Delayed Recovery of mid-latitude lower stratospheric Halogen Loading.

Andreas Engel, Harald Bönisch[1] and Jennifer Ostermöller

University of Frankfurt, Institute for Atmospheric and Environmental Sciences, Altenhöferallee 1, 60438 Frankfurt, Germany
5 [1]now at Karlsruhe Institute of Technology, Institute of Meteorology and Climate Research, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Correspondence to: Andreas Engel (an.engel@iau.uni-frankfurt.de)

Abstract. Chlorine and bromine atoms can lead to catalytic destruction of ozone in the stratosphere. Therefore the use and production of ozone depleting substances (ODS) containing chlorine and bromine is regulated by the Montreal Protocol to 10 protect the ozone layer. Equivalent Effective Stratospheric Chlorine (EESC) has been adapted as an appropriate metric to describe the combined effects of chlorine and bromine released from halocarbons on stratospheric ozone. Here we revisit the concept of calculating EESC. We derive a new formulation of EESC based on an advanced concept of ODS propagation into the stratosphere and reactive halogen release. A new transit time distribution is introduced in which the age spectrum for an inert tracer is weighted with the release function for inorganic halogen from the source gases. This distribution is termed the 15 "release time distribution". The improved formulation shows that EESC levels in the year 1980 for the mid latitude lower stratosphere were significantly lower than previously calculated. 1980 marks the year commonly defined as the onset of anthropogenic ozone depletion in the stratosphere. Assuming that the EESC value must return to the same level in order for ozone to fully recover, we show that it will take more than 10 years longer than currently assumed in this region of the stratosphere. Based on the improved formulation, EESC level at mid-latitudes will reach this landmark only in 2060. We also 20 present a range of sensitivity studies to investigate the effect of changes and uncertainties in the fractional release factors and in the assumptions on the shape of the release time distributions. We conclude that, under the assumptions that all other atmospheric parameters like stratospheric dynamics and chemistry are unchanged, the recovery of mid latitude stratospheric ozone would be expected to be delayed by about a 10 years, in a similar way as EESC.

1 Introduction

25 It is well established that chlorine and bromine atoms in the stratosphere enhance ozone depletion via catalytic reaction chains (Stolarski. and Cicerone, 1974;Solomon, 1999;Molina and Rowland, 1974;Wofsy et al., 1975). Ozone loss has been observed at mid latitudes (S. Pawson and W. Steinbrecht et al., 2014) and in particular at high latitudes during winter (Farman et al., 1985;M. Dameris and S. Godin-Beekmann et al., 2014). The chlorine and bromine atoms responsible for the ozone depletion are not injected directly into the stratosphere but are released from organic halocarbons, so called ozone depleting substances 30 (ODS), which are emitted in the troposphere. Ozone is thus not depleted by reactions with the chemicals emitted but, by

reaction with the inorganic halogen released from these chemicals. The effectiveness of the catalytic ozone destruction depends on the amount of inorganic halogen in the stratosphere. Equivalent Effective Stratospheric Chlorine (EESC) is a metric describing the combined effect of all chlorinated and brominated ODSs expressed as the equivalent amount of inorganic chlorine in the stratosphere. EESC depends on the transport from the troposphere into the stratosphere, the temporal trend of

5   the mixing ratios of the source gases in the troposphere and the release of inorganic halogen from these source gases. EESC has been used widely as a proxy to describe the combined effects of inorganic bromine and chlorine on stratospheric ozone, e.g. in the analysis of time series of ozone or when discussing the effects of volcanoes or geoengineering (Tilmes et al., 2009;Shepherd et al., 2014;Weatherhead and Andersen, 2006).

The transport into the stratosphere is described by the mean age of air, Γ (Hall and Plumb, 1994;Waugh and Hall, 2002;Kida,

10   1983). A stratospheric air parcel does not have a single transit time t' since its entry into the stratosphere, but is rather composed of a large number of irreversibly mixed fragments or fluid elements with varying transit times t', describing the variable times they already spent in the stratosphere. The distribution of transit times is called the age spectrum, the arithmetic mean (first moment) being the mean age Γ. The age spectrum is generally described by a Green's function G for one-dimensional advective diffusive transport and a parameterization of the width of the distribution as a function of the mean age (Hall and Plumb, 1994).

15   Together with the temporal trend of the trace gas in the troposphere, the age spectrum determines the mixing ratio of an inert trace gas in the stratosphere (1) at a certain time t and place r, $\chi_{inert,strat}(r,t)$, as the fluid elements will each contain the mixing ratio present in the troposphere at the time they entered the stratosphere, $\chi_0(t-t')$. Based on this concept, it is also possible to derive mean age of air (Hall and Plumb, 1994;Volk et al., 1997;Engel et al., 2002;Engel et al., 2009) based on observations of chemically inert tracers in the stratosphere, so called age tracer.

$$\chi_{inert,strat}(r,t) = \int_0^\infty \chi_0(t-t') \cdot G(r,t')dt' \tag{1}$$

20   For chemically active species, in addition to the transport, the chemical loss leading to the release of inorganic halogen needs to be considered. This release of inorganic chlorine and bromine from the halocarbon source gases is characterized by the fractional release factor f (FRF). The FRF describes which fraction of the source gas molecules originally present in an air parcel has already been released, i.e. transferred to the inorganic fraction. *1-f* will thus describe the fraction that is still in the form of the organic source gas. Fractional release factors for many relevant trace gases have been determined as a function of

25   mean age (Newman et al., 2007;Laube et al., 2013). Typically, a mean age value of 3 years is adapted for the lower stratosphere of the middle latitudes and a mean age value of 5.5 years is used for polar winter conditions in the lower stratosphere (Newman et al., 2007). The calculation of f relies on the difference of the observed mixing ratio of the source gases in the stratosphere to the amount of source gas originally present in this air-parcel (2). For this, a reference mixing $\chi_{ref}(\Gamma)$ ratio must be determined, based on temporal trends in the troposphere and transport into the stratosphere.

$$f(\Gamma) = \frac{\chi_{ref}(\Gamma) - \chi_{strat}(\Gamma)}{\chi_{ref}(\Gamma)} \tag{2}$$

This reference mixing ratio has typically been calculated using (1), i.e. assuming that the chemically active gas propagates in the same way as a chemically inert gas. Plumb et al. (1999) showed that the age spectrum G, which is representative for an inert gas is not well suited to describe the way that a chemical active gas is propagated into the stratosphere. The reason for this is that the remaining organic fraction of a chemically active species (CAS) is determined largely by the fluid elements

5   with shorter transit times, where chemical loss is less pronounced. The fluid elements with longer transit times on the other hand do not contribute as much to the remaining organic fraction, as more chemical loss has occurred. The combination of chemical loss and transport is described by a modified age spectrum, called the arrival time distribution. This arrival time distribution is weighted stronger at shorter transit times and has a different first moment than the age spectrum for an inert tracer. This first moment of the arrival time distribution is shorter than the mean age and is termed the mean arrival time.

10   Information on the mean arrival time was derived from 2-D model calculations by Plumb et al. (1999), who used the mean arrival time to detrend stratospheric correlations. They found that the detrended correlations from different years showed good agreement, if the mean arrival time was used in calculating the reference values, while this was not the case when using mean age. Ostermöller et al. (2017) could show that the arrival time distribution also allows to derive fractional release factors, which are not influenced by the tropospheric trend. These studies show that, due to the interaction of chemistry and transport, changes

15   in the tropospheric mixing ratios of source gases with chemical loss are reflected faster in their stratospheric mixing ratios than are changes in gases without chemical loss. The age spectrum for in inert tracer is not well suited for this purpose.

EESC is influenced by the temporal trends of the source gases, their fractional release factors and the transport into the stratosphere. As in the case of FRF, EESC is usually calculated as a function of mean age and again a mean age value of 3

20   years is adapted for the lower stratosphere of the middle latitudes and a mean age value of 5.5 years is used for polar winter conditions in the lower stratosphere (Newman et al., 2007). The formulation which is currently used to calculate EESC is based on the concept of fractional release and mean age, using the age spectrum G for an inert tracer. In this formulation EESC is calculated by multiplying the fractional release factor with the integral over the tropospheric time series χ_0 of the tracer and the age spectrum for an inert tracer (Newman et al., 2007; Velders and Daniel, 2014)

$$EESC_{current}(\Gamma,t) = \sum_{Cl}\left(n_i f_i(\Gamma)\int_0^\infty \chi_{0,i}(t-t')G(\Gamma,t')dt'\right) + \alpha\sum_{Br}\left(n_i f_i(\Gamma)\int_0^\infty \chi_{0,i}(t-t')G(\Gamma,t')dt'\right) \tag{3}$$

25   with n_i being the number of chlorine or bromine atoms in species i and f_i being the fractional release factor. α is a factor representing the higher effectivity of bromine to ozone destruction, typically taken as 60 for both high latitudes and mid latitudes (Newman et al., 2007). The age spectrum G used here is that for an inert tracer. As shown by Plumb et al. (1999) and Ostermöller et al. (2017), the arrival time distribution is better suited to describe the propagation of the organic fraction of a

source gas into the stratosphere. Consequently, it is also expected that the age spectrum for an inert tracer may not be the best way to describe the propagation and release of the inorganic fraction and thus EESC.

In this paper we discuss the interaction of chemistry and transport in the propagation of chemically active tracers with

5   tropospheric trends into the stratosphere and suggest an improved method for the calculation of EESC. The paper is organized as follows. In section 2 we present some general thoughts on the propagation of tropospheric trends taking into account chemical loss. In section 3 we derive a new mathematical formulation for EESC, based on the ideas developed in section 2. This new mathematical formulation is applied in section 4 to the scenario of source gas mixing ratios given in Velders and Daniel (2014) and the results are compared to their results for the estimated recovery of EESC to 1980 values. Finally we draw

10 some conclusion and present an outlook in section 5.

2. On the interaction between transport, chemistry and tropospheric trends.

In addition to transport and temporal trends in the troposphere, the stratospheric mixing ratio of a species with chemical loss in the stratosphere depends on the loss processes and on the interplay between transport, chemical loss and the temporal trend (Volk et al., 1997;Plumb et al., 1999). The age spectrum G, which is used to describe the propagation of chemically inert trace

15 gases into the stratosphere (Schauffler et al., 2003;Newman et al., 2007;Engel et al., 2002) and to calculate mean age does not take into account chemical loss. Chemical loss is not uniform throughout the stratosphere, as it depends in most cases on the actinic flux at short wavelength. In the seasonal mean, the chemical lifetime will in general decrease with altitude and increase with increasing latitude. The chemical loss is thus very inhomogeneous, but on average, it is expected that the longer a fluid element remains in the stratosphere, the larger the integrated chemical loss will be. Also, as the loss for most species with

20 photochemical sinks mainly occurs at higher altitudes, it is expected that, on average, longer transit times will be associated with shorter lifetimes. A transit time distribution in which the transit times are weighted with the transit time dependent chemical loss has been termed "arrival time distribution" (Plumb et al., 1999), G^* (4). The fractional chemical loss can be expressed in a very generalized way as $(1 - f(t'))$, where $f(t')$ is a fractional release function, which is specific for each trace gas and is of course a function of transit time. The first moment of the arrival time distribution is called the mean arrival

25 time Γ^*. This distribution describes the probability distribution for organic source gas molecules to arrive at some place r in the stratosphere, as a function of transit time t'.

$$G^*(r, t') \equiv (1 - f(t')) \cdot G(r, t') \qquad (4)$$

We can now define a second transit time distribution, $G^\#(r, t')$, which describes the probability for an inorganic halogen atom released from this source gas to arrive at this place r in the stratosphere, again as a function of transit time t'.

$$G^\#(r, t') \equiv f(t') \cdot G(r, t') \qquad (5)$$

For the calculation of G^* and $G^\#$ the integrated loss as a function of transit time needs to be known. Purely for illustrative purposes, we have constructed such a loss function using a sigmoid function, which changes from 0 (no loss) for short transit times to 1 (complete loss) for longer transit times. The function has been constructed in a way to match fractional release factors for CFC-11 for 3 and 5.5. years. CFC-11 is one of the most important chlorine source gases for the stratosphere. These

5   three different transit time distributions, G, G^* and $G^\#$ calculated using typical age spectra for 3 and 5.5 years of mean age are shown in Figure 1 and Figure 2. In both cases, the mean transit time for the inorganic fraction is longer than that for an inert tracer, while the lag of the remaining organic fraction is shorter than that of an inert tracer. The effect is much more pronounced for the 3 years mean age calculation, where the fractional release is about 0.5. i.e. the organic and the inorganic fraction are about equal. In the case of 5.5 years mean age, nearly all CFC-11 molecules are converted to the inorganic form and the

10   remaining organic fraction gets very small. The mean transit times for all three distributions are calculated as the arithmetic mean or first moment of the respective distribution functions. The mean transit time of the organic fraction is described by the mean arrival time Γ^* (Plumb et al., 1999), that of an inert tracer by the mean age Γ . The inorganic fraction is described by a third time scale, which represents a release weighted transit time distribution. We suggest the term "release time distribution", $G^\#$, for this transit time distribution with a first moment called the "mean release time", $\Gamma^\#$. In the example given in Figure 1

15   the mean age Γ is 3 years, the mean arrival time Γ^* for the organic fraction is 1.75 years and the mean release time $\Gamma^\#$ describing the inorganic fraction is 4.35 years. Inorganic chlorine thus lags the tropospheric time series more than expected from an inert tracer. Mean arrival time Γ^* and mean release time $\Gamma^\#$ differ for each tracer depending on their chemical loss behavior, which is described by the fractional release factor f. A parametrization of the mean arrival time Γ^* for all the relevant chlorine and bromine species has been calculated as a function of lifetime and mean age (Plumb et al., 1999). The mean release

20   time $\Gamma^\#$ can be derived from Γ, Γ^* and the fractional release factor (see section 3.1). As EESC is a proxy for inorganic halogen, we derive a new formulation of EESC which takes into account this interaction between chemistry and transport in an improved way.

3 Deriving a new formulation of EESC

The new mathematical formulation of EESC proposed here is derived based on the concept of how a trace gas of tropospheric

25   origin with a temporal trend and chemical loss in the stratosphere propagates into the stratosphere. The organic source gases of chlorine and bromine are such gases. In order to derive the amount of inorganic chlorine or bromine that has been released from such an organic source gas at some point r in the stratosphere, three different functions must be considered. First, the transit time distribution, i.e. how long it has taken for the individual fluid elements of this air parcel to travel from their entry point to the stratosphere to the location r in the stratosphere. We will denote transit time, i.e. the time a fluid element has spent

30   in the stratosphere as t', while the time itself will be denoted as t. Second, the temporal trend of the mixing ratios at the entry point has to be considered and, third, chemical loss during this transport. All three functions depend on the transit time t'. The integral over all possible transit times over these three functions will yield the remaining mixing ratio of the source gas. If we

denote the time series at the entry point to the stratosphere as $\chi_0(t - t')$, the transit time distribution for air to reach some point r in the stratosphere as $G(r, t')$ and the chemical loss term as $e^{-\frac{t'}{\tau(t')}}$ we can describe the mixing ratio of the organic source gas at that point r in the stratosphere as

$$\chi_{strat}(r, t) = \int_0^\infty \chi_0(t - t') \cdot e^{-\frac{t'}{\tau(t')}} \cdot G(r, t')dt' = \int_0^\infty \chi_0(t - t') \cdot \left(1 - f(t')\right) \cdot G(r, t')dt' \qquad (6)$$

The chemical loss term in (6) describes the loss by an exponential decay with lifetime $\tau(t')$, taking into account that the average lifetime is a function of the transit time. In a more general way, this loss can also be described by the factor $\left(1 - f(t')\right)$, where $f(t')$ describes the fraction which has been lost. Consequently, as $\left(1 - f(t')\right)$ is the remaining fraction of the organic source gas, the mixing ratio of inorganic chlorine released from the source gas would then be

$$\chi_{inorg,strat}(r, t) = \int_0^\infty \chi_0(t - t') \cdot f(t') \cdot G(r, t')dt' \qquad (7)$$

For simplicity, we have assumed here that the source gas releases only one atom of inorganic halogen. Transport and mixing are described by the transit time distribution, also known as the age spectrum or Green's function G. G describes the probability of a certain transit time since entry into the stratosphere at the tropical tropopause, and thus describes both net mass transport and mixing. G is a function of transit time t' and the location in the stratosphere, r. The integral over the probability of all transit times must be equal to 1.

$$\int_0^\infty G(r, t')dt' = 1 \qquad (8)$$

and the integral over all transit times weighted by their probability is the mean age of air Γ (Hall and Plumb, 1994).

$$\Gamma(r) = \int_0^\infty t' \cdot G(r, t')dt' \qquad (9)$$

We now use the new transit time distribution $G^\#$ that was introduced in section 2. $G^\#$ is defined as the product of the transit time dependent fractional release factor $f(t')$ and the age spectrum.

$$G^\#(r, t') \equiv f(t') \cdot G(r, t') \qquad (10)$$

As $G^\#$ is the product of the fractional release and the transit time distribution, it represents a release weighted transit time distribution. We will refer to this distribution as the release time distribution. Note that the integral over $G^\#$ is only unity in case of complete loss of the organic faction, i.e. $f(t')$ is 1 for all transit times t'. In all cases, the integral must be less or equal to 1.

$$\int_0^\infty G^\#(r,t')dt' \le 1 \tag{11}.$$

We can, however, define a new, normalized release time distribution $G_N^\#$, by dividing $G^\#$ through the integral of $G^\#$ over all possible transit times

$$G_N^\#(r,t') \equiv \frac{G^\#(r,t')}{\int_0^\infty G^\#(r,t')dt'} = \frac{G^\#(r,t')}{\int_0^\infty f(t') \cdot G(r,t')dt'} \tag{12}.$$

The integral over $G_N^\#$ over all possible transit times is now unity

$$\int_0^\infty G_N^\#(r,t')dt' = 1 \tag{13}$$

The integral over all transit times weighted by the normalized release time distribution $G_N^\#$ yields a "mean release time", $\Gamma^\#$, as also shown in Figures 1 and 2.

$$\int_0^\infty t' \cdot G_N^\#(r,t')dt' = \Gamma^\# \tag{14}$$

The integral in the denominator of (12) represents the first moment of the distribution of all fractional release factors, thus a mean fractional release factor, which is a function of the location r in the stratosphere (Ostermöller et al., 2017), but in contrast to $f(t')$, it is not a function of transit time anymore.

$$\int_0^\infty G^\#(r,t')dt' = \int_0^\infty f(t') \cdot G(r,t')dt' = \overline{f}(r) \tag{15}$$

Inserting (15) into (12) and solving for $G^\#$ yields:

$$G^\#(r,t') = G_N^\#(r,t') \cdot \overline{f}(r) \tag{16}$$

Using the definition of $G^\#$ (5) we can thus derive a relationship between G and $G^\#$

$$G^\#(r,t') = G_N^\#(r,t') \cdot \overline{f}(r) = G(r,t') \cdot f(t') \tag{17}$$

The term $f(t') \cdot G(r,t')$ in (7) can thus be replaced by $G_N^\#(r,t') \cdot \overline{f}(r)$ to derive a new relationship for inorganic chlorine

$$\chi_{inorg,strat}(r,t) = \int_0^\infty \chi_0(t-t') \cdot \overline{f}(r) \cdot G_N^\#(r,t')dt' \tag{18}$$

In contrast to $f(t')$, $\overline{f}(r)$ is independent of t' and it can be extracted from the integral and (18) can be rewritten:

$$\chi_{inorg,strat}(r,t) = \overline{f}(r) \cdot \int_0^\infty \chi_0(t-t') \cdot G_N^\#(r,t')dt' \qquad (19)$$

Instead of describing the mixing ratio of inorganic chlorine at some location r in the stratosphere, we can also describe it as a function of a certain mean age value Γ. The release time distribution is then expressed as a function of mean release time $\Gamma^\#$. Equation (19) then becomes

$$\chi_{inorg,strat}(\Gamma,t) = \overline{f}(\Gamma) \cdot \int_0^\infty \chi_0(t-t') \cdot G_N^\#(\Gamma^\#,t')dt' \qquad (20)$$

After multiplying the right hand side of (20) with the amount of halogen atoms released from a halocarbon (n_i) and in case of bromine with the factor α describing the relative efficiency of bromine and summing up over all halogen species i we arrive at

$$EESC_{new}(\Gamma,t) = \sum_{Cl}\left(n_i\overline{f}_i(\Gamma)\int_0^\infty \chi_{0,i}(t-t')G_{N,i}^\#(\Gamma^\#,t')dt' \right) + \alpha \sum_{Br}\left(n_i\overline{f}_i(\Gamma)\int_0^\infty \chi_{0,i}(t-t')G_{N,i}^\#(\Gamma^\#,t')dt' \right) \qquad (21),$$

which is the new formulation we suggest for the calculation of EESC. This formulation is similar to the one used by Velders and Daniel (2014) and Newman et al. (2007) and also in the most recent WMO ozone assessment reports (Harris et al., 2014;L.J. Carpenter and S. Reimann et al., 2014;Montzka and Reimann et al., 2011), but differs in two aspects. First, chemical loss is described by the new time independent fractional release factor $\overline{f}$ (Ostermöller et al., 2017) and, second, instead of the age spectrum G with mean age Γ for an inert tracer the normalized release weighted distribution function $G_N^\#$ with the corresponding mean release time $\Gamma^\#$ for a chemically active specie is used.

In order to apply this new formulation of EESC, the normalized release time distribution $G_N^\#$ and the time independent fractional release factors $\overline{f}$ (Ostermöller et al., 2017) for all relevant chlorine and bromine species need to be known. To our knowledge, so far only mean arrival times time Γ^* for most species are available from the literature (Plumb et al., 1999). In the following we therefore show how the first moment of $G_N^\#$ (the mean release time $\Gamma^\#$) and $\overline{f}$ can be derived from the information available.

3.1. Deriving the mean release time.

The arrival time distribution G^* (Plumb et al., 1999) and the release time distribution $G^\#$ used here are closely linked. By combining equation (4) and (5) it is easily shown that the sum of G^* and $G^\#$ is the age spectrum G.

$$G^\#(r,t') + G^*(r,t') = f(t') \cdot G(r,t') + \left(1-f(t')\right) \cdot G(r,t') = G(r,t') \qquad (22)$$

In a similar way as for G#, a normalized arrival time distribution G_N^* has been defined (Ostermöller et al., 2017).

$$G_N^*(r,t') = \frac{G^*(r,t')}{\left(1 - \overline{f}(r)\right)} \tag{23}$$

In a similar was as for the mean release time, a mean arrival time Γ^* (Plumb et al., 1999) can be derived as the first moment of the arrival time distribution (4). In the arrival time distribution the age spectrum is not weighted with the release term $f(t')$ (as is the case for $G^\#$), but rather with the loss term $\left(1 - f(t')\right)$,

$$\int_0^\infty t' \cdot G_N^*(r,t')dt' = \Gamma^* \tag{24}$$

Γ^* has been calculated in a 2D model and is available for all relevant halocarbons based upon a parametrization (Plumb et al.,
5   1999) as function of Γ and lifetime τ. $\Gamma^\#$, which is needed to calculate the release of inorganic halogen from a halocarbon can be derived from the knowledge of Γ, Γ^* and fractional release factors. To derive $\Gamma^\#$ we start with the relationship between $G^\#$ and G^* (22).

Multiplying (22) with t' and integrating over all possible transit times yields

$$\int_0^\infty t' \cdot G(r,t')dt' = \int_0^\infty t' \cdot G^*(r,t')dt' + \int_0^\infty t' \cdot G^\#(r,t')dt' \tag{25}$$

Replacing G^* and $G^\#$ with their normalized distributions G_N^* (23) and $G_N^\#$ (16) yields

$$\int_0^\infty t' \cdot G(r,t')dt' = \int_0^\infty t' \cdot \left(1 - \overline{f}(r)\right) \cdot G_N^*(r,t')dt' + \int_0^\infty t' \cdot \overline{f}(r) \cdot G_N^\#(r,t')dt' \tag{26}$$

10   Extracting the transit time independent fractional release factors (Ostermöller et al., 2017) from the integrals yields

$$\int_0^\infty t' \cdot G(r,t')dt' = \left(1 - \overline{f}(r)\right) \cdot \int_0^\infty t' \cdot G_N^*(r,t')dt' + \overline{f}(r) \cdot \int_0^\infty t' \cdot G_N^\#(r,t')dt' \tag{27}$$

All the integrals in (27) can be solved as they are the first moments of the respective distribution functions, thus mean age Γ (9), mean arrival time Γ^* (24) and mean release time $\Gamma^\#$ (14). (27) thus becomes

$$\Gamma = \left(1 - \overline{f}(r)\right) \cdot \Gamma^* + \overline{f}(r) \cdot \Gamma^\# \tag{28}$$

Again we express $\overline{f}$ as a function of mean age Γ instead of location r and then rearrange (28) to give an equation to calculate $\Gamma^\#$.

$$\Gamma^{\#} = \frac{\Gamma - \left(1 - \overline{f}(\Gamma)\right) \cdot \Gamma^{*}}{\overline{f}(\Gamma)} \tag{29}$$

$\Gamma^{\#}$, which is the first moment of $G_N^{\#}$, can thus be derived based on the mean fractional release factor, mean age and Γ^{*} for each compound. In the next section we now derive a formulation to calculate the mean fractional release factors $\overline{f}(\Gamma)$ from available fractional release factors.

3.2. Recalculating FRF values to yield time-independent mean FRF values $\overline{f}$.

5   For the calculation of mean release time $\Gamma^{\#}$, and also in the new formulation for EESC (21) the time independent mean fractional release factors $\overline{f}$ as derived by (Ostermöller et al., 2017) are needed.

$$\overline{f}(\Gamma) = \frac{\int_0^\infty \chi_0(t - t') \cdot G_N^*(\Gamma^*, t')dt' - \chi_{strat}(\Gamma, t)}{\int_0^\infty \chi_0(t - t') \cdot G_N^*(\Gamma^*, t')dt'} \tag{30}$$

The fractional release factors from the most recent WMO reports are largely based on observations from the time period 1996 to 2000 (Newman et al., 2007) and were derived using

$$f(\Gamma) = \frac{\int_0^\infty \chi_0(t - t') \cdot G(\Gamma, t')dt' - \chi_{strat}(\Gamma, t)}{\int_0^\infty \chi_0(t - t') \cdot G(\Gamma, t')dt'} \tag{31}.$$

In this formulation, the age spectrum for an inert tracer is used, which does not include chemical loss. Solving (31) for
10    $\chi_{strat}(\Gamma, t)$ and inserting this into (30) yields

$$\overline{f}(\Gamma) = \frac{\int_0^\infty \chi_0(t - t') \cdot G_N^*(\Gamma^*, t')dt' - (1 - f(\Gamma)) \cdot \int_0^\infty \chi_0(t - t') \cdot G(\Gamma, t')dt'}{\int_0^\infty \chi_0(t - t') \cdot G_N^*(\Gamma^*, t')dt'} \tag{32}$$

Equation (32) allows to convert fractional release factors f calculated according to Newman et al. (2007) to time-independent values $\overline{f}$ according to Ostermöller et al. (2017). We derived $\overline{f}$ for every month of the period 1996 to 2000 from f and then took the median of these values. The new $\overline{f}$ values and the spread of $\overline{f}$ values derived by the conversion during the different months of this period are shown in Tables 1 and 2. The spread is mostly very small, as temporal trends during this period were
15   small for many species. For the same reason, the $\overline{f}$ values derived in this way mostly do not differ very strongly from the f values, as f and $\overline{f}$ only differ due to tropospheric trends.

The fractional release factors used for the reference calculation presented in section 4 are those used by Velders and Daniel (2014), modified using equation (32) to be consistent with the new formulation given by Ostermöller et al. (2017). The mean release time Γ^{*} has been calculated according to the parameterization of Plumb et al. (1999) also using their model lifetimes.
20   For CFCs 114 and 115 which are not included in Plumb et al. (1999) we used stratospheric lifetimes from Ko et al. (2013),

while the stratospheric lifetimes for HCFC-142b and the halons halon-1301, halon-1202 and halon-2402, which are also not included in Plumb et al. (1999), are taken from Chipperfiled et al. (2013). For those species included in Plumb et al. (1999) we used the species specific fit parameters, while for other species we used the averaged fit parameters reported in Plumb et al. (1999). The values for lifetimes used in the calculations and for both mean arrival time and mean release time as well as

5   the mean fractional release factors $\bar{f}$ are given for all species used in this calculation in Tables 1 and 2.

4. Temporal evolution of EESC and implications for recovery to 1980 benchmark values.

The new formulation of EESC (21) uses a loss weighted transit time distribution, the release time distribution, and different fractional release factors from those used in the classical formulation (Newman et al., 2007). The new fractional release factors

10   are based on the formulation suggested by Ostermöller et al. (2017) and have been derived from available fractional release factors (see section 3.2),. No method to calculate the release time distribution is available so far. Both the mean release time $\Gamma^{\#}$ (first moment of the distribution) and the shape of the release time distribution $G_N^{\#}$ need to be known in order to use this distribution for the calculation of the propagation of tropospheric trends into the stratosphere. The age spectrum for an inert tracer, G, is commonly described by an inverse Gaussian function with a parameterization of the width as function of mean

15   age (Hall and Plumb, 1994;Schauffler et al., 2003;Newman et al., 2007). As no such parameterization has yet been established for $G_N^{\#}$ we have assumed that the general shape of $G_N^{\#}$ is similar to that of G, with $\Gamma^{\#}$ instead of Γ as mean value. The sensitivity of our calculations to these assumptions is discussed in section 4.2.

4.1. Comparison of different EESC formulations

As already mentioned, new time-independent fractional release factors and the release time distribution are needed for our new

20   formulation of EESC. The release time distribution is approximated assuming the form of an inverse Gaussian with a species specific first moment $\Gamma^{\#}$ and a width of $\lambda = \frac{\Delta^{\#^2}}{\Gamma^{\#}} = 0.7 \; years$.

The new time-independent fractional release factors are based on the concept of arrival time distribution (Plumb et al., 1999). Ostermöller et al. (2017) showed that using this concept, fractional release factors can be calculated, which are independent of time as long as stratospheric transport or photochemistry remain unchanged. More specifically, these fractional release factors

25   are independent of the tropospheric trend of the respective species. We have recalculated fractional release factors used in the most recent ozone assessment report (Harris et al., 2014) to be consistent with the new formulation of fractional release. The fractional release factors commonly used are largely based on observations (Newman et al., 2007), except for the hydrochlorofluorocarbons HCFC-141b and HCFC-142b (Daniel et al., 1995) (see Tables 1 and 2). Other observation based fractional release factors have been presented by Laube et al. (2013). The uncertainty due to the use of different fractional

30   release factors, different emissions and different lifetimes have been discussed in details by Velders and Daniel (2014) . Here,

we focus on the uncertainties due to the suggested new formulation for the calculation of EESC. Using these new FRF values and the mean arrival time Γ^* based on the available parameterization (Plumb et al., 1999) we have calculated values for $\Gamma^{\#}$ for all relevant chlorine and bromine containing source gases (see Tables 1 and 2).

Figures 3 and 4 show the calculation according to (21) using the new time independent FRF values for 3 and 5.5 years of mean age, respectively, and compares it with the calculation applying formulation (3) using the FRF values of the ozone assessment reports (Harris et al., 2014). All values given here are mole fractions given in ppt, which is equivalent to pmol/mol. The values are also summarized in Tables A1 and A2. The tropospheric time series and the future projection used for this calculation are based on Velders and Daniel (2014), where updated lifetimes (Ko et al., 2013) and assumptions on future emissions have been used as basis for the projection of tropospheric time series. For a mean age of air of 3 years, as used for mid-latitudes, there are significant differences between the two methods used for calculation of EESC (see Figure 3). In the case of our new formulation, there is a longer time lag between the troposphere and the arrival of the inorganic halogen in the stratosphere. The tropospheric halogen loading was increasing strongly during the time before 1980, and therefore EESC at that time was dominated by air masses that had a lower halogen content. As a consequence, we calculate 1980 EESC levels in the mid latitude lower stratosphere which are about 90 ppt lower (see Table 3 for details) than using the EESC formulation according to Newman et al. (2007). During the recovery phase of stratospheric halogen loading, temporal trends of halogenated source gases in the troposphere will be negative; EESC will thus be dominated by air masses with higher chlorine content and is higher in our new formulation. In combination with the lower level of EESC, which must be attained for recovery, a significantly later recovery date is calculated. According to our calculation, mid latitude lower stratospheric EESC levels will return to 1980 values in 2060 only, which is more than 10 years later than the recovery date of 2049 calculated using the current method (Velders and Daniel, 2014).

For polar winter conditions (5.5 years of mean age) shown in Figure 4, the recovery date calculated here is 2077, relative to a value of 2076 derived based on the currently used method using the same scenario (Velders and Daniel, 2014). The reason that only a very minor change is calculated for polar winter conditions is that under these conditions nearly all source gases are converted to their inorganic form and the differences between the age spectrum and the release time distribution become very small.

4.2. Sensitivity discussion and tests

As mentioned above, we will concentrate on the sensitivity of the new EESC method on the limited knowledge on the new release time distribution $G_N^{\#}$ and on the new fractional release factors (Ostermöller et al., 2017) used here. We have therefore performed sensitivity calculations to evaluate the sensitivity of our results on the changed fractional release factors and on the uncertainty in the knowledge of the release time distribution $G_N^{\#}$.

Sensitivity to new fractional release factors

To evaluate the changes due to the changes in fractional release factors, we use our new release time distribution $G_N^{\#}$ but use the same fractional release factors as in previous studies (Velders and Daniel, 2014;Harris et al., 2014). The comparison for a mean age of 3 years is shown in Figure 5 and Table 3 (bottom row). The estimated recovery year is 2058, instead of 2060

5   using our new fractional release factors. The change in maximum EESC is also small with a value of 1909 using our new fractional release factors and 1895 using the fractional release factors as in (Velders and Daniel, 2014). For 5.5 years of mean age (not shown), the same recovery date is calculated (2077) with about 20 ppt lower EESC during the maximum using the unmodified fractional release factors from (Velders and Daniel, 2014). The new time-independent fractional release factors are derived from the fractional release factors presented by Newman et al. (2007) as described in the Appendix. For this, a

10   correction needs to be applied (see Appendix) based on the year of the measurements from which the fractional release factors have been derived. The fractional release factors used by Newman et al. (2007) were derived from the measurements taken during the STRATcampaign (1996), the POLARIS campaign (1997) and from the SOLVE campaign (1999-2000) (Schauffler et al., 2003). We converted the fractional release factors assuming that they were taken during the time period 1996-2000, with the exception of HCFC-s 141b and 142b, where we used the values given in Velders and Daniel (2014). We performed the

15   conversion for every month of this period. The median of all values was taken as the best estimate for the new time-independent fractional release factors. We also derived a variability which was below 1% for most species. This variability is also presented in Tables 1 and 2 together with the new fractional release factors. As a sensitivity we performed the EESC calculation by shifting all fractional release values up or downwards by 1σ. Varying the new fractional release factors whitin this uncertainty range resulted in an upward (increased fractional release) or downward (decreased fractional release) shift of EESC by about

20   14 ppt during the maximum of EESC for the 3 year mean age calculation. The changes in the calculated recovery years were less than 0.2 years. For 5.5 years of mean age, the variation of the fractional release factors lead to even smaller changes. Overall, we conclude that the changes in the fractional release factors are rather small in comparison to the overall changes. Using the fractional release release factors recalculated according to the method of Ostermöller et al. (2017) leads to change of 2 years in the calculated recovery date for mid latitudes; varying the recalculated fractional released factors within their

25   uncertainties only led to very small changes. For polar winter conditions, the calculated changes were in all cases very small. The significant differences in recovery dates for the mid latitude lower stratosphere presented above are thus mainly due to the new release time distribution $G_N^{\#}$.

Sensitivity to new release time distribution $G_N^{\#}$

The new release time distribution $G_N^{\#}$ has not been calculated from models to our knowledge. We therefore have to make

30   assumptions on the shape and the width of $G_N^{\#}$. In the calculation presented above, we have assumed that the shape is similar as for G, i.e. an inverse Gaussian function. We then made the assumption that the width can be described in a similar way as

a function of the first moment, i.e. using a constant factor $\lambda = \frac{\Delta^2}{\Gamma} = \frac{\Delta^{\#2}}{\Gamma^{\#}} = 0.7 \; years$ (Hall and Plumb, 1994;Engel et al., 2002). In order to test the sensitivity of our results to these assumptions, we have varied this parameter between values of 0 and 2 years. The extreme case of 0 would mean that the release time distribution $G_N^{\#}$ collapses to one single transit time or lag time, i.e. $\Gamma^{\#}$ and that no mixing occurs during the transport in the stratosphere. In this case, stratospheric inorganic chlorine is simply

5   derived by time shifting the tropospheric time series of a source gas by the time lag $\Gamma^{\#}$ and multiplying it with the fractional release factor.

The scenarios with λ equal to 0 years (no mixing case), 0.7 years (reference case) and 2 years (strong mixing case) are compared in Figure 6 and 7 for mean age values of 3 and 5.5 years. It is obvious, that the calculation of the recovery year is not very sensitive to the width of the release time distribution $G_N^{\#}$. In the case of the pure lag time calculation assuming no

10   mixing ($\lambda = 0 \; years$) recovery is about 1 year later for both 3 and 5.5 years of mean age compared to the reference case ($\lambda = 0.7 \; years$). In the case of a very wide spectrum assuming strong mixing ($\lambda = 2 \; years$), recovery is expected about 1.5 years earlier at the mean age level of 3 years and 2.5 years earlier at the mean age level of 5.5 years.

The overall range of the calculated recovery dates is 2.2 years in the case of 3 years mean age and 3.8 years in the case of 5.5 years of mean age. The recovery dates and the maximum values of EESC calculated under the different assumptions are

15   compared in Table 4. This rather small dependence on the width of the applied transit time distribution even for the assumption of extreme cases is due to two factors. Firstly, the deviation of tropospheric trends from linearity in the years prior to the reference year of 1980 and during the recovery phase after 2030 are rather small, in which case the propagation values becomes independent on the shape of the distribution (Hall and Plumb, 1994) and only depend on the first moment, i.e. the mean release time $\Gamma^{\#}$. Secondly, during the period of the maximum EESC, tropospheric trends are rather small overall and thus the trend

20   correction becomes rather small. Therefore maximum differences are below 50 ppt both for 1980 values and for the maximum EESC values for 3 years of mean age and 73 ppt for 5.5 years of mean age. The largest dependence on the parameterization is thus derived for 5.5. years of mean age during the maximum of EESC, as tropospheric data from a large time period need to be taken into account here and there is significant non-linearity in the trends. In all cases, the lag time calculation yields higher EESC during the maximum, as would be expected.

25   Another source of uncertainty is, that the stratospheric lifetime of the individual compounds needs to be known in order to calculate the mean arrival time Γ^{*} from which the mean release time $\Gamma^{\#}$is derived (29). We tested the sensitivity of our calculation to that by systematically increasing all lifetimes by 20% or decreasing them by 20%. (see Table 5). Even if such rather large changes would go in the same direction for all species, the impact on our calculations is rather small. For 3 years of mean age, the calculated maximum in EESC varied by only 6 ppt and the calculated recovery date varied by 2.5 years. For

30   5.5 years of mean age the effect is even smaller with variation in maximum EESC of less than 1 ppt and a variation of less than half a year in the recovery date. This very small sensitivity at 5.5 years of mean age is due to most fractional release factors being close to 1 under these conditions. The reason for this small effect is that next to the parameterization of the mean

arrival time, the fractional release factor determines the mean release time. Therefore, the sensitivity of the mean arrival time to the assumed lifetime in our calculation is quite low. Consequently, the influence on the derived EESC is also rather small.

5. Conclusions and outlook

We have shown that for the calculation of the propagation of chlorine and bromine source gases with photochemical loss, different transit time distributions must be used to calculate the amount of organic, respective inorganic chlorine present at a given mean age level. First, treating the propagation of these tracers with the age spectrum for an inert tracer leads to fractional release values which show a strong temporal variability in case of large tropospheric trends of the respective gas (Ostermöller et al., 2017). Therefore, time-independent fractional release factors (Ostermöller et al., 2017) must be used to correctly describe the fraction that has been transferred from the organic source gas to the inorganic form and can then influence ozone chemistry. Secondly, changes in tropospheric mixing ratios lead to changes in stratospheric inorganic halogen with a time delay that is longer than the mean age, which describes the propagation of an inert tracer. This can be described by a modified transit time distribution, in which the transit times from the classical age spectrum are weighted with the chemical loss during this transport time. We suggest the term "release time distribution" for this modified tracer specific transit time distribution.

We developed a new formulation of EESC which uses the release time distribution and time-independent fractional release factors calculated by the method of Ostermöller et al. (2017). We suggest that this new method to calculate EESC should be adopted to estimate the time of recovery of inorganic halogen to 1980 values under otherwise unchanged conditions. This will lead to a delay of about 10 years in expected chlorine recovery in the lower mid-latitude stratosphere (mean age of 3 years) compared to the formulation currently used (Velders and Daniel, 2014;Newman et al., 2007), and also applied in the WMO ozone assessment reports (Harris et al., 2014;L.J. Carpenter and S. Reimann et al., 2014). If all other factors are unchanged, in particular stratospheric dynamics, the recovery of mid-latitude lower stratospheric ozone to unperturbed values is thus also expected to take about 10 years longer than previously estimated. In addition to this, increases in the concentrations of N_2O and short-lived chlorine containing halocarbons may further retard the recovery of the ozone layer (Hossaini et al., 2015b;Hossaini et al., 2015a;Chipperfield, 2009). The changes due to application of this new method for 5.5 years of mean age (representative of polar winter conditions) are rather small, as nearly all halogen is released under these conditions and the difference between age spectrum and release time distribution becomes small.

The two changes relative to the currently used formulation for EESC are the use of new time-independent fractional release factors and of the release time distribution. We have shown that the new time-independent fractional release factors do not differ very much from the fractional release factors currently used (Harris et al., 2014;Velders and Daniel, 2014), as they were derived during a period of rather small tropospheric trends for many species. Consequently, the projected EESC recovery dates vary by 2 years or less depending on which fractional release factors are used. We have also shown that the calculation of the recovery date shows some sensitivity to the assumed width of the release time distribution, with variations of about 2 years for the mid-latitude calculations and 3.5 years for the high latitude case. Varying the stratospheric lifetimes assumed for the calculation of $G^{\#}$ a similar influence on the projected recovery dates for 3 years mean age (mid-latitude conditions) and virtually

no effect for 5.5 years (high-latitude conditions). In general, the maximum EESC level is more sensitive to variations in the assumed width of the release time distribution than to the stratospheric lifetimes assumed in the calculation of the mean release time. The strongest dependence on the assumed width is observed during the maximum of EESC levels, especially for high polar winter conditions, as tropospheric trends were strongly non-linear during that time. A more realistic description of the

5   shape of the release time distribution would improve especially the prediction of EESC during its maximum. Age spectra for inert tracers in models for atmosphere and ocean have been derived from pulse experiments using tracers without chemical loss (Haine et al., 2008;Li et al., 2012b;Li et al., 2012a;Ploeger and Birner, 2016). For the derivation of the release time distribution and improved information on mean release time such pulse experiments for tracers with chemical loss should be performed. These release time distributions will be specific for each tracer, but should generally be similar for species with

10   similar lifetimes and similar loss processes. Using such an improved release time distributions a comparison of inorganic halogen levels from full model calculations with the new EESC method should be performed. For studies using EESC as a proxy for the halogen loading, e.g. in comparison to ozone time series, the new formulation of EESC suggested here should be used, as the timing of the recovery especially for mid latitudes is significantly different than in previous estimates.

15   *Data availability:* The work is based on the scenario developed by (Velders and Daniel, 2014). We have used the scenario "All_parameters_SPARC2013_mostlikely_mc.dat" given in the Appendix to that paper and available as supplement.

Author contribution:. Andreas Engel has performed all the calculation in the manuscript, has written the manuscript and has developed the ideas presented in the manuscript together with the co-authors in the frame of many open discussions. Jennifer Ostermöller and Harald Bönisch have both participated in the discussion and preparation of the manuscript.

20   *Acknowledgements.* This work was partly supported by DFG Research Unit 1095 (SHARP) under project numbers EM367/9-1 and EN367/9-2. We thank Tanja Schuck and Joachim Curtius for comments on the manuscript.

References

Chipperfield, M.: Atmospheric science: Nitrous oxide delays ozone recovery, Nature Geosci, 2, 742-743, 2009.

Chipperfiled, M., Qing, L., , Authors), L., Abraham, L., Bekki, S., Braesicke, P., Dhome, S., Di Genova, G., Fleming, E. L.,
25   Hardiman, S., Iachetti, D., Jackman, C. H., Kinnison, D. E., Marchand, M., Pitari, G., Rozanov, E., Stenke, A., and Tummon, F.: Model Estaimtes of Lifetimes, in SPARC Report N°6 (2013) Lifetimes of Stratospheric Ozone-Depleting Substances, Their Replacements, and Related Species; edited by M. K. W. Ko, P. A. Newman, S. Reimann, and S. E. Strahan, 2013.

Daniel, J. S., Solomon, S., and Albritton, D. L.: On the Evaluation of Halocarbon Radiative Forcing and Global Warming Potentials, Journal of Geophysical Research-Atmospheres, 100, 1271-1285, 1995.

Engel, A., Strunk, M., Muller, M., Haase, H. P., Poss, C., Levin, I., and Schmidt, U.: Temporal development of total chlorine in the high-latitude stratosphere based on reference distributions of mean age derived from CO_2 and SF_6, Journal of Geophysical Research-Atmospheres, 107, 10.1029/2001jd000584, 2002.

Engel, A., Mobius, T., Bonisch, H., Schmidt, U., Heinz, R., Levin, I., Atlas, E., Aoki, S., Nakazawa, T., Sugawara, S., Moore, F., Hurst, D., Elkins, J., Schauffler, S., Andrews, A., and Boering, K.: Age of stratospheric air unchanged within uncertainties over the past 30 years, Nature Geoscience, 2, 28-31, 10.1038/NGEO388, 2009.

Farman, J. C., Gardiner, B. G., and Shanklin, J. D.: Large Losses of Total Ozone in Antarctica Reveal Seasonal Clox/Nox Interaction, Nature, 315, 207-210, Doi 10.1038/315207a0, 1985.

Haine, T. W. N., Zhang, H., Waugh, D. W., and Holzer, M.: On transit-time distributions in unsteady circulation models, Ocean Modelling, 21, 35-45, https://doi.org/10.1016/j.ocemod.2007.11.004, 2008.

Hall, T. M., and Plumb, R. A.: Age as a diagnostic of stratospheric transport, Journal of Geophysical Research-Atmospheres, 99, 1059-1070, 10.1029/93jd03192, 1994.

Harris, N., Wuebbles, D., Daniel, J., Hu, J., Kuijpers, L., Law, K., Prather, M., and Schofield, R.: Scenarios and information for policymakers, Chapter 5 in Scientific Assessment of Ozone Depletion: 2014, Global Ozone Research and Monitoring Project–Report No. 55, World Meteorological Organization, Geneva, Switzerland, 2014.

Hossaini, R., Chipperfield, M. P., Montzka, S. A., Rap, A., Dhomse, S., and Feng, W.: Efficiency of short-lived halogens at influencing climate through depletion of stratospheric ozone, Nature Geosci, 8, 186-190, 10.1038/ngeo2363, 2015a.

Hossaini, R., Chipperfield, M. P., Saiz-Lopez, A., Harrison, J. J., von Glasow, R., Sommariva, R., Atlas, E., Navarro, M., Montzka, S. A., Feng, W., Dhomse, S., Harth, C., Mühle, J., Lunder, C., O'Doherty, S., Young, D., Reimann, S., Vollmer, M. K., Krummel, P. B., and Bernath, P. F.: Growth in stratospheric chlorine from short-lived chemicals not controlled by the Montreal Protocol, Geophysical Research Letters, 42, 4573-4580, 10.1002/2015GL063783, 2015b.

Kida, H.: General-Circulation of Air Parcels and Transport Characteristics Derived from a Hemispheric Gcm .2. Very Long-Term Motions of Air Parcels in the Troposphere and Stratosphere, Journal of the Meteorological Society of Japan, 61, 510-523, 1983.

Ko, M. K. W., Newman, P., Reimann, S., Strahan, S. E., Atlas, E. L., Burkholder, J. B., Chipperfield, M., Engel, A., Liang, Q., Mellouki, W., Plumb, R. A., Stolarski, R. S., and Volk, C. M.: Recommended Values for Steady-State Atmospheric Lifetimes and their Uncertainties , in SPARC Report N°6 (2013) Lifetimes of Stratospheric Ozone-Depleting Substances, Their Replacements, and Related Species; edited by M. K. W. Ko, P. A. Newman, S. Reimann, and S. E. Strahan, 2013.

L.J. Carpenter and S. Reimann, (Lead Authors), Burkholder, J. B., Clerbaux, C., Hall, B. D., Hossaini, R., Laube, J. C., and Yvon-Lewsi, S. A.: Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol, Chapter 1 in *Scientific Assessment of Ozone Depletion: 2014*, Global Ozone Research and Monitoring Project –Report No. 55, World Meteorological Organization, Geneva, Switzerland, 2014., 2014.

Laube, J. C., Keil, A., Bönisch, H., Engel, A., Röckmann, T., Volk, C. M., and Sturges, W. T.: Observation-based assessment of stratospheric fractional release, lifetimes, and ozone depletion potentials of ten important source gases, Atmos. Chem. Phys., 13, 2779-2791, 10.5194/acp-13-2779-2013, 2013.

Li, F., Waugh, D. W., Douglass, A. R., Newman, P. A., Pawson, S., Stolarski, R. S., Strahan, S. E., and Nielsen, J. E.: Seasonal variations of stratospheric age spectra in the Goddard Earth Observing System Chemistry Climate Model (GEOSCCM), Journal of Geophysical Research-Atmospheres, 117, Artn D05134

Doi 10.1029/2011jd016877, 2012a.

Li, F., Waugh, D. W., Douglass, A. R., Newman, P. A., Strahan, S. E., Ma, J., Nielsen, J. E., and Liang, Q.: Long-term changes in stratospheric age spectra in the 21st century in the Goddard Earth Observing System Chemistry-Climate Model (GEOSCCM), Journal of Geophysical Research-Atmospheres, 117, Artn D20119
5   Doi 10.1029/2012jd017905, 2012b.

M. Dameris and S. Godin-Beekmann, (Lead Authors), Alexander, S., Braesicke, P., Chipperfield, M., de Laat, A. T. J., Orsolini, Y., Rex, M., and Santee, M. L.: Update on Polar ozone: Past, present, and future, Chapter 3 in Scientific Assessment of Ozone Depletion: 2014, Global Ozone Research and Monitoring Project – Report No. 55, World Meteorological Organization, Geneva, Switzerland, 2014, 2014.

10   Molina, M. J., and Rowland, F. S.: Stratospheric Sink for Chlorofluoromethanes - Chlorine Atomic-Catalysed Destruction of Ozone, Nature, 249, 810-812, Doi 10.1038/249810a0, 1974.

Montzka and Reimann, Engel, A., Krüger, K., O'Doherty, S., Sturges, W. T., Blake, D., Dorf, M., Fraser, P., Froidevaux, L., Jucks, K., Kreher, K., Kurylo, M. J., Mellouki, A., Miller, J., Nielsen, O.-J., Orkin, V. L., Prinn, R. G., Rhew, R., Santee, M. L., and Verdonik, D.: Ozone-Depleting Substances (ODSs) and Related Chemicals, Chapter 1 in Scientific Assessment of
15   Ozone Depletion: 2010, Global Ozone Research and Monitoring Project-Report No. 52, World Meteorological Organization, Geneva, Switzerland, 516p., 1.1-1.108, 2011.

Newman, P. A., Daniel, J. S., Waugh, D. W., and Nash, E. R.: A new formulation of equivalent effective stratospheric chlorine (EESC), Atmos. Chem. Phys., 7, 4537-4552, 10.5194/acp-7-4537-2007, 2007.

Ostermöller, J., Bönisch, H., Jöckel, P., and Engel, A.: A new time-independent formulation of fractional release, Atmos.
20   Chem. Phys., 2017, 3785-3797, 10.5194/acp-17-3785-2017, 2017.

Ploeger, F., and Birner, T.: Seasonal and inter-annual variability of lower stratospheric age of air spectra, Atmos. Chem. Phys., 16, 10195-10213, 10.5194/acp-16-10195-2016, 2016.

Plumb, I. C., Vohralik, P. F., and Ryan, K. R.: Normalization of correlations for atmospheric species with chemical loss, Journal of Geophysical Research: Atmospheres, 104, 11723-11732, 10.1029/1999JD900014, 1999.

25   S. Pawson and W. Steinbrecht, (Lead Authors), Charlton-Perez, A. J., Fujiwara, M., Karpechko, A. Y., Petropavlovskikh, I., Urban, J., and Weber, M.: Update on global ozone: Past, present, and future, Chapter 2 in Scientific Assessment of Ozone Depletion: 2014, Global Ozone Research and Monitoring Project – Report No. 55, World Meteorological Organization, Geneva, Switzerland, 2014, 2014.

Schauffler, S. M., Atlas, E. L., Donnelly, S. G., Andrews, A., Montzka, S. A., Elkins, J. W., Hurst, D. F., Romashkin, P. A.,
30   Dutton, G. S., and Stroud, V.: Chlorine budget and partitioning during the Stratospheric Aerosol and Gas Experiment (SAGE) III Ozone Loss and Validation Experiment (SOLVE), Journal of Geophysical Research-Atmospheres, 108, -, 10.1029/2001jd002040, 2003.

Shepherd, T. G., Plummer, D. A., Scinocca, J. F., Hegglin, M. I., Fioletov, V. E., Reader, M. C., Remsberg, E., von Clarmann, T., and Wang, H. J.: Reconciliation of halogen-induced ozone loss with the total-column ozone record, Nature Geosci, 7, 443-
35   449, 10.1038/ngeo2155, 2014.

Solomon, S.: Stratospheric ozone depletion: A review of concepts and history, Reviews of Geophysics, 37, 275-316, 1999.

Stolarski., R. S., and Cicerone, R. J.: Stratospheric Chlorine - Possible Sink for Ozone, Canadian Journal of Chemistry-Revue Canadienne De Chimie, 52, 1610-1615, Doi 10.1139/V74-233, 1974.

Tilmes, S., Garcia, R. R., Kinnison, D. E., Gettelman, A., and Rasch, P. J.: Impact of geoengineered aerosols on the troposphere and stratosphere, Journal of Geophysical Research-Atmospheres, 114, 10.1029/2008jd011420, 2009.

5 Velders, G. J. M., and Daniel, J. S.: Uncertainty analysis of projections of ozone-depleting substances: mixing ratios, EESC, ODPs, and GWPs, Atmos. Chem. Phys., 14, 2757-2776, 10.5194/acp-14-2757-2014, 2014.

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, Journal of Geophysical Research-Atmospheres, 102, 25543-25564, 10.1029/97jd02215, 1997.

10 Waugh, D. W., and Hall, T. M.: Age of stratospheric air: Theory, observations, and models, Reviews of Geophysics, 40, 10.1029/2000rg000101, 2002.

Weatherhead, E. C., and Andersen, S. B.: The search for signs of recovery of the ozone layer, Nature, 441, 39-45, 2006.

Wofsy, S. C., McElroy, M. B., and Yung, Y. L.: The chemistry of atmospheric bromine, Geophysical Research Letters, 2, 215-218, 10.1029/GL002i006p00215, 1975.

Table 1: Mean arrival time Γ^*, mean release time $\Gamma^\#$, f and $\bar{f}$ for all relevant long lived chlorine and bromine species for a mean age of 3 years. The time independent fractional release factors were derived using equation (32). The measurements from which the original fractional release factors were derived are from the period 1996-2000. We calculated the conversion using eq. (32) for every month of this period for all species, except for HCFC-141b and 142b (see text). The 1σ variability of the converted fractional release factors is also shown.

	Stratospheric lifetime used for Γ^*[years]	mean arrival time Γ^* [years]	mean release time $\Gamma^\#$ [years]	fractional release factor f	time independent fractional release factor $\bar{f}$	1 σ variability of recalculated $\bar{f}$ in %
		Mean age Γ of 3 years				
CFC-11	55.7[a]	1.5	4.7	0.47[d]	0.47	0.23
CFC-12	102 [a]	2.0	6.2	0.23[d]	0.24	0.22
CFC-113	84.5 [a]	1.9	5.7	0.29[d]	0.3	0.69
CFC-114	189[b]	2.2	8.7	0.12[d]	0.13	0.11
CFC-115	1020[b]	2.5	12.1	0.04[d]	0.07	0.45
CCl$_4$	48.4 [a]	1.4	4.3	0.56[d]	0.56	0.08
CH$_3$CCl$_3$	48.8 [a]	1.4	4.1	0.67[d]	0.61	1.93
HCFC-22	217 [a]	2.6	5.6	0.13[d]	0.15	0.09
HCFC-141b	73 [a]	1.8	5.4	0.34[e]	0.34	n.a.[f]
HCFC-142b	212[c]	2.2	6.8	0.17[e]	0.17	n.a.[f]
halon-1211	39.5 [a]	1.3	4.0	0.62[d]	0.65	0.4
halon-1202	15.3[c]	0.5	5.0	0.62[d]	0.67	2.79
halon-1301	70.8[c]	1.7	6.0	0.28[d]	0.32	1.34
halon-2402	33.8[c]	1.2	4.0	0.65[d]	0.66	0.55
CH$_3$Br	40.2 [a]	1.3	4.1	0.60[d]	0.6	0.11
CH$_3$Cl	63.7 [a]	1.9	4.4	0.44[d]	0.44	0[g]

[a] stratospheric lifetime from the 2D model used in (Plumb et al., 1999)

[b] total atmospheric lifetime taken from recommendations in SPARC lifetime assessment (Ko et al., 2013), as tropospheric loss is negligible.

[c] stratospheric lifetime taken from modelling work for SPARC lifetime assessment (Chipperfiled et al., 2013).

[d] fractional release values based on Newman et al. (2007)

[e] fractional release value based on parameterization given in footnote to table 2 in Velders and Daniel (2014).

[f] not applicable, as the fractional release values have not been recalculated.

[g] no variability was derived as there is no trend in the tropospheric reference data applied.

Table 2: Mean arrival time Γ^*, mean release time $\Gamma^\#$, f and $\bar{f}$ for all relevant long lived chlorine and bromine species for a mean age of 5.5 years. In case of fractional release factor of 1, there is no remaining organic fraction and the concept of mean arrival time $\Gamma^*$is not applicable (n.a.). Inorganic chlorine can then be treated in a similar way as an inert tracer, using mean age Γ. The time independent fractional release factors were derived using equation (32). The measurements from which the original fractional release factors were derived are from the period 1996-2000. We calculated the conversion using eq. (32) for every month of this period for all species, except for HCFC-141b and 142b (see text). The 1σ variability of the converted fractional release factors is also shown.

	Stratospheric lifetime used for Γ^*[years]	mean arrival time Γ^* [years]	mean release time $\Gamma^\#$ [years]	fractional release factor f	time independent fractional release factor $\bar{f}$	1 σ variability of recalculated $\bar{f}$ in % [a]
		Mean age Γ of 5.5 years				
CFC-11	55.7[a]	1.8	5.5	0.99[d]	0.99	0.01
CFC-12	102 [a]	3.0	5.9	0.86[d]	0.87	0.11
CFC-113	84.5 [a]	2.7	5.8	0.90[d]	0.91	0.26
CFC-114	189[b]	3.6	8.3	0.40[d]	0.41	0.28
CFC-115	1020[b]	4.4	10.1	0.15[d]	0.2	0.58
CCl$_4$	48.4 [a]	n.a.	5.5	1.00[d]	1	0
CH$_3$CCl$_3$	48.8 [a]	1.7	5.6	0.99[d]	0.99	0.13
HCFC-22	217 [a]	4.3	7.0	0.41[d]	0.44	0.16
HCFC-141b	73 [a]	2.5	5.8	0.90[e]	0.9	n.a.[f]
HCFC-142b	212[c]	3.7	6.5	0.65[e]	0.65	n.a.[f]
halon-1211	39.5 [a]	n.a.	5.5	1.00[d]	1	0
halon-1202	15.3[c]	n.a.	5.5	1.00[d]	1	0
halon-1301	70.8[c]	2.2	6.2	0.80[d]	0.83	0.77
halon-2402	33.8[c]	n.a.	5.5	1.00[d]	1	0
CH$_3$Br	40.2 [a]	1.5	5.5	0.99[d]	0.99	0.01
CH$_3$Cl	63.7 [a]	2.9	5.8	0.91[d]	0.91	0[g]

stratospheric lifetime from the 2D model used in (Plumb et al., 1999)
[b] total atmospheric lifetime taken from recommendations in SPARC lifetime assessment (Ko et al., 2013), as tropospheric loss is negligible.
[c] stratospheric lifetime taken from modelling work for SPARC lifetime assessment (Chipperfiled et al., 2013).
[d] fractional release values based on Newman et al. (2007)
[e] fractional release value based on parameterization given in footnote to table 2 in Velders and Daniel (2014).
[f] not applicable, as the fractional release values have not been recalculated.
[g] no variability was derived as there is no trend in the tropospheric reference data applied.

Table 3: Recovery years for EESC to return to 1980 values and maximum EESC values using our new formulation and the current formulation (Newman et al., 2007), as shown in Figures 3 and 4. In all cases the width Δ is parametrized based a values of $\lambda = \frac{\Delta^2}{\Gamma} = \frac{\Delta^{\#2}}{\Gamma^\#} = \mathbf{0.7\ years}$ (see text for an explanation of the parameterization). In the new formulation, the time-independent fractional release values and the values for $\mathbf{\Gamma^\#}$ **shown in Tables A1 and A2** have been used. The results in the bottom row were derived using the same fractional release factors as in (Velders and Daniel, 2014), instead of the new time-independent fractional release factors, as shown in Figure 5 for 3 years of mean age. Decimal places are not meant to imply that recovery dates can be calculated to this accuracy rate, but are only given in order to show the sensitivity of the calculations to different parameters.

	3 years mean age			5.5 years mean age		
	EESC 1980 [ppt]	EESC max [ppt]	1980 recovery date	EESC 1980 [ppt]	EESC max [ppt]	1980 recovery date
New formulation, time independent fractional release factors (Table A1 and A2) and G#.	1065	1909	2059.9	2070	4107	2077.5
Current formulation, fractional release factors as in Velders and Daniel (2014), age spectrum G.	1154	1932	2048.6	2085	4102	2075.7
New formulation using G#, but unchanged fractional release factors as in Velders and Daniel (2014)	1070	1895	2057.8	2066	4088	2077.1

Table 4: Recovery years for EESC to return to 1980 values and maximum EESC values using different assumptions on the width of the release time distribution G# as shown in Figure 6 and 7. In all cases the general shape was assumed to be an inverse Gaussian function with different parameterizations of the width Δ, based on different values of $\lambda = \frac{\Delta^{\#2}}{\Gamma^\#}$ (see text for an explanation of the parameterization). The case of the pure lag time calculation is equal to $\lambda = \mathbf{0}$ years , i.e. the effect of mixing is completely ignored, $\lambda = \mathbf{2\ years}$ represents a case with strong mixing and a broad transit time distribution, while , $\lambda = \mathbf{0.7\ years}$ corresponds to our reference calculation. In all calculations, the same time-independent fractional release values have been used, as shown in Tables A1 and A2. Decimal places are not meant to imply that recovery dates can be calculated to this accuracy rate, but are only given in order to show the sensitivity of the calculations to different parameters.

	3 years mean age			5.5 years mean age		
	EESC 1980 [ppt]	EESC max [ppt]	1980 recovery date	EESC 1980 [ppt]	EESC max [ppt]	1980 recovery date
$\lambda = 0.7$ years reference	1065	1909	2059.9	2070	4107	2077.5
$\lambda = 2$ years , strong mixing	1101	1913	2058.5	2149	4103	2075.0
$\lambda = 0$, no mixing	1055	1941	2060.7	2046	4176	2078.8

Table 5: Recovery years for EESC to return to 1980 values and maximum EESC values varying the stratospheric lifetimes in the calculations of the mean arrival time $\mathbf{\Gamma}^{*}$ from which the mean release time time $\mathbf{\Gamma}^{\#}$ is calculated according to (A8). In these calculations, the width of the release time distribution G$^{\#}$ was kept constant at $\lambda = \frac{\Delta^{\#2}}{\Gamma^{\#}} = 0.7$ years. The lifetimes have been varied systematically up- and downward by 20% for this sensitivity test (see text for explanations). The reference case is the same as shown in Table 1. For the high τ and low τ calcuations the stratospheric lifetimes of all species have been increased systematically by 20% upwards and downwards respectively, when calculating the mean arrival times and the mean release times. Decimal places are not meant to imply that recovery dates can be calculated to this accuracy rate, but are only given in order to show the sensitivity of the calculations to different parameters.

	3 years mean age			5.5 years mean age		
	EESC 1980 [ppt]	EESC max [ppt]	1980 recovery date	EESC 1980 [ppt]	EESC max [ppt]	1980 recovery date
Reference	1064	1909	2059.9	2070	4107	2077.5
High τ	1073	1912	2058.8	2071	4107	2077.3
low τ	1054	1906	2061.3	2068	4107	2077.6
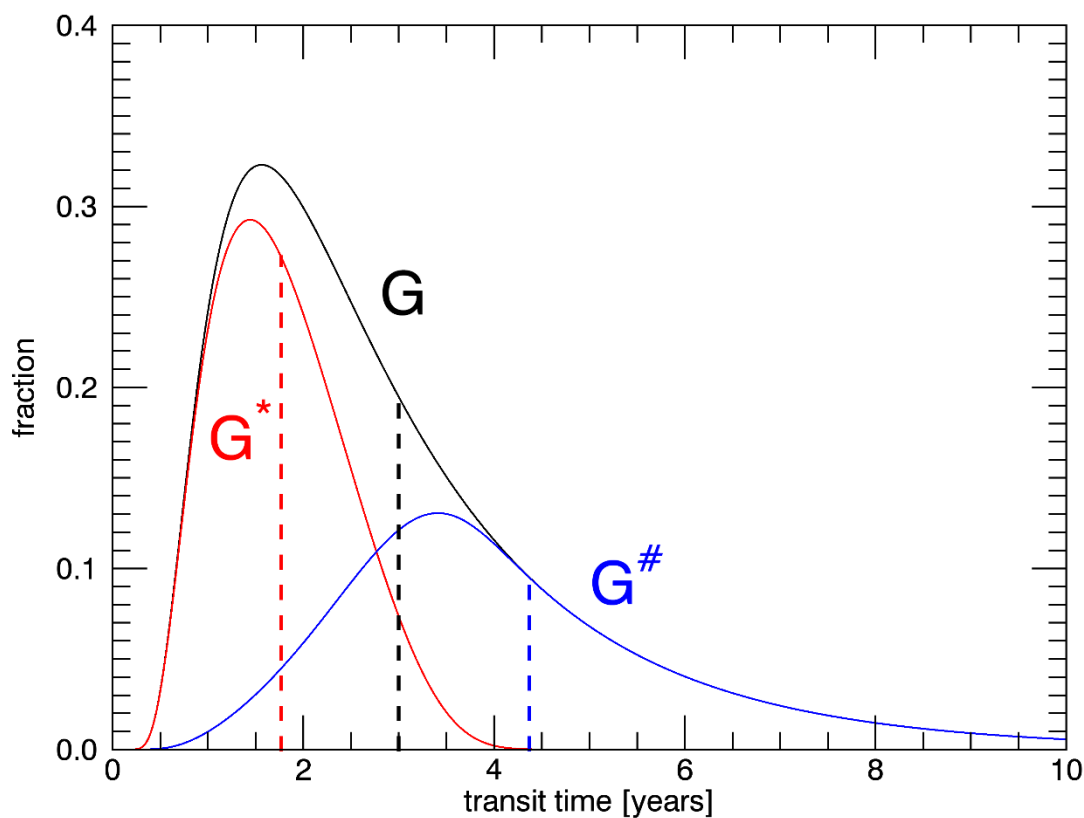
Figure 1: Age spectrum G (black line) for an inert tracer compared to the arrival time distribution G* (red line) and the release time distribution G# (blue line). The loss function has been approximated as a function of transit time in order to represent a tracer similar to CFC-11 (see supplementary information for more details). The first moments of the three functions differ substantially: while the black line (inert tracer) has a first moment of 3 years, the first moment for the red curve, representing the remaining organic fraction is 1.75 years and that of the blue curve describing the inorganic halogen released from the source gas is 4.35 years. Note that these values are not identical to those for CFC-11 in Table A1 as the loss function was only approximated and that this Figure is purely for illustrative purposes.
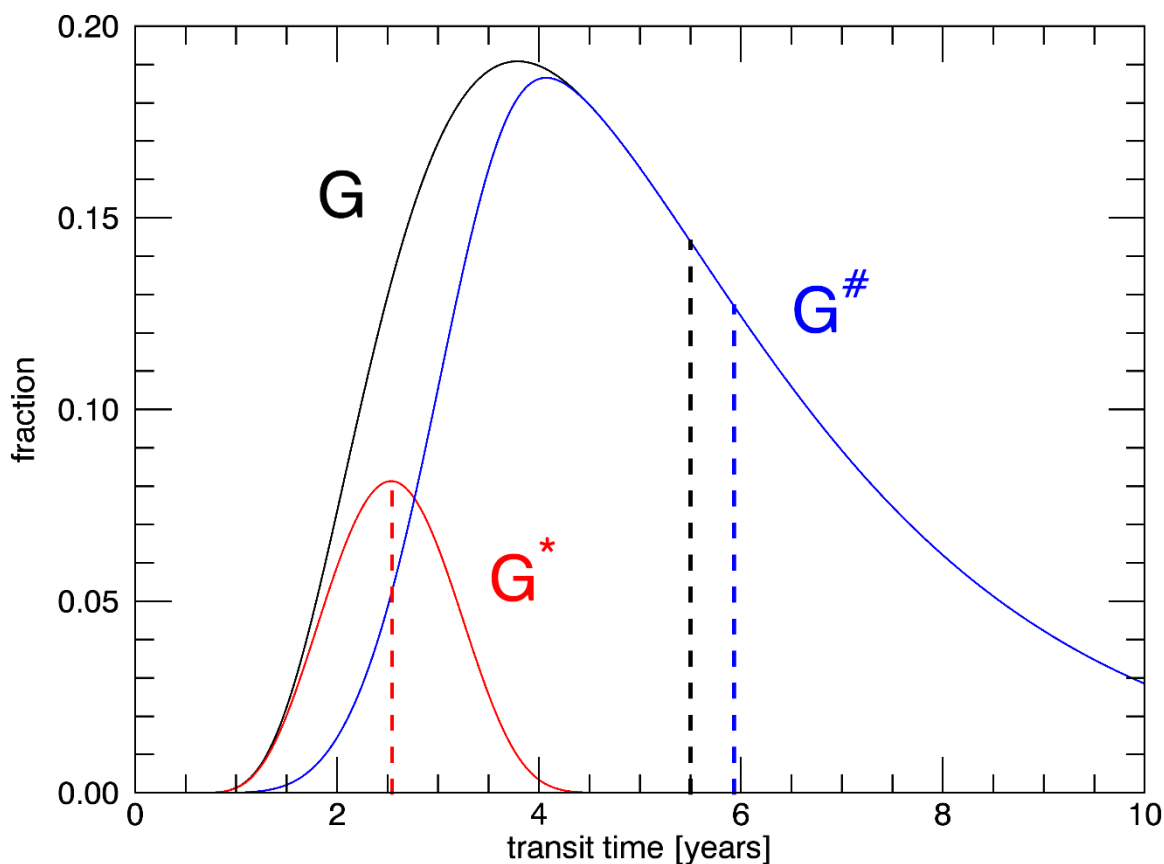
Figure 2: Age spectrum G (black line) for an inert tracer compared to the arrival time distribution G^* (red line) and the release time distribution $G^\#$ (blue line). The loss function has been approximated as a function of transit time in order to represent a tracer similar to CFC-11 (see supplementary information for more details). The first moments of the three functions differ substantially: while the black line (inert tracer) has a first moment of 5.5 years, the first moment for the red curve, representing the remaining organic fraction is 2.5 years and that of the blue curve describing the inorganic halogen released from the source gas is 5.9 years. Note that these values are not identical to those for CFC-11 in Table A2 as the loss function was only approximated and that this Figure is purely for illustrative purposes.
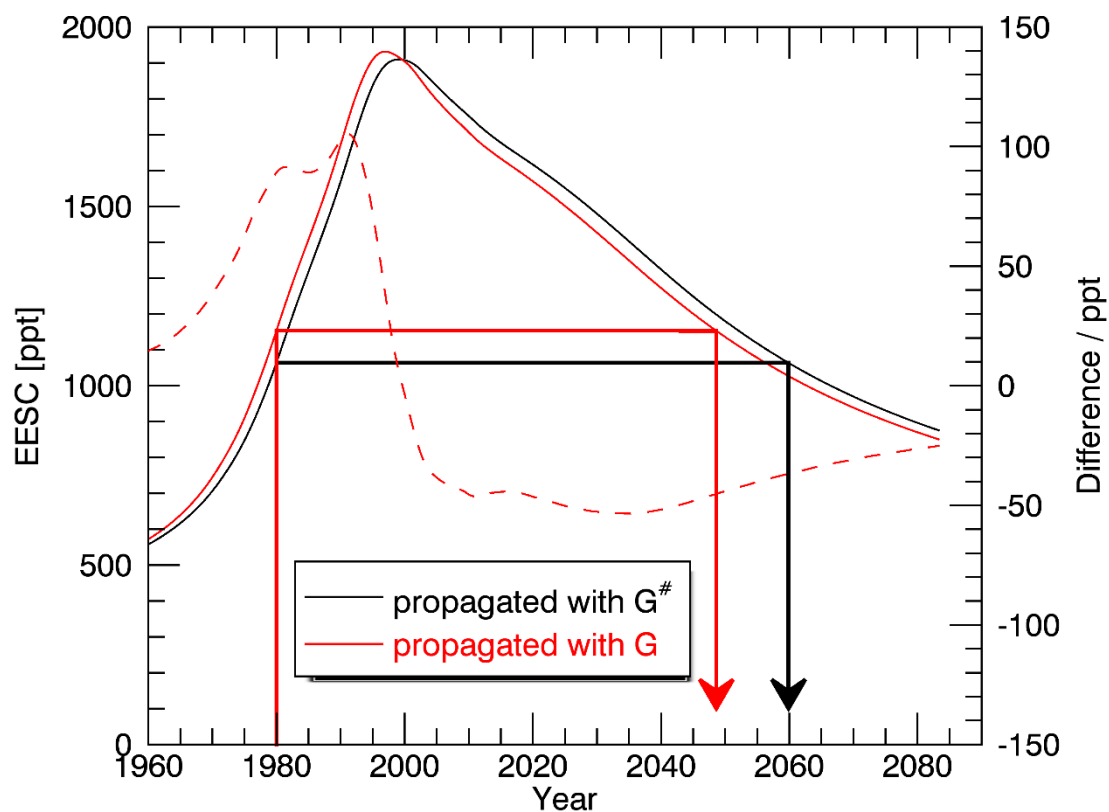
Figure 3: Estimated temporal evolution of EESC for a mean age of 3 years using the old (red line) and the new (black line) formulation of EESC. Also shown is the difference (red dashed line) and the recovery date to 1980 values for the old and the new formulation. Our new formulation yields a recovery date which is more than 10 years later than using the current formulation. This shift in recovery date is mainly caused by the lower EESC levels calculated for the increasing phase, i.e. the 1980 reference value.
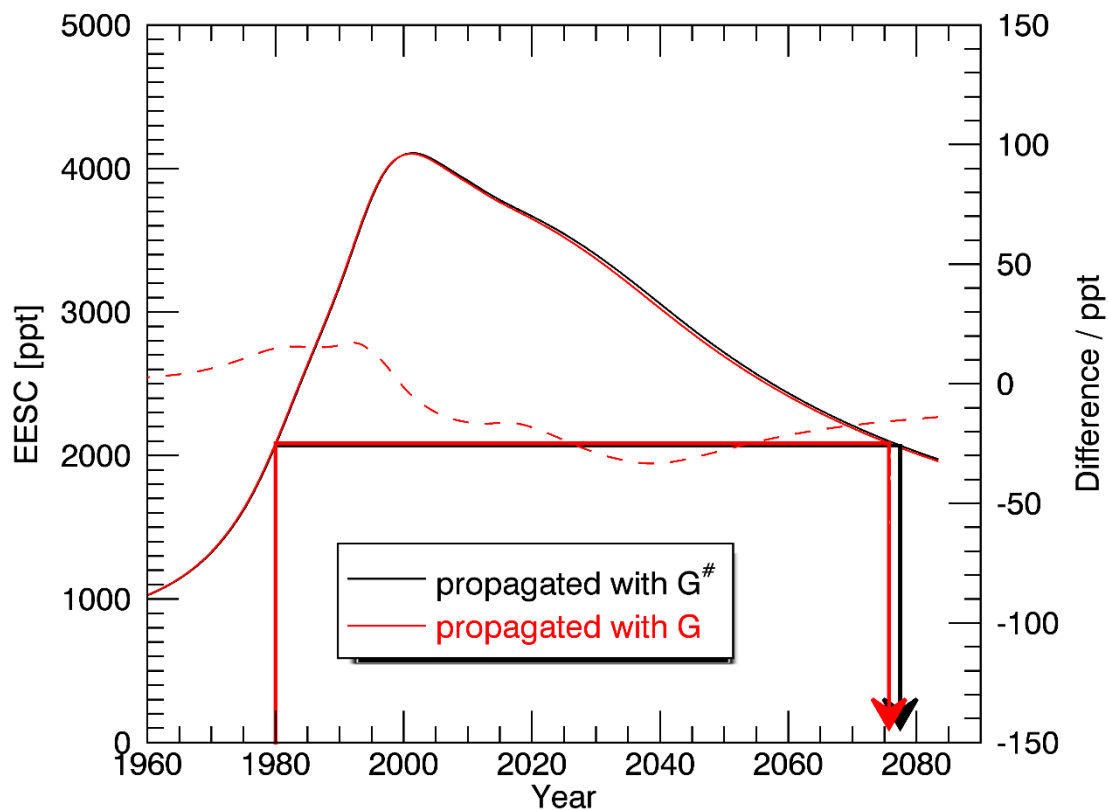
Figure 4: Estimated temporal evolution of EESC for a mean age of 5.5 years using the old (red line) and the new (black line) formulation of EESC. Also shown is the difference (red dashed line) and the recovery date to 1980 values for the old and the new formulation. Our new formulation yields a recovery date to 1980 values, which is about 2 years later than using the current formulation. The smaller shift in comparison to the calculation for 3 years of mean age is due to the near complete fractional release of most halogen source gases for these old air masses.
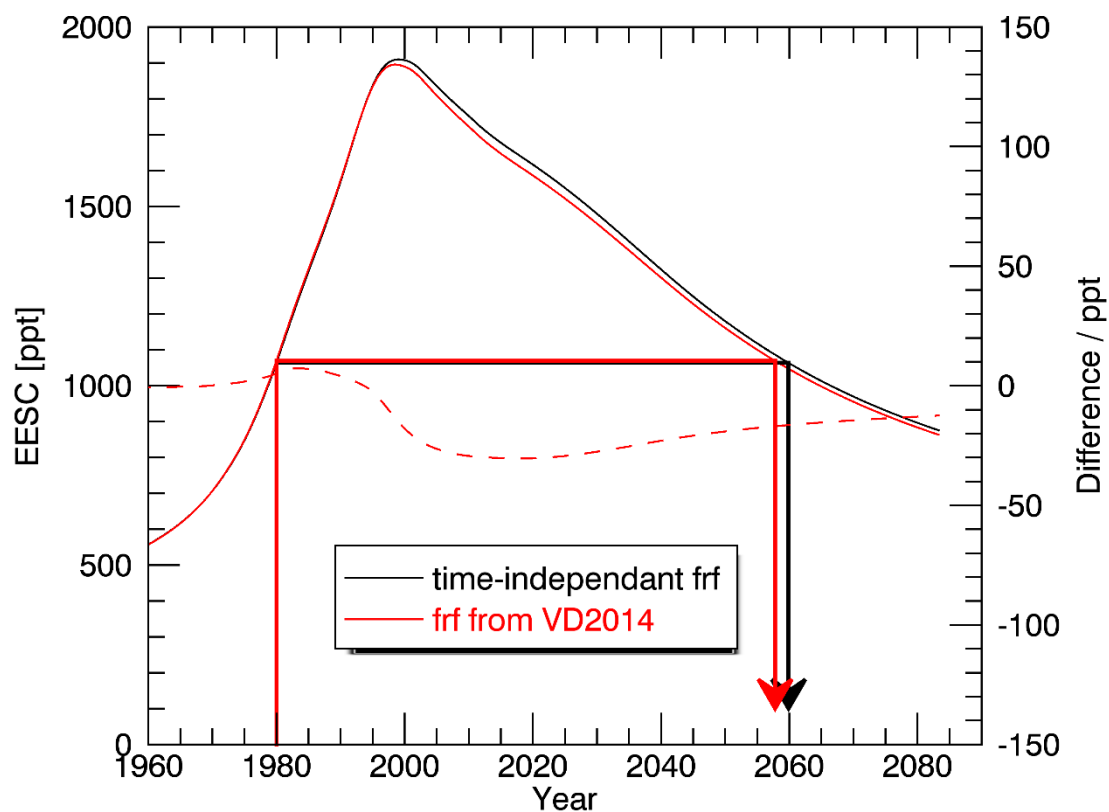
Figure 5: Influence of new fractional release factors for calculation of EESC at a mean age of 3 years. In both calculations the new formulation of EESC has been used, yet both calculations use different fractional release factors. The calculation using the new fractional release factors (Table A1) for 3 years of mean age is shown in black, while the calculation using the original values as used in Velders and Daniel (2014) (VD2014) is shown in red. As the fractional release factors currently used (Harris et al., 2014;Velders and Daniel, 2014) are largely based on measurements (Newman et al., 2007;Schauffler et al., 2003) which were taken during a period of rather small tropospheric trends for most species, the change due to the new formulation (Ostermöller et al., 2017) is rather small. For HCFCs 141b and 142b, uncertainties on observational fractional release factors are large and the same fractional release factors were used in both calculations, which are based on the parameterization given in Velders and Daniel (2014). The difference of the calculation using the VD2014 fractional release factors and our new time independent fractional release factors is shown as red dashed line. The fractional release factors used here are summarized in Table A1.
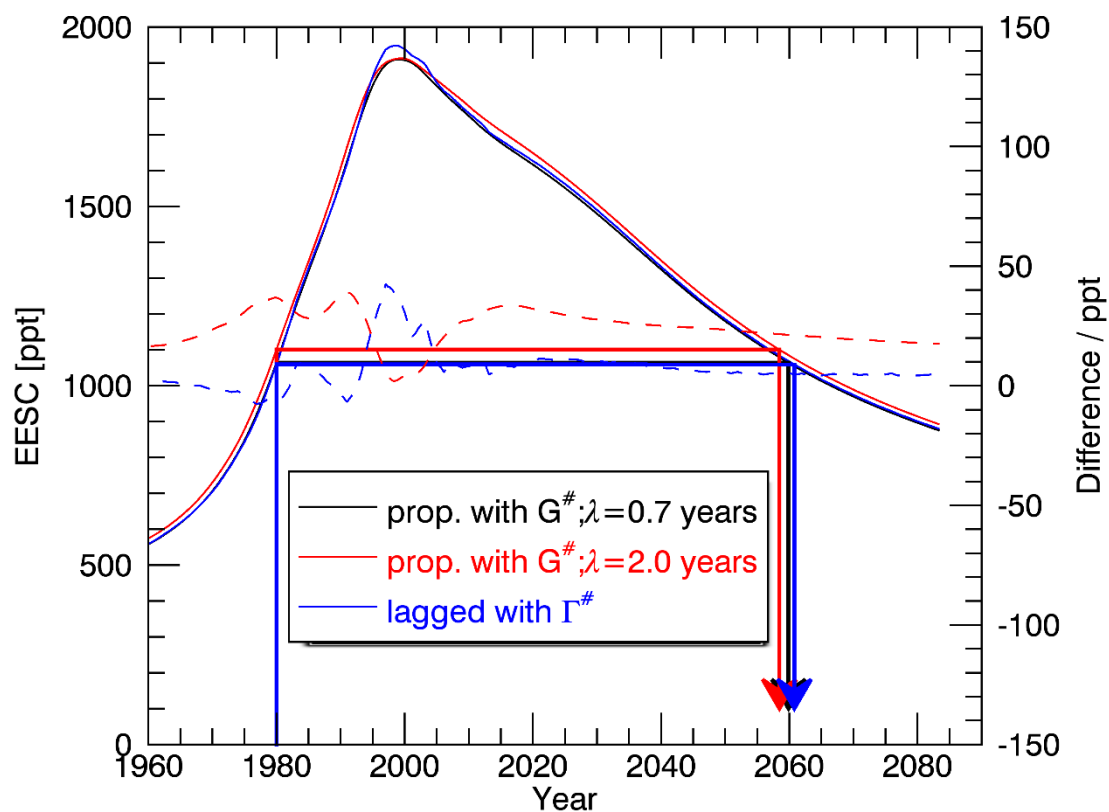
Figure 6: Sensitivity of EESC calculation using the new formulation for a mean age of 3 years on the parameterization of the shape of the release time distribution. In two cases the general shape was assumed to be an inverse Gaussian function with different parameterizations of the width Δ, based on different values of $\lambda = \frac{\Delta^2}{\Gamma}$ (see text for an explanation of the parameterization). The case of the pure lag time calculation
5   (blue line) is equal to $\lambda = 0$ years , i.e. the effect of mixing is completely ignored. The calculation using $\lambda = 2$ **years** (red line) represents a case with strong mixing and a broad transit time distribution, while $\lambda = 0.7$ **years** (black line) corresponds to our reference calculation. The influence is largest during the period of the maximum, when tropospheric trends showed a strong non-linear behavior and the tracer propagation strongly depends on the shape of the distribution function. The difference of the calculation to our reference calculations are shown as dashed lines.
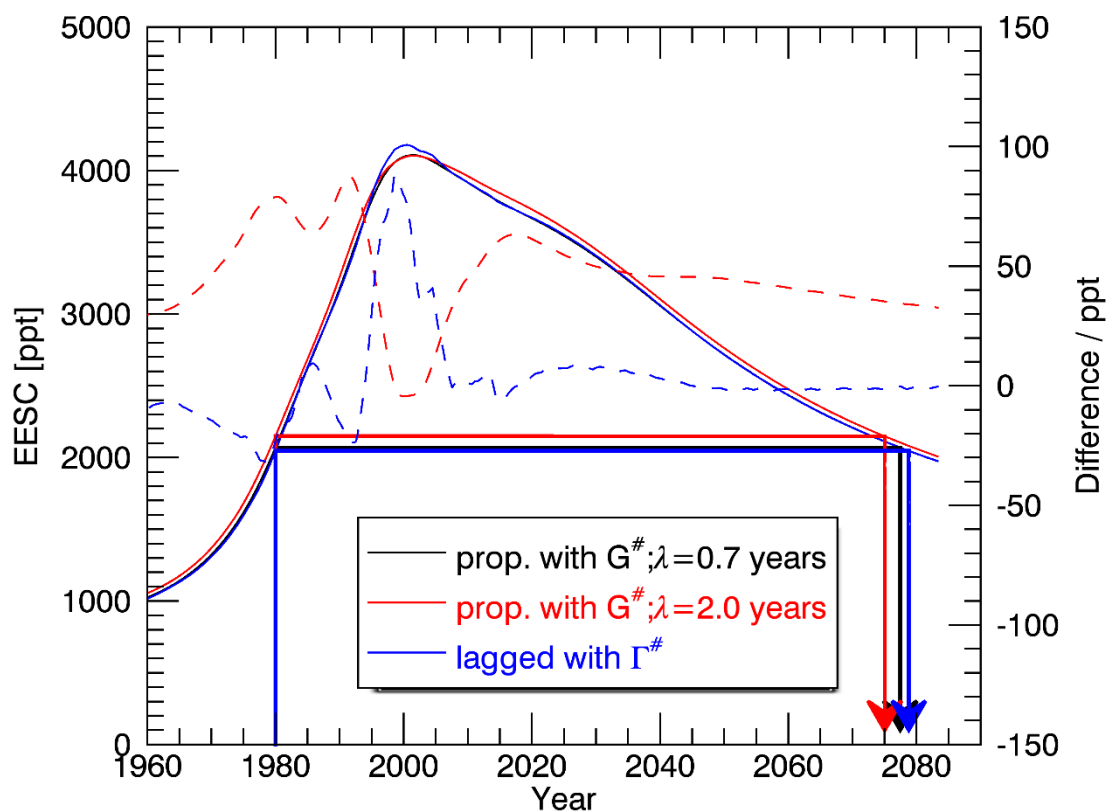
Figure 7: Sensitivity of EESC calculation using the new formulation for a mean age of 5.5 years on the parameterization of the shape of the release time distribution. In two cases the general shape was assumed to be an inverse Gaussian function with different parameterizations of the width Δ, based on different values of $\lambda = \frac{\Delta^2}{\Gamma}$ (see text for an explanation of the parameterization). The case of the pure lag time calculation (blue line) is equal to $\lambda = 0$ years , i.e. the effect of mixing is completely ignored. The calculation using $\lambda = 2$ **years** (red line) represents a case with strong mixing and a broad transit time distribution, while $\lambda = 0.7$ **years** (black line) corresponds to our reference calculation. The influence is largest during the period of the maximum, when tropospheric trends showed a strong non-linear behavior and the tracer propagation strongly depends on the shape of the distribution function. The difference of the calculations to our reference calculation are shown as dashed lines.