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Re-evaluation of the lifetimes of the major CFCs and CH_3CCl_3 using atmospheric trends

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Abstract. Since the Montreal Protocol on Substances that Deplete the Ozone Layer and its amendments came into effect, growth rates of the major ozone depleting substances (ODS), particularly CFC-11, -12 and -113 and CH_3CCl_3 , have declined markedly, paving the way for global stratospheric ozone recovery. Emissions have now fallen to relatively low levels, therefore the rate at which this recovery occurs will depend largely on the atmospheric lifetime of these compounds. The first ODS measurements began in the early 1970s along with the first lifetime estimates calculated by considering their atmospheric trends. We now have global mole fraction records spanning multiple decades, prompting this lifetime re-evaluation. Using surface measurements from the Advanced Global Atmospheric Gases Experiment (AGAGE) and the National Oceanic and Atmospheric Administration Global Monitoring Division (NOAA GMD) from 1978 to 2011, we estimated the lifetime of CFC-11, CFC-12, CFC-113 and CH_3CCl_3 using a multi-species inverse method. A steady-state lifetime of 45 yr for CFC-11, currently recommended in the most recent World Meteorological Organisation (WMO) Scientific Assessments of Ozone Depletion, lies towards the lower uncertainty bound of our estimates, which are 54_{48}^{61} yr (1-sigma uncertainty) when AGAGE data were used and 52_{45}^{61} yr when the NOAA net-

work data were used. Our derived lifetime for CFC-113 is significantly higher than the WMO estimates of 85 yr, being 109_{99}^{121} (AGAGE) and 109_{97}^{124} (NOAA). New estimates of the steady-state lifetimes of CFC-12 and CH_3CCl_3 are consistent with the current WMO recommendations, being 111_{95}^{132} and 112_{95}^{136} yr (CFC-12, AGAGE and NOAA respectively) and $5.04_{4.92}^{5.20}$ and $5.04_{4.87}^{5.23}$ yr (CH_3CCl_3 , AGAGE and NOAA respectively).

1 Introduction

Molina and Rowland (1974) proposed that stratospheric ozone could be depleted through catalytic cycles initiated by the photolytic release of chlorine radicals from chlorofluorocarbons (CFCs). Using a photochemical model, they estimated that the two most abundant CFCs, CFCl_3 (CFC-11) and CF_2Cl_2 (CFC-12), would remain in the atmosphere for between 40 and 150 yr. Subsequently, more advanced photochemical models have been used to estimate the lifetime of these important atmospheric constituents. For example, Park et al. (1999) compared a range of 2- and 3-dimensional models and found simulated CFC-11 lifetimes between 35

and 68 yr, CFC-12 lifetimes of 90 to 149 yr and CCl₂FCClF₂ (CFC-113) lifetimes of 55 to 101 yr.

Various observational constraints on trace gas lifetimes have also been attempted. Satellite observations of CFC abundances have allowed relative lifetimes to be derived using inter-species correlations in the lower stratosphere. Volk et al. (1997) estimated lifetimes of 96 ± 12 yr for CFC-12 and 112 ± 31 for CFC-113 using an assumed lifetime for CFC-11 of 50 yr.

Independently of these methods, lifetimes have been estimated by monitoring trends in CFC mole fractions measured at the Earth's surface. Even before the dangers associated with CFCs were discovered, Lovelock et al. (1973) measured CFC-11 using a gas chromatograph with an electron capture detector (GC-ECD) and estimated a lifetime of at least 10 yr. More precise lifetime estimates were not possible at the time because the cumulative emission rate was poorly quantified. The following decade, Cunnold et al. (1983) determined a CFC-11 lifetime of 83_{56}^{156} yr using a chemical transport model, emissions estimates and measurements from the Atmospheric Lifetime Experiment (ALE) which began in 1978 with the aim of measuring trends of CFCs and other trace gases (Prinn et al., 1983; Rasmussen and Lovelock, 1983). ALE, and subsequent projects, the Global Atmospheric Gases Experiment (GAGE) and Advanced Global Atmospheric Gases Experiment (AGAGE, Prinn et al., 2000) used automated GC-ECD systems to monitor CFC mole fractions at five background locations across the globe, and measurements are ongoing today. These data sets have primarily been used for emissions estimation in more recent years (e.g. Cunnold et al., 1994), although emissions derived using a chemical transport model and the ALE/GAGE/AGAGE measurements have been compared to inventory estimates to investigate the feasibility of particular lifetime estimates (e.g. a lifetime of 26 yr for CFC-113 was found to be largely inconsistent with estimated release rates in Fraser et al., 1996).

Based on these estimates derived from observations, laboratory data, and a range of modeling approaches, Prinn et al. (1999) recommended a lifetime of 45 yr for CFC-11 and 100 yr for CFC-12 in the 1998 World Meteorological Organisation (WMO) Scientific Assessment of Ozone Depletion. A lifetime of 85 yr is commonly used for CFC-113, based on the model inter-comparison of Ko et al. (1994). In the absence of a comprehensive re-evaluation of lifetimes since 1998, recent WMO Ozone Assessment Reports have reported these same values (Clerbaux et al., 2007; Montzka et al., 2011b).

The lifetime of CH₃CCl₃ (methyl chloroform) has also been the focus of much recent work. Although CH₃CCl₃ has a smaller ozone depletion potential than the major CFCs, its production is also controlled under the Montreal Protocol. Its lifetime is of interest because it can be used to determine the global concentration of its major sink, the hydroxyl radical (OH), which is responsible for removing many green-

house gases and other pollutants from the atmosphere, and plays a key role in atmospheric chemistry (Prinn et al., 2001, 2005; Bousquet et al., 2005; Montzka et al., 2011a). Most recently, Prinn et al. (2005) estimated an average lifetime for CH₃CCl₃ of 4.9 ± 0.3 yr, and similar lifetimes have been derived by other authors, leading to a recommendation of 5 yr in recent WMO assessments (e.g. Clerbaux et al., 2007; Montzka et al., 2011b).

Here, we present a new evaluation of the lifetimes of these gases using measurements by the ALE/GAGE/AGAGE and National Oceanic and Atmospheric Administration Earth System Research Laboratory Global Monitoring Division (NOAA GMD) networks. Measurements have now been made by these networks for over three decades, potentially allowing new insights. To infer lifetimes from the measured trends, we used a set of emissions estimates, a chemical transport model and a statistical “inverse” method, the details of which are given below. We only focus on CFC-11, -12 and -113 and CH₃CCl₃ in this paper, despite there being other measured trace species for which lifetimes are also poorly constrained. This is because our technique requires robust emissions estimates, which do not appear to be available for some important ozone-depleting gases such as CCl₄ (e.g. Xiao et al., 2010; Montzka et al., 2011b).

1.1 Atmospheric trace gas lifetimes

In a simple zero-dimensional model of the atmosphere, we can calculate the rate of change in the mass of a trace gas (the “burden”, B) from the difference between the sources into the atmosphere (S) and photochemical losses from it (L). Making the assumption that the loss rate can be represented by a lifetime (τ), we can write:

$$L = \frac{B(t)}{\tau} \quad (1)$$

$$\frac{dB(t)}{dt} = S(t) - \frac{B(t)}{\tau} \quad (2)$$

In this paper, we aim to derive lifetimes that represent the sum of all losses from the atmosphere (for example, the combination of photochemical losses and oceanic uptake for gases that have a stratospheric and oceanic sink).

It should be noted that in the real atmosphere, losses take place at different rates in different regions (e.g. the majority of CFC loss occurs in the stratosphere), and therefore, the global lifetime at a particular instant depends on the gas distribution relative to the loss processes. We refer to these distribution-dependent lifetimes as “transient lifetimes”. Lifetimes are only uniquely defined when the burden does not change (i.e. when sources balance sinks), which we refer to here as “steady-state lifetimes”.

2 Monitoring trends in ozone depleting substances

The mole fraction of CFCs and other substances have been monitored close to the earth's surface by the ALE/GAGE/AGAGE and NOAA GMD networks since 1978. The two networks aim to primarily sample air masses that are relatively free from the influence of recent pollution sources, and therefore sampling locations tend to be relatively remote (so-called “background” locations). The location of the 5 ALE stations was chosen to sample air that was thought to be representative of four atmospheric semi-hemispheres (90–30° N, 30–0° N, 0–30° S, 30–90° S, Prinn et al., 1983). ALE/GAGE/AGAGE measurements are made in situ with automated instruments, allowing measurements at approximately hourly frequency. The NOAA data used here is comprised of measurements made using automated and flask-sampling systems at 6 stations with additional flask sampling at four further locations. Measurements from some flask sampling locations have been omitted from this work as they were found to occasionally intercept “polluted” air masses, which would not be well represented by the chemical transport model used. Monitoring locations for both networks are shown in Fig. 1. Co-located flask samples are collected at all NOAA in situ and four ALE/GAGE/AGAGE stations, and simultaneous high-frequency measurements are made at the Cape Matatula, American Samoa station by both networks. These two measurement datasets are inter-compared in the Supplement.

Both sets of measurements are made primarily made using GC-ECD systems (Prinn et al., 2000; Elkins et al., 1993). The NOAA CFC-113 dataset includes additional in situ and flask measurements made using GC-mass spectrometry (MS) systems (Montzka et al., 1996), and the NOAA CH₃CCl₃ dataset is comprised of only GC-MS flask measurements (Montzka et al., 2011a). In this work, we preferentially used AGAGE CFC-113 measurements from the “Medusa” GC-MS systems, which began sampling in the mid-2000s (Miller et al., 2008) over the GC-ECD measurements, which suffer from poorer precision and potential co-elution problems in recent years at some sites. ALE/GAGE measurements of CFC-113 began at Cape Grim, Tasmania before the other ALE/GAGE stations (Fraser et al., 1996), however, we chose not to use these early measurements, because the inversion was found to be poorly constrained if measurements were not available all four semi-hemispheres. The ALE/GAGE/AGAGE CH₃CCl₃ time series used in this paper also includes Medusa measurements, which were averaged with GC-ECD measurements at all stations. CH₃CCl₃ measurements from the two sets of AGAGE instruments agree very well, with no significant biases.

ALE/GAGE/AGAGE measurements have been calibrated relative to standards prepared at the Scripps Institution of Oceanography (SIO) and are reported here on the SIO-2005 scale. Independent calibration scales have been prepared at NOAA, whose measurements are presented on the 1993,

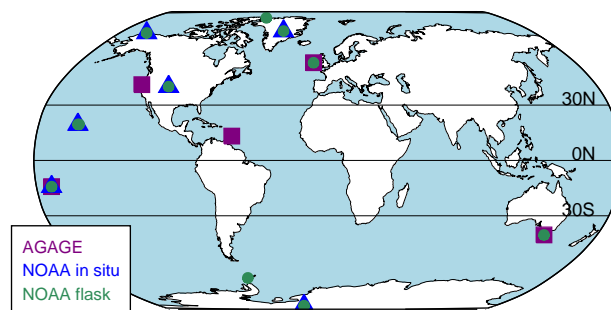


Fig. 1. Locations of AGAGE and NOAA CFC and CH₃CCl₃ measurements. Purple squares show locations of AGAGE (in situ) stations, blue triangles show the locations of NOAA in situ monitoring sites and green dots show NOAA flask sampling locations. Also shown are the boundaries of the chemical transport model “boxes”.

2008, 2002 and 2003 scales respectively for CFC-11, -12, -113 and CH₃CCl₃. Uncertainties in the absolute calibration scales are estimated to be around 2 % (Prinn et al., 2000) for the SIO scales. A comparison of the global difference between AGAGE and NOAA observations is consistent with a 2 % calibration scale uncertainty (see Supplement).

Average measurement repeatabilities are currently thought to be less than 1 % for the CFC and CH₃CCl₃ measurements for both networks. In this paper, we compare the measurements with a model of atmospheric chemistry and transport that represents only semi-hemispheric background mole fractions at monthly intervals. Therefore, in addition to measurement repeatability, we aimed to derive a measurement uncertainty statistic that included uncertainties due to the spatial and temporal sub-sampling of the monthly semi-hemispheric means by the measurement networks, as well as measurement repeatability and scale propagation errors. We estimated this from the difference between AGAGE and NOAA observations from the same latitudinal bands, around a global average offset (which we assumed to indicate network-wide calibration differences). We estimated this uncertainty in each decade to allow for improvements in measurement repeatability and changes in sub-sampling errors (e.g. due to the decrease in spatial gradients as emissions decrease). We find that an uncertainty function that begins at around 1.5 % in the 1970s and 1980s that then drops to 0.3 % from 2000 fits the AGAGE-NOAA differences well for CFC-11 and 12, whereas relatively constant uncertainties of around 0.3 % and 1 % fit the differences between the two networks for CFC-113 and CH₃CCl₃. More detailed analyses are presented in the Supplement.

Measurements and overall uncertainties (which include modelling uncertainties described below, but not calibration uncertainties), averaged into semi-hemispheres, are shown in Fig. 2. The figure shows monthly-mean observations in which “pollution events” have been removed from

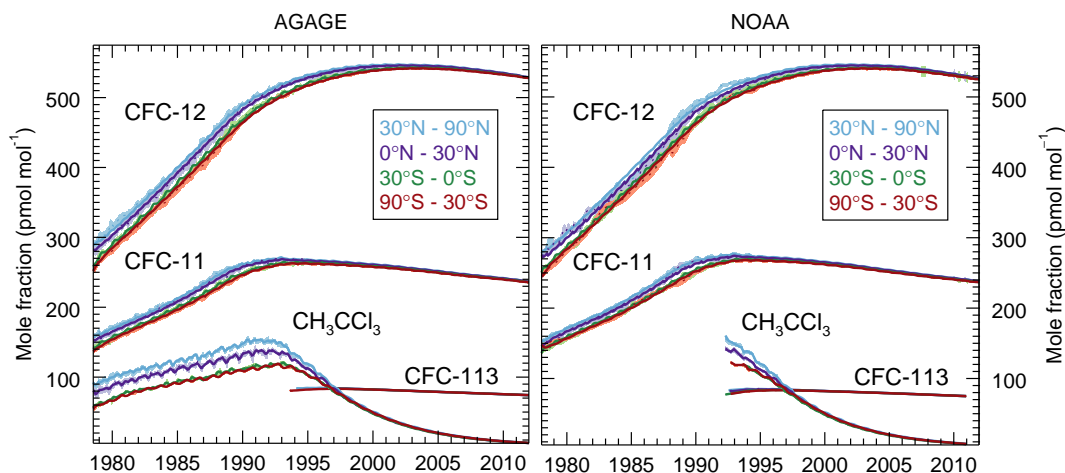


Fig. 2. Model prediction of AGAGE and NOAA CFC-11, -12, -113 and CH₃CCl₃ mole fractions in each semi-hemisphere (solid lines). Dotted lines and the surrounding shaded areas show the measurements and the model-measurement uncertainty limits (1-sigma). Uncertainties include measurement repeatability and subsampling errors, along with model representation uncertainties, but not network calibration uncertainties.

the AGAGE data using a statistical method outlined in O'Doherty et al. (2001).

After increasing sharply throughout the 1970s and 1980s, global mole fractions of CFC-11, -113 and CH₃CCl₃ began to decline in the early 1990s, indicating that emissions had fallen below the rate of destruction (Montzka et al., 1999; Prinn et al., 2000). Peak CFC-12 concentrations occurred in the early 2000s, and now all compounds show marked global reductions (Fig. 2). Similarly, the inter-hemispheric gradients of all species can be seen to decrease over time, reflecting a reduction in emissions, which predominantly originated in the Northern Hemisphere for these gases (e.g., McCulloch et al., 2001, 2003). CH₃CCl₃ mole fractions have declined the most sharply, reflecting the relatively short lifetime of this gas compared to the CFCs, and its limited use in slow-release applications (see below).

3 Lifetime estimation methodology

Measured trends in atmospheric ODS mole fractions are influenced by the lifetime of the compound, but also by emissions and atmospheric transport which must be accounted for if robust lifetimes are to be derived. In this section we describe the emissions inventories used in our analysis, before providing details on the chemical transport model and inverse method employed to determine lifetimes.

3.1 Emissions estimates

CFCs and CH₃CCl₃ have been primarily used for refrigeration, foam blowing, air conditioning and as solvents. Some of these uses involve relatively rapid release to the atmosphere and their emissions can be calculated by considering produc-

tion and usage statistics. However, some uses, such as refrigeration, lead to a release to the atmosphere that can take place (slowly or suddenly) many years after production. Emissions estimates from these sources must take account of the fraction of emissions stored in such “banks” and the timescales over which release is estimated to take place.

Using surveys, such as the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS), of industry in developed countries, plus the consumptions in all countries reported to the United Nations Environment Programme (UNEP) along with assumptions about releases from banks, past estimates and future projections of CFC emissions were prepared in 2006 based on methodologies outlined in McCulloch et al. (2001, 2003), and are shown in Fig. 3 and tabulated in the Supplement. Latitudinal distributions of CFC-11 and CFC-12 emissions were estimated for 1980–1990 in Cunnold et al. (1994). We use these gradients here, and assume they remained constant before 1980 and after 1990. Errors in the assumed emissions distribution were found to be less important than uncertainties in the overall emission rate as this paper focuses only on globally averaged lifetimes. We assumed that the latitudinal distribution of CFC-113 emissions was the same as the Cunnold et al. (1994) estimates for CFC-12.

We used an additional emissions dataset for CFC-11 and CFC-12 in our analysis, to investigate the influence of inventory errors on our lifetimes estimates. Using similar methodologies, global emissions were compiled by the UNEP Technology and Economic Assessment Panel (UNEP/TEAP, 2006) from 1991 to 2003. We applied the Cunnold et al. (1994) latitudinal gradients to these global values to estimate semi-hemispheric emissions. The two emissions datasets are compared in Fig. 3. The figure shows that for CFC-12,

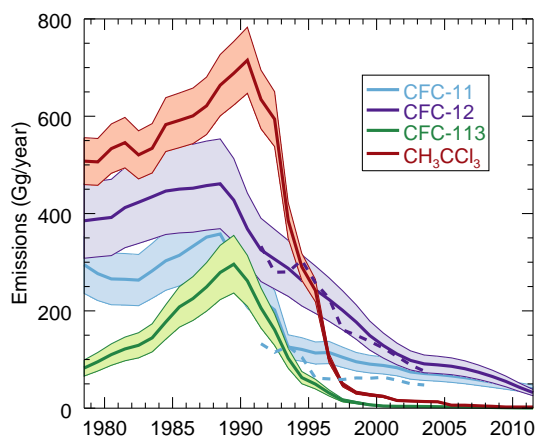


Fig. 3. Emissions estimates for CFC-11, -12, -113 and CH₃CCl₃ from 1978 to 2011. CFC estimates from 2005 to 2011 are projections (not based on reported data). Dashed lines show independently compiled emissions from UNEP/TEAP (2006). Shaded areas show 1-sigma uncertainties, which are estimated based on the root-mean-square difference between the two datasets.

overall discrepancies between the two datasets are relatively small (a few percent). However, for CFC-11, the UNEP/TEAP (2006) emissions are substantially lower for most years. When considering both the CFC-11 and CFC-12 datasets together, the root-mean-square (RMS) discrepancy between the two emissions estimates is 20 % for these years. This difference is larger than the uncertainty that has been estimated for this type of emissions estimate (e.g. Gamlen et al., 1986; Cunnold et al., 1994, estimate an uncertainty of around 5 % or better).

For lifetime estimates of CH₃CCl₃, we used the emissions estimates and associated uncertainties compiled in Prinn et al. (2005), which have been updated based on more recent UNEP submissions.

Figure 3 shows that since (and even before) the Montreal Protocol came into effect, emission rates slowed and eventually began to decline for all four gases. Emissions of CH₃CCl₃ have declined more rapidly than the three CFCs studied here, reflecting the smaller fraction that was stored in slow-release applications.

3.2 Chemical transport model

Previous studies have used low (1 or 2) dimensional models to determine global trace gas lifetimes or emissions using AGAGE and NOAA measurements (e.g., Cunnold et al., 1983; Montzka et al., 1999; Daniel et al., 2007; Montzka et al., 2011b). Whilst many important atmospheric processes must be parameterized in such models, they do offer two distinct advantages for simulations of the kind used here: (a) they are computationally very efficient, allowing estimation schemes to be used that can require many thousands of model runs (see below), and (b) the sensitivity to large-scale trans-

port features (e.g., stratosphere-troposphere exchange) can be investigated in a way that would be difficult in a three-dimensional model using reanalyzed meteorological fields.

We use a 12-box model of the atmosphere, similar to that of Cunnold et al. (1983, 1994), with box boundaries at the equator, 30° N and 30° S, and 500 and 200 hPa. This formulation was thought to parameterize atmospheric circulation sufficiently to resolve background mole fractions measured in each semi-hemisphere and provide useful information on processes such as stratosphere-troposphere exchange. A 9-box model that had a single stratospheric box was originally developed by Cunnold et al. (1983), using parameterizations of eddy diffusion and bulk advection from Newell et al. (1969). Subsequently, Cunnold et al. (1994) found that improved simulations could be obtained by sub-dividing the stratosphere into four boxes.

This AGAGE 12-box model has been re-coded for this work, using the original transport equations and parameters from Cunnold et al. (1983) and from Cunnold et al. (1994) for the stratosphere (further details are given in the Supplement). All of the eddy diffusion parameters (which dominate transport in the model) have been included in the estimation scheme as a priori constraints, allowing us to estimate model transport at the same time as determining lifetimes. These parameters were estimated in each season of each year. This improves on the approach of Cunnold et al. (1983) in which only three parameters were adjusted for the entire time period, leading to poor seasonal agreement with observations at some sites (e.g. Ragged Point, Barbados).

Stratospheric loss is parameterized by a loss rate in each of the stratospheric boxes in each season. The a priori seasonal cycle in the stratospheric lifetimes are based on model simulations by Golombek and Prinn (1986). Annually-repeating OH fields were specified a priori in the 8 tropospheric boxes based on the 3-dimensional model estimates of Spivakovsky et al. (2000), and adjustments to this OH field were derived in the inversion for each season in each latitudinal band. Oceanic uptake was parameterized by a loss timescale in the lowest boxes. A priori estimates of each of these parameters are given in the Supplement.

The model was used to simulate monthly-mean mole fractions in each semi-hemisphere, and was compared to semi-hemisphere averaged AGAGE and NOAA background observations.

3.3 Estimation method

To quantify the mismatch between the observed and modeled mole fractions and between any a priori information provided to the inversion (e.g. estimates of stratospheric lifetime), we define a scalar quantity (J) using the following “cost function”:

$$J = (\mathbf{y} - \mathbf{y}_{\text{obs}})^T \mathbf{R}^{-1} (\mathbf{y} - \mathbf{y}_{\text{obs}}) + (\mathbf{x} - \mathbf{x}_a)^T \mathbf{P}^{-1} (\mathbf{x} - \mathbf{x}_a) \quad (3)$$

The parameters vector \mathbf{x} contains the quantities that are to be estimated, for example stratospheric loss rates, OH concentrations, initial conditions and model transport parameters (see Sect. 3.5). Prior estimates of these quantities are contained in the vector \mathbf{x}_a . The vector \mathbf{y}_{obs} contains the observational dataset and the model-estimated value of these observations is given by \mathbf{y} .

The terms on the right-hand side of Eq. (3) correspond to the squared deviation of the model from the observations and of the parameters from the a priori estimates respectively. Each of these terms contains a weighting matrix, \mathbf{R} and \mathbf{P} , which are uncertainty covariances in the measurements (and model representation of the measurements) and the priors, respectively.

The sensitivity of the observations to the parameters investigated here can be non-linear and therefore an iterative solution to find the minimum of the cost function is required. We use a quasi-Newton method, in which the cost function is assumed to be locally linear with respect to small changes in the parameters vector \mathbf{x} as detailed in, for example, Tarantola (2005). At each iteration, a model prediction of the observations is made (\mathbf{y}), along with an estimate of the linearized sensitivity of the observations to small changes in the model parameters (\mathbf{H}). The sensitivity matrix is estimated by independently perturbing each parameter by an appropriately small amount and tracking the resulting perturbation through the model.

The recursion is given by, for iteration n :

$$\mathbf{x}_{n+1} = \mathbf{x}_n - \mu \mathbf{Q}_n \left(\mathbf{H}_n^T \mathbf{R}^{-1} (\mathbf{y}_n - \mathbf{y}_{\text{obs}}) + \mathbf{P}^{-1} (\mathbf{x}_n - \mathbf{x}_a) \right) \quad (4)$$

$$\mathbf{Q}_n = \left(\mathbf{H}_n^T \mathbf{R}^{-1} \mathbf{H}_n + \mathbf{P}^{-1} \right)^{-1} \quad (5)$$

The parameter μ determines the speed at which the cost function is descended ($\mu \lesssim 1$). The prior estimate of the parameters vector was used to initiate the scheme (i.e. $\mathbf{x}_1 = \mathbf{x}_a$).

Once a minimum in the cost function is reached (which we defined as the point where the change in the value of J dropped below 0.1 % of its initial value), the lifetime of each compound can be estimated by running the chemical transport model forward with the derived parameters. The transient lifetime at each model time step is then calculated using Eq. (1).

3.4 Linearity considerations

If we assume that emissions are negligible over some period (Δt) during which the lifetime is also constant, Eq. (2) can be integrated to give a change in atmospheric burden:

$$B \sim B_0 e^{-\frac{\Delta t}{\tau}} \quad (6)$$

By further assuming that the atmospheric burden can be linearly related to the observed mole fraction (χ), we find

that maximum linearity between the trace gas lifetime and the measured quantity (mole fraction) can be obtained by relating the log of mole fraction to inverse lifetimes:

$$\ln(\Delta \chi) \sim \tau^{-1} \quad (7)$$

Therefore, in our inversions, to formulate the problem as linearly as possible, the measurement vector (\mathbf{y} in the above section) contained the logarithm of AGAGE or NOAA mole fractions and we derived inverse lifetimes (as in Cunnold et al., 1983; Montzka et al., 2011a).

3.5 Inversion parameters, constraints and prior uncertainties

Transport parameters, stratospheric loss rates, initial conditions and OH concentrations were solved for in the inversion. Each of these parameters was subject to separate a priori constraints, with associated uncertainties, as outlined here and in Table 1. The value derived for each parameter depends on the sensitivity of the observations to the parameter, the a priori uncertainty assigned to it and the uncertainty assigned to the observations. Here we discuss how these constraints and uncertainties were formulated.

The uncertainty in the observations, including the model's ability to simulate the observations, is contained in the covariance matrix \mathbf{R} . We estimated the model-measurement uncertainty variance on measurement j (σ_j^2) as the quadratic sum of the overall measurement uncertainty ($\sigma_{M,j}$, which includes spatial and temporal sub-sampling by the networks as estimated as outlined in Sect. 2) and a model representation uncertainty ($\sigma_{RE,j}$):

$$\sigma_j^2 = \sigma_{M,j}^2 + \sigma_{RE,j}^2 \quad (8)$$

The model representation uncertainty was estimated from the variability in the (pollution filtered) monthly AGAGE measurements and is therefore a measure of the temporal variability that the model cannot resolve. The same representation uncertainty was applied to NOAA measurements.

Since each compound experiences the same transport parameters (although small differences are expected due to differing spatial distributions of the emissions parameterized in our 2-D model), we used a multi-species inverse method in which transport parameters were constrained by every gas. Transport is dominated by eddy diffusion in the model, so we adjusted only the 17 eddy-diffusion parameters, rather than the advection parameters. These parameters were solved for, using the Cunnold et al. (1983, 1994) values as an a priori constraint, in each season of each year. Similarly to Cunnold et al. (1983), due to numerical considerations, we opted to solve for the logarithm of these parameters. The uncertainty assigned to the a priori constraint was estimated from the mean seasonal cycle of the parameters (36 % according to the values in Cunnold et al., 1983).

The logarithm of initial mole fractions for each gas were estimated in each of the 12 boxes of the model at the first

Table 1. Parameters estimated in the inversion along with the constraints applied to each. All uncertainties are 1-sigma.

Parameter	Description	Constraint	Species
$\ln(\chi_0)$	Initial mole fraction in each model box	10-yr spin-up prior to first measurement, uncertainty of \pm the vertical gradient derived in the spin-up	All
τ_s^{-1}	Stratospheric loss rate (4 stratospheric boxes)	A priori stratospheric loss rate tuned to give overall lifetimes recommended by Prinn et al. (1999). Uncertainty based on range of photochemical model-derived lifetimes in (Park et al., 1999)	CFC-11, -12, -113
[OH]	OH concentration (each of 4 latitudinal bands)	Spivakovsky et al. (2000) estimates $\pm 100\%$ in each latitudinal band	CH ₃ CCl ₃
$\ln(T_{ij}^{-1})$	Eddy diffusion coefficients	Cunnold et al. (1983, 1994) \pm average seasonal cycle (36%)	All

time step. A priori estimates of the initial mole fraction were made by spinning-up the model for 10 yr. The uncertainty on the mole fraction in each box was then estimated as being equal to the vertical gradient obtained in the spun-up model. To ensure that the initial conditions did not have a significant influence on the derived lifetimes, lifetime estimates in the first 5 yr of each simulation were discarded.

Stratospheric loss rates were estimated in each stratospheric box in each year for CFC-11, -12 and -113. Prior estimates were obtained by iteratively searching for values that produced overall lifetimes consistent with the current WMO recommendations of 45, 100 and 85 yr for CFC-11, -12 and -113 respectively (Montzka et al., 2011b). We estimated the uncertainty in these values based on the range of model results from Park et al. (1999), which were around 25 % to 30 % of the mean values. The a priori uncertainties in overall lifetimes are shown in Table 2.

The hydroxyl radical concentrations from Spivakovsky et al. (2000) were adjusted in the inversion by a multiplying factor in each season (inter-annually varying) in each latitudinal band. Similar to Prinn et al. (2005), an uncertainty of 100 % of the OH concentration in each band in each season was assumed. A 43 yr stratospheric lifetime for CH₃CCl₃ was assumed, based on the calculations of Naik et al. (2000) and was not estimated in the inversion. Oceanic uptake lifetimes of 85 yr from Butler et al. (1991) were also assumed.

3.6 Uncertainty quantification

A linearized estimate of the posterior uncertainty in the inversion parameters is given by Eq. (5). However, we ultimately want to determine the uncertainty in the overall lifetime of each of the species, rather than in the model param-

eters that contribute to the lifetime calculation. We used the model to calculate the sensitivity of the inverse lifetimes to each inversion parameter ($\mathbf{H}_{\tau^{-1}}$) at the cost function minimum, and then calculated a linearized estimate of the uncertainty in τ^{-1} as:

$$\mathbf{Q}_{\tau^{-1}} = \mathbf{H}_{\tau^{-1}}^T \mathbf{Q}_N \mathbf{H}_{\tau^{-1}} \quad (9)$$

where \mathbf{Q}_N is the posterior parameter uncertainty after the final (N -th) iteration.

Emissions were not estimated as part of the inversion scheme. However, errors in the chosen emissions will have a dominant impact on the derived lifetimes. This source of uncertainty is likely to contain a “bias” component that cannot easily be quantified in the \mathbf{R} and \mathbf{P} matrices in the inversions, which assume random, unbiased uncertainties. To estimate the sensitivity of the inversion to erroneous emissions estimates, we ran an ensemble of 100 inversions in which the supplied emissions were scaled by factors randomly selected from a Gaussian distribution with a standard deviation of 1 % of the emissions for each species. We assumed that errors in the emissions were likely to be autocorrelated with time-scales of the order of emissions from “slow-release” applications such as refrigeration, which we assumed to be 10 yr. Therefore, the random scaling applied to each year of emissions in each ensemble member was chosen from a randomly generated time series with an autocorrelation length of 10 yr. This ensemble of inversions generates an ensemble of perturbed posterior inverse global lifetimes, the standard deviation of which was taken to be the sensitivity of the derived inverse lifetimes to changes in emissions. Overall inverse lifetime uncertainties that are due to emissions uncertainties were then calculated by scaling this sensitivity by the estimated uncertainty in the emissions datasets.

Table 2. A priori and derived lifetimes using AGAGE and NOAA measurements. A priori lifetime uncertainties are the mean aggregated uncertainties in steady-state lifetimes due to each parameter solved for in the inversion (stratospheric loss rates, transport parameters and OH concentration). Optimised lifetimes are shown for inversions using either AGAGE or NOAA data. For each measurement dataset, mean steady-state ($\overline{S.S.}$) and transient lifetimes ($\overline{Trans.}$) from peak burden onwards are shown. Also shown are mean steady-state lifetimes when UNEP/TEAP emissions were used instead of McCulloch et al. emissions for CFC-11 and CFC-12 ($\overline{S.S.}_{TEAP}$). The optimised lifetime uncertainties include the aggregate influence of inversion parameter uncertainties and emissions uncertainties.

Gas	Lifetimes (years)						
	A priori	AGAGE			NOAA		
		$\overline{S.S.}$	$\overline{Trans.}$	$\overline{S.S.}_{TEAP}$	$\overline{S.S.}$	$\overline{Trans.}$	$\overline{S.S.}_{TEAP}$
CFC-11	45 ⁵⁶ ₃₅	54 ⁶⁴ ₄₈	53 ⁶³ ₄₈	64 ⁷⁶ ₅₁	52 ⁶¹ ₄₅	51 ⁶¹ ₄₄	57 ⁶⁸ ₄₇
CFC-12	100 ¹²³ ₇₈	111 ¹³² ₉₅	110 ¹³² ₉₅	136 ^{385*} ₈₁	112 ¹³⁶ ₉₅	112 ¹³⁵ ₉₅	134 ^{313*} ₇₉
CFC-113	85 ¹⁰³ ₆₉	109 ¹²¹ ₉₉	105 ¹¹⁷ ₉₅		109 ¹²⁴ ₉₇	109 ¹²⁴ ₉₇	
CH ₃ CCl ₃	5.0 ^{6.8} _{3.5}	5.04 ^{5.20} _{4.92}	5.14 ^{5.29} _{5.02}		5.04 ^{5.23} _{4.87}	5.13 ^{5.32} _{4.97}	

* 2003 average only, since UNEP/TEAP emissions were only available for one year after maximum CFC-12 burden.

We estimated this uncertainty as being equal to the overall root-mean-square (RMS) difference between the two emissions datasets presented above (20%). We note that this uncertainty can only be treated as an approximation of the true uncertainty since each ensemble member used to generate the sensitivity to emissions uncertainties will not provide a truly independent estimate of the lifetime, because each inversion shares the same prior parameter estimates.

Uncertainties in the measurement calibration scales must also be accounted for. To first order, the uncertainty in the derived inverse lifetime due to calibration scale errors will be proportional to the calibration scale uncertainty. For the four gases studied here, this uncertainty is around 2% or better for both networks.

The overall uncertainty in inverse lifetime was calculated as the squared sum of each of these uncertainties. Where time-averaging was performed, the off-diagonal terms in \mathbf{Q}_T were included in the summation and the uncertainty was reduced by the square root of the number of seasons that were averaged. However, the emissions and calibration scale uncertainties were not similarly reduced since these errors act more like biases than random errors. For these, the mean uncertainty over the averaging period was used.

3.7 Estimating steady-state lifetimes

As described in Sect. 1.1, lifetimes are only uniquely defined in “steady-state” conditions, when sources balance sinks. However, the inversions outlined here produce estimates of transient lifetimes in each season of the simulation. To estimate steady-state lifetimes from the derived parameters, we ran 1000-yr constant-emission simulations for the model parameters derived in each season (i.e. emissions, stratospheric lifetimes, OH concentrations and transport parameters were held constant at the values derived in a particular season for

1000 yr). Using these model runs, an estimate of the steady-state lifetime was produced for each season of the simulation. Multi-year averages of these seasonal estimates are presented below.

4 Lifetime re-evaluation

Using the framework outlined above, we used AGAGE and NOAA observations to derive stratospheric loss rates for CFC-11, -12 and -113 from 1978 (1993 for CFC-113) to 2011, along with OH concentrations, initial conditions and chemical transport model parameters. The model-predicted mole fractions are shown in Fig. 2 and a detailed measurement-model inter-comparison is presented in the Supplement. The Supplement also contains a discussion of derived transport parameters and the time-variation of the derived lifetimes. Using the parameters determined in the inversion, we estimated global lifetimes for each gas and the associated uncertainties.

The sensitivity of the inversion to errors in the emissions inventories was found to decrease as emissions declined (see Supplement for detailed discussion). Therefore, we chose to make our lifetime recommendations using averages of the estimated steady-state lifetimes from the time of peak burden onwards, i.e. during the period when emissions were lowest. Averages are therefore taken from 1994, 2002, 1997 and 1992 until 2011 for CFC-11, -12, -113 and CH₃CCl₃, respectively. Table 2 shows the derived lifetimes and uncertainties for each species.

For CFC-11, the average steady-state lifetime estimated from peak burden onwards was 54⁶⁴₄₈ yr using the AGAGE network and 52⁶¹₄₅ yr when NOAA data were used. These estimates are somewhat higher than the current WMO estimate of 45 yr (Prinn et al., 1999), although a 45 yr estimate lies

towards the lower end of our uncertainty bounds. Our estimates are lower than those of Cunnold et al. (1983), who estimated a lifetime of 83_{56}^{156} yr using ALE data from 1978 to 1982 with a similar estimation scheme to ours. There are several possible reasons for the difference: firstly, the calibration scale used in their work is different to that of the current ALE/GAGE/AGAGE dataset (Cunnold et al., 1994), and a calibration “factor” was also solved for in their inversion; secondly, they used a different set of prior estimates for stratospheric lifetimes; thirdly, their inversion procedure had a smaller degree of “flexibility” with fewer transport parameters being adjusted and only one stratospheric box, which may have led to a poorer representation of atmospheric transport and loss processes; fourthly, their inversion was carried out during a period of relatively high emissions, and therefore the sensitivity of the inversion to emissions errors was significantly larger than in this work.

The estimated mean steady-state lifetime of CFC-12 since its burden began to decrease was 111_{95}^{132} yr (AGAGE) and 112_{95}^{136} yr (NOAA). The uncertainties in the CFC-12 lifetime are larger than those for CFC-11, primarily due to its longer lifetime (Cunnold et al., 1978), but also because of the smaller averaging period used here (peak burden occurred later for CFC-12). Our estimates are consistent with the value of 100 yr recommended in recent WMO assessments (Prinn et al., 1999) and estimates using stratospheric observations (Volk et al., 1997).

We performed a separate inversion for the lifetimes of CFC-11 and CFC-12 using the UNEP/TEAP (2006) emissions estimates. Somewhat higher lifetimes are derived for CFC-11 when this dataset was used (64_{51}^{76} for AGAGE and 57_{47}^{68} for NOAA), as would be expected given that the TEAP emissions are lower on average than the McCulloch et al. emissions. For CFC-12, we obtained lifetimes of 136_{81}^{385} (AGAGE) and 134_{79}^{313} (NOAA) when UNEP/TEAP emissions were used. The very large uncertainty on these estimates is because there was only one year where CFC-12 UNEP/TEAP emissions estimates were available after peak-burden, leading to little uncertainty reduction due to averaging. The lifetimes derived using these emissions estimates are not statistically different from the lifetimes derived using the McCulloch et al. emissions, which is expected, given that our emissions uncertainty is based on the inter-comparison of these two datasets.

Our estimate for the steady-state lifetime of CFC-113 is 109_{99}^{121} yr when AGAGE data are used, compared to 109_{97}^{124} when NOAA data are used. Our derived values are more in line with Volk et al. (1997) than the current WMO recommendation of 85 yr.

The lifetime of CH₃CCl₃ since peak atmospheric burden was found to be $5.04_{4.92}^{5.20}$ yr (AGAGE) and $5.04_{4.87}^{5.23}$ yr (NOAA). These values agree well the current WMO recommendation of 5.0 yr (Montzka et al., 2011b), and previous estimates of 4.9 ± 0.3 yr made using AGAGE observations

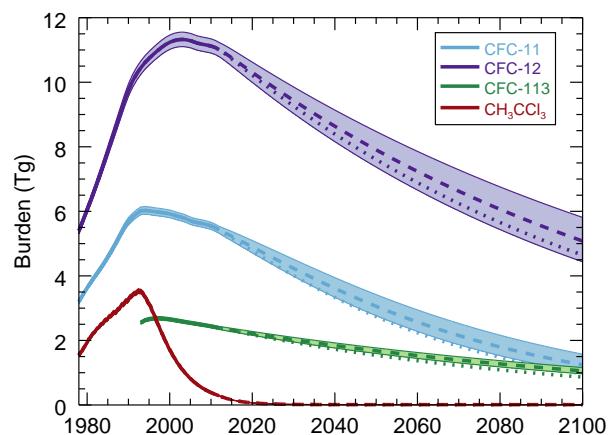


Fig. 4. Historical atmospheric burdens of CFCs and CH₃CCl₃ (solid lines) and future projections (dashed lines) based on AGAGE observations. Shaded areas indicate 1-sigma uncertainties. Dotted lines show the projections if WMO-recommended lifetimes are used.

(Prinn et al., 2005). The time-variation of the CH₃CCl₃ lifetime and of the global average OH concentrations is explored in detail in the Supplement and are also similar to previous estimates.

Using our derived OH field, we ran the model forward using reaction rates, molecular masses and stratospheric lifetimes for CH₄ (as in Rigby et al., 2008). Based on this simulation, the derived OH field was found to lead to an overall CH₄ steady-state lifetime of 9.7 ± 0.4 yr and a lifetime with respect to OH loss of 10.6 ± 0.4 yr. Similar calculations have been performed for the major CFC replacement compounds and their lifetimes are shown in the Supplement.

In addition to the mean steady-state lifetimes, Table 2 shows the average transient lifetimes for each gas since the time of peak burden. The table shows that the steady-state lifetimes differ from the post-peak-burden time-averaged transient lifetimes by less than 2% percent in all cases. This shows that, for these gases in the years following peak burden, the gas distributions relative to the loss processes are less important than the loss processes themselves in determining the transient lifetimes.

The uncertainties in these estimates are dominated by uncertainties in the emissions estimates, and therefore their magnitude is largely determined by the assumptions we make about the emissions error. However, this term is often poorly quantified. Here, we have used an estimate of 20% for the CFCs, based on the mean RMS difference between the McCulloch et al. and UNEP estimates. If, in contrast, we used the mean difference between the two estimates for CFC-11 alone, for example, the AGAGE-derived CFC-11 lifetime would be 54_{42}^{73} yr compared to the above estimate of 54_{48}^{64} yr. We therefore caution that the above uncertainties must be considered approximations that are sensitive to the choices

made about the emissions uncertainty, along with the assumptions of linearity outlined in Sect. 3.6.

The uncertainties in each of these lifetimes is relatively large, being on the order of decades for CFC-12. As emissions continue to decline in the future, there is scope for these uncertainties to be further reduced, as emissions remain the major contributor to the overall lifetime uncertainty. Uncertainty reduction may also be obtained by incorporating trace gas measurements from the upper atmosphere into the chemical transport model. In particular, these measurements may help to constrain model stratosphere-troposphere exchange timescales.

5 Future trends in the atmospheric burden of CFCs and CH₃CCl₃

Using the estimated transport parameters, stratospheric loss rates and OH concentrations, we calculated the atmospheric CFC and CH₃CCl₃ burden since 1978, along with associated uncertainties (Fig. 4, solid line). Based on our calculated parameters (derived using the AGAGE network alone in this case) and the emissions projections based on the McCulloch et al. (2001, 2003) methodology, we then ran the model to the end of the 21st century (Fig. 4, dashed line), assuming that the loss processes do not change inter-annually.

The figure shows that at the end of 2011, the burden of CH₃CCl₃ had already declined to 5 % of its peak value. In contrast, the burden of CFC-11, -12 and -113 remained at 90 %, 97 % and 89 % of their peaks. We predict that the burden of CFC-11 will reach half of its peak value by 2051²⁰⁵⁹₂₀₄₆, compared to 2087²¹⁰⁰₂₀₇₅ for CFC-12 and 2074²⁰⁸³₂₀₆₇ for CFC-113.

The figure also shows the projected burden of the CFCs if lifetimes of 45, 100 and 85 yr were used, respectively for CFC-11, -12 and -113 (Prinn et al., 1999). For each gas, a longer “recovery time” is predicted in our analysis, with half the maximum burden arriving between 5 (CFC-11) and 13 (CFC-113) years later using our estimates.

6 Conclusions

We have re-evaluated the lifetimes of CFC-11, -12 and -113 and CH₃CCl₃ using more than three decades of surface observations from the AGAGE and NOAA networks and a multi-species inverse method. Steady-state lifetimes of 54⁶⁴₄₈ (52⁶¹₄₅) yr were determined for CFC-11 using AGAGE (NOAA) observations and 111¹³²₉₅ (112¹³⁶₉₅), 109¹²¹₉₉ (109¹²⁴₉₇) and 5.04^{5.20}_{4.92} (5.04^{5.23}_{4.87}) yr for CFC-12, CFC-113 and CH₃CCl₃, respectively.

Supplementary material related to this article is available online at: <http://www.atmos-chem-phys.net/13/2691/2013/acp-13-2691-2013-supplement.zip>.

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