Atmos. Chem. Phys. Discuss., 9, 20283–20307, 2009
www.atmos-chem-phys-discuss.net/9/20283/2009/

Atmospheric Chemistry and Physics Discussions

This discussion paper is/has been under review for the journal *Atmospheric Chemistry and Physics (ACP)*. Please refer to the corresponding final paper in *ACP* if available.

Fractional release factors of long-lived halogenated organic compounds in the tropical stratosphere

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Received: 28 August 2009 – Accepted: 11 September 2009 – Published: 28 September 2009

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Fractional release factors (FRFs) of organic trace gases are time-independent quantities that influence the calculation of Global Warming Potentials and Ozone Depletion Potentials. We present the first set of vertically resolved FRFs for 15 long-lived halocarbons in the tropical stratosphere up to 34 km altitude. They were calculated from measurements on air samples collected on board balloons and a high altitude aircraft. We compare the derived dependencies of FRFs on the mean stratospheric transit times (the so-called mean ages of air) with similarly derived FRFs originating from measurements at higher latitudes and find significant differences. Moreover a comparison with averaged FRFs currently used by the World Meteorological Organisation revealed the latter to be imprecise measures due to their observed vertical and latitudinal variability. The presented data set could thus be used to improve future ozone level and climate projections.

1 Introduction

Many halocarbons are strong greenhouse gases and/or are able to enhance the catalytic decomposition of ozone. Moreover, the chemical composition of the stratosphere interacts with its radiative balance and the distribution and abundance of ozone (e.g. Brasseur and Solomon, 1986). The tropical stratosphere is very important for the climate of this planet – e.g. most of the ozone is produced there. Thus it is important to quantify the vertical distributions of halocarbons in this atmospheric region.

Very few measurements of halocarbons in the tropical stratosphere have been performed (e.g. Goldan et al., 1980; Schauffler et al., 1993, 1999; Volk et al., 1997; Laube et al., 2008). Due to the elevated tropopause in the tropics (between about 15 and 18 km depending on the meteorological conditions) aircraft-based investigations such as those of Volk et al. (1997) and Schauffler et al. (1999) were only able to investigate the lower stratosphere there (up to 21 km). Satellite instruments provide only limited

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precision and/or vertical resolution and have also not been able to quantify many halocarbons up to now (e.g. Moore and Remedios, 2008; Allen et al., 2009; Rinsland et al., 2009). Thus whole-air-samples collected on board balloons, which reach high altitudes up to 38 km represent a unique opportunity for high precision middle stratospheric measurements.

A fractional release factor (FRF) is a relative quantity. It can be described as the inorganic halogen fraction released from a halocarbon at a given location and time in the stratosphere. It is time-independent as long as the general stratospheric circulation and actinic flux spectrum are not changing. For a FRF calculation according to Eq. (1) (taken from Daniel and Velders, 2007) two quantities must be known: the mixing ratio of a compound at a given altitude and the corresponding mixing ratio of the compound when it entered the stratosphere. The former was measured for this work and the latter can be calculated from the mean age of the air (i.e. the mean stratospheric transit time) and tropospheric concentration time series for long-lived compounds. In principle, a calculation is also possible for very short lived substances (VSLS), but the corresponding FRFs are highly variable and depend on the season and location of the respective emissions in the troposphere (Ko and Poulet, 2003). For these reasons no FRFs could be calculated for VSLS from the limited available data set for this work.

$$f_i(x,y,z,t) = \frac{\rho_{i,\text{entry}} - \rho_i(x,y,z,t)}{\rho_{i,\text{entry}}} \quad (1)$$

$\rho_i(x,y,z,t)$ – mixing ratio of the halocarbon at a given stratospheric location (x,y,z) at time t; $\rho_{i,\text{entry}}$ – mean initial mixing ratio of the halocarbon in the air parcel when it entered the stratosphere.

A number of different methods to derive fractional release factors of halocarbons have been described in the literature. The quantity itself was first defined by Solomon and Albritton (1992) according to Eq. (1). As few stratospheric measurements of halocarbons were available at this time Solomon et al. (1992) used models and a semi-empirical analysis of measured stratospheric profiles for methane and other gases to

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estimate FRFs. Daniel et al. (1995) combined measurements of air samples originating from the arctic stratosphere and model calculations to derive FRFs relative to $CFCl_3$ (F11) by assuming that most halocarbons show linear correlations with this compound throughout the stratosphere. Schauffler et al. (2003) and Newman et al. (2006) improved this calculation by deriving the FRFs as a function of mean age of air from aircraft-based observations in the lower stratosphere in middle and high latitudes. Moreover they included the effect of an age spectrum in their calculations which will be explained in the following.

Each stratospheric air parcel can be assumed to consist of a large number of infinitesimally small parcels, which have experienced different transport pathways since crossing the tropical tropopause. Thus, a probability distribution function of transit times to the given location in the stratosphere can be assigned to the air parcel which is the so-called age spectrum (Hall and Plumb, 1994). It describes how the composition of an air parcel is altered by mixing processes with older and newer air parcels. Schauffler et al. (2003) and Newman et al. (2006) used the estimated age spectra to calculate the amount of a halocarbon for a given mean age that would be present without decomposition of the compound in the stratosphere. This amount represents the stratospheric entry mixing ratio $\rho_{i,\mathrm{entry}}$ of the compound for an air parcel taking into account the mixing processes during transport from the tropical tropopause (the entry region) to its location in the stratosphere.

To calculate $\rho_{i,\mathrm{entry}}$ the past tropospheric distributions of the respective trace gas must be known. A number of longer-lived halocarbons are continuously measured by the NOAA-ESRL (National Oceanic Atmospheric Administration – Earth System Research Laboratory) global ground-based network (see http://www.esrl.noaa.gov/gmd/). Globally averaged tropospheric time series can be derived for these compounds on a monthly basis and the data are publicly accessible at the above mentioned internet address. Schauffler et al. (2003) and Newman et al. (2006) used such temporal trends and an age spectra method described by Waugh and Hall (2002) to simulate stratospheric transport and mixing.

Global Warming Potentials (e.g. Daniel et al., 1995) and the semi-empirical calculation of Ozone Depletion Potentials (ODPs, Solomon et al., 1992; Schauffler et al., 1999) are measures of the ability of a trace gas to influence future climate and to deplete stratospheric ozone. FRFs contain time-independent information on vertical trace gas distributions and thus influence the calculation of both measures e.g. via the atmospheric lifetimes or Radiative Forcings assigned to the respective compound. The FRF data set derived here includes six CFCs, four HCFCs, three Halons and two longer-lived non-fluorinated Chlorocarbons and uses new data from the middle stratosphere at tropical latitudes, where few data exist for halocarbons. These FRFs could improve calculations of Equivalent Effective Stratospheric Chlorine (EESC), a term used to quantify the effects of chlorinated and brominated organic compounds on stratospheric ozone depletion. Moreover, they could be used for the parameterisation and evaluation of models (such as Chemical Transport Models, CTMs, see e.g. Avallone and Prather, 1997; McKenna et al., 2002; Grooß et al., 2002) and thus help to predict future ozone levels and climate.

2 Analytical section

The data presented here originate from measurements on air samples collected a) with three balloon-borne whole-air-samplers launched in June 2005 from Brazil (5°04′ S, 42°52′ W) and in October 2006 from Southern France (44° N, 0.4° E) and b) during flights of the high altitude aircraft Geophysica between 43° N and 22° S. An overview is given in Table 1. Three cryogenic whole-air-samplers (named BONBON-I, BONBON-II and CLAIRE) are operated by the University of Frankfurt. These samplers are brought into the stratosphere with large balloons launched by the French Space Agency CNES (Centre National d'Etudes Spatiales). To avoid contamination from out-gassing of the balloon or gondola parts (due to the low pressures and high radiation in the stratosphere) BONBON samples are preferentially taken during the slow descent of the balloon if the meteorological conditions permit. The BONBON cryo-samplers consist of

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a Dewar which contains 15 stainless steel containers (300–500 ml volume) that are electro-polished inside to provide a smooth and inert surface. The Dewar is filled with liquid neon before the balloon flights and cools to about 27 K. This allows sampling of large amounts of air even at low outside pressures because the containers work as cryopumps (almost all air components are condensed inside). More technical details are given in Schmidt et al. (1987) and Engel (1993). The new cryosampler CLAIRE built in 2006 is based on the same principle, but it was designed to take samples during balloon ascent and can collect 26 samples.

Other air samples were collected with the whole air sampler (WAS) of Utrecht University operated onboard the Geophysica high altitude research aircraft. These samples were collected into evacuated stainless steel containers (two litre volume) using a trace gas free metal bellows pump. The whole air samples were analysed in Frankfurt using cryogenic pre-concentration followed by Gas Chromatography with Electron Impact Mass Spectrometric detection (GC-EI-MS). Please refer to Laube et al. (2008) and Kaiser et al. (2006) for further details on sampling and measurement techniques as well as calibration scales.

3 Calculation of fractional release factors and error bars

We calculated FRFs using a procedure which is similar to those of Schauffler et al. (2003) and Newman et al. (2006). The applied method was described by Engel et al. (2002) and includes effects from an age spectrum as well as from global tropospheric temporal concentration trends for the calculation of mean age and the propagation of a species without chemical loss. First, for every sample the mean age of air (i.e. the first moment of the age spectrum) was derived from mixing ratios of SF_6 which were measured within the workgroup for flight B42 and by the University of Heidelberg for flights B43 and C1, all using GC-ECD techniques. SF_6 mixing ratios can be used to calculate a mean stratospheric transit time by assigning the mixing ratio observed in the stratosphere to a certain time of the past tropospheric SF_6 trend (e.g. Strunk

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et al., 2000). As the corresponding age spectra cannot be measured directly they were derived from the mean ages via a parameterisation according to Laube et al. (2008) who based their calculations on Engel et al. (2002), Hall and Plumb (1994) and Volk et al. (1997). Subsequently the corrected stratospheric entry mixing ratio was calculated for each compound and sample by assigning mixing ratio distributions to the age spectra via the above mentioned tropospheric time series similar to the calculation of total chlorine in Engel et al. (2002).

For five compounds no monthly tropospheric trend data was available from NOAA-ESRL: C_2F_5Cl (F115), CF_2ClCF_2Cl (F114), CF_3CFCl_2 (F114a), CF_2BrCF_2Br (Halon 2402) and $CHFClCF_3$ (F124). Thus, a temporal trend was derived via linear regression from the annually averaged mixing ratios back to 1998 which were taken from Table 1-1 of Montzka and Fraser, 2003 and Table 1-2 of Clerbaux and Cunnold, 2007 (AGAGE, in situ data was used except for Halon 2402: UEA, flasks). However, the mixing ratios for 2005 derived from these trend functions did not match with the measured mixing ratios originating from air samples collected in the Tropical Tropopause Layer (TTL, i.e. the main stratospheric entrance region) in 2005. This is likely to be caused by differences in absolute calibration scales. However, the FRFs are only fractions i.e. relative values to the entrance mixing ratios. Thus, the trend functions were shifted to match the mixing ratios observed in the TTL using a conversion factor.

No SF_6 data was available for the samples collected from the high altitude aircraft (Flights R3, S3, S8 and T3). To assign a mean age of air to these samples a correlation of mean age of air and a tracer was derived for the tropical stratosphere. A polynomial of the form of Eq. (2) best reflected the correlation of mean ages Γ and CF_2Cl_2 (F12) mixing ratios (MR_{F12}) of the lower stratospheric data resulting from the balloon flights B42 and B43.

$$\Gamma = 28.71 - 0.19 \cdot MR_{F12} + 5.08 \times 10^{-5} \cdot (MR_{F12})^2 - 4.55 \times 10^{-7} \cdot (MR_{F12})^3 \quad (2)$$

Please note, that this function is only valid for the tropical stratosphere in 2005 for air having mean ages below 3.5 years and a F12 mixing ratio range from 545 to 350 ppt.

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The FRFs were then calculated according to those of the other flights but using the "F12 mean age" instead of SF_6.

For the calculation of tropical FRFs all data between 22°S and 22° N and above potential temperatures of 360 K were used. These criteria were chosen to include a) only tropical mixing ratios and b) the variability of the compounds in the TTL.

FRF uncertainties (error bars in the Figures) include the 1σ measurement uncertainties, the sample instability errors (only for flight B42) and the standard deviations of the global mixing ratios averaged over 2001 as provided by NOAA-ESRL (source: http://www.esrl.noaa.gov/gmd/). They were calculated according to those in Laube et al. (2008). An additional uncertainty originating from interhemispheric mixing ratio gradients was accounted for by adding the average percent difference between the 2001 data from the NOAA-ESRL stations in Tutuila, American Samoa (14.25° S, 170.56° W) and Mauna Loa, Hawaii, United States (9.54° N, 155.58° W).

3.1 Results and discussion

The correlation between the mixing ratios of two trace gases that are both long-lived (so-called tracers) is compact in the stratosphere (Plumb and Ko, 1992). But transport barriers, chemical processes and also latitudinal and seasonal variations in the vertical distributions of tracers cause different correlation curves between these compounds for different stratospheric regions (e.g. Plumb, 1996; Volk et al., 1997; Engel et al., 2002; Waugh and Hall, 2002). Due to the major transport barriers the stratosphere can be subdivided into three regions which show characteristic correlations between the tracers: tropics, mid-latitudes and the polar vortex which forms at high-latitudes around the respective winter-pole. The correlations in these regions vary with season. For example Boering et al. (1994) performed stratospheric measurements of CO_2 and N_2O in northern mid-latitudes and found the correlations between these tracers to be seasonally dependent indicating that vertical transport above 20 km is slower in northern summer than in winter. The highest seasonal variability is observed in polar regions where an isolated vortex forms in winter inside which characteristic correlations

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are found (e.g. Waugh et al., 1997). In contrast, seasonal correlation changes in the tropical stratosphere are believed to be smaller (Plumb, 2002, 2007) which is why the analysed air samples collected in different seasons in 2005 were combined in one data set here.

To summarise, the correlations between two long-lived halocarbons are characteristic for different stratospheric regions in which the air masses have experienced similar transport pathways. This can also be observed for FRFs when plotted against the corresponding mean ages of air as shown in Fig. 1 for $CFCl_3$ (F11). In the tropics F11 shows a greater decrease with increasing mean age than at mid-latitudes. The highest FRF differences are observed for mean ages of air between two and five years. Also displayed in Fig. 1 is the mid- and high-latitude correlation derived by Newman et al. (2006) which consists of two functions: a quadratic polynomial to calculate FRFs for low ages of air up to 1.5 years and a cubic polynomial for older ages. The derived mid-latitudinal and subtropical FRFs are comparable with the fit functions of Newman et al. (2006) but the tropical FRFs are considerably larger for older ages of air. The faster decomposition of F11 in the tropical stratosphere at higher altitudes is most likely caused by the enhanced radiation relative to regions at higher latitudes. Calculations and model studies predict loss rates of CFCs that are significantly larger in the tropics compared to mid-latitudes (e.g. Rowland and Molina, 1975; Plumb and Ko, 1992; Lee, 1994).

Not all long-lived halocarbons show such a characteristic behaviour in different stratospheric regions. In Fig. 2 the FRFs of CHF_2Cl (F22) are depicted. F22 decomposes very slowly compared to F11 and thus its FRF correlation with mean age is comparable for different stratospheric regions. The corresponding correlation function derived by Newman et al. (2006) is comparable with the one derived here.

To quantify the observed latitudinal differences polynomials were derived which allow the calculation of tropical FRFs from the mean age of air (see Figs. 1–6 and Table 2). The order of the polynomial was increased stepwise. If the corresponding Pearson correlation coefficient did not increase significantly (less than ≈0.05) the polynomial

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with the lower order was chosen in most cases. A second visual criterion was the agreement of the curve for older ages as the data set is weighted towards younger ages.

In general, good agreement with the correlation functions derived by Newman et al. (2006) was found for lower ages of air (up to 0.5–2 years depending on the individual compound). This agrees with other observations indicating strong transport from the lower tropical stratosphere (below potential temperatures of about 450 K) into the extra-tropics (Rosenlof et al., 1997). For older ages most compounds were found to decompose faster in the tropics than in the extratropics. The only exceptions were halocarbons with low stratospheric decomposition rates which showed comparable or even slightly lower FRFs: F22, F142b, F115 and F114. Two compounds, F114a and F124, could not be compared as no functions for these compounds were derived by Newman et al. (2006). FRFs can be assumed to be constant in time for a given mean age-of-air (e.g. Newman et al., 2007) but depend on the respective stratospheric region. Therefore the derived tropical correlation functions can be used for a wider temporal range than correlation functions and are valid as long as there are no major changes to general stratospheric circulation and composition.

For the semi-empirical calculation of ODPs averaged FRF values are used (Daniel and Velders, 2007). Moreover, these values are calculated relative to the averaged FRF of F11. Table 3 shows a comparison of these WMO values (which are mainly those derived by Daniel et al., 1995) with the relative tropical FRFs averaged for all ages between 2 and 4.8 years. The latter were derived according to a method described in Schauffler et al. (2003) and are thus comparable. The error bars represent the variability of the relative FRFs over the averaged mean age range. Most of the compounds were observed to decompose relatively quickly with increasing mean age in the tropics. Because the ratio of this decomposition relative to that of CFC-11 is not constant a high variability is introduced when the FRFs are averaged over a wide mean age range. Consistently most of the relative FRF means agree with those of the WMO within this uncertainty criterion. However, four compounds were found to have

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significantly different relative mean FRFs in the tropics. Halon 2402 showed a larger relative mean FRF which is caused by its rapid decomposition; the compound is already depleted to values below detection limits at mean ages of two years. F114, F22 and F142b showed lower relative mean FRFs in the tropics. For F114 (see Fig. 3) the WMO used the averaged relative FRF of Schauffler et al. (2003) (i.e. 0.28±0.02) but our calculations resulted in a tropical value which is lower by a factor of two (0.14±0.09). This issue remains unresolved because CFC's are mainly destroyed by photolysis and reactions with O^1D and thus they should decompose faster in the tropical stratosphere. The tropical values of F22 and F142b derived here (0.23±0.11 and 0.12±0.07) agree with those of Schauffler et al. (2003) derived from mid- and high-latitudes (0.29±0.02 for F22 and 0.08±0.04 for F142b) but disagree with the greater values used in Daniel and Velders (2007) (see Table 3).

4 Conclusions

The measured set of air samples originating from the lower and middle tropical stratosphere enabled characterisation of the vertical distribution of 15 long-lived halocarbons. The data were used to derive Fractional Release Factors (FRFs) and relate these to the mean age of air in this region of the atmosphere. The tropical FRFs were internally and externally compared with mid- and high-latitude FRFs. Characteristic differences were found for air masses which entered the stratosphere more than 0.5 to 2.5 years prior to sample collection (depending on the individual compound). The mid-latitude FRFs were found to increase at a considerably lower rate with mean age than tropical FRFs for 9 out of 13 long-lived halocarbons (F114a and F124 could not be compared). Moreover, FRFs averaged over an age range were calculated relative to an average FRF of F11. They were compared with averaged values originating from observations in the mid- and high-latitude stratosphere which are currently used by the World Meteorological Organization for the semi-empirical calculation of Ozone Depletion Potentials (ODPs). Most values were in agreement though highly variable in the tropics. There-

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fore the ODPs calculated by the WMO (based on FRFs calculated by Daniel et al., 1995) can be considered as globally representative, with the exceptions of F114, F22 and F142b. Our data suggests that the fractional release of these three compounds should be reassessed for the non-tropical stratosphere where most ozone loss occurs. Daniel et al. (1995) assumed for simplification, that all tracer-tracer-correlation functions relative to F11 are linear and thus the FRFs relative to F11 are valid throughout the stratosphere. However, this simplification was found to be of very limited use in the tropical stratosphere. Averaged FRFs relative to F11 calculated accordingly are highly imprecise and thus questionable. For improved ODP calculations the FRF correlations with mean age as derived by Schauffler et al. (2003), Newman et al. (2006) and in this work should be used. Further, we present FRFs for F115 and F114a which are not available in the respective literature (Daniel and Velders, 2007).

For the first time correlations of the FRFs of a set of 15 halocarbons were calculated as functions of the mean age of air for the lower and middle tropical stratosphere. These correlations can be considered as time-independent and are recommended for the parameterisation of models in order to reassess the chemical composition and the radiative balance in this region. Changes to these quantities could be of interest to policy makers as they influence not only the ODPs but also the Global Warming Potential (GWP) values (via Radiative Forcing values) which are currently assigned to the corresponding halocarbons.

Acknowledgements. The work of Ingeborg Levin (University of Heidelberg), the CNES balloon team, the Geophysica team and of the NOAA-ESRL GMD teams (who provided global tropospheric data) is much appreciated. Furthermore we thank the European Space Agency, the Deutsches Zentrum fuer Luft- und Raumfahrt (project 50EE0016), the European Union (SCOUT-O3 project GOCE-CT-2003-505390), the Deutsche Forschungsgesellschaft (CAWSES project EN 367/4) as well as the British Natural Environment Research Council for funding.

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Table 1. Overview of analysed air samples collected at altitudes above 10 km. Only uncontaminated samples were used for the calculation of FRFs i.e. 31 samples from balloon-borne whole-air-samplers and 42 samples from the Geophysica high altitude research aircraft.

Flight no.	Sampler	Location	Flight date	No. of samples	Sample altitude range [km]
B42	BII	Teresina, Brazil, 5°04′ S, 42°52′ W	08.06.2005	11	15–34
B43	B I	Teresina, Brazil, 5°04′ S, 42°52′ W	25.06.2005	14	15–34
C1	CLAIRE	Aire Sur l'Adour, 44° N, 0.4° E	15.10.2006	6	12–28
R3a	WAS	Dubai–Larnaca, 25–33° N, 38–53° E	16.12.2005	6	17.2–17.8
R3b	WAS	Larnaca–Oberpfaffenhofen, 35–43° N, 14–33° E	17.12.2005	7	16.7–17.1
S3	WAS	Survey Indonesia, 8–12° S, 130–134° E	23.11.2005	13	15.5–18.3
S8	WAS	Survey South, 13–22° S, 131–134° E	06.12.2005	11	13.9–19.7
T3	WAS	Tapao–Brunei, 5–13° N, 101–115° E	11.11.2005	5	12.7–17.5

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Table 2. Correlation functions to derive FRFs of long-lived halocarbons from the mean age of air in the lower and middle tropical stratosphere (between 22°N and 22°S and above 360 K potential temperature). The polynomials of the form $y=a+bx+cx^2+dx^3$ are only valid for the given FRF (y) and mean age (x) ranges. If a function is not valid down to a mean age of 0.0 this means the FRF is negligible in the corresponding lower stratospheric region. R^2 is the Pearson correlation coefficient.

Compound	a	b	c	d	R^2	Validity ranges (FRF & mean age in years)
F12	0.001	–0.0013	0.00880	0.006733	0.98	0.00–0.94 0.0–4.8
F11	0.056	–0.2540	0.26905	–0.036559	0.98	0.0–1.0 0.8–3.9
F113	0.004	–0.0208	0.04907	–0.000171	0.97	0.0–1.0 0.3–4.8
F114	–0.013	-0.0046	0.00150	0.001691	0.93	0.0–0.23 1.4–4.8
F115	0	–0.0006	–0.00324	0.001711	0.61	0.0–0.11 2.1–4.8
F114a	0.013	–0.0337	0.02434	0.007381	0.90	0.0–1 0.6–4.5
F22	0.008	0.0454	–0.01160	0.003169	0.92	0.0–0.31 0.0–4.8
F141b	–0.018	–0.0475	0.05714	0	0.95	0.0–1.0 1.2–4.7
F142b	0.007	0.0093	0.00375	0	0.65	0.0–0.14 0.0–4.8
F124	–0.091	0.1590	0	0	0.92	0.0–0.7 0.6–4.8
CCl_4	0.060	0.2426	0	0	0.87	0.0–1.0 0.0–3.9
CH_3CCl_3	–0.125	0.3256	0	0	0.69	0.0–1.0 0.4–3.6
H-1211	–0.044	0.0642	–0.00422	0.049419	0.87	0.0–1.0 0.6–2.7
H-1301	–0.006	–0.0184	0.01851	0.014456	0.95	0.0–1.0 0.9–3.9
H-2402	–0.223	0.5555	0	0	0.88	0.0–1 0.4–2

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Table 3. Comparison of averaged FRFs relative to the averaged FRF of $CFCl_3$ (F11) in the tropics with current WMO values that are based on observations at mid and high latitudes (see Table 8-1 of Daniel and Velders, 2007). The stated tropical errors do not include measurement or calculation uncertainties but represent only the 1σ variability of the FRF within the mean age range used for averaging. The bold numbers are significantly different from those presented in Daniel and Velders, 2007.

Compound	tropical mean FRF relative to F11[a]	mean FRF relative to F11 (from Daniel and Velders, 2007)
F12	0.56±0.38	0.60
F11[b]	0.74±0.28	0.55
F113	0.72±0.39	0.75
F114	**0.14±0.09**	0.28±0.02
F115	0.05±0.06	n. a.
F114a	0.69±0.51	n. a.
F22	**0.23±0.11**	0.35
F141b	0.76±0.41	0.72
F142b	**0.12±0.07**	0.36
F124	0.64±0.20	0.52
CH_3CCl_3	1.21±0.25	1.08
CCl_4	1.14±0.31	1.06
H-1211	1.26±0.28	1.18
H-1301	0.90±0.49	0.62
H-2402	**1.36±0.00**	1.22

[a] averaged for mean ages between 2.0 to 4.8 years;
[b] F11: absolute averaged FRF is given
n.a.: not available, model derived values were used for ODP calculations.

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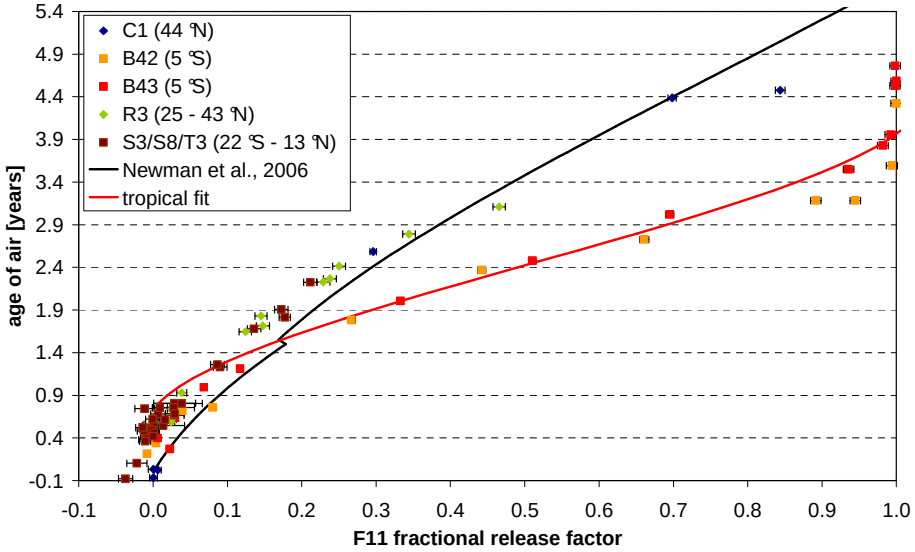

Fig. 1. Fractional release factors (FRFs) and mean ages of air for F11. The mean age is plotted on the y-axis because it increases with altitude. The cold colours (blue and green) represent data of mid-latitudinal origin while the warm colours (orange, red and brown) represent tropical and subtropical data. Small negative values that occur for low ages and FRFs are caused by atmospheric variability and measurement uncertainties. The black curves are the correlation functions derived by Newman et al. (2006) using data from lower stratospheric aircraft observations in middle and high latitudes. The derived mid-latitudinal and subtropical FRFs are comparable to the fit functions of Newman et al. (2006) but the tropical FRFs increasingly differ for older ages.

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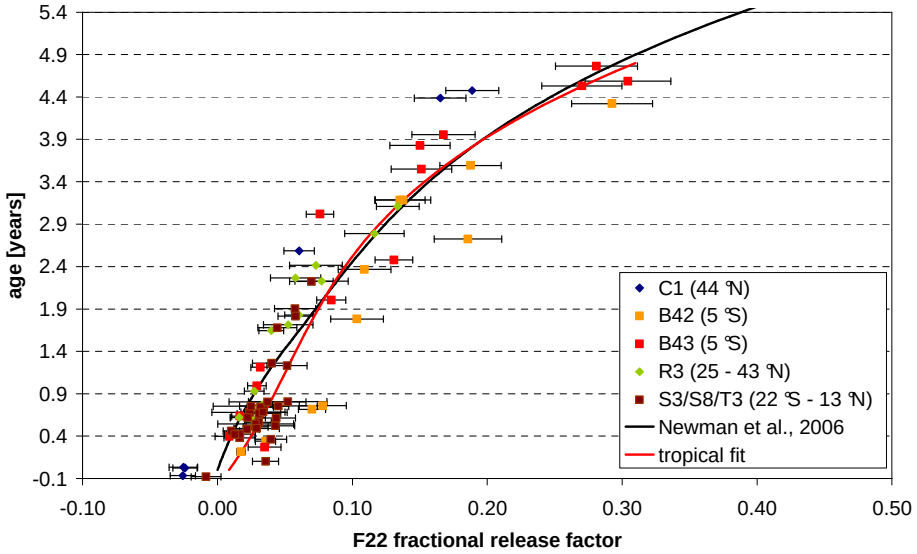

Fig. 2. The same as in Fig. 1 but for F22. This compound is found to decompose very slowly in the stratosphere. Thus, its FRF-mean-age correlation is less influenced by different transport pathways or radiation and shows no differences for stratospheric regions that are separated by transport barriers.

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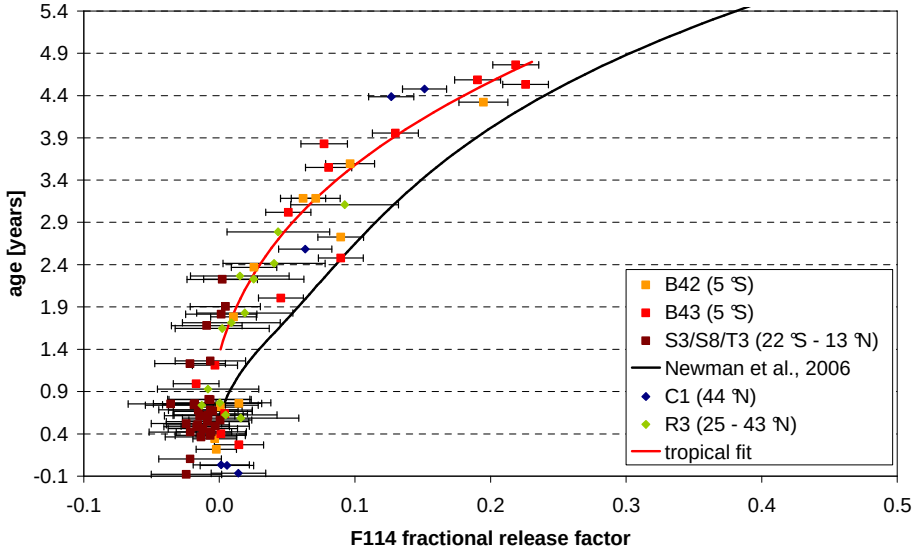

Fig. 3. The same as in Fig. 1 but for F114. The observed tropical FRF values are lower than those derived by Newman et al. (2006) for mid- and high latitudes.

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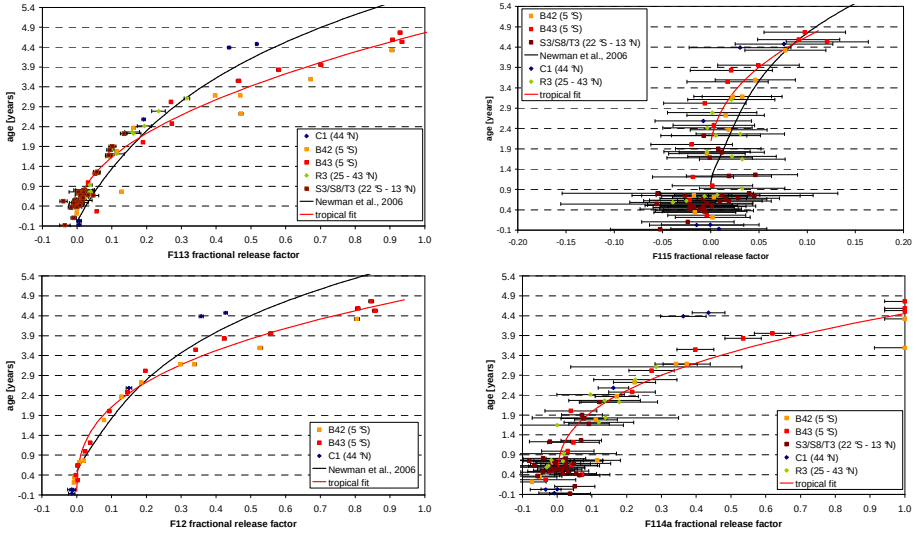

Fig. 4. The same as in Fig. 1 but for the CFCs F12, F113, F114a and F115.

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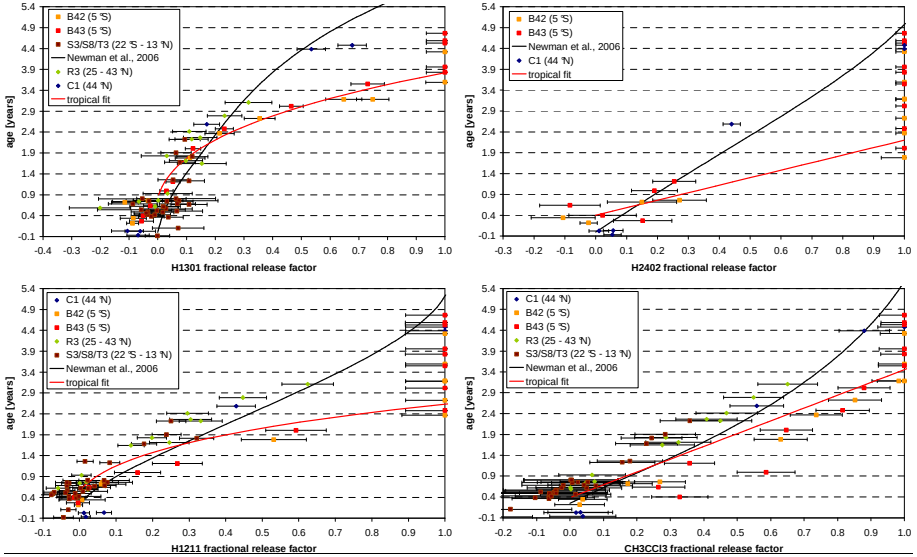

Fig. 5. The same as in Fig. 1 but for the Halons 1301, 1211 and 2402 as well as methyl chloroform.

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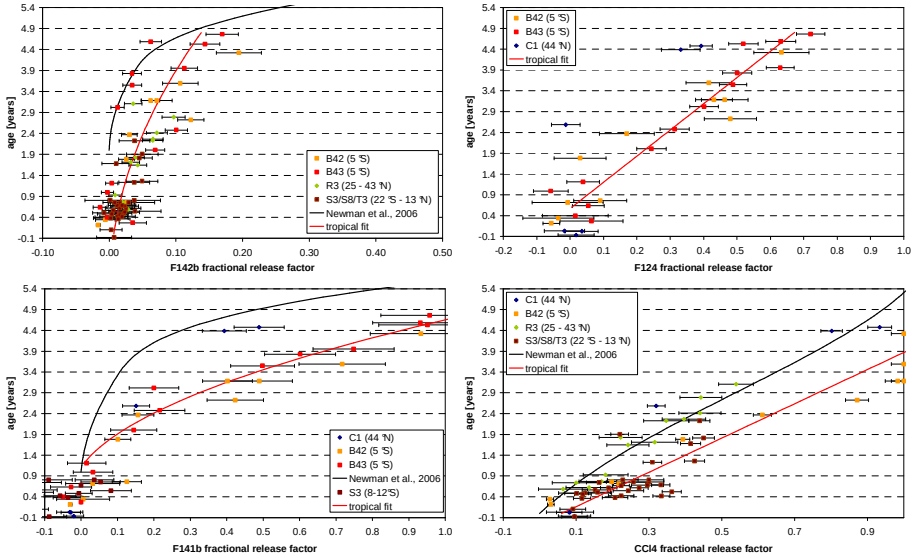

Fig. 6. The same as in Fig. 1 but for the HCFCs F142b, F141b and F124 as well as carbon tetrachloride.

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Fractional release factors of long-lived halogenated organic compounds

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