetime (Chapter 2). Figure 1.2 presents a schematic overview of the procedure used in this report to estimate atmospheric lifetimes. A more detailed explanation is provided in Chapter 6. Input variables needed for the different models and methods are discussed in Chapters 3

and 4. These include photochemical constants (e.g., photolytic and kinetic rates), observations (e.g., atmospheric distribution of ODSs, climatological data), and emission data. The best lifetimes estimates and related uncertainties from Chapter 4 and Chapter 5 are aggregated using a statistical method to produce a recommended atmospheric lifetime and its uncertainty. In Chapter 5, results from extensively evaluated three-dimensional (3-D) coupled chemistry climate models (CCMs) are presented that were not available for previous assessments. Brief descriptions of the chapters are given below.
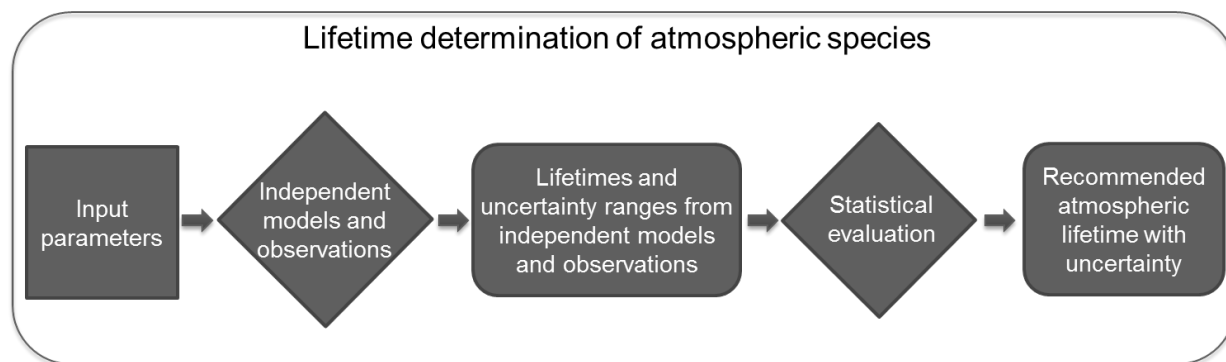

Figure 1.2. Schematic procedure for deriving recommended lifetimes of atmospheric species. Input and output parameters are shown in rectangles and processes in diamonds.

Chapter 2: The Theory of Estimating Lifetimes Using Models and Observations

While Equations 1.3 and 1.4 give a simple description of a lifetime, the theoretical basis of lifetimes is much more complex. For example, in Equation 1.3 we assume that the loss can be represented as a linear process that is proportional to the global burden of the trace gas. In reality, the removal is only linear in the local concentration, and *R(t)* depends on location and time. In Chapter 2 of this document, the theoretical basis of lifetimes is extensively explored and updated. It is pointed out that, while the reactivity of the molecule determines its lifetime to a large extent, the lifetime also depends on reactants in the atmosphere, atmospheric transport, and emission histories. Various techniques for estimating lifetimes are examined.

This theory chapter sets the stage for subsequent chapters by introducing concepts and approaches that have been used to estimate global lifetimes. For each approach, the observational information and the modeling capabilities required are presented, along with general concepts about the most important factors in determining lifetimes. Discussions are presented on the different definitions of lifetimes (e.g., steady-state vs. instantaneous), the general strengths and weaknesses of the various approaches used to derive the values, and how those values are used. Past and projected future deviations of lifetimes from steady-state values are addressed. Differences between the decay of a tracer pulse and the global lifetime of that tracer are differentiated.

Chapter 3: Evaluation of Atmospheric Loss Processes

This chapter provides a comprehensive evaluation and recommendations for kinetic and photochemical parameters relevant for the atmospheric loss processes of the molecules listed in Table 1.1. Kinetic and photochemical data evaluations include Lyman-α and UV absorption cross sections and OH radical, O(^{1}D), and Cl reaction rate coefficients. A critical evaluation of the uncertainties in the kinetic and photochemical parameters, and the resulting range in calculated atmospheric lifetimes is also evaluated using a 2-D model.

Box 1.2. Evolution of Modeling Approaches in Lifetime Estimates

Prior to 1988, the results in Figure 1.1 are indicative of the range and means from 1-D models. After 1988, the ranges and means are from two-dimensional (2-D) models. As each model class matured in its ability to simulate the physical processes, and as more observations became available to evaluate the performance of the models, the model ranges for lifetimes have generally become smaller. The Kaye *et al.* (1994) lifetimes assessment used six 2-D and one 3-D model to calculate ODS lifetimes based on global atmospheric burdens and loss rates ($\tau = B/R$). The range of model-calculated CFC-11 lifetimes was 40-61 years, which was attributed to model differences in both photochemistry and transport. This assessment revealed that models used different CFC photolysis rates, and a comparison of simulated N_2O and CFC-11 profiles with mid-latitude data from balloons illustrated large differences in transport representation. The 1994 lifetime assessment noted that sparse global stratospheric data with large uncertainties in the middle stratosphere was a limiting factor in evaluating model transport and reducing the effect of transport uncertainty on the lifetime calculation.

Since the Kaye *et al.* (1994) assessment, an abundance of stratospheric trace gas observations from satellites (e.g., NASA's UARS and Aura, CSA's SCISAT, and ESA's Envisat) and high-flying aircraft campaigns has dramatically improved the understanding of stratospheric chemistry and transport. This in turn has allowed major improvements in the performance of 2-D and 3-D models. The concept of stratospheric mean age permits evaluation of model transport independent of chemistry. Hall *et al.* (1999) evaluated stratospheric transport in nearly two dozen 2-D and 3-D models using mean age derived from aircraft observations of CO_2 and SF_6 and the distribution of water vapor in the tropical lower stratosphere using satellite observations (Mote *et al.*, 1996). This study showed that most models had mean age younger than observed (i.e., had circulations that were too fast) along with too much horizontal mixing (i.e., not enough isolation of the stratospheric tropical upwelling region). They also demonstrated that distributions of long-lived trace gases such as N_2O and the CFCs were highly correlated with mean age, concluding that most models had significant transport inaccuracies.

The recent availability of multi-year global stratospheric constituent data sets has provided additional information necessary for model improvements. The advent of faster computers and inexpensive data storage has made it practical for 3-D models to be run at higher resolution and with more complete chemistry, allowing a more physical representation of atmospheric processes. In 2010, a comprehensive chemistry climate model evaluation project, the SPARC CCM Validation (CCMVal) (SPARC 2010), used observationally derived diagnostics to evaluate the representation of radiation, dynamics, chemistry, and transport in 18 CCMs. This project produced an unprecedented look 'under the hood' of the sophisticated 3-D models used in WMO (2011). Using diagnostics developed during CCMVal, chemical and transport processes essential for realistic representation of stratospheric composition and hence lifetimes are evaluated for the models used in this report.

Evaluating the uncertainties in a molecule's lifetime involves modeling its distribution in the atmosphere. Current 3-D coupled chemistry-climate models are time-consuming and expensive to run. Hence, a 2-D model is used in this chapter to estimate lifetimes and

uncertainties due solely to the uncertainties in the kinetic and photochemical parameters recommended in this chapter and compared with values obtained using the JPL10-6 recommended parameters (Sander *et al.,* 2011). The 2-D model produces an excellent simulation of stratospheric transport (e.g., age of air), and is an efficient tool for performing multiple simulations for the evaluation of lifetime uncertainties. The 2-D model is also used as an effective transfer standard between the more complex 3-D models in Chapter 5 and the complex photochemical and kinetic information of Chapter 3.

Chapter 4: Inferred Lifetimes from Observed Trace Gas Distributions

The aim of this chapter is to update atmospheric lifetimes (and uncertainties) using recent measurements from all observation platforms (surface *in-situ*, high-altitude (aircraft, balloon), and satellite retrievals) and appropriate models that utilize these observations.

Several approaches have been applied in the past to calculate atmospheric lifetimes of gases listed in Table 1.1 either by using atmospheric observations on their own or in combination with emission inventories. These methods are re-evaluated in Chapter 4 using both new measurement data and updated observation inversion models. Some methods derive instantaneous lifetimes, which then can be converted to steady-state lifetimes. In addition to the methods using *in-situ* and aircraft/balloon data this chapter gives a comprehensive overview of satellite observations and their ability to contribute new independent estimates of atmospheric lifetimes for ODSs and greenhouse gases.

Chapter 5: Model Estimates of Lifetimes

Analogous to the goals of Chapter 4, Chapter 5 uses CCMs (six 3-D models and one 2-D model) to estimate lifetimes of the gases listed in Table 1.1. In contrast to the methods used in Chapter 4, CCMs only use the atmospheric observations as boundary conditions so the lifetime estimates are purely model-based. Since the Kaye *et al.* (1994) lifetimes assessment, 3-D chemical-dynamical models have advanced significantly and are now more appropriate tools for lifetime estimates. The CCMs use an agreed-upon set of photochemical data (Sander *et al.,* 2011) and many have a realistic description of the transport, as judged by their ability to reproduce stratospheric distributions of a variety of long-lived trace gases and mean age-of-air (SPARC 2010). Chapter 5 applies key transport and photochemical diagnostics to the participating models, which were developed during the CCMVal-2 effort (SPARC, 2010). Model lifetime estimates for present-day conditions are interpreted in light of each model's ability to realistically represent essential stratospheric processes. Model simulations are also used to predict how lifetimes may change for a year 2100 atmosphere.

Chapter 6: Recommended Steady-State Lifetimes and Their Uncertainties

Key results relevant to the determination of steady-state lifetimes from Chapters 2 through 5 are presented. The lifetime estimates and other results from these chapters are merged to produce a recommended set of lifetimes along with their uncertainties (Tables 6-1 to 6-3). The methodology for merging the lifetime estimates and calculating uncertainties is given in the Appendix. In order to improve future lifetime estimates, research recommendations are made for closing scientific gaps in our understanding that limit the determination of lifetimes.

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