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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. The CFC-11 lifetime of 45 yr, currently recommended in the World Meteorological Organisation (WMO) Scientific Assessment of Ozone Depletion, lies at the lower uncertainty bound of our estimates which are 52^{66}_{40} yr (1-sigma uncertainty) when AGAGE data were used, and 50^{66}_{40} yr when the NOAA network data were used. Our derived lifetime for CFC-113 is higher than the WMO estimates of 85 yr (104^{123}_{88} using AGAGE, 103^{122}_{87} using NOAA). Our estimates of the lifetime of CFC-12 and CH_3CCl_3 agree well with other recent estimates being 108^{137}_{85} and 104^{135}_{84} yr (CFC-12, AGAGE and NOAA, respectively) and $5.2^{5.6}_{4.8}$ and $5.2^{5.7}_{4.8}$ 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 CCl_2FCClF_2 (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 mole fractions 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 yr (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 (Fraser et al., 1996, e.g. a lifetime of 26 yr for CFC-113 was found to be largely inconsistent with estimated release rates in).

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 CH_3CCl_3 (methyl chloroform) has also been the focus of much recent work. Although CH_3CCl_3 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 greenhouse 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) estimate an average lifetime for CH_3CCl_3 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 (Clerbaux et al., 2007; Montzka et al., 2011b, e.g.)

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 CH_3CCl_3 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 CCl_4 (Xiao et al., 2010; Montzka et al., 2011b, e.g.).

1.1 Trace gas lifetimes

Viewing the atmosphere as a single box, 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 (Q) and photochemical losses from it (L). Making the assumption that the loss rate can be represented by an instantaneous lifetime (τ), we can write:

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

$$\frac{\mathrm{d}B}{\mathrm{d}t} = Q(t) - \frac{B(t)}{\tau(t)} \tag{2}$$

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 atmosphere, in contrast to the “one-box” view, losses take place at different rates in specific regions (e.g. the majority of CFC loss occurs in the stratosphere), and therefore, the lifetime at a particular instant depends on the gas distribution relative to the loss processes. Lifetimes are only uniquely defined when the burden does not change (i.e. when sources balance sinks). However, in this paper, we will derive only time-averaged instantaneous lifetimes of the three major CFCs and CH_3CCl_3.

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

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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° N–30° N, 30° N–0° N, 0° S–30° S, 30° S–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 systems at 6 stations with additional flask sampling at four additional 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 measurements have been regularly inter-compared throughout the period investigated (comparisons shown 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 CH_3CCl_3 dataset is comprised of only GC-MS flask measurements (Montzka et al., 2011a). 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, 2008, 2002 and 2003 scales, respectively for CFC-11, -12, -113 and CH_3CCl_3. 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 CH_3CCl_3 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 CH_3CCl_3. 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 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 CH_3CCl_3 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). CH_3CCl_3 mole fractions have declined the most sharply, predominantly reflecting the relatively short lifetime of this gas compared to the CFCs.

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 CH_3CCl_3 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 production 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 “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 advance of Daniel et al. (2007) based on methodologies outlined in McCulloch et al. (2001, 2003), and are shown in Fig. 3 and tabulated in the Supplement. Uncertainties in these estimates were calculated based on the findings of Gamlen et al. (1986) and subsequent analysis of Cunnold et al. (1994) and are shown in Fig. 3. However, we chose not to use these uncertainty estimates in our analysis (see Sect. 3.6). Latitudinal distributions of the CFC-11 and CFC-12 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 thought to be less important than uncertainties in the overall emissions rate as this paper focuses only on globally averaged lifetimes. Furthermore, the derived lifetimes are much greater than the inter-hemispheric mixing times. We assumed that the latitudinal distribution of CFC-113 emissions was the same as the Cunnold et al. (1994) estimates for CFC-12, and that uncertainties in the CFC-113 emission rate were also the same as 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 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, agreement between the two datasets is generally within the estimated uncertainty. However, for CFC-11, the UNEP/TEAP (2006) emissions are substantially lower for most years. The mean discrepancy between the two emissions estimates is 32 % for these years.

For lifetime estimates of CH_3CCl_3, 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 CH_3CCl_3 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, 2011b; Daniel et al., 2007). 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 transport 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 derived by 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, 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 month of the year, but are annually-repeating in this version of the model. This improves on the approach of Cunnold et al. (1983) in which only three parameters were adjusted, leading to poor seasonal agreement with observations at some sites (e.g. Ragged Point, Barbados).

Stratospheric loss is parameterized by a lifetime in each of the stratospheric boxes in each season. 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 box.

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":

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

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

The terms on the right-hand side of Eq. (3) correspond to the squared deviation of the model from the observations and the deviation 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 $\boldsymbol{x}$ as detailed in, for example, Tarantola (2005). At each iteration, a model prediction of the observations is made ($\boldsymbol{y}$), along with an estimate of the linearized sensitivity of the observations to small changes in the model parameters (**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:

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

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

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. $\boldsymbol{x}_1 = \boldsymbol{x}_a$).

Once a minimum in the cost function is reached (5–10 iterations in our case), the lifetime of each compound can be estimated by running the chemical transport model forward with the derived parameters. The instantaneous lifetime at each model timestep 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 (***y*** in the above section) contained the logarithm of AGAGE or NOAA mole fractions and we aimed to derive inverse lifetimes (as in Cunnold et al., 1983; Montzka et al., 2011a). However, it was found that the inversion could be made more stable by solving for the logarithm of the inverse lifetime. This is due to numerical considerations: because of the finite time-stepping in the chemical transport model, the model will diverge if lifetimes less than or close to zero were obtained in the inversion. By formulating the inverse problem in this way we ensure positive lifetimes and improve numerical stability at the cost of some linearity. The mean lifetimes derived in the inversion were not found to be significantly affected by this modification, however, the derived uncertainties can only be considered linearized approximations of the "true" uncertainties. Similar considerations were also applied to the model mixing timescales (see below).

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 values derived for each parameter depends on the a priori uncertainty assigned to the parameter 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 **R**. We estimated the model-measurement uncertainty variance on measurement j (σ_j^2) as the quadratic sum of the overall measurement uncertainty ($\sigma_{\mathrm{M},j}$, which includes spatial and temporal sub-sampling by the networks as estimated as outlined in Sect. 2) and a model representation uncertainty ($\sigma_{\mathrm{RE},j}$):

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

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 month of the year. Because the transport parameters were not inter-annually varying in the inversion, we note that errors may be obtained in instantaneous lifetimes derived during some periods where anomalous transport caused anomalous mole fractions at some measurement sites. However, since the ultimate aim of this work is to determine an overall lifetime, rather than to examine lifetime variations, the error due to this simplification should be minimal. The uncertainty assigned to the a priori constraint was estimated from the mean seasonal cycle of those parameters that were assumed to have a seasonal cycle (36 % according to the values in Cunnold et al., 1983). Since these parameters cannot be negative in the model, we solved for their logarithm in the inversion.

Initial mole fractions for each gas were estimated in each of the 12 boxes of the model at the first 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.

Stratospheric inverse lifetimes were estimated in each stratospheric box in each season (inter-annually varying) for CFC-11, -12 and -113. Prior estimates of the CFC stratospheric lifetimes were obtained by iteratively searching for values that produced an overall lifetime in line 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), although note that our ranges differ slightly from theirs, because our inversion assumes symmetric uncertainties in inverse lifetime. The a priori uncertainties in overall lifetimes are shown in Table 2

The hydroxyl radical concentrations from Spivakovsky et al. (2000) were adjusted by a multiplying factor in each season (inter-annually varying) in each tropospheric box. Again, the logarithm of this multiplying factor was solved for to ensure positive OH concentrations. Similar to Prinn et al. (2005), an uncertainty of 100 % of the OH concentration in each box in each season was assumed. The stratospheric lifetime of CH_3CCl_3 was taken from model calculations by Naik et al. (2000) and was not estimated in the inversion. Oceanic uptake lifetimes from Butler et al. (1991) were used. The overall a priori lifetime derived when these parameters were used was somewhat higher than recent estimates ($6.3^{12.5}_{4.0}$ yr, see Table 2). However, the estimated uncertainty in the overall lifetime more than encompasses the values derived by, for example, Prinn et al. (2005).

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

$$\mathbf{Q}_\tau = \mathbf{H}_\tau^T \mathbf{Q}_N \mathbf{H}_\tau \tag{9}$$

where $\mathbf{Q}_N$ is the posterior parameter uncertainty after the final (Nth) iteration.

Emissions were not estimated as part of the inversion scheme. However, errors in the chosen emissions will have a significant impact on the derived lifetimes. Furthermore, uncertainties in the measurement calibration scales must also be accounted for.

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We treat these two sources of uncertainty as biases that cannot be accounted for in the uncertainty covariances **R** and **P**, which assume random errors. To account for them we opted to run an ensemble of 100 inversions in which the supplied emissions or measurements were scaled in each member by factors randomly selected from a Gaussian distribution with a standard deviation given by their respective uncertainties. Given that the uncertainty on the emissions datasets presented in Sect. 3.1 to not encompass both estimates for CFC-11, we chose the mean difference between the two datasets as the emissions uncertainty for all three CFCs (32 %). We further assumed that errors in the emissions are likely to be autocorrelated with time-scales of the order of emissions from "slow-release" applications such as refrigeration (which we assume 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. The ensemble of inversions generates an ensemble of perturbed posterior lifetimes, the standard deviation of which was added to all inverse lifetimes estimates. However, we note that this uncertainty can only be treated as an approximation of the true uncertainty since each ensemble member will not provide a truly independent estimate of the lifetime, because each inversion shares the same prior parameter estimates.

4 Lifetime re-evaluation

Using the framework outlined above, we used AGAGE and NOAA observations to derive initial conditions and stratospheric lifetimes for CFC-11, -12 and -113 and CH_3CCl_3 from 1978 (1993 for CFC-113) to 2011. Simultaneously, we determined OH concentrations and chemical transport model parameters. The model-predicted mole fractions are shown in Fig. 2 and a more detailed measurement-model inter-comparison is presented in the Supplement. An analysis of the optimized model parameters is also shown in the Supplement. Using the derived parameters, we determined instantaneous lifetimes for each gas and the associated uncertainties.

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Annual running mean lifetimes derived using AGAGE and NOAA observations are shown in Fig. 4. Two sets of 1-sigma uncertainty bounds are shown in the figure, one showing the uncertainties derived in the inversion, which includes the influence of measurement and model uncertainties, and a second showing the influence of emissions uncertainties. Lifetimes derived in the first two years of the investigation were ignored, to remove the influence of spin-up errors. The figure shows that the lifetimes derived using the two networks are not statistically different from one another for all gases at all times. Since errors due to unaccounted-for emissions can be seen to decline as emissions decreased, we chose to make our lifetime recommendations using an average of instantaneous lifetimes from the time of peak burden for each species. Averages are therefore taken from 1994, 2002, 1997 and 1992 until 2011 for CFC-11, -12, -113 and CH_3CCl_3, respectively. The uncertainties presented below include lifetime uncertainties due to emissions.

The maximum likelihood lifetime of CFC-11 can be seen to remain relatively stable throughout the inversion with a mean value of close to 50 yr over the entire time series. The average lifetime from peak burden is estimated as 52_{40}^{66} yr using the AGAGE network and 50_{40}^{66} 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 year estimate lies within 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, although it should be noted that our uncertainty estimates for the period used by Cunnold et al. (1983) encompass their estimates: 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.

The estimated lifetime of CFC-12 shows relatively large, but not statistically significant, changes over timescales on the order of decades. The magnitude of the change in derived CFC-12 lifetime is unlikely to be physically realistic (e.g. the ∼50 year increase during the 1980s). Since the same changes are seen for both networks, they are likely caused by errors in the emissions estimates that our lifetime derivation relies on. Our emissions uncertainty estimates appear to account for these changes. The estimated lifetime since the burden of CFC-12 began to decrease is 108_{85}^{137} yr (AGAGE) and 104_{84}^{135} yr (NOAA). The uncertainties on the CFC-12 lifetime are significantly larger than those for CFC-11, primarily due to its longer lifetime (Cunnold et al., 1978), but also due to the smaller averaging period used here. Our estimates agree well 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 lifetime of CFC-11 and CFC-12 using the UNEP/TEAP (2006) emissions estimates (Fig. 4). Somewhat higher lifetimes are derived for CFC-11 when this dataset was used, as would be expected given that the emissions are lower. However, the average derived lifetime is not statistically different from those values presented above. This is also expected, given that our emissions uncertainty is based on the inter-comparison of these two datasets.

Our estimate for the lifetime of CFC-113 since peak burden is 104_{88}^{123} yr when AGAGE data are used, compared to 103_{87}^{122} when NOAA data are used. No significant deviations from these estimates are seen during the period investigated, although relatively large deviations from the mean are seen during the late 1990s. Our derived values are more in line with Volk et al. (1997) than the current WMO recommendation of 85 yr, although a value of 85 yr is only just outside our uncertainty estimates.

The lifetime of CH_3CCl_3 since peak atmospheric burden was found to be $5.2_{4.8}^{5.6}$ yr (AGAGE) and $5.2_{4.8}^{5.7}$ 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 (Prinn et al., 2005, also shown in Fig. 4).

We find a similar timing to inter-annual fluctuations and trends in CH_3CCl_3 lifetimes to those found by Prinn et al. (2005) from 1980 to 2003 also using AGAGE data. These changes will be due to changes in OH concentration and/or measurement and emissions errors. The standard deviation of the annual mean, relative to the overall mean lifetime is around 4.2 % in our estimates from 1980–2003, compared to 5.3 % in Prinn et al. (2005). The Prinn et al. (2005) estimates used a similar model to that used here and the same observations. However, the reason for the slightly smaller variability is likely to be due to the smaller number of degrees of freedom used in the Prinn et al. (2005) estimates, compared to ours (one OH concentration was solved for per year, compared to 8 "boxes" per season here). Since more parameters were solved for, our inversion should suffer from smaller "aggregation error" than the Prinn et al. (2005) inversion. Similarly to Prinn et al. (2001, 2005), no statistically significant trend in CH_3CCl_3 lifetime could be inferred in this work. From 1992 to 2010, we derive inter-annual fluctuations of 3 % and 2.5 % when AGAGE or NOAA data are used, respectively. This relatively small inter-annual variability agrees with the findings of Montzka et al. (2011a).

The uncertainties in each of these lifetimes is relatively large, being on the order of decades for CFC-12 and CFC-113. As emissions continue to decline in the future, there is scope for these uncertainties to be further reduced, and emissions remain a 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 inter-annual variability in CFC lifetimes.

5 Future trends in the atmospheric burden of CFCs and CH_3CCl_3

Using the estimated transport parameters, stratospheric lifetimes and OH concentrations, we calculated the atmospheric CFC and CH_3CCl_3 burden since 1978, along with associated uncertainties (Fig. 5, 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. 5, dashed line), assuming that the loss processes do not change inter-annually.

The figure shows that at the end of 2011, the burden of CH_3CCl_3 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 its peak value by 2050^{2061}_{2042}, compared to $2085^{>2100}_{2070}$ for CFC-12 and 2073^{2084}_{2064} 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 (but not statistically significantly different) "recovery time" is predicted in our analysis, with half the maximum burden arriving between 5 (CFC-11) and 13 (CFC-113) yr later using our estimates.

6 Conclusions

We have re-evaluated the lifetimes of CFC-11, -12 and -113 and CH_3CCl_3 using more than three decades of surface observations from the AGAGE and NOAA networks and a multi-species inverse method. A lifetime of 52^{66}_{40} (50^{66}_{40}) yr was determined for CFC-11 using AGAGE (NOAA) observations and 108^{137}_{85} (104^{135}_{84}), 104^{123}_{88} (103^{122}_{87}) and $5.2^{5.6}_{4.8}$($5.2^{5.7}_{4.8}$) yr for CFC-12, CFC-113 and CH_3CCl_3, respectively.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/24469/2012/acpd-12-24469-2012-supplement.zip.

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References

Bousquet, P., Hauglustaine, D. A., Peylin, P., Carouge, C., and Ciais, P.: Two decades of OH variability as inferred by an inversion of atmospheric transport and chemistry of methyl chloroform, Atmos. Chem. Phys., 5, 2635–2656, doi:10.5194/acp-5-2635-2005, 2005. 24472

Butler, J. H., Elkins, J. W., Thompson, T. M., Hall, B. D., Swanson, T. H., and Koropalov, V.: Oceanic Consumption of CH_3CCl_3: implications for tropospheric OH, J. Geophys. Res., 96, 22347–22355, 1991. 24483, 24494

Clerbaux, C., Cunnold, D. M., Derson, J., Engel, A., Fraser, P. J., Mahieu, E., Manning, A., Miller, J., Montzka, S. A., Nassar, R., Prinn, R., Reimann, S., Rinsland, C. P., Simmonds, P., Verdonik, D., Weiss, R., Wuebbles, D., and Y. Yokouchi.: Long-lived compounds, in: Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project-Report No. 50, chapter 1, World Meteorological Organization, Geneva, 2007. 24472

Cunnold, D., Alyea, F., and Prinn, R. G.: A methodology for determining the atmospheric lifetime of fluorocarbons, J. Geophys. Res., 83, 5493–5500, 1978. 24486

Cunnold, D. M., Prinn, R. G., Rasmussen, R. A., Simmonds, P. G., Alyea, F. N., Cardelino, C. A., Crawford, A. J., Fraser, P. J., and Rosen, R. D.: The atmospheric lifetime experiment, 3. Lifetime methodology and application to three years of $CFCl_3$ data, J. Geophys. Res., 88, 8379–8400, 1983. 24471, 24477, 24478, 24481, 24482, 24485

Cunnold, D. M., Fraser, P. J., Weiss, R. F., Prinn, R. G., Simmonds, P. G., Miller, B. R., Alyea, F. N., and Crawford, A. J.: Global trends and annual releases of CCl_3F and CCl_2F_2 estimated from ALE/GAGE and other measurements from July 1978 to June 1991, J. Geophys. Res., 99, 1107–1126, 1994. 24471, 24476, 24477, 24478, 24482, 24485

Daniel, J. S., Velders, G. J. M., Douglass, A. R., Forster, P. M. D., Hauglustaine, D. A., Isaksen, I. S. A., Kuijpers, L. J. M., McCulloch, A., and Wallington, T. J.: Halocarbon scenarios, ozone depletion potentials, and global warming potentials, in: Scientific Assessment of

cc BY

Ozone Depletion: 2006, edited by: Ajavon, A.-L. N., Albritton, D. L., and Watson, R. T., World Meteorological Organization, Geneva, Switzerland, 2007. 24476, 24478

Elkins, J. W., Thompson, T. M., Swanson, T. H., Butler, J. H., Hall, B. D., Cummings, S. O., Fishers, D. A., and Raffo, A. G.: Decrease in the growth rates of atmospheric chlorofluorocarbons 11 and 12, Nature, 364, 780–783, 1993. 24474

Fraser, P., Cunnold, D., Alyea, F., Weiss, R., Prinn, R. G., Simmonds, P. G., Miller, B., and R. Langenfelds.: Lifetime and emission estimates of 1,1,2-trichlorotrifluorethane (CFC-113) from daily global background observations June 1982–June 1994, J. Geophys. Res., 101, 12585–12599, 1996. 24471

Gamlen, P. H., Lane, B. C., and Midgley, P. M.: The production and release to the atmosphere of CCl_3F and CCl_2F_2 (chlorofluorocarbons CFC 11 and CFC 12), Atmos. Environ., 20, 1077–1085, 1986. 24476

Ko, M. K. W., Jackman, C. H., Boville, B. A., Bruehl, C., Connell, P., Golombek, A., Levy, J., Rodriquez, J. M., Sasaki, T., and Tung, K. K.: Model calculations of atmospheric lifetime, in: Report on Concentrations, Lifetimes, and Trends of CFCs, Halons, and Related Species, edited by: Kaye, J. A., Penkett, S. A., and Ormond, F. M., chapter 5, National Aeronautics and Space Administration, Washington D. C., 1994. 24472

Lovelock, J. E., Maggs, R. J., and Wade, R. J.: Halogenated hydrocarbons in and over the atlantic, Nature, 241, 194–196, 1973. 24471

McCulloch, A., Ashford, P., and Midgley, P. M.: Historic emissions of fluorotrichloromethane (CFC-11) based on a market survey, Atmos. Environ., 35, 4387–4397, 2001. 24475, 24476, 24488

McCulloch, A., Midgley, P. M., and P. Ashford.: Releases of refrigerant gases (CFC-12, HCFC-22 and HFC-134a) to the atmosphere, Atmos. Environ., 37, 889–902, 2003. 24476, 24488

Molina M. J. and Rowland, F. S.: Stratospheric sink for chlorofluoromethanes: chlorine atomcatalysed destruction of ozone, Nature, 249, 810–812, June 1974. 24470

Montzka, S. A., Butler, J. H., Myers, R. C., Thompson, T. M., Swanson, T. H., Clarke, A. D., Lock, L. T., and Elkins, J. W.: Decline in the tropospheric abundance of halogen from halocarbons: implications for stratospheric ozone depletion, Science, 272, 1318–1322, 1996. 24474

Montzka, S. A., Butler, J. H., Elkins, J. W., Thompson, T. M., Clarke, A. D., and Lock, L. T.: Present and future trends in the atmospheric burden of ozone-depleting halogens, Nature, 398, 690–694, 1999. 24475, 24478

Montzka, S. A., Krol, M., Dlugokencky, E., Hall, B., Jockel, P., and J. Lelieveld.: Small interannual variability of global atmospheric hydroxyl, Science, 331, 67–69, 2011a, 24472, 24474, 24481, 24487

Montzka, S. A., Reimann, S., Engel, A., Krüger, K. O'Doherty, S., and Sturges, W. T.: Ozone-depleting substances (ODSs) and related chemicals, in: Scientific Assessment of Ozone Depletion, chapter 1, World Meteorological Organization, Geneva, 2011b. 24472, 24473, 24478, 24482, 24486

Naik, V., Jain, A. K., Patten, K. O., and Wuebbles, D. J.: Consistent sets of atmospheric lifetimes and radiative forcings on climate for CFC replacements: HCFCs and HFCs, J. Geophys. Res., 105, 6903–6914, 2000. 24483, 24494

Newell, R. E., Vincent, D. G., and Kidson, J. W.: Interhemispheric mass exchange from meteorological and trace substance observations, Tellus, 21, 641–647, 1969. 24478

O'Doherty, S., Simmonds, P. G., Cunnold, D. M., W ang, H. J., Sturrock, G. A., Ryall, D., Derwent, R. G., Weiss, R. F., Salameh, P., Miller, B. R., and G. Prinn.: In situ chloroform measurements at advanced global atmospheric gases experiment atmospheric research stations from 1994 to 1998, J. Geophys. Res., 106, 20429–20444, 2001. 24475

Park, J. H., Ko, M. K. W., Jackman, C. H., Plumb, R. A., Kaye, J. A., and Sage, K. H. (Eds.): Models and Measurements Intercomparison II, National Aeronautics and Space Administration, Hampton, Virginia, 1999. 24471, 24483, 24493, 24494

Prinn, R. G., Simmonds, P. G., Rasmussen, R. A., Rosen, R. D., Alyea, F. N., Cardelino, C. A., Crawford, A. J., Cunnold, D. M. , Fraser, P. J., and Lovelock, J. E.: The atmospheric lifetime experiment 1. Introduction, instrumentation, and overview, J. Geophys. Res., 88, 8353–8367, 1983. 24471, 24474

Prinn, R. G., Zander, R., Cunnold, D. M., Elkins, J. W., Engel, A., Fraser, P. J., Gunson, M. R., M. K. W.Ko, Mahieu, E., Midgley, P. M., Russell, J. M. III, Yolk, C. M., and Weiss, R. F.: Long-lived ozone-related compounds, in: Scientific Assessment of Ozone Depletion, Global Ozone Research and Monitoring Project, Report No. 44, edited by: Albritton, D. L., Aucamp, P. J., Megie, G., and Watson, R. T., chapter 1, World Meteorological Organization, 1999. 24472, 24485, 24486, 24488, 24493, 24494

Prinn, R. G., Weiss, R. F., Fraser, P. J., Simmonds, P. G., Cunnold, D. M., Alyea, F. N., O'Doherty, S., Salameh, P., Miller, B. R., Huang, J., Wang, R. H. J., Hartley, D. E., Harth, C., Steele, L. P., Sturrock, G., Midgley, P. M., and McCulloch., A.: A history of chemically and

cc BY

radiatively important gases in air deduced from ALE/GAGE/AGAGE, J. Geophys. Res., 105, 17751–17792, 2000. 24471, 24474, 24475

Prinn, R. G., Huang, J., Weiss, R. F., Cunnold, D. M., Fraser, P. J., Simmonds, P. G., McCulloch, A., Harth, C., Salameh, P., O'Doherty, S., Wang, R. H., Porter, L., and Miller, B. R.: Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades. Science, 292, 1882–8, 2001. 24472, 24487

Prinn, R. G., Huang, J., Weiss, R. F., Cunnold, D. M., Fraser, P. J., Simmonds, P. G., Mcculloch, A., Harth, C., Reimann, S., Salameh, P., Wang, R. H., Porter, L. W., Miller, B. R., and Krummel, P. B.: Evidence for variability of atmospheric hydroxyl radicals over the past quarter century, Geophys. Res. Lett., 32, L07809, doi:10.1029/2004GL022228, 2005. 24472, 24477, 24483, 24486, 24487, 24498

Rasmussen, R. A., and Lovelock, J. E.: The Atmospheric Lifetime Experiment 2. Calibration, J. Geophys. Res., 88, 8369–8378, 1983. 24471

Spivakovsky, C. M., Logan, J. A., Montzka, S. A., Balkanski, Y. J., M. Foreman-Fowler, Jones, D. B. A., Horowitz, L. W., Fusco, A. C., Brenninkmeijer, C. A. M., Prather, M. J., Wofsy, S. C., and McElroy, M. B.: Three-dimensional climatological distribution of tropospheric OH: Update and evaluation, J. Geophys. Res., 105, 8931–8980, 2000. 24478, 24483, 24494

Tarantola, A: Inverse Problem Theory, Society for Industrial and Applied Mathematics, Philadelphia, USA, 2005. 24479

UNEP/TEA P.: Task Force on Emissions Discrepancies Report, Technical Report October, United Nations Environment Programme/Technology and Economic Assessment Panel, Nairobi, Kenya, 2006. 24477, 24486, 24497, 24498

Volk, C. M., Elkins, J. W., Fahey, D. W., Dutton, G. S., Gilligan, J. M., Loewenstein, M., Podolske, J. R., Chan, K. R., and Gunson, M. R.: Evaluation of source gas lifetimes from stratospheric observations, J. Geophys. Res., 102, 25543–25564, 1997. 24471, 24486

Xiao, X., Prinn, R. G., Fraser, P. J., Weiss, R. F., Simmonds, P. G., O'Doherty, S., Miller, B. R., Salameh, P. K., Harth, C. M., Krummel, P. B., Golombek, A., Porter, L. W., Butler, J. H., Elkins, J. W., Dutton, G. S., Hall, B. D., Steele, L. P., Wang, R. H. J., and Cunnold, D. M.: Atmospheric three-dimensional inverse modeling of regional industrial emissions and global oceanic uptake of carbon tetrachloride, Atmos. Chem. Phys., 10, 10421–10434, doi:10.5194/acp-10-10421-2010, 2010. 24473

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

Parameter	Description	Constraint	Frequency	Species
χ_0	Initial mole fraction in each model box	10-yr spin-up prior to first measurement, uncertainty of ± the vertical gradient derived in the spin-up		All
$\ln(\tau_s^{-1})$	Instantaneous stratospheric lifetime (each of 4 stratospheric boxes)	A priori stratospheric lifetime tuned to give overall lifetimes recommended by Prinn et al. (1999). Uncertainty based on range of photochemical model-derived lifetime in (Park et al., 1999)	Seasonal	CFC-11, -12, -113
ln([OH])	OH concentration (each of 8 tropospheric boxes)	Spivakovsky et al. (2000) estimates ±100 % in each box	Seasonal	CH_3CCl_3
$\ln(T_{ij}^{-1})$	Eddy diffusion coefficients	Cunnold et al. (1983, 1994) ± average seasonal cycle (36 %)	Monthly (inter-annually repeating)	All

Table 2. Emissions uncertainties, a priori lifetimes and lifetimes derived using AGAGE and NOAA measurements. Overall prior lifetime uncertainties are the aggregated uncertainties due to each parameter solved for in the inversion (e.g. stratospheric lifetime, OH concentration). The optimised lifetime uncertainties include the aggregate influence of inversion parameter uncertainties and emissions uncertainties.

Gas	Lifetime (years)		
	Prior	AGAGE	NOAA
CFC-11	[a]45_{33}^{63}	52_{40}^{66}	50_{40}^{66}
CFC-12	[a]100_{77}^{128}	108_{85}^{137}	104_{84}^{135}
CFC-113	[a]85_{62}^{127}	104_{88}^{123}	103_{87}^{122}
CH_3CCl_3	[b]$6.3_{4}^{12.5}$	$5.2_{4.8}^{5.6}$	$5.2_{4.8}^{5.7}$

[a] Stratospheric lifetimes adjusted to match overall instantaneous lifetimes in Prinn et al. (1999), uncertainties based on photochemical model ranges in Park et al. (1999). [b] Based on model forward run using Spivakovsky et al. (2000) OH field, Naik et al. (2000) stratospheric lifetime and Butler et al. (1991) oceanic uptake lifetime. Uncertainties derived assuming 100 % uncertainty on OH concentrations in each model box during each season.

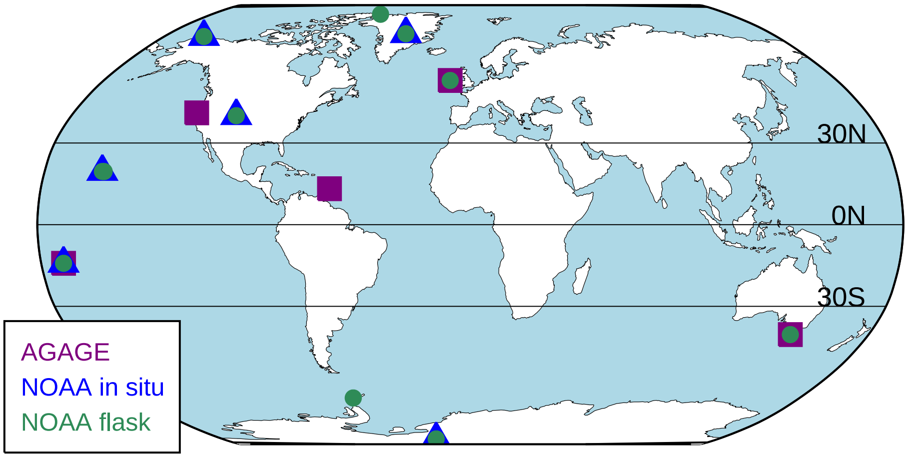

Fig. 1. Locations of AGAGE and NOAA CFC and CH_3CCl_3 measurements. Purple squares show locations of AGAGE (in situ) stations, blue triangles show the locations of NOAA in situ monitoring sites and green dots show NOAA flask sampling locations. Also shown are the boundaries of the chemical transport model "boxes".

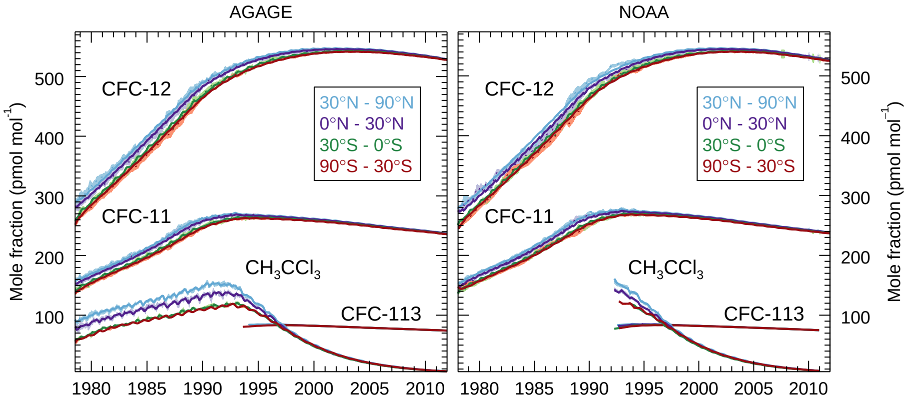

Fig. 2. Model prediction of AGAGE and NOAA CFC-11, -12, -113 and CH_3CCl_3 mole fractions in each semi-hemisphere (solid lines). Dotted lines and the surrounding shaded areas show the measurements and the model-measurement uncertainty limits (1-sigma). Uncertainties include measurement repeatability and subsampling errors, along with model representation uncertainties, but not network calibration uncertainties.

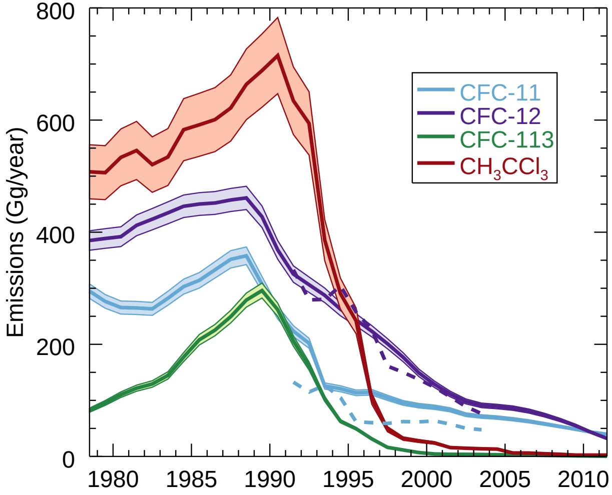

Fig. 3. Emissions estimates for CFC-11, -12, -113 and CH_3CCl_3 from 1978 to present day. CFC estimates from 2005 to present are projections (not based on reported data). Shaded areas show estimated 1-sigma uncertainties, although these uncertainties were not used in the inversion. Dashed lines show independently compiled emissions from UNEP/TEAP (2006).

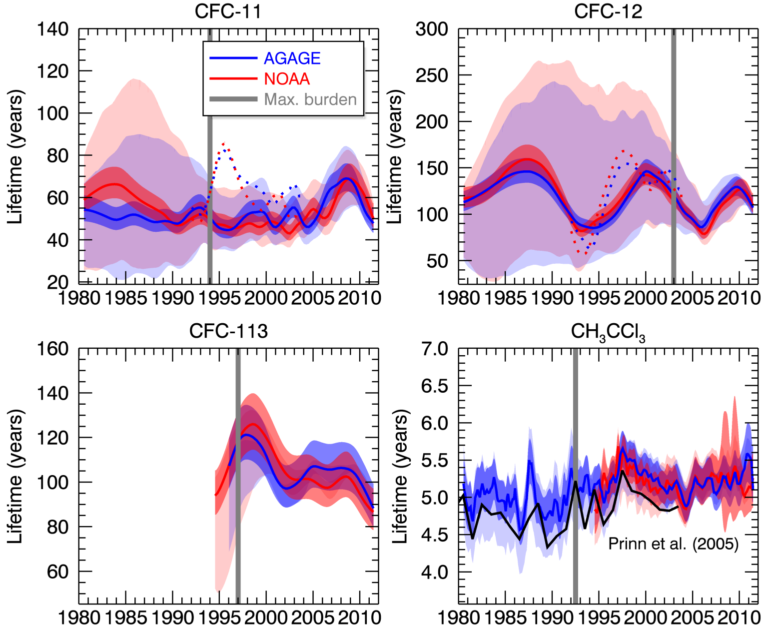

Fig. 4. 1-yr running mean lifetimes as derived in inversions using AGAGE (blue) and NOAA (red) observations. 1-sigma uncertainties that include the influence of measurement and modelling errors, but not emissions errors are shown in the boldly shaded areas. The more faintly shaded areas show the 1-sigma range of derived lifetimes from the ensemble of inversions run with perturbed emissions. The grey line indicates the time of maximum atmospheric burden of each gas. Dotted lines in the top two figures show the lifetimes derived when UNEP/TEAP (2006) emissions were used. The black line in the lower-right plot shows the CH$_3$CCl$_3$ lifetime derived by Prinn et al. (2005).

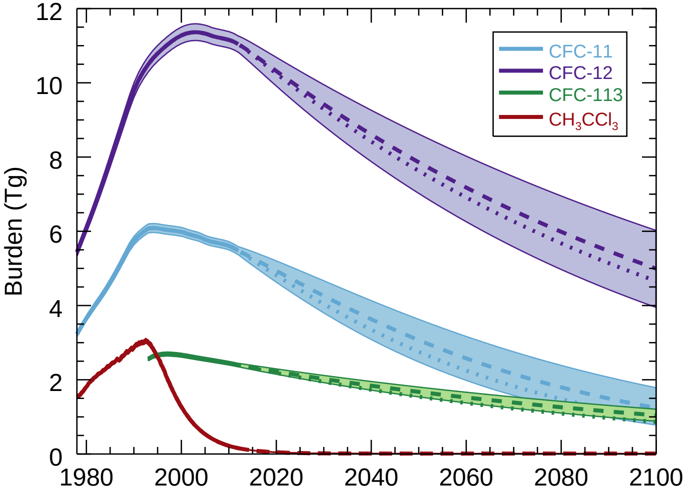

Fig. 5. Historical atmospheric burdens of CFCs and CH_3CCl_3 (solid lines) and future projections (dashed lines) based on AGAGE observations. Shaded areas indicate 1-sigma uncertainties. Dotted lines show the projections if WMO-recommended lifetimes are used.

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