A new time-independent formulation of fractional release

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Abstract. The fractional release factor (FRF) gives information on the amount of a halocarbon that is released at some point in the stratosphere from its source form to the inorganic form, which can harm the ozone layer through catalytic reactions. The quantity is of major importance because it directly affects the calculation of the Ozone Depletion Potential (ODP). To apply FRF in this context, steady-state values are needed, thus representing a molecular property for a given atmospheric situation.

5 In particular, these values should be independent of the tropospheric trends of the respective halogenated trace gases.

We analyzed the temporal evolution of FRF from ECHAM/MESSy Atmospheric Chemistry (EMAC) model simulations for several halocarbons and nitrous oxide between 1965–2011 on different mean age levels and found that the current formulation of FRF yields highly time-dependent values. We show that this is caused by the way that the tropospheric trend is handled in the current calculation method of FRF.

10 Taking into account chemical loss in the calculation of stratospheric mixing ratios reduces the time-dependence in correlations of different tracers. Therefore we implemented a loss term in the formulation of FRF and applied the parameterization of a "mean arrival time" to our data set.

We find that the time-dependence in FRF can almost be compensated by applying a new trend correction in the calculation of FRF. We suggest that this new method should be used to calculate time-independent FRF, which can then be used e.g. for

15 the calculation of ODP.

1 Introduction

Ozone depletion in the stratosphere is forced predominantly by chlorine- and bromine-containing substances with anthropogenic sources. The gases are emitted into the troposphere, where many of them are nearly inert before they enter the stratosphere at the tropical tropopause. In the stratosphere, many of the molecules will be photochemically broken down and release

20 halogen radicals that intensify ozone destruction reactions.

The amount of a halocarbon at some point in the stratosphere that is released from the organic (source) into the inorganic (reactive) form is quantified by its fractional release factor (FRF). The quantity was defined by Solomon et al. (1992) as "the fraction of the halocarbon species x injected into the stratosphere that has been dissociated". It can be calculated by comparing the original mixing ratio of a tracer that entered the stratosphere to the mixing ratio that is still left in the stratosphere. The

25 difference of the entry mixing ratio and the stratospheric mixing ratio is equal to the released amount of the species.

When entering the stratosphere at the tropical tropopause, ozone depleting substances (ODS) have a FRF that is close to zero. As they follow the stratospheric circulation, the air parcels get distributed by different transport pathways and pass through their loss regions, where the molecules get dissociated. The FRF increases until it reaches the value of 1 when the ODS is completely depleted.

FRF thus depends on the location in the stratosphere and thus on the time the air mass has spent in the stratosphere. Fractional release is not only sensitive to transport times but also to transport pathways. Once an air parcel has entered the stratosphere, it is distributed by the different branches of the Brewer-Dobson circulation (BDC). Depending on its transport pathway, it experiences different stages of chemical or photolytic loss. An air parcel that travels through the upper part of the stratosphere will suffer stronger photolytic degradation, especially in the tropics, than an air parcel in the lower stratosphere. In this way, the air parcel carries information on both chemical and transport processes via its FRF.

FRF is commonly assumed to be a time-independent quantity, meaning that as long as transport and chemical processes do not change, FRF shows no change and in particular is independent of the tropospheric trend. This is a prerequisite e.g. for its application in the calculation of the Ozone Depletion Potential (ODP), which is a steady state quantity.

For every tracer with changing tropospheric mixing ratios, we need to consider that this trend needs to be corrected for in the way that the FRF for a chemical active species (CAS) is calculated. As different transit pathways contributing to the air parcel are associated with different transit times, the complex interplay between transport and mixing needs to be described correctly for this purpose.

In the current formulation for the calculation of FRF, the transport of a CAS is treated in a similar way as for chemically inert species, which are used to derive mean age of air. However, Plumb et al. (1999) showed that the concepts are only valid for inert tracers, thus not for CAS. In particular, the transit time distribution G and the mean age of air Γ only describe the transport of inert species.

For CAS, the chemical loss during the transport needs to be considered, which leads to a different weighting of different transit pathways and associated transit times. Based on that finding, Plumb et al. (1999) introduced species dependent arrival time distributions (ATD) to characterize the propagation of tracers undergoing chemical loss and with changing tropospheric abundances. This ATD gives less weight to long transit times as the CAS, which were originally in these air parcels, have been photochemically degraded and thus contribute to a lesser extend to the observable remaining fraction of the CAS.

Plumb et al. (1999) used a two dimensional model to calculate the species dependent mean arrival time Γ^*, which is the first moment of the species dependent ATD. A parameterization of Γ^* was then derived, based on mean age and the stratospheric lifetime of the tracers. Plumb et al. (1999) showed that there is a large difference between Γ and Γ^*. Using Γ^* instead of Γ in the calculation of the stratospheric mixing ratio, a much better agreement between detrended correlations from different time periods was achieved.

It is the purpose of this paper to find a steady state formulation for the FRF. This would allow the comparison of measurements from different dates. Especially in the late 1990s many tracers showed rapid changes in their tropospheric trend due to the decline of the substances induced by the regulations of the Montreal Protocol. Thus it is necessary to find a proper

trend correction for the calculation of FRF values, which are used in the determination of the ODP and Effective Equivalent Stratospheric Chlorine (EESC).

In Sect. 2 we present the classical and current calculation methods of FRF. A description of the ECHAM/MESSy Atmospheric Chemistry (EMAC) model and the simulations follows in Sect. 3. We then calculate FRF with the model data (Sect. 4) 5 and show that the current calculation method yields time-dependent values. In Sect. 5 we present a new formulation of FRF and give an overview of the results of the new calculation method in Sect. 6. In the last section we discuss our results.

2   Calculation methods of FRF

The quantity of FRF was first introduced by Solomon and Albritton (1992) as "the fraction of the halocarbon species x injected into the stratosphere that has been dissociated". This can be expressed by the following equation

$$10 \quad f_i(r,t) = \frac{\chi_{i,entry} - \chi_{i,strat}(r,t)}{\chi_{i,entry}}. \tag{1}$$

Herein, $\chi_{i,entry}$ is the mixing ratio of an air parcel when it entered the stratosphere and $\chi_{i,strat}(r,t)$ is the mixing ratio at a certain location and time in the stratosphere. The latter is an observable quantity and can be measured from balloon or aircraft samples. It is influenced by temporal trends in the troposphere, stratospheric loss, and transport and mixing in the stratosphere.

In the classical formulation of FRF, the entry mixing ratio is calculated from the tropospheric time series by estimating the 15 time lag of the tracer mixing ratios between the troposphere and the stratosphere

$$\chi_{i,entry} = \chi_{i,trop}(t - \Gamma), \tag{2}$$

where Γ is the mean age of air, which is the mean time elapsed since the entry of an air parcel at the tropical tropopause.

The concept of age of air (AOA) can be understood as follows: We consider a stratospheric air parcel that consists of infinitesimal fluid elements. These are so small that they cannot exchange components with each other and are thus not influenced by 20 mixing for all timescales of interest (Waugh and Hall, 2002). When entering the stratosphere, the fluid elements get distributed by different transport pathways. If we consider an air parcel at some location r in the stratosphere, it will contain fluid elements with longer and shorter transit times t' depending on the pathway they took. The chemical composition of such an air parcel for a species whose mixing ratio changes with time in the troposphere is thus influenced by a distribution of transit times, the so-called age spectrum, $G(r,t')$ rather than one single transit time (Hall and Plumb, 1994). G describes the probability of a 25 certain transit time since the entry into the stratosphere and is thus influenced by net mass transport and mixing.

As the sum of the probabilities of all transit times must be unity, $G(r,t')$ is normalized so that

$$\int_0^\infty G(r,t')dt' = 1 \tag{3}$$

and the arithmetic mean of the distribution can be calculated by its first moment and is called the mean age of air

$$\Gamma(r) = \int_0^\infty t' G(r,t')dt'. \tag{4}$$

Mean age is not a directly observable quantity but it can be deduced from observations of passive tracers like CO_2 or SF_6 (Schmidt and Khedim, 1991; Hall and Plumb, 1994; Strunk et al., 2000; Engel et al., 2009).

FRFs show compact correlations with mean age of air Γ. Newman et al. (2006) presented FRF as a function of mean age including the age spectrum in the calculation. In this formulation, the entry mixing ratio on a certain age isosurface is calculated

5 by the convolution of the tropospheric time series with the age spectrum

$$\chi_{entry}(r,t) = \int_0^\infty \chi_{trop}(t-t')G(t')dt'. \tag{5}$$

where $\chi_{trop}(t-t')$ represents the mixing ratio at time $t-t'$, thus t' before the observed date.

The entry mixing ratios calculated by Eq. (2) and Eq. (5) coincide, if the species mixing ratio does not depend on time, or in the case of the age spectrum being a delta function at $t = \Gamma$. In the latter case, the stratospheric transport would be without

10 mixing and controlled by uniform advection of all fluid elements in the specific air parcel.

In general, a tracers *stratospheric* mixing ratio $\chi_{strat}(r,t)$ can be formulated via its fractional release factor f if we consider that it is the remaining fraction of the tracer which is not yet dissociated. This fraction f will be a function of the transit pathway and the transit time t'. For simplification, we assume that longer transit pathways will be linked with more chemical loss and longer transit times, thus we consider f to be a function of t' only:

15 $$\chi_{strat}(r,t) = \int_0^\infty \chi_{trop}(t-t')\left(1-f(t')\right)G(r,t')dt'. \tag{6}$$

In the case of an inert tracer, $f(t') = 0$ for all possible transit times and transport pathways. Thus the loss term disappears and we again receive Eq. (5).

If one supposes that f does not depend on time, the factor $(1-f)$ can be extracted from the integral

$$\chi_{strat} = (1-f)\int_0^\infty \chi_{trop}(t-t')G(r,t')dt'. \tag{7}$$

20 We then receive the following equation for the calculation of the fractional release factor

$$f = \frac{\int_0^\infty \chi_{trop}(t-t')G(r,t')dt' - \chi_{strat}}{\int_0^\infty \chi_{trop}(t-t')G(r,t')dt'}. \tag{8}$$

This is the current representation of fractional release, as it is applied by Newman et al. (2007). Subsequently we will refer to it as the "current formulation".

The stratospheric mixing ratio χ_{strat} in Eq. (8) can be deduced from observations or from model data, as well as the

25 tropospheric time series χ_{trop}. The transit time distribution G can be parameterized according to Waugh and Hall (2002).

It was accepted so far that the formulation of the entry mixing ratio according to Eq. (5) is an adequate correction for tropospheric trends. Laube et al. (2010) treated FRFs as a time-independent quantity at least "as long as the general stratospheric circulation and actinic flux spectrum are not changing". Differences in FRF values from different measurement campaigns were attributed to vertical and latitudinal variabilities or could be influenced by uncertainties in the derivation of mean age.

In recent years inconsistencies were identified and it was found that FRF calculated by Eq. (8) are not generally time-independent (Laube et al., 2013). The concept is only valid "as long as there are no major changes in stratospheric transport or relative tropospheric growth rates".

In our opinion, a further explanation for the discrepancy between FRFs derived from different data sets could be the method how the entry mixing ratio was calculated, thus the correction for the tropospheric trend. In particular, the inherent assumption that f is independent of t', which is needed to derive Eq. (8) is certainly an oversimplification. Errors in this calculation will lead to differences in the FRF derived, especially if data from different time periods are compared, where trends differ in magnitude and sometimes even in the direction (positive/ negative trend).

We therefore analyzed the temporal evolution of FRF in model data to evaluate, whether the approach of Eq. (8) really produces time-independent values. The EMAC model and the related simulations will be presented in the next section before we show first results of the FRF calculations.

3   The EMAC Model

The ECHAM/MESSy Atmospheric Chemistry (EMAC) model is a numerical chemistry and climate simulation system that includes submodels describing tropospheric and middle atmosphere processes and their interaction with oceans, land and human influences (Jöckel et al., 2006). It uses the second version of the Modular Earth Submodel System (MESSy2) to link multi-institutional computer codes. The core atmospheric model is the 5th generation European Centre Hamburg general circulation model (ECHAM5, Roeckner et al. (2006)). For the present study we applied EMAC (ECHAM5 version 5.3.02, MESSy version 2.51) in the T42L90MA-resolution, i.e. with a spherical truncation of T42 (corresponding to a quadratic Gaussian grid of approximately 2.8 by 2.8 degrees in latitude and longitude) with 90 vertical hybrid pressure levels up to 0.01 hPa.

3.1   Simulations

In this study we analyse a reference simulation performed by the Earth System Chemistry integrated Modelling (ESCiMo) initiative (Jöckel et al., 2016). The simulation RC1-base-07 is a free-running hindcast simulation from 1950 to 2011. It is forced by prescribed sea surface temperatures (SSTs) and sea ice concentrations (SICs) merged from satellite and in-situ observations. The initialization of the simulation starts in January 1950 and is followed by a spin-up period of 10 years. Therefore we will analyze the data after 1965.

The model uses observed surface mixing ratios for boundary conditions that were taken from the Advanced Global Atmospheric Gases Experiment (AGAGE, http://agage.eas.gatech.edu) and the National Oceanic and Atmospheric Administration/ Earth System Research Laboratory (NOAA/ESRL, http://www.esrl.noaa.gov).

An important point in the model set-up is the additional implementation of idealized tracers with mixing ratios relaxed to $\chi_{trop} = 1$ ppt in the lowest model layer above the surface. These idealized tracers have no tropospheric trend but the chemical kinetics in the stratosphere follow the same mechanisms as for realistic tracers. However, there is no feedback of these tracers

into the chemistry, radiation or dynamics of the model. For all tracers, the chemistry is controlled by the submodel MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere, Sander et al. (2011)) and the photolysis rate coefficients are calculated by the submodel JVAL (Sander et al., 2014).

Idealized tracers with constant tropospheric mixing ratios have been implemented for the halocarbons CFC-11 ($CFCl_3$),

5   CFC-12 (CF_2Cl_2), methyl chloroform (CH_3CCl_3), Halon 1211 (CF_2ClBr) and Halon 1301 (CF_3Br), as well as for nitrous oxide (N_2O).

A detailed description of ECHAM/ MESSy development cycle 2 can be found in Jöckel et al. (2016), and references therein.

4   Time-dependence of FRF in EMAC simulations

FRFs are often analyzed as a function of mean age of air Γ (Schauffler et al., 2003). Figure 1 shows as an example the

10   correlations of the FRF of nitrous oxide and methyl chloroform with mean age of air using monthly mean EMAC model data and the current calculation method (cf. Eq. (8)). The correlations are compact, but not time-independent. Especially for methyl chloroform there are large differences in the correlations depending on the year. This is a first hint that there is a time-dependence in the current representation of FRF.

There may be several reasons for this time-dependency. On the one hand, changes in the stratospheric circulation or chemistry

15   could cause changes in the correlations, on the other hand it is possible that the tropospheric trend of the species has an impact on the correlations.

In order to separate the two possible effects from each other, we make use of the idealized tracers described in Sect. 3.1. These tracers have nearly constant mixing ratios of 1 ppt throughout the troposphere, but in the stratosphere they experience the same transport and chemical depletion mechanisms as the realistic tracers. The FRF of the idealized tracers can easily be

20   calculated by Eq. (1) with $\chi_{i,entry} =1$ ppt. FRF calculated by the idealized tracers gives a very good proxy of a quasi steady state value of FRF in the model.

We study the temporal behavior of zonal mean FRF values derived from monthly mean data on the constant mean age of air surfaces $\Gamma = 2$ yr, 3 yr and 4 yr in the northern hemisphere mid-latitudes between 32° N and 51° N. In this latitude band several observations were analyzed by Laube et al. (2013). In order to avoid possible spin-up effects, the analysis is restricted

25   to data after 1965.

On older mean age of air surfaces we find higher FRF values, which is reasonable, because older air has had more time to travel through the photochemical loss regions than younger air. The value of FRF depends on the species and their photolytic lifetimes. CFC-12 (CF_2Cl_2) and nitrous oxide (N_2O) are long-lived with a similar stratospheric lifetime of 95.5 yr and 116 yr respectively (Ko et al., 2013). Even on the 4 yr age isosurface about half of the original amount remains in the organic form.

30   In contrast, CFC-11 ($CFCl_3$) and methyl chloroform (CH_3CCl_3) are shorter-lived with stratospheric lifetimes of 57 yr and 37.7 yr respectively (Ko et al., 2013). These species are largely depleted on the 4 yr age isosurface with FRF values of around 0.8.

We notice a seasonality in FRF, which can be explained by seasonal variations in transport and mixing. These are stronger in the upper stratosphere, due to shorter local lifetimes. Beside this, we can see that the FRFs for idealized tracers only slightly

vary with time. The increase of FRF is in the order of about 5 % per decade, which is in agreement to Li et al. (2012), who analyzed changes in FRF in the Goddard Earth Observing System Chemistry-Climate Model (GEOSCCM). These changes are consistent with an an acceleration of the Brewer-Dobson Circulation due to climate change, which is found in EMAC calculations consistent with most other models. A stronger circulation leads to a faster transport of air parcels to their loss

5 regions and thus to an increased FRF on a given mean age level. Nevertheless, the FRF of the idealized tracers can be assumed to be a good proxy for a quasi steady state value in the model, as they are not influenced by tropospheric trends. To analyze the realistic tracers (with tropospheric trend), we need to solve Eq. (8) and make some assumptions on the tropospheric time series and the shape of the age spectrum. Calculating the entry mixing ratio in the current FRF formulation, Eq. (5) is integrated 30 years back in time. This is necessary to correct for the influence of the troposphere on the stratosphere. The tropospheric

10 time series before 1950 can be taken from the RCP6.0 scenario (Meinshausen et al., 2011). For most of the considered tracers the mixing ratio before 1950 was close to zero, except for the nearly linearly increasing tracer nitrous oxide (N_2O). N_2O is increasing very slowly and nearly constantly by 0.8 ppb/ yr. The tropospheric mixing ratios of N_2O before 1950 are assumed to decrease by the same magnitude.

In this study we use an inverse Gaussian function for the transit time distribution G with a constant ratio of the squared

15 width to mean age of $\Delta^2/\Gamma = 0.7$ according to Hall and Plumb (1994) and as used in previous studies (Engel et al., 2002). This parameterization can be used throughout most of the stratosphere, but varies between stratospheric models (Waugh and Hall, 2002).

The temporal evolution of the FRF of the realistic tracers is analyzed on the same latitude band and AOA surfaces as for the idealized tracers. The results can be seen in Fig. 3. The colored lines in Fig. 3 show the results of the FRF calculation for

20 realistic tracers according to the current formulation. The results of the idealized tracers are plotted in solid black lines and the tropospheric trends are added by dashed black lines.

We can divide the results for tracers with a weak and a strong tropospheric trend.

For N_2O, which has a very small linear tropospheric trend of about only 0.2 %/yr, the realistic and the idealized tracer are in good agreement, which means that the current formulation of FRF works well as long as the trends are small.

25 The situation is different, if we consider the anthropogenically emitted chlorofluorocarbons and methyl chloroform, which had strong trends in the 1980s (growth rate 3.7 %/yr, Albritton et al. (1995)) and phased out in the 1990s due to the Montreal Protocol. For those tracers, the FRF is strongly time-dependent and obviously depends on the tropospheric trends of the species: In times of positive trends (before 1995), FRF is underestimated in comparison to the idealized tracer. For methyl chloroform, whose positive trend is followed by a strong negative trend since the middle of the 1990s, we notice that the FRF

30 is overestimated during the period of the negative trend compared to the idealized tracer. The chlorofluorocarbons CFC-11 and CFC-12 have a much weaker negative trend due to their longer stratospheric lifetimes. Here, we do not notice an overestimation of FRF during the negative trend period.

To sum up, our model experiments show that the tropospheric trend influences the current FRF calculation and imposes a time-dependence. This time-dependence could also explain the differences between FRF values deduced from measurements at

35 different dates. If we for instance compare CFC-12 data on the 3 yr isosurface in 1980 and in 2000, there is an increase of about

50 % on the FRF value (see Fig. 3). The result of the calculation cannot be regarded as a steady state value and the possible change due to variations in the stratospheric circulation cannot explain this magnitude of the difference (see idealized tracers). Therefore, we conclude that it is caused by an incomplete correction of tropospheric trends and develop a new formulation of FRF in the following section.

5   A new formulation of FRF

We consider the propagation of a CAS with solely tropospheric sources into the stratosphere. Air parcels enter the stratosphere at the tropical tropopause. In the stratosphere, the CAS gets distributed by the meridional overturning circulation (Brewer-Dobson circulation), which includes residual circulation and mixing. During this transport, the CAS will also be chemically depleted by sunlight or radicals. The mixing ratio of the CAS at a certain location in the stratosphere is thus influenced by different factors like the temporal trend in the troposphere, transport and mixing in the stratosphere, as well as loss processes.

The effect of transport is described by the transit time distribution $G(r,t)$, which is a function of transit time t' and the location in the stratosphere r. The transit time distribution is also often referred to as the "age spectrum" because it is a probability density function of the age of each fluid element in the air parcel since it entered the stratosphere. The age spectrum describes both residual circulation and mixing.

The mixing ratio of an inert tracer in the stratosphere can then be calculated by the convolution of the age spectrum and the tropospheric time series χ_{trop}, which describes the changing abundances of the tracer in the troposphere that propagate into the stratosphere. Hence, we receive Eq. (5) for the determination of the entry mixing ratio, as discussed in Sect. 2.

This equation will be valid throughout the stratosphere only for an inert tracer. For CAS we also need to take into account that the tracer will be depleted during its propagation through the loss regions. Using a 2D chemical transport model, Plumb et al. (1999) showed that the chemical loss modifies the transit time distribution for each CAS in a different way. Strongest modifications were calculated for the species with shortest stratospheric lifetimes.

In general, the fraction of a species which has been released from its source gas will increase with time, especially the time spent in the loss region. For simplicity we therefore assume that FRF will only be a function of the time spent in the stratosphere. The different fractional losses for different pathways are ignored in this approach, following the "average lagrangian path" concept proposed by Schoeberl et al. (2005).

As shown in Eq. (6), the stratospheric mixing ratio of a CAS can then be expressed in the following way

$$\chi_{strat}(r,t) = \int\limits_{0}^{\infty} \chi_{trop}(t-t')\,(1-f(t'))\,G(r,t')dt'. \tag{9}$$

Within this formulation of the stratospheric mixing ratio, we can define a new loss weighted distribution function G^*, which combines G with the chemical loss term $(1-f(t'))$:

$$G^*(r,t') \equiv (1-f(t'))\,G(r,t'). \tag{10}$$

We will refer to G^* as the arrival time distribution, as it represents the distribution of arrival times of molecules, which have not been photochemically degraded.

The arrival time distribution G^* is only normalized for inert tracers without chemical loss. In this case, the loss term $f(t')$ disappears in Eq. (9) and the arrival time distribution coincides with the age spectrum $G^* = G$.

5   In general it satisfies the relation

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

For this reason we define a normalized arrival time distribution G_N^* by normalizing G^*

$$G_N^*(r,t') = \frac{G^*(r,t')}{\int_0^\infty G^*(r,t')dt'} \tag{12}$$

so that

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

with a corresponding mean arrival time Γ^* that can be calculated from the first moment of G_N^*

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

We now solve the integral over G^*

$$\int_0^\infty G^*(r,t')dt' = \int_0^\infty (1-f(t'))\, G(r,t')dt' = \int_0^\infty G(r,t')dt' - \int_0^\infty f(t')G(r,t')dt' = 1 - \bar{f} \tag{15}$$

15   with $\bar{f}$ being the first moment of the probability density function of all fractional releases, thus the arithmetic mean or average fractional release.

Replacing the integral in (12) with (15) yields

$$G_N^*(r,t') = \frac{G^*(r,t')}{(1-\bar{f})}. \tag{16}$$

Solving (16) for G^* and inserting this relation into (10) yields

20    $$G_N^*(r,t')\left(1-\bar{f}\right) = (1-f(t'))\, G(r,t'), \tag{17}$$

and inserting in (9) yields

$$\chi_{strat}(r,t) = \int_0^\infty \chi_{trop}(t-t')\left(1-\bar{f}\right) G_N^*(r,t')dt' = \left(1-\bar{f}\right)\int_0^\infty \chi_{trop}(t-t')G_N^*(r,t')dt'. \tag{18}$$

Note that in this formulation $\bar{f}$ is a constant and can thus be extracted from the integral.

From this equation we can now calculate the mixing ratio of a chemical active tracer at any location and time in the stratosphere. Presupposed that the tropospheric time series, the FRF and the arrival time distribution are known. The other way around it is possible to infer steady state FRFs $\bar{f}$ from Eq. (18).

This can be done by simply rearranging Eq. (18) and solving for $\bar{f}$

$$\bar{f} = \frac{\int_0^\infty \chi_{trop}(t-t') G_N^*(r,t') dt' - \chi_{strat}(r,t)}{\int_0^\infty \chi_{trop}(t-t') G_N^*(r,t') dt'}. \tag{19}$$

We interpret $\bar{f}$ as the mean fractional release factor on a given age isosurface. It corresponds to a quasi steady state value. Of course, FRF still depends on the mean age of air, which gives information on how long the air parcel is already located in the stratosphere. In addition, by using the arrival time distribution, the effect of chemical loss is taken into account.

The calculation of this expression requires the knowledge of the normalized arrival time distribution $G_N^*(r,t)$. Following Plumb et al. (1999), we call the first moment of this distribution the "mean arrival time" Γ^* which takes into account the chemical loss of the species. A possible parameterization of Γ^* was described by Plumb et al. (1999). It was received from a normalization scheme within a 2-D chemical transport model. Γ^* is a substance specific quantity and depends on mean age and the stratospheric lifetime of the tracers. In the following section we test the new formulation of $\bar{f}$ by applying it to EMAC model data. We compare the results to the current formulation of FRF.

6 Results of the new formulation

To use the FRF in the calculation of ODP and EESC a trend independent formulation is necessary. Thus we apply our new formulation Eq. (19) which includes chemical loss to the same data set as for the analysis of the current FRF formulation presented in Sect. 4. This means we examine the temporal evolution of FRF on the same latitude band and age of air isosurfaces.

To solve Eq. (18) it is necessary to find a good description of G_N^*. A parameterization of the first moment of the distribution is given by Plumb et al. (1999), for a wide range of species and in addition as a function of the stratospheric lifetime. With respect to the shape of the distribution we have chosen to use the same shape as for G, i.e. an inverse Gaussian distribution with the width Δ of $\Delta^2/\Gamma^* = 0.7$ yr.

The result of the new calculation according to Eq. (19) can be seen in Fig. 4. We clearly notice the improvement of the new calculation method. The tropospheric trend of the species is almost corrected for and FRF values for the idealized and the realistic tracers show a much better agreement.

In contrast to the current formulation (cf. Fig. 3), FRF is slightly overestimated compared to the idealized tracer in times of positive trends for CFC-12 (CF_2Cl_2) and methyl chloroform (CH_3CCl_3). For CFC-11 ($CFCl_3$), the FRF according to the new formulation is somewhat underestimated on the 2 and 3 yr age isosurface but fits the idealized tracer well on the 4yr age isosurface. Furthermore, the FRF of methyl chloroform is underestimated when tropospheric mixing ratios are declining. The reason for this feature is a too large correction between Γ and Γ^*.

As we would expect, the fractional release of N_2O is nearly unaffected by the new calculation method, because of its small tropospheric trend. For CFC-11 and CFC-12 there are still small deviations between the realistic and the idealized tracer but the steady state value is reached much earlier than in the current formulation and overall the differences are much smaller. Indeed, we do expect species and age dependent differences in the results, as the same parameterization is used to derive Γ^* from Γ for all mean age values and different parameters are used for different species.

The largest change can be seen for methyl chloroform, which is the analyzed substance with the largest variation in the tropospheric trend. The realistic tracer now approaches the idealized tracer and we can see the improvement especially for the highest considered age isosurface ($\Gamma = 4$ yr) in comparison to the current formulation of FRF used in Fig. 3.

To sum up, we conclude that including chemical loss into the calculation reduces the time-dependence of the FRF value substantially. The parameterization of loss was adopted from Plumb et al. (1999) who derived the parameterization from a simple 2D model. It could still be improved to obtain an even better adaption to the idealized tracer. Besides this, we also kept an inverse Gaussian distribution with a similar parameterization as for mean age, which might not be the optimal choice for the new arrival time distribution.

7 Summary and discussion

In this paper we presented a study on fractional release factors (FRF) and their time-dependence. We analyzed the temporal evolution of FRF between 1965 and 2011 for the halocarbons CFC-11, CFC-12 and methyl chloroform, as well as for nitrous oxide. FRF is often treated to be a steady state quantity, which is a necessary assumption to use it in the calculation of ODP and EESC. In the current formulation of FRF, the transit time distribution and the tropospheric time series of the substances are taken into account, but the coupling between trends, chemical loss and transit time distribution is not included.

For chemical active species, the fraction of the air with very long transit times (the "tail" of the transit time distribution) will have passed the chemical loss region and therefore only contributes very little to the remaining organic fraction, but is to a large degree in the inorganic form. On the other hand, the fraction of the air with short transit times will be to a large degree still in the form of the organic source gas, as it has not been transported to the chemical loss region. This must be taken into account when folding the transit time distribution with the tropospheric time series to derive the fraction still residing in the organic (source) form. For this we used an arrival time distribution, based on the concept and parameterization suggested by Plumb et al. (1999).

We applied the two FRF calculation methods (current and new) on EMAC model data and studied the differences. For both methods we used exemplarily (but without loss of generality) zonally averaged monthly mean stratospheric mixing ratios in a latitude band between 32° N and 51° N.

A special feature of the used model simulation are the implemented idealized tracers with nearly constant tropospheric mixing ratios. We showed that the use of the new formulation of the propagation of chemical active species with tropospheric trends into the stratosphere results in FRF values, which are to a large degree independent of the tropospheric trend of the

respective trace gas and thus gives a quasi steady state value of FRF. This is shown by a much better agreement with the FRF of the idealized tracers, which have no tropospheric trend.

In contrast, the classical approach yields FRF values that depend on tropospheric trends, which change with time. This might be an explanation for the discrepancies between FRF values deduced from observations at different dates. The reason for the non steady behavior is obviously based on an incomplete trend correction. In times of strong tropospheric trends, the realistic tracers deviate most from the idealized tracers. On the other hand, the FRF of the realistic N_2O tracer hardly differs from the idealized tracer, because it has a very small tropospheric trend.

To include chemical loss into the transit time distribution, we applied the parameterization described by Plumb et al. (1999). Using the new formulation of the stratospheric mixing ratio (with loss) we constructed a new expression of the FRF and validated it with EMAC data.

The newly calculated FRF values fit well to the results of the idealized steady state tracers and the influence of the tropospheric trend can almost completely be corrected. This is remarkable, because we have to keep in mind that the parameterization was derived from a completely different and independent 2D model and that we used the same shape parameters as for the classical age spectrum.

We suggest to use the new formulation and reassess former FRF data. Especially FRF values calculated from observations at times of strong tropospheric trends will profit from the new calculation method. Many fully halogenated CFCs showed strong trends prior to 1990, while many HCFCs still show very strong positive trends. This implies that FRF values currently used for HCFCs are likely to be underestimated, which would lead to an underestimation of their ODP values.

We suggest that this new method should be refined by calculating the arrival time distributions in state-of-the-art models and deriving parameterizations from these models. These new methods should be tested by including idealized tracers in the same models and subsequently be applied to observations, which have been used to derive FRF values. Using these new FRF values, a reassessment of ODP values for halogenated source gases and also a re-evaluation of temporal trends of EESC are necessary.

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References

Albritton, D. L., Watson, R., and Aucamp, P.: Scientific assessment of ozone depletion: 1994, 1995.

Engel, A., Strunk, M., Müller, 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 CO2 and SF6, Journal of Geophysical Research: Atmospheres, 107, ACH 1–1–ACH 1–11, doi:10.1029/2001JD000584, http://dx.doi.org/10.1029/2001JD000584, 2002.

Engel, A., Möbius, T., Bönisch, H., Schmidt, U., Heinz, R., Levin, I., Atlas, E., Aoki, S., Nakazawa, T., Sugawara, S., et al.: Age of stratospheric air unchanged within uncertainties over the past 30 years, Nature Geoscience, 2, 28–31, 2009.

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

Jöckel, P., Tost, H., Pozzer, A., Brühl, C., Buchholz, J., Ganzeveld, L., Hoor, P., Kerkweg, A., Lawrence, M., Sander, R., Steil, B., Stiller, G., Tanarhte, M., Taraborrelli, D., van Aardenne, J., and Lelieveld, J.: The atmospheric chemistry general circulation model ECHAM5/MESSy1: consistent simulation of ozone from the surface to the mesosphere, Atmospheric Chemistry and Physics, 6, 5067–5104, doi:10.5194/acp-6-5067-2006, http://www.atmos-chem-phys.net/6/5067/2006/, 2006.

Jöckel, P., Tost, H., Pozzer, A., Kunze, M., Kirner, O., Brenninkmeijer, C. A. M., Brinkop, S., Cai, D. S., Dyroff, C., Eckstein, J., Frank, F., Garny, H., Gottschaldt, K.-D., Graf, P., Grewe, V., Kerkweg, A., Kern, B., Matthes, S., Mertens, M., Meul, S., Neumaier, M., Nützel, M., Oberländer-Hayn, S., Ruhnke, R., Runde, T., Sander, R., Scharffe, D., and Zahn, A.: Earth System Chemistry integrated Modelling (ESCiMo) with the Modular Earth Submodel System (MESSy) version 2.51, Geoscientific Model Development, 9, 1153–1200, doi:10.5194/gmd-9-1153-2016, http://www.geosci-model-dev.net/9/1153/2016/, 2016.

Ko, M., Newman, P., Reimann, S., Strahan, S., Plumb, R., Stolarski, R., Burkholder, J., Mellouki, W., Engel, A., Atlas, E., et al.: Lifetimes of stratospheric ozone-depleting substances, their replacements, and related species, SPARC Report, 2013.

Laube, J. C., Engel, A., Bönisch, H., Möbius, T., Sturges, W. T., Braß, M., and Röckmann, T.: Fractional release factors of long-lived halogenated organic compounds in the tropical stratosphere, Atmospheric Chemistry and Physics, 10, 1093–1103, doi:10.5194/acp-10-1093-2010, http://www.atmos-chem-phys.net/10/1093/2010/, 2010.

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, Atmospheric Chemistry and Physics, 13, 2779–2791, doi:10.5194/acp-13-2779-2013, http://www.atmos-chem-phys.net/13/2779/2013/, 2013.

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, 2012.

Meinshausen, M., Smith, S. J., Calvin, K., Daniel, J. S., Kainuma, M. L. T., Lamarque, J.-F., Matsumoto, K., Montzka, S. A., Raper, S. C. B., Riahi, K., Thomson, A., Velders, G. J. M., and van Vuuren, D. P.: The RCP greenhouse gas concentrations and their extensions from 1765 to 2300, Climatic Change, 109, 213–241, doi:10.1007/s10584-011-0156-z, http://dx.doi.org/10.1007/s10584-011-0156-z, 2011.

Newman, P. A., Nash, E. R., Kawa, S. R., Montzka, S. A., and Schauffler, S. M.: When will the Antarctic ozone hole recover?, Geophysical Research Letters, 33, n/a–n/a, doi:10.1029/2005GL025232, http://dx.doi.org/10.1029/2005GL025232, 112814, 2006.

Newman, P. A., Daniel, J. S., Waugh, D. W., and Nash, E. R.: A new formulation of equivalent effective stratospheric chlorine (EESC), Atmospheric Chemistry and Physics, 7, 4537–4552, doi:10.5194/acp-7-4537-2007, http://www.atmos-chem-phys.net/7/4537/2007/, 2007.

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, 11 723–11 732, doi:10.1029/1999JD900014, http://dx.doi.org/10.1029/1999JD900014, 1999.

Roeckner, E., Brokopf, R., Esch, M., Giorgetta, M., Hagemann, S., Kornblueh, L., Manzini, E., Schlese, U., and Schulzweida, U.: Sensitivity of simulated climate to horizontal and vertical resolution in the ECHAM5 atmosphere model, J. Clim., 19, 3771–3791, 2006.

5 Sander, R., Baumgaertner, A., Gromov, S., Harder, H., Jöckel, P., Kerkweg, A., Kubistin, D., Regelin, E., Riede, H., Sandu, A., Taraborrelli, D., Tost, H., and Xie, Z.-Q.: The atmospheric chemistry box model CAABA/MECCA-3.0, Geoscientific Model Development, 4, 373–380, doi:10.5194/gmd-4-373-2011, http://www.geosci-model-dev.net/4/373/2011/, 2011.

Sander, R., Jöckel, P., Kirner, O., Kunert, A. T., Landgraf, J., and Pozzer, A.: The photolysis module JVAL-14, compatible with the MESSy standard, and the JVal PreProcessor (JVPP), Geoscientific Model Development, 7, 2653–2662, doi:10.5194/gmd-7-2653-2014, http://
10 www.geosci-model-dev.net/7/2653/2014/, 2014.

Schauffler, S. M., Atlas, E. L., Donnelly, S. G., Andrews, A., Montzka, S. A., Elkins, J. W., Hurst, D. F., Romashkin, P. A., 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, n/a–n/a, doi:10.1029/2001JD002040, http://dx.doi.org/10.1029/2001JD002040, 4173, 2003.

15 Schmidt, U. and Khedim, A.: In situ measurements of carbon dioxide in the winter Arctic vortex and at midlatitudes: An indicator of the 'age' of stratopheric air, Geophysical Research Letters, 18, 763–766, 1991.

Schoeberl, M. R., Douglass, A. R., Polansky, B., Boone, C., Walker, K. A., and Bernath, P.: Estimation of stratospheric age spectrum from chemical tracers, Journal of Geophysical Research: Atmospheres, 110, n/a–n/a, doi:10.1029/2005JD006125, http://dx.doi.org/10.1029/2005JD006125, d21303, 2005.

20 Solomon, S. and Albritton, D. L.: Time-dependent ozone depletion potentials for short-and long-term forecasts, Nature, 357, 33–37, 1992.

Solomon, S., Mills, M., Heidt, L. E., Pollock, W. H., and Tuck, A. F.: On the evaluation of ozone depletion potentials, Journal of Geophysical Research: Atmospheres, 97, 825–842, doi:10.1029/91JD02613, http://dx.doi.org/10.1029/91JD02613, 1992.

Strunk, M., Engel, A., Schmidt, U., Volk, C., Wetter, T., Levin, I., and Glatzel-Mattheier, H.: CO2 and SF6 as stratospheric age tracers: Consistency and the effect of mesospheric SF6-loss, Geophysical research letters, 27, 341–344, 2000.

25 Waugh, D. and Hall, T.: AGE OF STRATOSPHERIC AIR: THEORY, OBSERVATIONS, AND MODELS, Reviews of Geophysics, 40, 1–1–1–26, doi:10.1029/2000RG000101, http://dx.doi.org/10.1029/2000RG000101, 1010, 2002.
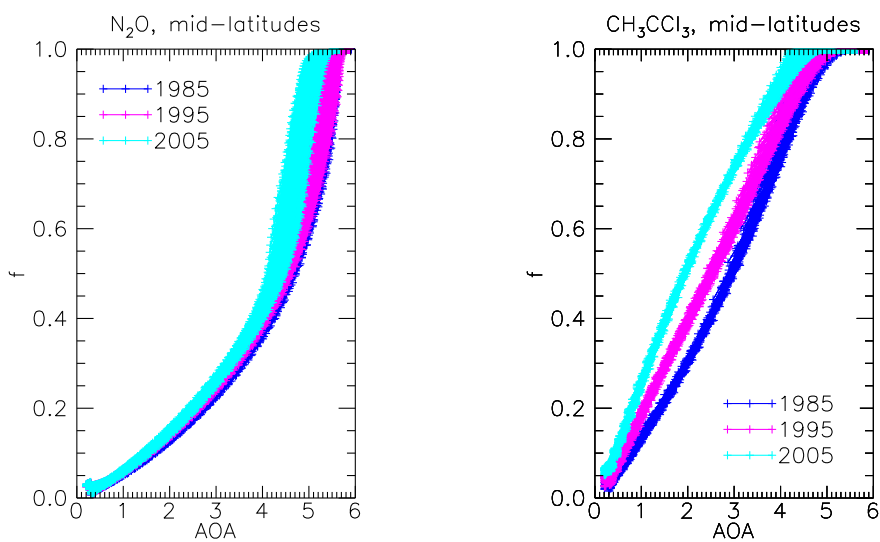
Figure 1. Fractional release (f) as a function of mean age of air (AOA) in the mid-latitudes between 32° N and 51° N for nitrous oxide (left) and methyl chloroform (right) derived from monthly mean EMAC model data. The FRF was calculated by the current formulation for different dates. It can be observed that the correlations vary with time.
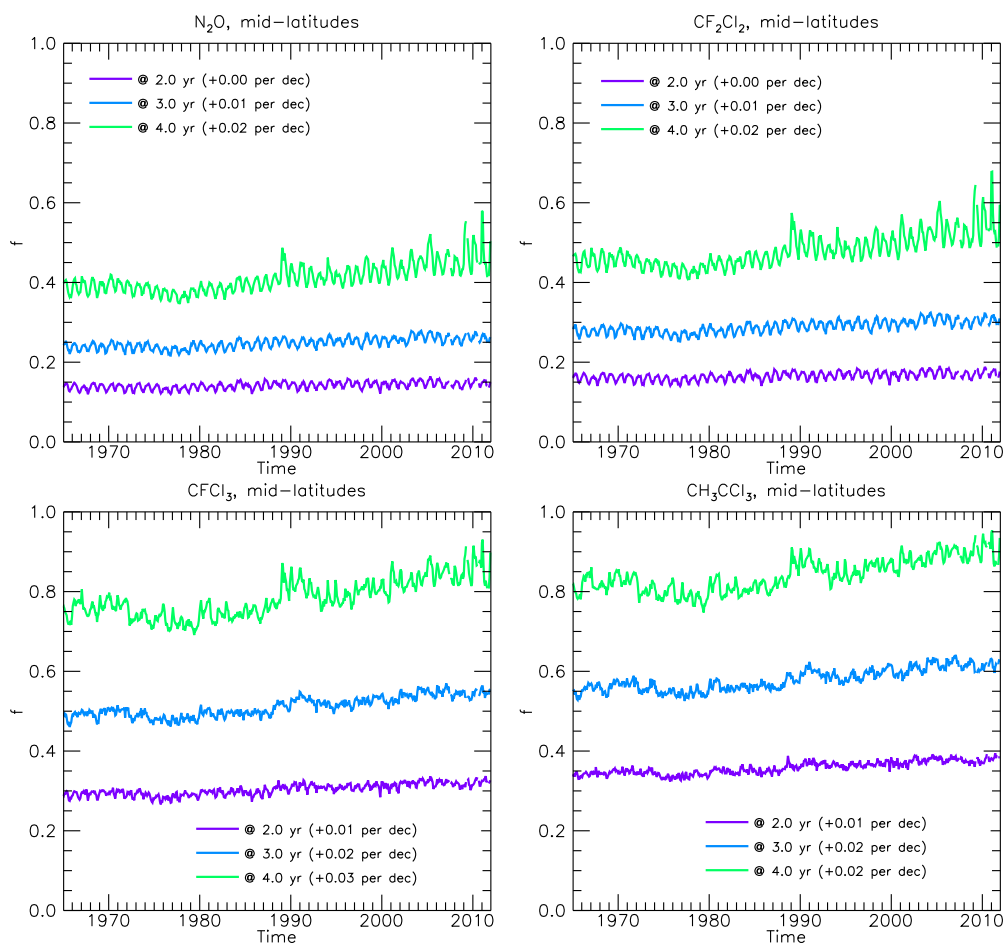
Figure 2. FRF calculated from the idealized tracers (without tropospheric trends) of the EMAC model in the mid-latitudes between 32° N and 51° N. The FRF is calculated on the 2 (purple), 3 (blue) and 4 yr (green) age isosurface. The absolute change of FRF per decade is noted in parentheses.
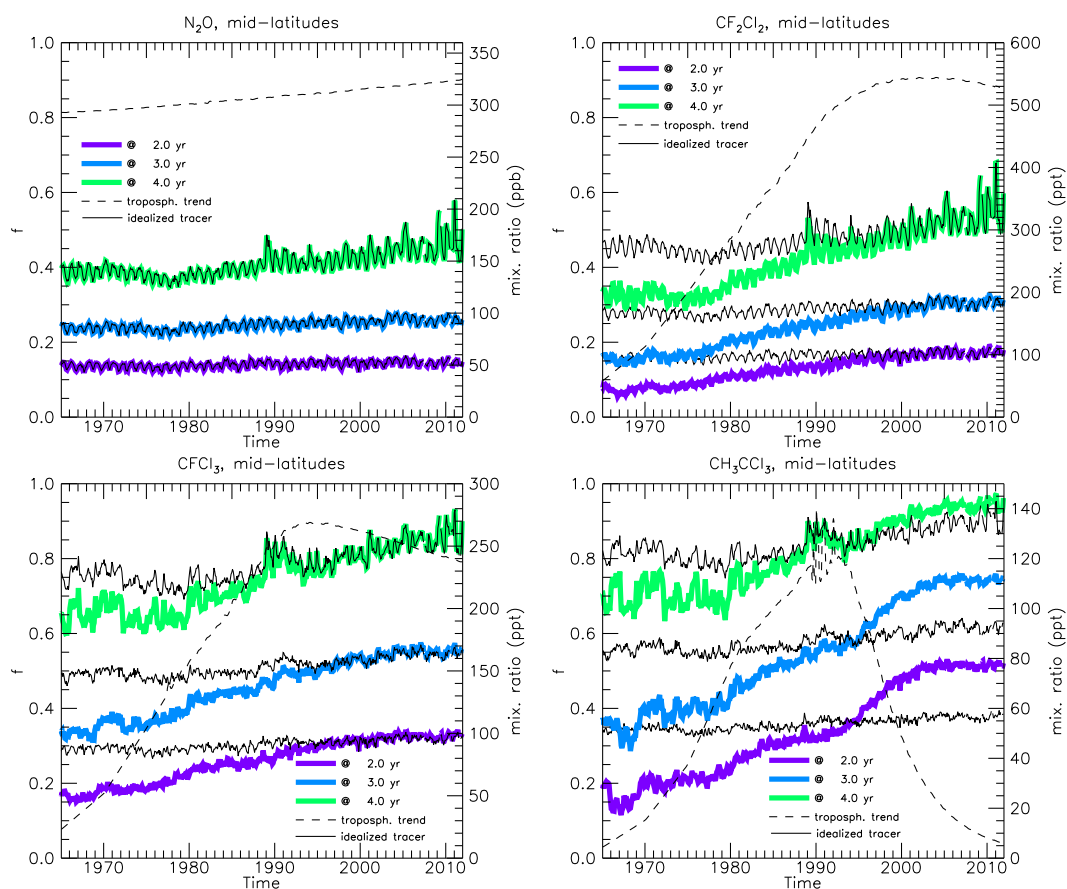
Figure 3. Temporal evolution of FRF calculated by the current formulation. Results for the realistic tracers are shown in color. The results for the idealized tracers (cf. Fig. 2) are shown as black lines for comparison. The related tropospheric trend of the species is plotted in dashed lines over the entire range in order to compare the magnitudes. There are obvious deviations between realistic and idealized tracers that depend on the tropospheric trends of the species (see text for explanation).
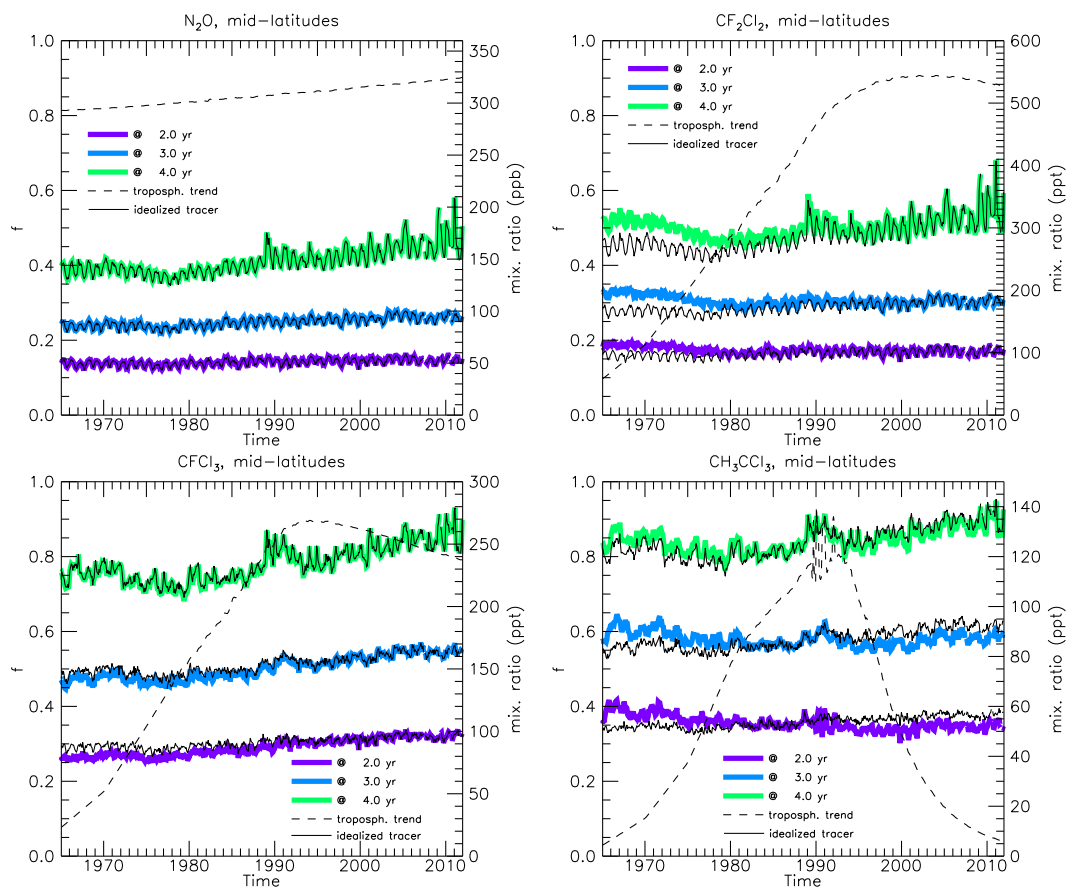
Figure 4. Temporal evolution of FRF calculated by the new formulation, taking into account chemical loss. The results of the realistic tracers are shown in color on different age isosurfaces. The results of the idealized tracers are shown in solid black lines whereas the tropospheric trend is plotted in dashed lines. We find a much better agreement between idealized and realistic tracers compared to the current formulation of FRF (cf. Fig. 3).