

CHAPTER 2

The Theory of Estimating Lifetimes Using Models and Observations

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CHAPTER 2

The Theory of Estimating Lifetimes Using Models and Observations

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This chapter sets the stage for subsequent chapters by defining lifetime and other metrics with units of time such as inverse loss frequency and mode time scales that apply to atmospheric constituents. It describes the approaches that have been used to estimate global lifetimes, and recognizes that definitions and interpretations in the literature (e.g., Junge, 1974; O'Neill *et al.*, 1994) have not always been consistent. For example, the lifetime of an atmospheric trace gas is often reported in assessments as a single constant, and here we show that the state of the atmosphere and the history of emissions can change the lifetime.

The chapter covers the underlying theory and methods, and not specific methods of implementation. The chapter begins with the definitions of loss frequency, time scales, and the various usages of lifetime. The lifetime of an emitted species is defined in terms of budgets, and as such it depends in general on the history and location of emissions, as well as on loss rates and the atmospheric circulation. When emissions balance losses, the budget is steady in time, and the steady-state lifetime of a gas is derived as the ratio of its global burden to net emissions (or sinks). For gases of interest in this assessment, we examine how the lifetime manifests itself in some simple instances such as constant source strength or source-free decay, and assess the general applicability of the steady-state lifetime. The application becomes more complex when the chemical loss of the gas is non-linear or is coupled with other gases. The second section of the chapter introduces the primary loss terms by region, considering stratosphere-mesosphere, troposphere, and the land surface/soils or ocean mixed layer as a third trace-gas reservoir. The third section of the chapter deals with the application of basic theory to the practical derivation of lifetimes with major subsections addressing lifetimes derived solely from model simulations (see Chapter 5) and lifetimes derived from a combination of measurements and models (see Chapter 4). A summary and recommendations conclude this chapter.

2.1 Time Scales and Lifetimes

2.1.1 Local Loss Rates and Global Lifetime

The concentration n of an atmospheric chemical constituent is governed by the continuity equation:

$$\frac{\partial n}{\partial t} + \nabla \cdot F = s - l \quad (2.1)$$

where n is the concentration (molecules per unit volume), F is the transport flux, and s and l represent local sources and sinks in molecules per unit volume per unit time. An important concept is the local loss rate, the rate at which a gas at a specific locality is destroyed due to chemical reaction at that location. Thus, assuming a first order, linear, loss ($l = \alpha n$ with α constant) and local chemical production to be independent of the constituent ($ds/dn = 0$), we can rewrite Equation (2.1) as:

$$\frac{\partial n}{\partial t} + \nabla \cdot F = s - \alpha n \quad (2.2)$$

where α is the local loss frequency. The local loss rate for dichlorodifluoromethane (CF_2Cl_2), for example, is essentially zero in the troposphere, as it has no local sinks. In the upper stratosphere, by contrast, its local loss rate is very fast ($\alpha^{-1} \ll 1$ year), as is evident in Figure 2.1. In fact, most of the loss of CF_2Cl_2 (or of N_2O or similar gases with stratospheric loss)

occurs in a fairly narrow region, indicated by the shaded area in Figure 2.1, where the inverse of the local loss rate starts to become comparable with or less than transport time scales.

The spatial distribution of such gases, with surface sources and stratospheric loss, is controlled by a balance between emissions, transport, and chemical destruction. For long-lived gases, the tropospheric time scales for vertical mixing (weeks) and global latitudinal mixing (months) tend to produce a nearly well-mixed troposphere with almost uniform mixing ratio (or mole fraction). For example in the 1980s when chlorofluorocarbons (CFCs) were increasing globally at 5-10% per year from northern sources, the largest gradients in the troposphere were 5-10% across the equatorial region.

As illustrated schematically in Figure 2.2, the stratospheric circulation picks up trace gases at the tropical tropopause and is characterized by tropical upwelling and extratropical downwelling. There appear to be two branches of the circulation (e.g., Birner and Boenisch, 2011; Volk *et al.*, 1996), the shallower branch extending into both hemispheres, while the deeper branch is concentrated in the winter hemisphere. This circulation is not the only factor affecting transport of trace gases; there is also quasi-horizontal (in fact, almost isentropic) mixing that acts more rapidly than the mean advection. Accordingly, tropospheric source gases are advected upward in the tropical stratosphere, and mixed outward into extratropical latitudes where the air subsides.

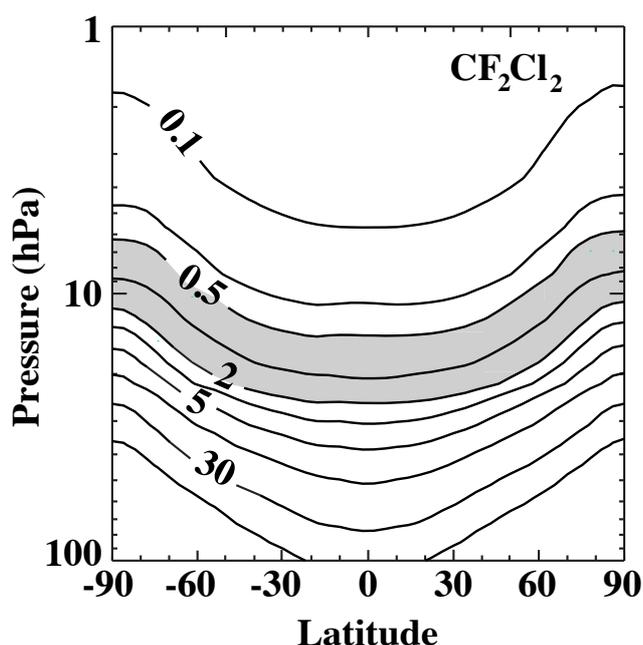


Figure 2.1. The inverse loss frequency (α^{-1} ; yr) of CF_2Cl_2 as a function of latitude and altitude from Douglass *et al.* (2008). Within the shaded region, the inverse loss rate is between 0.5 – 2 yr and comparable with typical time scales for vertical transport in this part of the stratosphere.

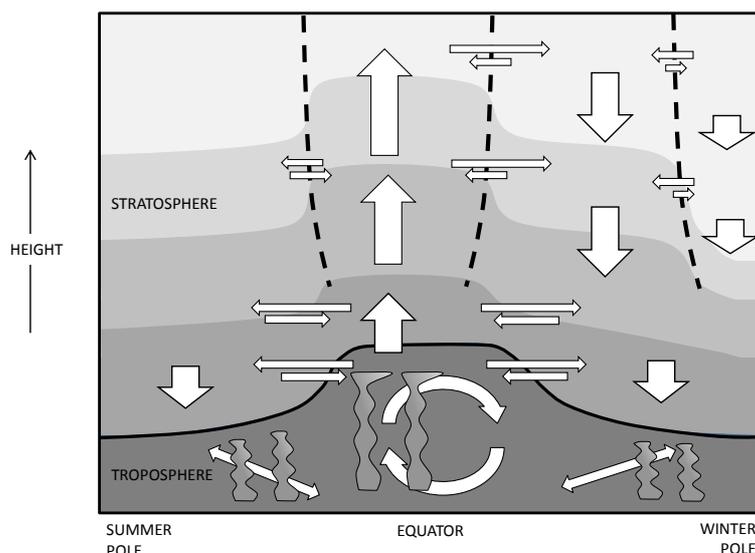


Figure 2.2. Schematic representation of stratospheric transport. The large upward/downward arrows depict vertical (diabatic) advection by the mean circulation: air ascends in the tropical stratosphere and descends within the horizontally well-mixed “surf zone” of the midlatitude winter hemisphere and within the winter polar vortex. The heavy dashed lines mark the partial transport barriers at the edges of the tropics, and the edge of the polar vortex; the heavy continuous curve marks the tropopause. Air is exchanged asymmetrically across the transport barriers, as depicted by the smaller horizontal arrows. These transport characteristics lead to characteristic poleward/downward slopes of the isopleths on long-lived tracers, which are depicted schematically by the background grey-scale shading, with slopes being greatest at the transport barriers.

The characteristic shape of the mixing ratio isopleths, bulging upward in the tropics and downward at high latitude, is determined primarily by transport, while the general decrease of mixing ratio with altitude is a consequence of chemical loss.

Integration of the local continuity equation over the entire globe gives the equation for the time evolution of the global atmospheric burden of a species:

$$\frac{\partial B}{\partial t} = S(t) - L(t) \quad (2.3)$$

where $B = \int n \cdot dV$ is the global burden (e.g., total number of molecules), $S = \int s \cdot dV$ is the globally integrated source (molecules/yr), and $L = \int l \cdot dV = \int \alpha n \cdot dV$ is the globally integrated loss (molecules/yr). Defining the global lifetime to be:

$$\tau = B/L \quad (2.4)$$

Equation (2.3) becomes:

$$\frac{\partial B}{\partial t} = S(t) - \frac{B}{\tau} \quad (2.5)$$

The global lifetime τ satisfies:

$$\tau^{-1} = \frac{\int \alpha n \cdot dV}{\int n \cdot dV} \quad (2.6)$$

so that the inverse of the global lifetime is a tracer-mass-weighted mean of the local loss frequencies (α).

In steady state, when emissions are exactly balanced by losses, the steady lifetime satisfies:

$$\tau_{ss} = \frac{B}{L} = \frac{B}{S} \quad (2.7)$$

As Equation (2.6) makes clear, the lifetime of any trace gas depends not only on the magnitude and distribution of chemical loss frequencies, but also on the spatial distribution of the trace gas itself. This in turn depends on loss rates, on transport, and on the history and location of emissions, and will therefore evolve with time as any or all of these factors change. There is, therefore, no unique lifetime for a given gas. After sources are removed, for example, decay of concentrations occurs at rates dictated by the modes of the unforced problem (i.e., of Equation (2.2) with $s=0$), so that, eventually, decay becomes dominated by the slowest decaying mode (Prather, 1994, 2007; Farrell and Ioannou, 2000). The time scale of this decay can be quite distinct from the steady lifetime τ_{ss} given by Equation (2.7) (Prather 1994; 1997; 1998). Accordingly, in principle one cannot rely on determinations of lifetime in near-steady state to predict rates of decay following removal of sources.

In practice, however, the distinction between steady lifetime and the time scale of decay may be very small, especially for long-lived gases with stratospheric sinks. Figure 2.3 illustrates this point with results from a one-dimensional model calculation for a gas with a surface source and a constant loss rate (i.e., constant α) confined to altitudes above 22 km. The source is introduced at $t=0$, and held constant until 50,000 days (137 years) of integration, at which time it is suddenly turned off. The figure shows the global burden B and the lifetime τ , as given by Equation (2.6), through the integration. During the period in which the source is present, the burden asymptotes toward steady state, and the lifetime rapidly adjusts to the steady value of 35.2 years. Following removal of the source, the burden exhibits near-perfect exponential decay; correspondingly, the lifetime, following a brief period of adjustment, arrives at the constant value 34.5 years, the time scale of the slowest eigenmode. The transition from steady state to decay, too rapid to be visible in Figure 2.3, is more complex as seen in Figure 2.4. The lifetime is slightly longer when forced to steady state by surface sources because there is more burden in the lower troposphere driving the flux into the stratosphere; and when left to decay, the troposphere becomes more uniformly mixed. The application of eigenvalues and eigenmodes in atmospheric chemistry is discussed in Prather (1994, 2007); Daniel and Solomon (1998); Manning (1999); Farrell and Ioannou (2000); Waugh and Hall (2002); and Ehhalt *et al.* (2004).

Such close correspondence between steady lifetime and decay times is in fact typical of long-lived gases with constant stratospheric sinks. A wide range of calculations with the same model, but sinks at different stratospheric altitudes, reveals that these two time scales differ by no more than 2% for gases with lifetimes greater than 10 years. (Note that this statement is not valid if the loss rate changes with time, as it can in coupled systems, even when the lifetime is long; such systems are addressed in Section 2.1.2, below.)

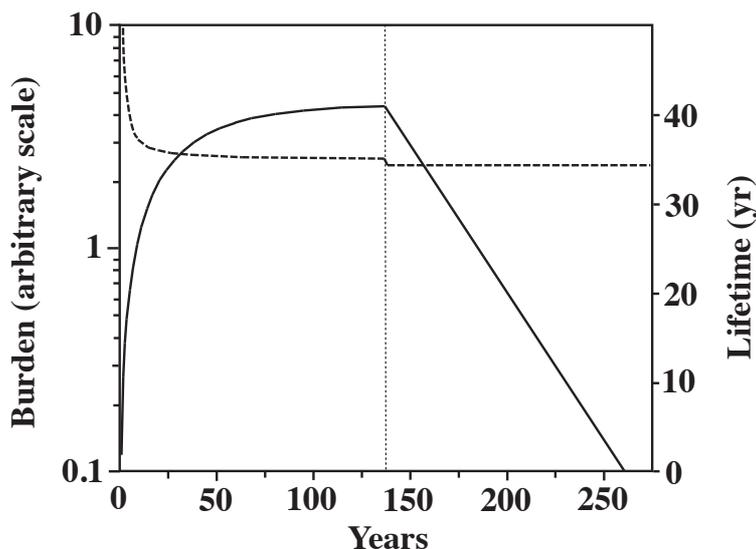


Figure 2.3. Results from a calculation from a one-dimensional model for a species with a surface source and stratospheric sink (in this case, above 22 km). The source is held constant for $t < 137$ years, at which point it is suddenly removed. The solid curve shows the global burden, the dashed curve shows the lifetime defined by Equation (2.4).

For shorter-lived gases with tropospheric sinks, however, the differences become more substantial. An example is shown in Figure 2.4, for methyl bromide (Prather, 1997). The figure shows the evolution of the global burden and lifetime during decay of an initially steady solution following removal of sources. The decay of the burden is not quite exponential, the lifetime increasing from the steady value of 1.75 years to almost 2.1 years after 14 years. (Note this example does not include the oceanic reservoir and sink, which reduces the lifetime to about 0.8 year) In free decay, the abundance decreases fastest in the vicinity of the sinks, thereby reducing the total loss relative to the global burden and, thus, increasing the lifetime.

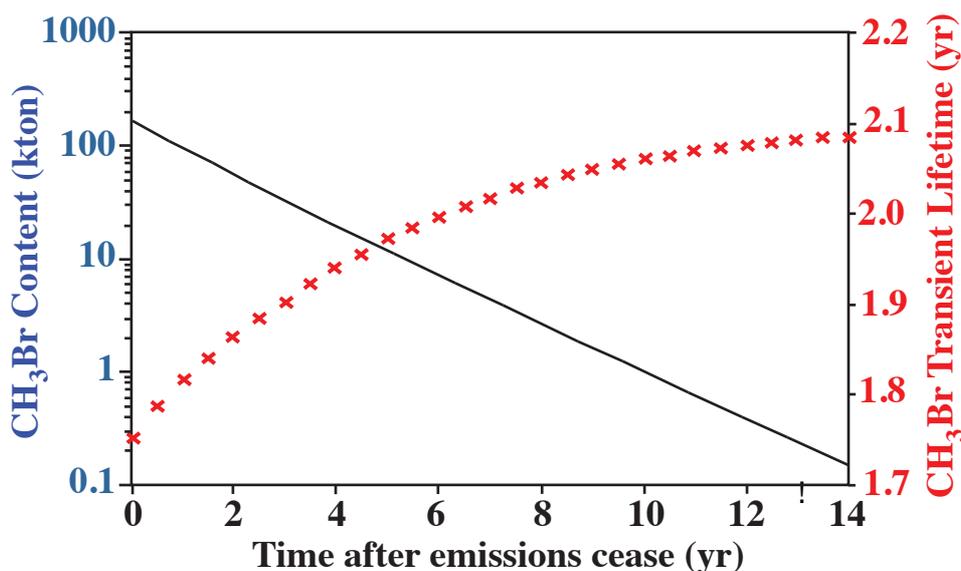


Figure 2.4. Evolution of methyl bromide (CH_3Br) following removal of sources. (After Prather, 1997) This case is atmosphere only; the inclusion of oceanic sinks and reservoirs drops the lifetime to 0.8 yr (see Hu *et al.*, 2012).

Accordingly, lifetimes determined from calculations of burden/loss in the presence of sources can be used with a good degree of accuracy to predict the source-free decay of long-lived gases with constant stratospheric sinks. Not so, however, for those shorter-lived gases with sinks in the troposphere, nor for coupled systems. The procedure for determining τ , using Equation (2.6), given good estimates for emissions and the global burden, will be addressed in Section 2.3.

2.1.2 Coupled Lifetimes

The recognition that atmospheric chemistry was coupled, that abundances of one gas could perturb those of another, was recognized early by Isaksen and Hov (1987). Prather (1994) developed this concept further by demonstrating theoretically that this coupling could change the inherent times scales of the system. He showed with eigenvalue decomposition that the methane (CH_4), carbon monoxide (CO), hydroxyl radical (OH) chemical system had a time scale for a CH_4 perturbation that was 1.4 times longer than the lifetime of CH_4 in the system. The basic idea is that an increase in CH_4 will increase CO and that both of these will decrease OH. The decrease in OH will slow the loss of CH_4 thus giving it an extended lifetime as seen in Figure 2.5. In fact, since a small change in OH affects the entire burden of CH_4 and not just the perturbation, the effect can be quite large. Thus the response time of methane to a perturbation will be longer than would be predicted from the steady-state lifetime.

A similar example for CO was shown by Daniel and Solomon (1998). They considered the characteristics of the CH_4 , CO, OH chemical system in response to a CO pulse and showed that the CO steady-state lifetime was 52 days while the pulse-decay time averaged over the first 10 days of the model experiment was 58 days. These results follow directly from a simple linearization of the system and demonstrate that the longer time scale is nearly independent of the magnitude of the perturbation. As a result of these considerations, the greenhouse warming potentials (GWPs) for direct CH_4 emissions were revised upward by 40% in the Intergovernmental Panel on Climate Change (IPCC) Second Assessment Report (1996). An important corollary was that perturbations were coupled across species and hence emissions of the relatively short-lived species CO and nitrogen oxides (NO_x), for example, would produce a perturbation to atmospheric CH_4 that lasts more than a decade (Prather, 1996; Daniel and Solomon, 1998; Wild *et al.*, 2001; Derwent *et al.*, 2001). This resulted in indirect GWPs being assessed for direct emissions of NO_x , CO, and volatile organic compound (VOC).

The analysis of time scales was extended to more complex coupled systems like that of stratospheric nitrous oxide (N_2O), total reactive nitrogen (NO_y), and ozone (O_3) (Prather, 1998) where the coupling through transport (nearest neighbors) and radiation (non-local, overhead column O_3) was now included. An increase in N_2O increases NO_x , which reduces O_3 locally, allowing more ultraviolet (UV) penetration to layers below and increases N_2O loss by photolysis, thus decreasing its lifetime. N_2O in the coupled N_2O - NO_y - O_3 system thus responds to an increase with a time constant that is shorter than the steady-state N_2O lifetime. This 8% reduction in the effective GWP of N_2O was adopted in the IPCC Third Assessment Report (2001) based on 2-D model corroboration by AER, Goddard, and Oslo. Prather and Hsu (2010) completed similar century-long N_2O perturbation studies in a 3-D model with both stratospheric and tropospheric chemistry. Results confirmed the 8% offset between N_2O lifetime and time scale, and further identified the coupling of N_2O perturbations with tropospheric OH, whereby +10 molecules of N_2O induce -3.6 molecules of CH_4 . This coupled CH_4 perturbation decays with the long-term N_2O primary time scale of a century,

rather than the decade time scale for CH_4 . Similar assessment of CFC ozone depleters, focusing on the upper stratosphere where $\text{ClO}+\text{O}$ reactions are important, has not yet been made.

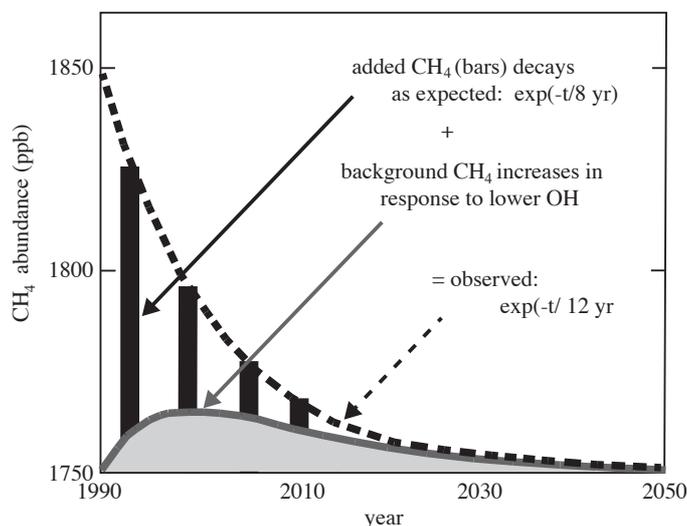


Figure 2.5. From Prather (2007), showing the decay response of pulses of CH_4 and the response of the background to the lower OH concentration caused by the CH_4 perturbation.

Why are chlorofluorocarbon (CFC) lifetimes so long?

- Time lag for transport from surface to stratosphere for chlorine release is 3-5 years.
- Stratospheric age of air ranges up to ~5 years.
- Loss rates in mid-stratosphere-to-mesosphere loss region are short (can be less than 1 year).
- So how do we get a 50- or 100-year lifetime?
- The loss region itself is a small fraction of the atmosphere.

Lifetime is governed by the rate of delivery of air containing the CFC to the loss region. Some of that air can be delivered rather quickly (3-5 years) in tropical upward motion. But no more than about 1% of air can be delivered from the troposphere (say, 200-1000hPa) to the atmosphere above 10 hPa in one cycle of the circulation, since the latter region contains 1/80 of the air mass of the former. The rest of the air will be detrained from the upward motion and re-circulated into the lower stratosphere or troposphere with no loss of CFC. The air will eventually be re-injected into the upward flow whence another fraction of the CFCs will be destroyed in the loss region. Thus the overall lifetime is extended by recirculation. The higher in the atmosphere that a species must go to experience the loss process, the longer will be the lifetime.

2.2 Loss Processes

Long-lived tracers (τ several decades or longer) have loss processes dominated by stratospheric photolysis with additional contributions in some cases from reaction with OH and O(¹D). In general compounds with shorter lifetimes will be less effective at making it to the stratosphere. These molecules tend to be those with significant reactions with tropospheric OH. Finally, many species have both sources and sinks at the surface. A prime example is the methyl bromide (CH₃Br).

2.2.1 Stratospheric Loss

Stratospheric loss for many of the long-lived species, such as N₂O, trichlorofluoromethane (CFCl₃) and CF₂Cl₂, is dominated by photolysis, particularly in the spectral interval from 190 to 215 nm (Minschwaner *et al.*, 1993). The cross sections for absorption by long-lived species in this wavelength region vary slowly with wavelength compared to the extreme variation of the Schumann-Runge bands of molecular oxygen (O₂) that determine the amount of UV flux that penetrates into the stratosphere.

Figure 2.6 from Minschwaner *et al.* (1993) illustrates the altitude and wavelength dependence of the loss rate for CFCl₃ calculated using measured profiles of CFCl₃ and ozone for tropical noontime, equinox conditions.

At 40 km the loss rate has significant contributions between 190 and 220 nm. By 20 km the loss rate is constrained to wavelengths between 195 and 210 nm because both the shorter and longer wavelengths have been absorbed by O₂ and O₃. Note that the contours in Figure 2.4 represent changes of orders of magnitude. This was emphasized in Douglass *et al.* (2008) as shown previously in Figure 2.1, where it was pointed out that the effective photolysis occurs over a narrow range of altitudes.

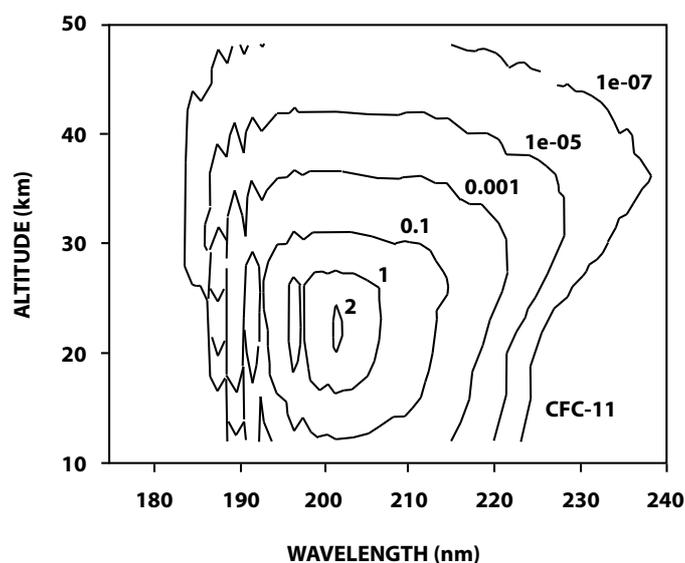


Figure 2.6. CFCl₃ loss rate (molecules cm⁻³sec⁻¹ per nm) as a function of wavelength (nm) calculated with a photochemical model using measured concentrations of ozone and CFCl₃ (Minschwaner *et al.*, 1993). Calculations are for the tropics at local noon for equinox conditions. This calculation effectively combines the loss frequencies (shown for CF₂Cl₂ but not CFCl₃ in Figure 2.1) and the profile of the CFC.

The calculations of Minschwaner *et al.* (1993) illustrated that we can calculate loss rates from a photochemical model based on data in locations where we have measurements. Model output can be used to examine the spatial and temporal distribution of calculated loss rates in more detail. Figure 2.7 shows the loss rates for CCl_4 , CFCl_3 , CF_2Cl_2 and N_2O as a function of altitude and latitude. The results come from one of the models in Chapter 5 (GEOSCCM) and have been averaged over 6 years (2000-2005) of a time-dependent simulation. They thus represent annually averaged loss rates.

A problem with combining observations with a model for the photochemical loss frequency is that they may not be consistent with each other, and error in the photochemical model may induce biases in the integrated loss used to calculate the lifetime. One advantage of using a complete chemistry-transport model is self-consistency in that transport limits the fluxes of the trace gas to the regions of rapid loss. In all, the best solution is finding a self-consistent model that matches the measured abundances and thus should give the best value for integrated loss.

We can see from Figure 2.7 that the loss rates maximize at the lower altitude (higher pressure) for CFCl_3 , and significantly higher altitude for CF_2Cl_2 and N_2O . The order of the altitude of maximum loss is in the same order as the increase in the lifetime of the species. Thus one of the major determinants of lifetime is the altitude at which loss occurs. This results from the fact that the lifetime for species that have only stratospheric losses, such as those in Figure 2.7, is dependent on the rate at which those species can be transported to the loss region. Once air containing these species reaches the loss region, loss occurs rapidly.

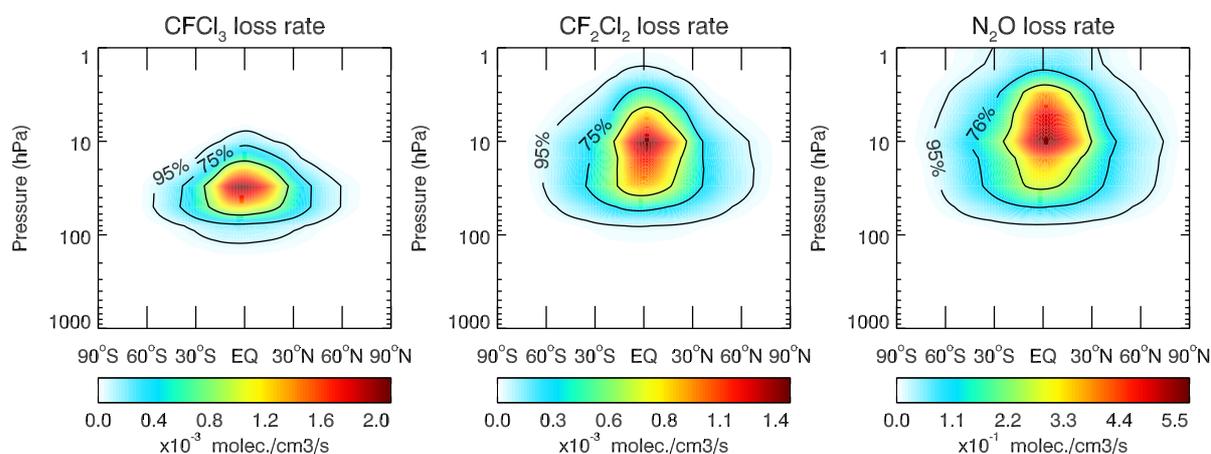


Figure 2.7. An example of latitude-pressure cross section of zonally integrated annual loss rates (molecules $\text{cm}^{-3} \text{ s}^{-1}$) of CFCl_3 , CF_2Cl_2 , N_2O between 2000 and 2005 from the WACCM REF-C1 simulation (see Chapter 5) with warm colors indicating faster loss rates. The solid contours outline the regions within which 95%, 75% and 50% of the loss occurs. Loss rates values are given by the colors as indicated in the color bars below each panel.

2.2.2 Tropospheric Loss by Reaction with OH

Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), along with methane, methyl chloride, and other hydrogen-containing compounds have losses dominated by reaction with tropospheric OH. Given the short time scale for odd hydrogen (HO_x) chemistry and large variations in OH concentration, there is no way to measure directly the global abundance of tropospheric OH. Most evaluations of lifetimes of these compounds depend on estimates of tropospheric OH from models that inform us on how to scale the integrated loss from one gas to another (Prather and Spivakovsky, 1990; Spivakovsky *et al.*, 2000; Lawrence *et al.*, 2001). When calculating a “mean OH concentration” it is important to carefully define the weighting kernel and recognize that even tropospheric mean OH varies almost a factor of 2 for different weightings (Prather and Spivakovsky, 1990; Lawrence *et al.*, 2001). The modeled mean OH is weighted by mass and the loss rate that is dependent on temperature (for methyl chloroform (CH_3CCl_3) the temperature dependence is $e^{-1520/T}$). The resulting OH concentrations have been tested by comparisons to estimates derived from methyl chloroform and its time trend (e.g., Prinn *et al.*, 1995; Montzka *et al.*, 2011). Going from the observed decay of methyl chloroform to an estimate of its lifetime against OH-loss and then deriving the similar lifetime for CH_4 requires careful attention to the loss by other processes (e.g., ocean exchange (Wennberg *et al.*, 2004) and stratospheric photolysis) and the correct atmospheric burden, see Prather *et al.* (2012). These scaling approaches do not work for short-lived halocarbons, some of which are important to lower stratospheric ozone, for which the lifetime depends on where and when emissions occur. Investigation of very short-lived halocarbons (Ko *et al.*, 1997) was spurred by the U.S. EPA workshop in 1999 (Bridgeman *et al.*, 2000; Wuebbles *et al.*, 2001; Olsen *et al.*, 2000). A theoretical framework for handling the geographic dependence of such short-lived species is discussed in Pisso *et al.* (2010) and Brioude *et al.* (2010).

If the emissions of CH_3CCl_3 are well known, then an average OH concentration can be derived from knowledge of the reaction rate coefficient for $\text{OH} + \text{CH}_3\text{CCl}_3$.

The average obtained for tropospheric loss of methyl chloroform or of methane will be heavily weighted towards the tropical lower troposphere as illustrated in Figure 2.8. The reactions of these molecules with OH are strongly temperature dependent ($\exp(-1775/T)$ for methane and $\exp(-1520/T)$ for methyl chloroform (from the JPL-2010 kinetics evaluation (Sander *et al.*, 2011)). Although each of these molecules will have its loss weighted towards the tropical lower troposphere, the differences in temperature dependence of their reaction rates with OH will lead to a difference in the effective average OH concentration (Prather and Spivakovsky, 1990; Lawrence *et al.*, 2001).

While both methane and methyl chloroform have their predominant losses in the troposphere, they also have stratospheric losses. It is sometimes beneficial to separate these losses and calculate individual losses and lifetimes for the troposphere and stratosphere. Thus we can rewrite Equation (2.4) as:

$$\frac{1}{\tau} = \frac{L_{strat} + L_{trop}}{B} = \frac{1}{\tau_{strat}} + \frac{1}{\tau_{trop}} \quad (2.8)$$

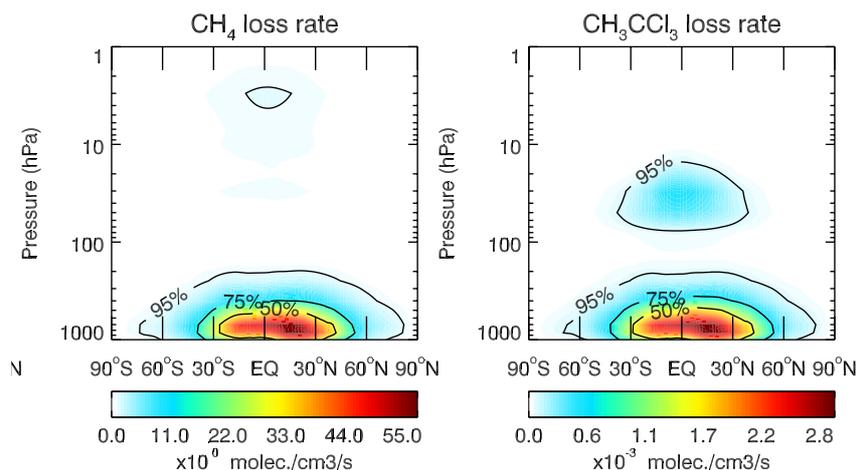


Figure 2.8. Same as Figure 2.7, but for CH_4 and CH_3CCl_3 . These species are destroyed primarily through reaction with OH, except in the stratosphere where CH_3CCl_3 is destroyed primarily through photolysis.

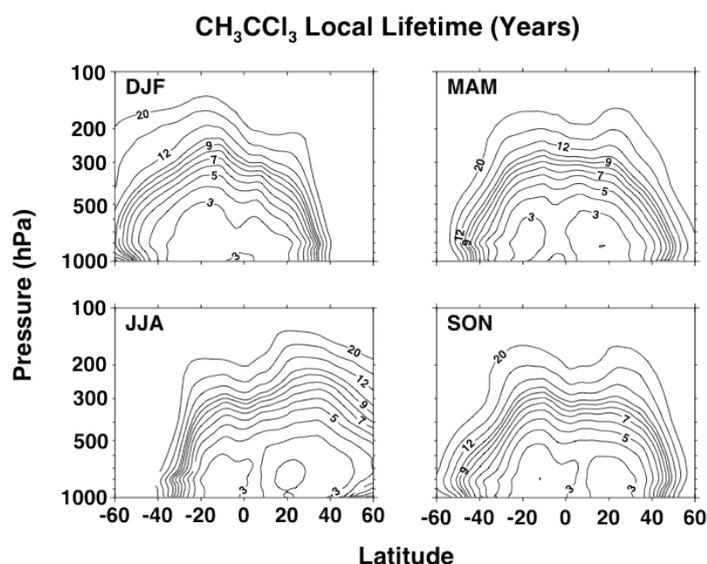


Figure 2.9. Inverse loss frequencies (yr) for methyl chloroform (CH_3CCl_3) as a function of latitude and pressure, averaged zonally and over a season. Computation is for 2005 conditions in GEOSCCM.

Local lifetimes for loss by reaction with OH calculated from the inverse of the loss frequency are shortest in the tropical lower troposphere. Figure 2.9 illustrates the seasonal variation of the local lifetime for methyl chloroform reaction with OH. The local lifetimes are somewhat less than 3 years in the tropical lower troposphere and the minimum shifts toward the summer hemisphere as a function of time of year.

When a molecule has a tropospheric lifetime of less than a year (e.g., bromoform, CHBr_3), the average loss frequency over all seasons would not correctly represent the lifetime. The actual lifetime would depend both on the time of year of the release and on the location of the release relative to the primary region for loss. Even with uniform emissions the abundance

and losses are less in the summer season. Brioude (2010) and Pisso *et al.* (2010) considered the impact of emission location on the calculated ozone depletion potential for several short-lived species. If a short-lived species is emitted at mid or high latitudes, much of it will be lost before it reaches the tropics where it can be injected into the stratosphere to have a potential impact on ozone. Conversely, emissions in the tropics near the region of injection into the stratosphere can make a larger contribution to potential ozone depletion. The same principle affects the lifetime of a short-lived species, but in the other direction. Emissions far from the tropical lower troposphere will result in longer lifetimes while emissions in the tropical lower troposphere will have shorter lifetimes.

2.2.3 Loss at the Surface and Additional Reservoirs

For species such as methyl bromide (CH_3Br) the ocean mixed layer is an additional reservoir, having both internal production and loss, and being able to serve as either source or sink for the atmosphere (Butler, 1994; Prather, 1997; Yvon-Lewis and Butler, 1997). The impact of changed emissions of methyl bromide must take into account this additional reservoir, both in terms of integrating losses and in terms of integrating the total burden of CH_3Br that is used in the lifetime definition. The lifetime will be determined by a combination of the lifetimes for loss in the troposphere and stratosphere as before but with inclusion of the ocean layer and soil uptake (Rhew *et al.*, 2003):

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{ocean}}} + \frac{1}{\tau_{\text{soil}}} + \frac{1}{\tau_{\text{trop}}} + \frac{1}{\tau_{\text{strat}}}$$

Hu *et al.* (2012) have recently shown that the measured oceanic saturation anomalies for CH_3Br are significantly smaller than those measured previously. They attribute this to the decrease in the atmospheric concentrations of CH_3Br under the provisions of the Montreal Protocol. They point out that a further decrease in the atmospheric concentration could result in the ocean becoming a net source for CH_3Br . These results indicate a limitation in the conceptual model of considering the ocean (or possibly even the land) as a boundary condition with known fluxes. A more complete conceptual model would include oceanic boxes for CH_3Br that could react with changes in the atmosphere.

In the case of CH_4 (and several other gases), we need to consider also the lifetime against loss by soil uptake and by tropospheric Cl radicals:

$$\frac{1}{\tau_{\text{CH}_4}} = \frac{1}{\tau_{\text{OH}}} + \frac{1}{\tau_{\text{Cl}}} + \frac{1}{\tau_{\text{soil}}} + \frac{1}{\tau_{\text{strat}}}$$

2.3 Methods for Calculating Lifetimes and Time Scales

2.3.1 Model-Based Computations from Burden over Loss

2.3.1.1 Atmospheric Variability

The standard method for determining global lifetimes from model computations is to use the definition (2.4) of lifetime as the global atmospheric burden divided by the global atmospheric loss. This method is an extension of the method of instantaneous rates applied by Minschwaner *et al.* (1993) to a limited set of measurements. For model output or a modern global satellite data set, a full year (or even several years) is used to calculate the

annual average burden of the molecule in question and to calculate the annual average loss rate. Calculating total loss from data is not completely model free as the photolysis must be determined using a radiative transfer code and ozone concentrations obtained from either data or models. A molecule with a lifetime of many decades (such as CFCs or N₂O) will be subject to many seasonal cycles during its time in the atmosphere and the average over these seasonal cycles will give an accurate representation of its lifetime. A lifetime calculated in this manner may still be referred to as an “instantaneous” lifetime although it was actually averaged over one or more years. A similar concept is applicable to variations over the quasi-biennial oscillation and El Niño cycles.

2.3.1.2 Atmospheric Change over Time

Butchart *et al.* (2006) demonstrated that all of the climate models they diagnosed predicted an increase in the speed of the Brewer-Dobson circulation as CO₂ was added to the model’s atmosphere. Douglass *et al.* (2008) showed that, in their chemistry climate model (CCM), the speed-up of the Brewer-Dobson circulation corresponded to a decrease in the atmospheric lifetime of CFC-11 by 5 to 10% by the year 2100 and almost no change in the CFC-12 lifetime. They also deduced a current lifetime for CFC-11 that was ~20% greater (56 years) than that used in recent assessments (45 years). They attributed the difference to the modern general circulation models that have a slower stratospheric circulation than those that were in use at the time the 45-year lifetime was established, but it could also be that the value of 45 years determined from the observed CFC-11 vs. age relationship (Volk *et al.*, 1997) needs revision (Section 2.3.3). The above discussion emphasizes that the lifetime of a molecule is dependent on the state of the atmosphere. For long-lived CFCs we saw above that the lifetime was controlled by the rate of transport to the region of primary loss. Changing the underlying atmospheric dynamics will change the atmospheric distribution of the gas and therefore the “instantaneous” lifetime that we deduce.

Aside from changes in the transport patterns, climate change can also affect tracer lifetimes through redistribution of ozone and resulting effects on ultra-violet radiation and ozone transport into the troposphere (Stevenson *et al.*, 2006; Hegglin and Shepherd, 2009) or through changes in climatological temperature distributions. In the stratosphere, temperatures are predicted to decrease due to increasing greenhouse gases, which leads to an increase in ozone due to a slowing down of ozone loss reactions (Li *et al.*, 2009). In the troposphere, increasing temperatures are expected to affect the lifetime of methane due to effects of rising atmospheric water vapour content on OH-abundances, the effect of rising temperature on the OH + CH₄ reaction rate, and the effects of increasing NO_x sources from lightning, fires, and soil emissions (John *et al.*, 2012) as discussed further below.

2.3.1.3 Source Variability over Time

Instantaneous lifetimes can be calculated from either observations or a model simulation by evaluating the total loss term and dividing it into the total burden as indicated by Equation (2.3). As mentioned earlier, the instantaneous lifetime is not exactly the same as the steady-state lifetime. We can estimate the difference by solving Equation (2.5) for τ without invoking the steady-state approximation:

$$\tau(t) = \frac{B(t)}{S(t) - \partial B/\partial t} \quad (2.9)$$

Thus, for example, during the 1980s when CFCs were increasing at about 5%/year, the calculated instantaneous lifetime using the steady relationship (2.7) based on net emissions, $\tau=B/S$, would be biased about 5% high compared to the definition (2.4). In 2010 CFCs were decreasing and the instantaneous lifetime would be biased low by the current decay rate, ~2% for CFC-11 and ~1% for CFC-12. In the context of the discussion above, following Equation (2.7), these differences reflect the impact of growth and decay of the CFC abundances on their spatial distributions. In general, note that Equation (2.9) still yields the instantaneous lifetime, not the steady-state lifetime, since the spatial structure of the gas within the atmosphere will differ in the two cases (cf. Equation (2.6) and subsequent discussion).

As discussed above, the lifetime of methane can be strongly affected by changes in methane emissions itself due to the potential feedbacks on OH abundances. For different climate change scenarios John *et al.* (2012) found that the methane lifetime decreases between 5 and 13% between 1960 and 2100, except for the most extreme warming case (RCP8.5), where the lifetime increased by 4%. This increase was due to a near doubling of CH₄ emissions in this simulation. On shorter timescales, source variability is especially hard to assess in the case of methane due to relatively large natural and intermittent sources such as volcanic eruptions, wildfires, permafrost, oceans, low-latitude wetlands, and termites (Lelieveld *et al.*, 1998).

2.3.2 Inverse Methods

In forward models, of the type just discussed, the tracer continuity Equation (2.2) is used to calculate concentrations from given atmospheric transport parameters, sources and loss rates as the drivers of the system. Inverse modeling, by contrast, is an approach used to estimate these drivers based on observed concentrations as constraints to the model output. The relationship between the model variables (called state vector x) and the observed variables (called the observational vector y) is given by the forward model F

$$y = F(x, b) + \epsilon \quad (2.10)$$

where b represents the known model parameters and ϵ is the error vector describing the uncertainty in the observations, the known model parameters, and the forward model. The choice of which variables to include in x or b is dependent on the variable that needs to be optimized. x can then be calculated given y from the inversion of Equation (2.10).

The forward model used in inverse modeling approaches can be of different complexity, from simple single-box (e.g., Cunnold *et al.*, 1983; Montzka *et al.*, 1999, 2011) or multi-box models (Rigby *et al.*, 2012) to full chemistry transport models (e.g., Hartley and Prinn, 1993; Bergamaschi *et al.*, 2009; Lee *et al.*, 2011; Patra *et al.*, 2011). In the single- to multi-box models, the model parameters are strongly simplified, but offer the advantage that the computational costs are small and large sets of runs can be carried out easily to test the sensitivity to changes in the different model parameters. Accurate knowledge of the emissions is necessary in order to obtain meaningful lifetime estimates, which is not readily available for all species of interest (see Montzka *et al.*, 2011). Chemistry transport models (CTMs) on the other hand rely on the quality of model transport, which is known to have limitations and can lead to error growth as many studies on inverse modeling of emission sources have shown (Hartley and Prinn, 1993), also a valid concern for inverse modeling used to estimate lifetimes. An advantage is that these models can be used also for shorter-lived species that are not well mixed in the atmosphere.

Sufficiently simple forward models can sometimes be inverted, either exactly or statistically. But especially for CTMs, the forward model is too nonlinear to invert and so a linearization of the forward model is employed. The simplest case is provided by sequential estimation. Let the gridded concentrations in the CTM at time t be the state vector $x(t)$, and the observations be the observational vector $y(t)$. Given an initial condition, the CTM is used to produce a forecast or an a priori (x_a) at a subsequent time. The forward model is linearized around this *a priori* estimate yielding

$$y = F(x_a, b) + K(x - x_a) + O((x - x_a)^2) \quad (2.11)$$

where $K = \partial y / \partial x$ is the Jacobian matrix of the forward model evaluated at $x = x_a$.

If the dimension of $y(t)$ equals the dimension of $x(t)$, then (assuming no error) the Jacobian is invertible, yielding the state vector

$$x = x_a + K^{-1}(y - F(x_a, b)) \quad (2.12)$$

In practice, however, the observations are usually sparse so the dimension of $y(t)$ is much smaller than the dimension of $x(t)$. Then the Jacobian is not invertible, and the estimate of x can only be optimal, not exact, i.e., representing the most likely state given knowledge of the uncertainties in both observations and forward model parameters, taking account of any expected correlations between parameters. For a full discussion of the inverse modeling approach the reader is referred to Kalnay (2003).

Examples, and further discussion, of the application of the inverse modelling approach to the determination of lifetimes is given in Chapter 4.2.1.

2.3.3 Relative Lifetimes: Tracer-Tracer Method

Plumb and Ko (1992) showed that the compact relationships between two long-lived stratospheric species could be used to determine their relative lifetimes. (In this context, “long-lived” implies that local loss rates are slow compared to transport rates.) Under their assumption that rapid isentropic mixing is global in extent, then the ratio of net global fluxes of two species of mixing ratio χ_1, χ_2 , through a surface of constant mixing ratio (such surfaces coincide where the species are locally long-lived) is

$$\frac{F_1}{F_2} = \frac{d\chi_1}{d\chi_2} \quad (2.13)$$

i.e., the slope of the tracer-tracer relationship evaluated at the mixing ratios on the surface. If this surface is chosen to lie below all sinks of the two tracers then, in equilibrium, these fluxes balance the net losses. Hence, if the atmospheric burden of each is known, the ratio of lifetimes is

$$\frac{\tau_1}{\tau_2} = \frac{B_1}{B_2} \cdot \frac{d\chi_2}{d\chi_1} \quad (2.14)$$

where B_1 and B_2 are the respective burdens.

In fact, if the tracer surface chosen is located very close to the tropopause (and the tropopause does indeed appear to coincide with isopleths of long-lived species; Prather *et al.* (2011)), then the local mixing ratios are approximately representative of tropospheric values, and the net atmospheric burden of each tracer is approximately the product of the mixing ratio and the atmospheric mass. In that case, the ratio of lifetimes is

$$\frac{\tau_1}{\tau_2} \approx \frac{\chi_2}{\chi_1} \frac{d\chi_1}{d\chi_2} \quad (2.15)$$

The greatest advantage to this approach is that it can be applied from local observations without model input, i.e., that observations in the extratropical lower stratosphere are sufficient to determine the slope of the tracer-tracer relationship and thence to obtain the lifetime ratio. The disadvantage is that Equation (2.15) delivers the ratio of two lifetimes, and not the absolute value of either. However, Volk *et al.* (1997) used “age,” determined from the temporal tracer SF₆, as a reference, since its flux is known from first principles. For a linearly growing, transient, tracer the local age is just the time lag of mixing ratio $\chi(t)$ relative to that, $\chi_o(t)$, at the tropical tropopause, i.e.,

$$\Gamma = \frac{\chi_o(t) - \chi(t)}{\partial\chi/\partial t} \quad (2.16)$$

from which age (using (2.1)) can be treated itself as a tracer with a unit source,

$$\nabla \cdot F_r = 1 \quad (2.17)$$

and a boundary condition $\Gamma_0=0$ (Boering *et al.*, 1996; Waugh and Hall, 2002). In equilibrium, the global flux of age through any global surface is known from first principles to equal the mass of the atmosphere M_u above the surface (Volk *et al.*, 1997; Neu and Plumb, 1999; Plumb, 2002). Equation (2.13) can be used to derive the net flux of any species from the slope of the tracer vs. age (or tracer vs. transient tracer) relationship, thus yielding an absolute estimate of tracer lifetime, i.e.,

$$\tau = -\frac{d\Gamma}{d\chi} \cdot \frac{B}{M_u} \quad (2.18)$$

However, Plumb and Ko’s result (2.13) rests on assumptions about stratospheric transport (specifically, the absence of transport barriers) that are now known to be invalid. In particular, the assumption that isentropic mixing has global reach led to the conclusion that net vertical transport of tracers (through surfaces of constant mixing ratio) is equivalent to vertical diffusion, and hence that the net vertical flux is proportional to the vertical gradient of mixing ratio. It is this equivalence on which the result (2.13) rests.

The theory of tracer-tracer relationships for the more realistic case with leaky subtropical barriers was outlined in detail in Plumb (2007; see also Volk *et al.*, 1996, 1997; Neu and Plumb, 1999). For the issues of interest here, the most important consequence of the presence of barriers is that the net vertical tracer flux is not purely diffusive, but partly advective, thus undermining (2.13). The implications for these developments for the determination of lifetimes have not been fully addressed in the literature. However, Plumb (2007) argued that the flux-gradient relation remains approximately valid for *locally*

conserved tracers in equilibrium, thus allowing determination of *relative* lifetimes of such tracers via Equation (2.14). However, since age has a source everywhere, no similar relationship has been demonstrated under such circumstances when age is one of the tracers. At present, therefore, use of tracer-age slopes to determine *absolute* tracer lifetimes is open to question.

Aside from such unresolved conceptual matters, there are also practical difficulties with the application of the absolute method. These difficulties, discussed by Volk *et al.* (1997), include the errors inherent in determining age from observations of transient tracers such as SF₆ or CO₂ (neither of which is growing perfectly linearly, although correction can be made for this) and in calculating the tracer-age slope at the tropopause, given the observed fact that the age-tracer relationship for many species of interest is curved in the lower stratosphere. (Both of these issues are evident in, e.g., Figure 6 of Volk *et al.* (1997).)

Another limitation of the applicability of both Equations (2.15) and (2.18) is the requirement of an equilibrium situation, which is rarely met in practice. Atmospheric growth of a tracer adds curvature to its correlation with another tracer (or with age) resulting in a change of the correlation slope at the tropopause on the order of $\sim 0.1\tau$ times the relative growth rate, e.g., $\sim 10\%$ for a lifetime of 100 years and a growth rate of 1% per year (Volk *et al.*, 1997). A formalism to correct the correlation slopes for tracer transience has been developed by Volk *et al.* (1997). Taking advantage of the fact that tracer mixing ratios are tightly correlated with age in the extratropical lowermost stratosphere, the method derives tracer-age slopes representative of a steady-state situation using the observed (transient) tracer-age slopes at the *extratropical tropopause* along with the temporal development of the tropospheric mixing ratio and information on the width of the stratospheric age spectrum. Use of these corrected (steady) slopes in Equations (2.15) and (2.18) then yields, in principle, (relative) steady-state lifetimes (within the various conceptual and practical limitations discussed above).

Finally, the theoretical basis of the tracer-tracer method has not, as yet, taken account of the seasonal variability of transport. At this stage, therefore, there is little if any theoretical guidance on how best to deal with such variability when applying the technique to observations or model output.

2.4 Summary

Lifetime is a combined property of the molecule, the background atmosphere (combined chemistry and transport), and the emission scenario. The lifetime can be defined from the global budget as the total burden in the atmosphere divided by the integrated loss over the entire atmosphere. The result depends on loss processes for the specific gas and on the distribution of the gas, which can depend on the emission scenario. The lifetime computed from the global budget is sometimes referred to as an instantaneous lifetime as it is calculated from the state of the atmosphere at a specific time or averaged over a short time interval such as a single year or a few years.

When emissions are continued long enough for the system to reach a steady state in which the average source equals the average loss, we can define a steady-state lifetime from the burden over the loss. The steady-state lifetime depends in principle on the emission pattern used to create that steady-state pattern of abundance, though for long-lived gases it is insensitive to the pattern of surface sources.

A response lifetime is defined simply from the change in burden divided by the change in loss caused by a given perturbation and will differ from the global lifetime when there are chemical feedbacks. The lifetime can be represented as a weighted mix of the time scales (e-folding times) that describe the temporal response of the atmosphere to a single pulse of a gas. It is not in general equal to any one of the time scales. These individual time scales depend on both transport times and local chemical time scales but not on the emission pattern. When the source of a gas is suddenly eliminated, the decay rate of the gas will evolve from the inverse of its instantaneous lifetime to that of a freely decaying mode (the longest time scale).

For gases that are well mixed in the troposphere, lifetime is a reasonably robust concept. The steady-state lifetime is then nearly independent of where the gas is emitted within the troposphere. Well-mixed gases have lifetimes (against surface emissions) of a couple years or more, and steady-state tropospheric variability of about ten percent or less. Thus, well-mixed gases include both long-lived CFCs and relatively short-lived gases like CH_3CCl_3 and some HFCs.

For gases that are not well mixed, the lifetime and time scales must be carefully diagnosed for emissions that vary with time, either systematically or seasonally, and location. The difference between lifetime and decay time can be substantial, making problematic the use of steady lifetimes to predict the future evolution. These not-well-mixed gases include gases like CH_3Br and $\text{NO}+\text{NO}_2$.

Comprehensive atmospheric chemistry-transport models provide the most self-consistent framework for calculating lifetimes, but the accuracy of such lifetimes can only be based on the corresponding ability of the models to simulate the observed abundances and atmospheric distributions of many trace species, thus requiring accurate transport and chemistry.

Determination of lifetimes from observation has improved greatly with the availability of global, satellite-based retrievals of important trace gases and *in situ* campaign data with simultaneous, high precision measurements of multiple species.

Direct determination of lifetimes from global burdens and loss rates via Equation (2.4) requires global information about both over a large altitude and temporal range, and the accuracy of any such determination depends on the availability of such data. Models provide this information, but the reliability of lifetimes thus calculated rests on the accuracy with which the models represent reality. Determination via (2.4) from observations has become feasible, as global satellite-based retrievals of many of the important trace gases are now available, but theoretical loss rates (to calculate L) or accurate source information (if Equation (2.7) is used) are also required.

Tracer-tracer methods appear to be theoretically justified, and useful in practice, as a route to calculating *relative* lifetimes against stratospheric loss and they are applied as such in Chapter 6. However, use of age, or of a transient conservative tracer, as a reference in order to yield *absolute* lifetimes is problematic, given current perspectives on the nature of stratospheric transport, and is likely to yield inaccurate answers. Specifically, model experiments conducted for Chapter 5 imply that lifetimes thus calculated are likely to be underestimated by about 20%. This systematic error is in addition to errors incurred as a result of the difficulty in determining accurate tracer-age slopes, both from observations (Volk *et al.*, 1997) and models (Chapter 4).

By whichever means lifetime is calculated, temporal variability – of the atmosphere, or of sources – must be borne in mind. The stratosphere, especially, exhibits a high degree of interannual variability and the impact of such variability on calculated lifetimes should not be ignored. Moreover, lifetimes can also change with time if the sources change, because of the dependence of net loss on the spatial distribution of the gas. For a source gas whose source is suddenly eliminated, its decay rate will evolve from the inverse of its steady-state lifetime to that of a freely decaying mode. For long-lived gases with stratospheric sinks, the difference between steady lifetime and decay time is very small; hence lifetimes determined for current conditions are useful as predictors of future decay if sources are removed. For shorter-lived gases with tropospheric sinks, however, the differences are substantial, making problematic the use of current lifetimes to predict future evolution.

Table 2.1 below is a short guide to connect the description of the theory of various methods for determining lifetime to the subsequent chapters that describe and apply those methods.

Table 2.1. Short guide to the use of methods in subsequent chapters of this report.

Section	Method	Chapter
2.3.1	Model-based computations from burden over loss	3, 5
2.3.1	Observation-based computations from burden over loss	4
2.3.2	Inverse methods	4
2.3.3	Tracer-tracer methods	4

In the box below we summarize the definitions of lifetime used throughout this report.

Lifetime Definitions

Global Atmospheric Lifetime (τ): Calculated from the global budget equation of a species as global atmospheric burden divided by global loss rate. This is also called an **instantaneous lifetime** and has been referred to as a **turnover time**.

Transient lifetime (τ): Another term for global atmospheric lifetime or instantaneous lifetime of a gas that is not in steady state.

Steady-state lifetime (τ_{ss}): Special case of global atmospheric lifetime calculated for a system that is at or near steady state. In steady state, the source and loss rates are equal.

Local lifetime: Inverse loss frequency at a specific point in the atmosphere.

Response lifetime: The time scale characterizing the decay of an instantaneous pulse input added to the atmosphere. This has also been referred to as an adjustment time.

Partial lifetimes:

OH (τ_{OH}): Global atmospheric burden divided by loss due to OH reaction rate

Cl (τ_{Cl}): Global atmospheric burden divided by loss due to Cl atom reaction rate

O(¹D) (τ_{O1D}): Global atmospheric burden divided by loss due to O(¹D) reactions rate

Photolysis (τ_{phot}): Global atmospheric burden divided by loss due to photolysis rate

Tropospheric (τ_{trop}): Global atmospheric burden divided by tropospheric loss rate

Stratospheric (τ_{strat}): Global atmospheric burden divided by stratospheric loss rate

Mesospheric (τ_{meso}): Global atmospheric burden divided by mesospheric loss rate

Oceanic (τ_{ocean}): Global atmospheric burden divided by loss to ocean surface rate

Soil (τ_{soil}): Global atmospheric burden divided by loss to land surface rate

In this report the global atmospheric lifetime will be referred to as just lifetime with symbol τ . Partial lifetimes and pulse-response lifetimes will be referred to with their specific subscripted symbols.

2.5 References

- Bergamaschi, P., C. Frankenberg, J. F. Meirink, M. Krol, M. G. Villani, S. Houweling, F. Dentener, E. J. Dlugokencky, J. B. Miller, L. V. Gatti, A. Engel, and I. Levin, Inverse modeling of global and regional CH₄ emissions using SCIAMACHY satellite retrievals, *J. Geophys. Res.*, *114*, D22301, doi: 10.1029/2009JD012287, 2009.
- Birner, T., and H. Boenisch, Residual circulation trajectories and transit times into the extratropical lowermost stratosphere, *Atmos. Chem. Phys.*, 11817-11827, doi: 10.5194/acp-11-817-2011, 2011.
- Boering, K. A., S. C. Wofsy, B. C. Daube, H. R. Schneider, M. Loewenstein, J. R. Podolske, and T. J. Conway, Stratospheric mean ages and transport rates from observations of CO₂ and N₂O, *Science*, *274*, 1340-1343, doi: 10.1126/science.274.5291.1340, 1996.
- Bridgeman, C. H., J. A. Pyle, and D. E. Shallcross, A three-dimensional model calculation of the ozone depletion potential of 1-bromopropane (1-C₃H₇Br), *J. Geophys. Res.*, *105*, 26493, 2000.
- Brioude, J., R. W. Portmann, J. S. Daniel, O. R. Cooper, G. J. Frost, K. H. Rosenlof, C. Granier, A. R. Ravishankara, S. A. Montzka, and A. Stohl, Variations in ozone depletion potentials of very short-lived substances with season and emission region, *Geophys. Res. Lett.*, *37*, L19804, doi: 10.1029/2010GL044856, 2010.
- Butchart, N., A. A. Scaife, M. Bourqui, J. de Grandpré, S. H. E. Hare, J. Kettleborough, U. Langematz, E. Manzini, F. Sassi, K. Shibata, D. Shindell, and M. Sigmond, Simulations of anthropogenic change in the strength of the Brewer–Dobson circulation, *Clim. Dyn.*, *27* (7-8), 727-741, doi: 10.1007/s00382-006-0162-4, 2006.
- Butler, J. H., The potential role of the ocean in regulating atmospheric CH₃Br, *Geophys. Res. Lett.*, *21*, 185-189, 1994.
- Cunnold, D., R. Prinn, R. Rasmussen, P. Simmonds, F. Alyea, C. Cardelino, A. Crawford, P. Fraser, and R. Rosen, The Atmospheric Lifetime Experiment 3. Lifetime Methodology and Application to Three Years of CFCl₃ Data, *J. Geophys. Res.*, *88* (C13), 8379-8400, 1983.
- Daniel, J. S., and S. Solomon, On the climate forcing of carbon monoxide, *J. Geophys. Res.*, *103*, 13249-13260, 1998.
- Derwent, R. G., W. J. Collins, C. E. Johnson, and D. S. Stevenson, Transient behaviour of tropospheric ozone precursors in a global 3-D CTM and their indirect greenhouse effects, *Clim. Change*, *49* (4), 463-487, 2001.
- Douglass, A. R., R. S. Stolarski, M. R. Schoeberl, C. H. Jackman, M. L. Gupta, P. A. Newman, J. E. Nielsen, and E. L. Fleming, Relationship of loss, mean age of air and distribution of CFCs to stratospheric circulation and implications for atmospheric lifetimes, *J. Geophys. Res.*, *113*, D14309, doi: 10.1029/2007JD009575, 2008.
- Ehhalt, D. H., R. Rohrer, S. Schaufli, and M. Prather, On the decay of stratospheric pollutants: Diagnosing the longest-lived eigenmode, *J. Geophys. Res.*, *109*, D08102, doi: 10.1029/2003JD004029, 2004.
- Farrell, B. F., and P. J. Ioannou, Perturbation dynamics in atmospheric chemistry, *J. Geophys. Res.*, *105*, 9303-9320, 2000.

- Hartley, D. and R. Prinn, Feasibility of determining surface emissions of trace gases using an inverse method in a three-dimensional chemical transport model, *J. Geophys. Res.*, *98*, 5183-5198, 1993.
- Hegglin, M. I., and T. G. Shepherd, Large climate-induced changes in UV index and stratosphere-to-troposphere ozone flux, *Nature Geoscience* *2*, 687-691, 2009.
- Hu, L., S. Yvon-Lewis, Y. Liu, and T. S. Bianchi, The ocean in near equilibrium with atmospheric methyl bromide, *Global Biogeochem. Cycles*, *26*, GB3016, doi: 10.1029/2011GB004272, 2012.
- IPCC (Intergovernmental Panel on Climate Change), *Climate Change 1995: The Science of Climate Change*, edited by J. T. Houghton, L. G. Meira Filho, B. A. Callander, N. Harris, A. Kattenberg, and K. Maskell, 572 pp., Cambridge University Press, Cambridge, U. K., 1996.
- IPCC (Intergovernmental Panel on Climate Change), *Climate Change 2001: The Scientific Basis, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by J. T. Houghton, Y. Ding, D. J. Griggs, M. Noguer, P. J. van der Linden, X. Dai, K. Maskell, and C. A. Johnson, 881 pp., Cambridge University Press, Cambridge, U. K., 2001.
- Isaksen, I. S. A., and O. Hov, Calculation of trends in tropospheric O₃, OH, CH₄, and NO_x, *Tellus B*, *39*, 271-285, 1987.
- John, J. G., A. M. Fiore, V. Naik, L. W. Horowitz, and J. P. Dunne, Climate versus emission drivers of methane lifetime from 1860–2100, *Atmos. Chem. Phys. Discuss.*, *12*, 18067-18105, doi: 10.5194/acpd-12-18067-2012, 2012.
- Junge, C. E., Residence time and variability of tropospheric trace gases, *Tellus*, *26*, 477-488, 1974.
- Kalnay, E., Atmospheric modeling, data assimilation and predictability, Cambridge University Press, 2003.
- Ko, M. K. W., N. D. Sze, C. J. Scott, and D. K. Weisenstein, On the relation between stratospheric chlorine/bromine loading and short-lived tropospheric source gases. *J. Geophys. Res.*, *102*, 25507-25517, doi: 10.1029/97JD02431, 1997.
- Lawrence, M. G., P. Jöckel, and R. von Kuhlmann, What does the global mean OH concentration tell us?, *Atmos. Chem. Phys.*, *1*, 37-49, doi: 10.5194/acp-1-37-2001, 2001.
- Lee, C., R. V. Martin, A. van Donkelaar, H. Lee, R. R. Dickerson, J. C. Hains, N. Krotkov, A. Richter, K. Vinnikov, and J. J. Schwab, SO₂ emissions and lifetimes: Estimates from inverse modeling using *in situ* and global, space-based (SCIAMACHY and OMI) observations, *J. Geophys. Res.*, *116*, D06304, doi: 10.1029/2010JD014758, 2011.
- Lelieveld, J., P. J. Crutzen, and F. J. Dentener, Changing concentration, lifetime and climate forcing of atmospheric methane, *Tellus, Ser., B*, *50*, 128-150, 1998.
- Li, F., R. S. Stolarski, and P. A. Newman, Stratospheric ozone in the post-CFC era, *Atmos. Chem. Phys.*, *9*, 2207-2213, <http://www.atmos-chem-phys.net/9/2207/2009/>, 2009.
- Manning, M. R., Characteristic modes of isotopic variations in atmospheric chemistry. *Geophys. Res. Lett.*, *26*, 1263-1266, doi: 10.1029/1999GL900217, 1999.

- Minschwaner, K., R. J. Salawitch, and M. B. McElroy, Absorption of solar Radiation by O₂; Implications for O₃ and Lifetimes of N₂O, CFCl₃, and CF₂Cl₂, *J. Geophys. Res.*, *98*, 10543-10561, 1993.
- Montzka, S. A., J. H. Butler, J. W. Elkins, T. M. Thompson, A. D. Clarke, and L. T. Lock, Present and future trends in the atmospheric burden of ozone-depleting halogens, *Nature*, *398*, 690-694, 1999.
- Montzka, S. A., M. Krol, E. Dlugokencky, B. Hall, P. Jöckel, and J. Lelieveld, Small interannual variability of global atmospheric hydroxyl, *Science*, 7 January 2011, 67-69, doi: 10.1126/science.1197640, 2011.
- Neu, J. L., and R. A. Plumb, Age of air in a “leaky pipe” model of stratospheric transport, *J. Geophys. Res.*, *104* (D16), 19243-19255, doi: 10.1029/1999JD900251, 1999.
- Olsen, S. C., B. J. Hannegan, X. Zhu, and M. J. Prather, Evaluating ozone depletion from very short-lived halocarbons, *Geophys. Res. Lett.*, *27*, 1475-1478, 2000.
- O’Neill, B. C., Gaffin, S. R., Tubiello, F. N. and Oppenheimer, M., Reservoir timescales for anthropogenic CO₂ in the atmosphere, *Tellus-B*, *46*, 378-389, 1994.
- Patra, P. K., S. Houweling, M. Krol, P. Bousquet, D. Belikov, D. Bergmann, H. Bian, P. Cameron-Smith, M. P. Chipperfield, K. Corbin, A. Fortems-Cheiney, A. Fraser, E. Gloor, P. Hess, A. Ito, S. R. Kawa, R. M. Law, Z. Loh, S. Maksyutov, L. Meng, P. I. Palmer, R. G. Prinn, M. Rigby, R. Saito, and C. Wilson, TransCom model simulations of CH₄ and related species: Linking transport, surface flux and chemical loss with CH₄ variability in the troposphere and lower stratosphere, *Atmos. Chem. Phys.*, *11*, 12813-12837, 2011.
- Pisso, I., P. H. Haynes, and K. S. Law, Emission location dependent ozone depletion potentials for short-lived halogenated species, *Atmos. Chem. Phys.*, *10*, 12025-12036, 2010.
- Plumb, R. A., Stratospheric Transport, *J. Meteor. Soc. Japan*, *80*, 793-809, 2002.
- Plumb, R. A., Tracer interrelationships in the stratosphere, *Rev. Geophys.*, *45*, RG4005, doi: 10.1029/2005RG000179, 2007.
- Plumb, R. A., *et al.*, in preparation, 2013.
- Plumb, R. A., and M. K. W. Ko, Interrelationships between mixing ratios of long-lived stratospheric constituents, *J. Geophys. Res.*, *97*, 10140-10156, 1992.
- Prather, M. J., Lifetimes and eigenstates in atmospheric chemistry, *Geophys. Res. Lett.*, *21*, 801-804, 1994.
- Prather, M. J., Time scales in atmospheric chemistry: Theory, GWPs for CH₄ and CO, and runaway growth, *Geophys. Res. Lett.*, *23*, 2597-2600, 1996.
- Prather, M. J., Timescales in atmospheric chemistry: CH₃Br, the ocean, and ozone depletion potentials, *Global Biogeochem. Cycles*, *11* (3), 393-400, 1997.
- Prather, M. J., Time scales in atmospheric chemistry: Coupled perturbations to N₂O, NO_y, and O₃, *Science*, *279*, 1339-1341, 1998.
- Prather, M. J., Lifetimes and time scales in atmospheric chemistry, *Phil. Trans. Roy. Soc. A*, *365* (1856), 1705-1726, 2007.
- Prather, M. J., and J. Hsu, Coupling of nitrous oxide and methane by global atmospheric chemistry. *Science*, *330* (6006), 952-954, 2010.

- Prather, M. J., and C. Spivakovsky, Tropospheric OH and the lifetimes of hydrochlorofluorocarbons, *J. Geophys. Res.*, *95*, 18433-18439, doi: 10.1029/JD095iD11p18723, 1990.
- Prather, M. J., X. Zhu, Q. Tang, J. N. Hsu, and J. L. Neu, An atmospheric chemist in search of the tropopause, *J. Geophys. Res.*, *116*, D04306, doi: 10.1029/2010JD014939, 2011.
- Prather, M. J., C. D. Holmes, and J. Hsu, Reactive greenhouse gas scenarios: Systematic exploration of uncertainties and the role of atmospheric chemistry, *Geophys. Res. Lett.*, *39*, L09803, doi: 10.1029/2012GL051440, 2012.
- Prinn, R., R. Weiss, B. Miller, J. Huang, F. Alyea, D. Cunnold, P. Fraser, D. E. Hartley, and P. G. Simmonds, Atmospheric trends and lifetime of CH₃CCl₃ and global OH concentrations, *Science*, *269* (5221), 187-192, 1995.
- Rhew, R. C., M. Aydin, and E. S. Saltzman, Measuring terrestrial fluxes of methyl chloride and methyl bromide using a stable isotope tracer technique, *Geophys. Res. Lett.*, *30* (21), 2103, doi: 10.1029/2003GL018160, 2003.
- Rigby, M., R. G. Prinn, S. O'Doherty, S. A. Montzka, A. McCulloch, C. M. Harth, J. Mühle, P. K. Salameh, R. F. Weiss, D. Young, P. G. Simmonds, B. D. Hall, G. S. Dutton, D. Nance, D. J. Mondeel, J. W. Elkins, P. B. Krummel, L. P. Steele, and P. J. Fraser, Re-evaluation of the lifetimes of the major CFCs and CH₃CCl₃ using atmospheric trends, *Atmos. Chem. Phys.*, *13*, 2691-2702, doi: 10.5194/acp-13-2691-2013, 2013.
- Sander, S. P., J. Abbatt, J. R. Barker, J. B. Burkholder, R. R. Friedl, D. M. Golden, R. E. Huie, C. E. Kolb, M. J. Kurylo, G. K. Moortgat, V. L. Orkin and P. H. Wine, *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17*, JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, <http://jpldataeval.jpl.nasa.gov/>, 2011.
- Spivakovsky, C. M., J. A. Logan, S. A. Montzka, Y. J. Balkanski, M. Foreman-Fowler, D. B. A. Jones, L. W. Horowitz, A. C. Fusco, C. A. M. Brenninkmeijer, M. J. Prather, S. C. Wofsy, and M. B. McElroy, Three-dimensional climatological distribution of tropospheric OH: Update and evaluation, *J. Geophys. Res.*, *105* (D7), 8931-8980, doi: 10.1029/1999JD901006, 2000.
- Stevenson, D. S., F. J. Dentener, M. G. Schultz, K. Ellingsen, T. P. C. van Noije, O. Wild, G. Zeng, M. Amann, C. S. Atherton, N. Bell, D. J. Bergmann, L. Bey, T. Butler, J. Cofala, W. J. Collins, R. G. Derwent, R. M. Doherty, J. Drevet, H. J. Eskes, A. M. Fiore, M. Gauss, D. A. Hauglustaine, L. W. Horowitz, I. S. A. Isaksen, M. C. Krol, J.-F. Lamarque, M. G. Lawrence, V. Montanaro, J.-F. Müller, G. Pitari, M. J. Prather, J. A. Pyle, S. Rast, J. M. Rodriguez, M. G. Sanderson, N. H. Savage, D. T. Shindell, S. E. Strahan, K. Sudo, and S. Szopa, Multimodel ensemble simulations of present-day and near-future tropospheric ozone, *J. Geophys. Res.*, *111*, D08301, doi: 10.1029/2005JD006338, 2006.
- Volk, C. M., J. W. Elkins, D. W. Fahey, R. J. Salawitch, G. S. Dutton, J. M. Gilligan, M. H. Proffitt, M. Loewenstein, J. R. Podolske, K. Minschwaner, J. J. Margitan, and K. R. Chan, Quantifying transport between the tropical and mid-latitude lower stratosphere, *Science*, *272*, 1763-1768, 1996.
- Volk, C. M., J. W. Elkins, D. W. Fahey, D. S. Dutton, J. M. Gilligan, M. Loewenstein, J. R. Podolske, K. R. Chan, and M. R. Gunson, Evaluation of source gas lifetimes from stratospheric observations, *J. Geophys. Res.*, *102*, 25543-25564, 1997.

- Waugh, D. W., and T. M. Hall, Age of stratospheric air: Theory, observations, and models, *Rev. Geophys.*, *40* (4), 1010, doi: 10.1029/2000RG000101, 2002.
- Wennberg, P. O., S. Peacock, J. T. Randerson, and R. Bleck, Recent changes in the air-sea gas exchange of methyl chloroform, *Geophys. Res. Lett.*, *31*, L16112, doi: 10.1029/2004GL020476, 2004.
- Wild, O., M. J. Prather, and H. Akimoto, Indirect long-term global cooling from NO_x emissions, *Geophys. Res. Lett.*, *28*, 1719-1722, doi: 10.1029/2000GL012573, 2001.
- Wuebbles, D. J., K. O. Patten, M. T. Johnson, and R. Kotamarthi, New methodology for ozone depletion potentials of short-lived compounds: n-propyl bromide as an example, *J. Geophys. Res.*, *106*, 14551-14571, 2001.
- Yvon-Lewis, S. A., and J. H. Butler, The potential effect of oceanic biological degradation on the lifetime of atmospheric CH₃Br, *Geophys. Res. Lett.*, *24* (10), 1227-1230, 1997.