**Atmospheric
Chemistry
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Discussions**

Southern hemispheric halon trends and global halon emissions, 1978–2011

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Abstract

The atmospheric records of four halons, H-1211 ($CBrClF_2$), H-1301 ($CBrF_3$), H-2402 ($CBrF_2CBrF_2$) and H-1202 (CBr_2F_2), measured from air collected at Cape Grim, Tasmania between 1978 and 2011, are reported. Mixing ratios of H-1211, H-2402 and H-1202 began to decline in the early to mid-2000s but those of H-1301 continue to increase throughout the record. These trends are compared to those reported by NOAA (National Oceanic and Atmospheric Administration) and AGAGE (Advanced Global Atmospheric Experiment). The continued increase of H-1301 mixing ratios means that the contribution of the halons to total tropospheric bromine is not declining. Top-down global annual emissions of the halons were derived using a two-dimensional atmospheric model. The emissions of all four have decreased since peaking in the late 1980s–mid 1990s but this decline has slowed recently, particularly for H-1301 and H-2402 which have shown no decrease in emissions over the past five years. The UEA top-down model derived emissions are compared to those reported using a top-down approach by NOAA and AGAGE and the bottom-up estimates of HTOC (Halons Technical Options Committee). Additionally results are presented that suggest that H-1202 emissions are linked to H-1211 emissions rather than H-1211 production. Finally revised steady state atmospheric lifetimes are reported as 14 yr for H-1211, 75 yr for H-1301, 17 yr for H-2402 and 2.6 yr for H-1202. These revised lifetimes would reduce the estimated existing bank of H-1211 by over 80 % to 10 Gg while increasing the H-1301 bank by 15 % to 49 Gg.

1 Introduction

Halons were produced from the 1950s until the end of 2009 and are used mainly in fire extinguishing equipment and explosion protection applications because of their highly inert chemical nature. The two main halons produced for these purposes were H-1211 ($CBrClF_2$) and H-1301 ($CBrF_3$). A third halon, H-2402 ($CBrF_2CBrF_2$), was produced

and used mainly in the Soviet Union (McCulloch, 1992). H-1202 (CBr_2F_2) is thought to have had very little direct use but was produced as a by-product from over-bromination during H-1211 manufacture (HTOC, 1999).

The halons have relatively long atmospheric lifetimes (H-1211 – 16 yr, H-1301 – 65 yr, H-2402 – 20 yr, H-1202 – 2.9 yr, Montzka and Reimann, 2011). The main atmospheric loss is by photolysis. This occurs almost entirely in the troposphere for H-1202, in both the troposphere and the stratosphere for H-1211 and H-2402 and almost entirely in the stratosphere for H-1301. The bromine released from breakdown in the stratosphere contributes to stratospheric ozone depletion, with bromine being 60–65 times more effective than chlorine at depleting ozone on a per molecule basis (Daniel and Velders et al., 2007). Because of this, production of halons for non-essential use in non-Article 5 countries (i.e. North America, Europe, Australia and Japan) was banned under the Montreal Protocol in 1994 and production for use in Article 5 countries was banned from 2010. However halons continue to be released to the atmosphere from the existing installed capacity and from users with critical use exemptions (CUEs) such as civil aviation and military applications. Significant halon supply for CUE comes from recycling (HTOC, 2011). H-1301 is still being produced as a chemical feedstock for the production of the pesticide Fipronil (HTOC, 2011).

Previous studies of the halons in air extracted from deep firn snow (Butler et al., 1999; Sturrock et al., 2002; Reeves et al., 2005) have shown them to be entirely anthropogenic in origin with concentrations near zero in the early 1960s. Atmospheric mixing ratios of the halons increased rapidly from the late 1970s up to the late 1990s (Butler et al., 1999; Fraser et al., 1999; Sturrock et al., 2002). They have since levelled off or begun to decline, with the exception of H-1301 which continues to grow (based on data reported up to 2008) (Reeves et al., 2005; Montzka and Reimann, 2011).

The contribution from the halons to total tropospheric bromine was 8.2–8.5 ppt in 2008, with a similar amount being contributed by methyl bromide (Montzka and Reimann, 2011).

This paper reports atmospheric measurements from Cape Grim, Tasmania from 1978 up to 2011, updating the record reported in Fraser et al. (1999), and compares the measurements from 1998 to 2011 to similar measurements by NOAA (National Oceanic and Atmospheric Administration) and AGAGE (Advanced Global Atmospheric Gases Experiment, Prinn et al., 2000). A two-dimensional atmospheric chemical transport model is used to derive top-down global annual emissions of the halons. These derived emissions are compared to those derived by NOAA and AGAGE using a top-down approach and by HTOC (Halons Technical Options Committee) using a bottom-up approach. The paper also reconsiders the source of H-1202. The values of the recommended lifetimes of the four halons, and the effect that uncertainties in these values could have on the remaining halon banks, are investigated. Finally the current and future contribution of the halons to tropospheric bromine mixing ratios is discussed.

2 Analytical methods

2.1 Sampling

Approximately 130 samples collected at Cape Grim, Tasmania (40.4° S, 144.4° E) have been analysed for the 4 major halons (1211, 1301, 2402, 1202). Prior to 1993 these samples were predominantly sub-samples of the Cape Grim air archive (see Fraser et al., 1999) but from 1994 onwards are from flask samples collected directly at Cape Grim. These latter samples were collected in either electropolished (Rasmussen) or silcosteel-treated (Restek) stainless steel canisters (Rasmussen) and were only taken during baseline atmospheric conditions (with prevailing winds from the south-westerly sector) so as to be representative of background conditions rather than sampling air coming from the landmasses of mainland Australia or Tasmania (Fraser et al., 1991; Weeks et al., 1992; Langenfelds et al., 1996). As discussed in Fraser et al. (1999) and elsewhere, we are confident that the Cape Grim archive contains representative

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samples of background air and that the halons (and many other halocarbons) can be stored without significant changes to their concentrations.

2.2 Analysis

2.2.1 Cape Grim

Up until 2006, the Cape Grim samples were analysed using an Agilent 5890 gas chromatograph coupled to a trisector mass spectrometer (V.G./Micromass Autospec) operated in single ion, electron ionisation mode. During this period the halon gases were separated on a KCl-passivated alumina (Al_2O_3/KCl) PLOT column (see Fraser et al., 1999 for further details). As detailed in Oram et al. (2012), since 2006 samples have been analysed using a similar method but with an updated GC-MS instrument (Waters Autospec Premier) and a slightly modified pre-concentration procedure. In addition, the post 2006 samples have been processed using an Agilent GS GasPro column (see Laube et al., 2010 for further details).

The GasPro/Autospec Premier combination has also been used to reanalyse selected samples from before 2006 to ensure comparability with the original record measured using the Al-PLOT/Autospec combination. This analysis appears to show a small unexplained non-linearity at low mixing ratios for H-1211 and H-2402 which affects the earlier (pre-1989) part of the record. During the 1978–2005 period several different alumina-PLOT columns were used for the Cape Grim analyses. Initially these were supplied by Chrompak but subsequently by Agilent. In 2004 seven samples covering the period 1978–1993 were reanalysed on the Agilent column, and these show very good agreement with the more recent GasPro measurements (see Supplement), suggesting that the non-linearity stems from one particular GC column, which is no longer in use, and not from the analytical system itself. Indeed a static dilution series derived from a background air sample (see Laube et al., 2012a) and analysed with the current GasPro setup showed no detectable non-linearity. Consequently we have excluded the

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pre-1989 H-1211 and H-2402 data which was analysed on the Chrompack alumina-PLOT column.

The mean precisions of the measurements of the four halons were 2.2 % (H-1301), 1.2 % (H-1211), 3.7 % (H-1202) and 2.1 % (H-2402).

2.2.2 Calibrations

The measurements of H-1211 and H-1301 are presented in the NOAA Climate Monitoring and Diagnostics Laboratory (NOAA-CMDL) NOAA-2006 gravimetric scale, the H-1301 calibration is based on GC-MS analyses (S. Montzka, personal communication, 2012), for ease of comparison with the most recent reported measurements and emissions in Montzka and Reimann et al. (2011). The ratios of the UEA volumetric scale, used in previous work, to the NOAA-2006 gravimetric scales are 1.13 and 0.84 for H-1211 and H-1301, respectively. H-1202 and H-2402 are presented on the UEA volumetric scale as described in Fraser et al. (1999).

2.3 Atmospheric modeling

2.3.1 Model transport and chemistry

The chemical transport model used is two-dimensional with twenty-four equal area latitudinal bands and twelve equal height vertical layers extending to an altitude of 24 km. The atmospheric circulation used in the model is that derived by Plumb and Mahlman (1987). The absorption cross sections are calculated for each grid box as a function of seasonally varying temperature for the wavelengths 200–400 nm. They are the mean of the temperature dependent absorption cross sections reported by Gillotay and Simon (1989), Gillotay et al. (1988) and Burkholder et al. (1991). Note that this is different to Fraser et al. (1999) in which a function, defined by Sander et al. (1994), was used which represented a combination of the cross sections reported by Gillotay and Simon (1989), Gillotay et al. (1988) and Burkholder et al. (1991). However

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this function has not appeared in more recent reports and Sander et al. (2011) just present the functions defined by Gillotay and Simon (1989), Gillotay et al. (1988) and Burkholder et al. (1991). This difference accounts for the slight difference between the lifetimes calculated in Fraser et al. (1999) and those calculated in this work (see Sect. 6).

The OH values are input monthly and interpolated in between these times for each grid cell using a sine smoothing function. The OH field is based on modeling by Hough (1991) and has then been adjusted to give a lifetime for methyl chloroform with respect to reaction with OH of 6.1 yr, as given by the most recent WMO review (Montzka and Reimann, 2011), using a reaction rate of $1.2 \times 10^{-12} e^{(-1440/T)}$ (Atkinson et al., 2008).

The diffusive loss of gases from the top of the model is governed by defining the ratio, F, of the concentration of the species in the top box of the model (23 km) to that of a box directly above the model domain (25 km). The value of this ratio was adjusted for H-1211, H-1301 and H-2402 so that, in combination with the loss from photolysis and reaction with OH, the steady-state lifetimes of the halons within the model domain were equal to those given in Montzka and Reimann et al. (2011) (H-1211 – 16 yr, H-1301 – 65 yr, H-2402 – 20 yr). To achieve these steady-state lifetimes values of 0.952 (H-1211), 0.736 (H-1301) and 0.820 (H-2402) were used for the ratio F. For H-1202, the lifetime reported in Montzka and Reimann (2011) was originally derived by Fraser et al. (1999) using the model used in this work. However due to changes in the calculation of absorption cross-sections (discussed above), the lifetime of H-1202 within the model domain is revised to 2.6 yr.

2.3.2 Emissions

The model has two main adjustable input functions, the total global annual emissions and the latitudinal distribution of these emissions.

The latitudinal distribution of halon production changed considerably during the early-mid 1990s when the Montreal Protocol came into force banning the further

production of halons in non-Article 5 countries. The major area of production since 1994 has been South-East Asia, namely China (HTOC, 2006). However the emission distribution would not have changed so dramatically since the use of halons for fire protection applications was phased out gradually in non-Article 5 countries with some

5 use for critical exemptions still ongoing.

H-2402 was produced almost exclusively in Russia and former Soviet countries (HTOC, 2011). Emissions of H-2402 are now limited largely to these countries and to countries which use ex-Soviet military equipment.

The emissions distributions used in the model for H-1211 and H-1301 were varied

10 according to the reported regional annual emissions of these halons in HTOC (2011). The distribution used for H-1202 emissions was the same as that of H-1211 since the emissions appear to be related (see Sect. 5). H-2402 emissions were assumed to have a constant distribution throughout the period over which the model was run.

The annual emissions input to the model were adjusted manually so that the model

15 output for the box representing 35.7° S–41.8° S simulated mixing ratios comparable to the measurements from Cape Grim (40.4° S). The model has previously been shown to reproduce southern hemispheric observations to within about 5 % for gases emitted mostly in the Northern Hemisphere and for which there have been well reported emission inventories such as CFC-11 and CFC-12 (e.g. Reeves et al., 2005).

20 ## 3   Cape Grim mixing ratio time series

The mixing ratios of the four halons measured at Cape Grim between 1998 and 2011 are shown in the main panels of Fig. 1, as well as measurements by NOAA and AGAGE at Cape Grim where available. The entire records from Cape Grim (1978–2011) are shown as insets in the main panels. The measurements made on the Al-PLOT column

25 (brown circles) have previously been reported by Fraser et al. (1999) up to 1998. However the mixing ratios of H-1211 and H-1301 are presented here on the NOAA-2006 gravimetric calibration scale as opposed to the UEA volumetric scale used in Fraser

et al. (1999). The measurements made using the GasPro column are shown as black diamonds. It is evident that the data obtained from the two different analytical setups agree very well and can be combined. The Cape Grim mean annual mixing ratios from the model fit are available in the supplementary information.

Table 1 shows the mean mixing ratios of the halons between January and June 2011 at Cape Grim and the mean growth rates during the periods 1985–1999 (when the mixing ratios were all increasing), 1999–2005 (when growth rates began to slow or turn over) and 2005–2011 (when the mixing ratios of three of the halons were decreasing).

3.1 H-1211

The mixing ratio of H-1211 grew rapidly during the 1980s and 1990s from about 1.3 ppt (parts per trillion) in 1985 to a mean of 3.9 ppt in 1999 at an average growth rate of 0.19 ppt yr^{-1}. The mixing ratio began to level off after 1999 reaching a maximum of 4.2 ppt and concentrations at Cape Grim began to slowly decline. The mean mixing ratio in the first half of 2011 was 4.0 ppt.

NOAA report a similar trend in mixing ratios for H-1211 from measurements by GC-MS of Cape Grim background samples (mean of flask pairs) between 1998 and mid-2011 (Montzka and Elkins, 2012). These measurements are about 1 % higher than UEA measurements between 1998 and 2003 and about 1 % lower between 2003 and 2011. The mixing ratios reported by AGAGE from in-situ baseline measurements by GC-MS at Cape Grim since 1998 (http://agage.eas.gatech.edu) are very similar to those reported here but are consistently about 2–3 % higher which could be caused by differences in calibration scales.

3.2 H-1301

The H-1301 mixing ratio grew steadily from a mean of 0.7–0.8 ppt in 1985 to a mean of 2.65 ppt in 1999 at an average growth rate of 0.14 ppt yr^{-1}. The mean mixing ratio in the first half of 2011 was 3.15 ppt with a mean growth rate since 2000 of 0.045 ppt yr^{-1}.

H-1301 is the only one of the halons reported here to have atmospheric mixing ratios that are still increasing. This continued growth is consistent with predictions in Fraser et al. (1999) and Montzka and Fraser et al. (2003) which show H-1301 mixing ratios peaking around 2020 before beginning to decline.

5   The mixing ratios reported by NOAA from ECD measurements on Cape Grim flask pair mean samples are almost 5 % higher than those of UEA between 1998 and 2000 but then steadily converge with those reported here during 2001 and 2002 and from 2003 the two trends are virtually identical up to the middle of 2006 when NOAA's ECD measurements stopped (Montzka and Elkins, 2012). Since 2004 NOAA have

10 also measured the flask samples by GC-MS. These mixing ratios agree very well with those reported here (S. Montzka, personal communication, 2012). The baseline mixing ratios reported by AGAGE since 1998, measured by GC-MS in-situ at Cape Grim (http://agage.eas.gatech.edu/), are consistently about 3 % higher than those reported here with the exception of a period between 2001 and 2003 in which the AGAGE mea-

15 surements show a high degree of variability.

3.3   H-2402

The mixing ratio of H-2402 increased from about 0.21 ppt in 1985 to a mean of 0.42 ppt in 1999 at a mean growth rate of 0.016 ppt yr^{-1}. The mixing ratio levelled off during the late 1990s–early 2000s at a peak of 0.42–0.44 ppt. It began to fall around 2005 and

20 reached a mean of 0.39 ppt during the first half of 2011.

    NOAA reports measurements of H-2402 from 2004 onwards and for a brief period from 1995 to the start of 1997. The declining trend since 2004 agrees well with the trend observed in this work but the mixing ratios reported by NOAA are consistently 10–15 % higher. This is again probably caused by a calibration difference.

25   AGAGE H-2402 data are not currently available from the publically-accessible data archive (http://agage.eas.gatech.edu), but monthly global means were presented in Montzka and Reimann et al. (2011).

3.4   H-1202

The mixing ratio of H-1202 at Cape Grim grew from an annual mean of 14–15 ppq (parts per quadrillion) in 1985 to a mean of 45 ppq in 1999 with a mean growth rate of 2.2 ppq yr^{-1}. The mean annual mixing ratio remained fairly stable between 1999 and
5 2001 and has since fallen sharply to a mean mixing ratio of about 20 ppq in the first half of 2011.

UEA is the only institution to have reported measurements of H-1202.

4   Model derived emissions

The annual global emissions of the halons, as derived from the model runs in Fig. 1,
10 are shown in Fig. 2. Also shown, where available, are the emissions reported by NOAA and AGAGE (Montzka and Reimann, 2011), both derived using a one box atmospheric model with global measurements, and the emissions derived using a 12-box model in conjunction with AGAGE measurements (from the Cape Grim archive air before 2004 and global measurements thereafter, Montzka and Reimann, 2011). Finally the bottom
15 up estimates of HTOC are shown (HTOC, 2011); these emission estimates are calculated based on emissions modeling taking into account industry reported production, usage and destruction.

Uncertainties in the measurements and fitting the model output to those measurements, the atmospheric lifetimes of the halons, and in the model transport all contribute
20 to uncertainties in the model derived emissions. Figure 2 shows the annual emissions estimated in this work with error bars based on the measurement errors associated with each individual data point (see supplementary material) and errors in the transport within the model (which are taken as a constant 5 % throughout the run based on previous work with the model, e.g. Reeves et al., 2005). These errors should allow
25 comparison with other top-down derived emissions (i.e. NOAA and AGAGE), assuming that similar atmospheric lifetimes were used. Errors associated with the lifetimes of the

halons are not shown in Fig. 2; a discussion of lifetimes and uncertainties is presented in Sect. 6.

4.1 H-1211

The model derived annual emissions of H-1211 are 3.0 Gg in 1978, they then increase at an average growth rate of 0.58 Gg yr^{-1} to maximum emissions of 12.8 Gg in 1995. Emissions have since decreased at an average rate of 0.52 Gg yr^{-1} to 5.0 Gg in 2010.

The emissions derived here show a similar trend to those derived by NOAA and AGAGE. The cumulative emissions derived from the model for the period 1979–2009, shown in Table 2, are 253 Gg compared to those using the AGAGE measurements and a 12-box model which are 11 % lower at 225 Gg. The emissions reported by HTOC are similar to those reported here with cumulative emissions for the period 1979–2009 of 234 Gg, 8 % lower than those derived in this work and 4 % higher than those derived by AGAGE.

4.2 H-1301

The model derived annual emissions of H-1301 in 1978 are 1.5 Gg. Annual emissions then increase gradually to 2.5 Gg in 1984 at an average rate of 0.17 Gg yr^{-1} before a more rapid increase up to a maximum of 6.0 Gg in 1987 at a rate of 1.2 Gg yr^{-1}. They then decline steadily to annual emissions between 2007 and 2010 of 1.8–1.9 Gg.

The NOAA record shows a great deal of variability and though it agrees with the general decline in recent years, the exact features are often quite different. The AGAGE emissions display far less variability and a more similar trend. Emissions derived by both AGAGE and HTOC display a steady rise from 1978 to the mid-late 1980s, whereas we derive a slower growth in the early 1980s followed by a steep increase beginning around 1985. This was also commented on in Fraser et al. (1999).

The cumulative emissions derived in this work for the period 1979–2009 (97 Gg) (Table 2) are similar to those of HTOC (99 Gg) and those derived using a 12-box model with AGAGE measurements (96 Gg).

4.3   H-2402

The model derived annual emissions are 0.9 Gg in 1978 and increase steadily up to a peak of 1.9 Gg in 1990 at a growth rate of 0.08 Gg yr^{-1}. They then decline to 1.0 Gg in 1996 and remain around this level until 2000. They then begin to decline again to 0.7 Gg in 2006 and have remained around this level up to 2010.

The emissions derived by AGAGE for the period 1979–2009 (Table 2) using a 12 box model display a very similar trend and calculate very similar cumulative emissions for the period 1979–2009 of 36 Gg compared to 35 Gg in this work. HTOC does not report annual emissions of H-2402.

4.4   H-1202

The model derived annual emissions of H-1202 are 0.16 Gg in 1978. They increase steadily up to 0.52 Gg in 1993 at a rate of 0.024 Gg yr^{-1} and then increase steeply to a peak of 0.84 Gg in 1997 before declining to 0.26 Gg in 2010.

5   The Source of H-1202

Unlike the other halons, H-1202 has negligible reported direct usage and has been produced mainly as an unwanted by-product caused by over bromination during the production of H-1211 (e.g. Fraser et al., 1999). Using a combination of northern and Southern Hemisphere measurements, Reeves et al. (2005) concluded that the latitudinal emission distribution of H-1202 shifted southward in the early 1990s. Based on the premise that H-1202 emissions are released at source (i.e. directly from H-1211 production plants) they linked this shifting of H-1202 emissions to the cessation of

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production of H-1211 in non-Article 5 countries and the movement of production to south-east Asia.

If H-1202 emissions were released as H-1211 is produced then they should have fallen to zero since the beginning of 2010 when global H-1211 production should have ceased (HTOC, 2011). However Fig. 2 shows that this is not the case; annual emissions in 2010 were 0.26 Gg. So if H-1202 emissions are directly related to H-1211 production then this suggests one of two things: either that there is still significant global production of H-1211 or that there is another source of H-1202. Based on reported efficiencies of Chinese H-1211 plants during an audit in 2002, in which 0.02–0.03 Gg of H-1202 were reported to be produced per Gg of H-1211 (E. Pedersen, World Bank, personal communication, 2002), annual emissions of 0.26 Gg of H-1202 would suggest an unreported global H-1211 production in 2010 on the order of 10 Gg. This seems very unlikely since there should have been no H-1211 production in 2010 and based on the reported production by HTOC in recent years (Fig. 3).

We propose that H-1202 emissions are actually associated with H-1211 emissions as opposed to production. This association has the corollary that all H-1211 currently installed and in banks is contaminated with a certain percentage of H-1202. This result would not be incongruous with the assertion of Reeves et al. (2005) that H-1202 emissions have moved to more southerly latitudes since the mid-1990s since H-1211 emissions also shifted toward Article 5 countries (mainly China and South Korea) from the more northerly latitudes of Europe and North America during this time period. Furthermore the degree to which H-1211 is contaminated by H-1202 will almost certainly vary according to where it is produced.

Figure 3 shows the ratio of H-1202 emissions to H-1211 emissions (both derived in Sect. 4) between 1978 and 2010, this fluctuates between 0.04 and 0.08. These fluctuations are likely to be related to the production efficiency of H-1211 which in turn might be related to the changing location of production (also shown in Fig. 3). During the period from 1978 to the early 1990s, when the majority of the production of H-1211 was in non-Article 5 countries, the ratio is seen to gradually fall as production

presumably becomes more efficient (i.e. there is less H-1202 contamination). As production decreased in non-Article 5 countries and increased in Article 5 countries in the early 1990s the ratio increases, presumably due to less efficient H-1211 production in these countries. The changes in the ratio appear to lag those in the production by a couple of years as would be expected if they were related to emissions rather than production. The subsequent decline in the ratio after 2000 suggests one of two things: either the production efficiency of H-1211 increased in Article 5 countries, or the H-1211 produced in Article 5 countries (high ratio) was used up preferentially to stocks produced in non-Article 5 countries (low ratio).

If all H-1211 is contaminated with H-1202 then this will reduce the estimated H-1211 bank. The percentage of H-1202 contamination can be calculated by dividing the H-1202 emissions (Fig. 2) by the "total H-1211" emissions, i.e. the sum of H-1211 and H-1202 emissions. This calculation shows that the current emissions of "total H-1211" are about 4 % H-1202. Assuming this to be the case then the reported 65 Gg bank (HTOC, 2011) of H-1211 would be reduced to 62.4 Gg and leave a H-1202 bank of 2.6 Gg (see Sect. 7 for further discussion on the halon banks).

The hypothesis that the source of H-1202 is as a minor component of H-1211 production could be tested by analysing some existing H-1211-charged fire extinguishers.

6 Atmospheric lifetimes

The emissions of H-1211, H-1301 and H-2402 derived in Sect. 4 are based on atmospheric lifetimes for the molecules of 16, 65 and 20 yr, respectively, as given by Montzka and Reimann et al. (2011). These lifetimes were all originally derived by Burkholder et al. (1991) using a 1-D photochemical model extending to an altitude of 60 km. There have been various other estimates of the tropospheric, stratospheric and total lifetimes, in particular the recent re-evaluation of the stratospheric lifetimes of H-1211 and H-1301 by Laube et al. (2012b). Here we re-evaluate the atmospheric lifetimes for the halons using the 2-D atmospheric model and considering the stratospheric lifetimes

reported in Laube et al. (2012b). The implications of such changes on the model derived emissions and on the sizes of the remaining halon banks are considered in Sect. 7.

6.1 Tropospheric lifetimes

The modeled tropospheric lifetimes (τ_{trop}) are calculated by running the model to steady state and then dividing the global atmospheric burden of the molecule by the global emissions. The model was run with the photolysis and OH sinks only active in the troposphere and the diffusive loss from the top of the model switched off. A range of tropospheric lifetimes were calculated by changing the defined height of the tropopause (Z_{trop}). These are shown in Table 3. The uncertainties associated with the absorption cross-sections used were also investigated. The cross-sections measured by Gillotay and Simon (1989), Gillotay et al. (1988) and Burkholder et al. (1991) generally agree to within 10 % at room temperature though this error tends to increase at wavelengths longer than 265 nm. At low temperatures the agreement is generally within 20 % but again differences tend to increase at wavelengths longer than 265 nm. Tropospheric lifetimes were calculated with the photolysis rates adjusted by ±20 % for Z_{trop} = 14 km (Table 3). This estimate is considered to account for both uncertainties in the absorption cross sections and other uncertainties in the photolysis rates calculated by the model such as the solar photon flux and attenuation of the flux by molecular oxygen and ozone. Errors in the rate constant for recation with the hydroxyl radical and in the OH field are not considered since this loss is at least 20 times smaller than photolysis for all four halons.

It is seen that the given height of the tropopause does not affect the calculated tropospheric lifetimes greatly. Moving the tropopause from 12 km to 16 km changes the H-1211 tropospheric lifetime from 25.6 yr to 24.6 yr, the H-2402 lifetime from 42.9 to 39.1 yr and the H-1202 lifetime from 3.1 to 2.9 yr. H-1301 has a tropospheric lifetime greater than 10 000 yr for all studied tropopause heights. The tropospheric lifetime of H-1211 calculated here, 25–26 yr, agrees reasonably with the figure of 23 yr calculated by

Burkholder et al. (1991), while that of H-2402 is slightly higher (39–43 versus < 34 yr) and that of H-1202 slightly lower (2.9–3.1 versus 3.2 yr), compared to Burkholder et al. (1991).

Adjusting the photolysis rates by 20 % has a relatively large effect on the tropospheric lifetimes giving a tropospheric lifetime range for H-1211 of 21.0 yr to 30.9 yr, for H-2402 of 34.0 to 50.8 yr and for H-1202 lifetime of 2.5 to 3.7 yr.

6.2 Stratospheric lifetimes

To calculate the stratospheric lifetimes (τ_{strat}) the photolysis and OH sinks were only active in the stratosphere and the effect of a range of values for F (the ratio of the mixing ratio of the molecule at the centre of a box directly above the model domain (25 km) to that at the centre of the top box (23 km)) was investigated (Table 3). The stratospheric lifetime calculated in this way is an approximation since the atmospheric burden above the model domain is not known and so cannot be included in the calculation. However use of a 1-D atmospheric model extending up to 50 km suggests that this is less than 1.5 % of the total atmospheric burden for H-1211 and H-1301 at steady state with no tropospheric loss.

The stratospheric lifetimes calculated using the full range of possible values for F are presented in Table 3. The value of F can, however, be compared to actual measurements of the halons at 23 and 25 km. Very few such measurements at these altitudes exist, but we do have measurements from three midlatitude balloon flights; two from Aire sur l'Adour, France in October 1994 and March 1999, and one from Gap, France in June 1997, and a tropical balloon flight from Teresina, Brazil. The midlatitude data are previously unpublished, but were collected and analysed in essentially identical manner to other balloon flights from the same series reported by Pfeilsticker et al. (2000). The tropical measurements were reported by Laube et al. (2008). For H-1211, based on three flights, the mean value of F for H-1211 was 0.21 with a standard deviation of 0.01. For H-1301, based on four flights, the mean value of F was 0.74 with a standard

deviation of 0.1. For H-2402 only one flight detected the molecule above 25 km and gave a value for F of 0.19. H-1202 was not detected above 25 km on any of the flights.

The stratospheric steady state lifetimes of H-1211 and H-1301 have recently been re-evaluated by Laube et al. (2012b) based on tracer analysis using samples collected by the high altitude research aircraft, Geophysica, and a range of balloon flights. Laube et al. (2012b) report two calculated stratospheric lifetimes, relative to a CFC-11 lifetime of 45 yr and of 53.6 yr. For H-1211 these are 25 ± 2 yr and 30 ± 2 yr and for H-1301 they are 63 (+10, −7) years and 75 (+11, −8) yr (Table 4). The lifetime of CFC-11 is given in Montzka and Reimann et al. (2011) as 45 yr but recent work has suggested a steady state lifetime of 56–64 yr (Douglass et al. 2008). This is acknowledged in Montzka and Reimann et al. (2011) as they note that, "evidence is emerging that lifetimes for some important ODSs (e.g. CFC-11) may be somewhat longer than reported in past assessments". In this study we use the stratospheric lifetimes calculated for a CFC-11 lifetime of 53.6 yr (30 yr, H-1211; 75 yr H-1301).

The value of the ratio F required to be used in the model to give the stratospheric lifetimes from Laube et al. (2012 b) was examined. For H-1211 a value of 0.04 was required, and for H-1301 a value of 0.797. For H-1301 this is within the 1σ range of the balloon measurements reported here. For H-1211 this is outside the 1σ range but it is noted that a value for F of 0.2, as suggested by the balloon data, gives a stratospheric lifetime of 31 yr, within the range given by Laube et al. (2012b).

There have been no stratospheric lifetimes derived from measurements for H-2402 or H-1202. Consequently the value of F used for the best estimate of the stratospheric lifetime of H-2402 was constrained using the one relevant balloon flight. For H-1202 there are no relevant balloon flight data but it seems likely that mixing ratios are decreasing rapidly with height at this height and so a value for F of 0.2, as measured for H-1211 and H-2402, was used for the best estimate of stratospheric lifetime.

6.3 Total atmospheric lifetimes

The total atmospheric lifetimes (τ_{atm}) are calculated by combining the inverse of the tropospheric and stratospheric lifetimes. The tropospheric lifetimes used for the revised total lifetimes are those calculated for Z_{trop} = 14 km. For H-1211 and H-1301 the stratospheric lifetimes derived by Laube et al. (2012b) relative to a CFC-11 lifetime of 53.6 yr were used. For H-2402 and H-1202 the stratospheric lifetimes calculated in the model, with the value of F constrained by the balloon data as described above, were used.

This gives total atmospheric lifetimes of 14 (12–16) yr for H-1211, 75 (67–86) yr for H-1301, 17 (16–20) yr for H-2402, and 2.6 (2.2–3.2) yr for H-1202. This is likely to be a maximum lifetime for H-2402 since, unlike for H-1211 and H-1202, Burkholder et al. (1991) did not extrapolate the absorption cross sections to wavelengths longer than 320 nm due to the non-systematic nature of the cross sections calculated between 300–320 nm. Uncertainty ranges are calculated by combining the uncertainties in the tropospheric and the stratospheric lifetimes given in Table 4.

7 Cumulative emissions and halon banks

The production of halons for direct use has ceased globally as of 1 January 2010 (HTOC, 2011) with the People's Republic of China stopping production of H-1211 by the end of 2005 and H-1301 by the end of 2009 and the Republic of Korea halting production of both by the end of 2009 (HTOC, 2011). There is still some limited production of H-1301 for use as a chemical feedstock in the preparation of the fertilizer Fipronil. Such usage is not controlled under the Montreal Protocol.

Assuming no resumption of production, emissions are likely to continue to fall year on year. However many countries have their own halon recycling programs whereby unused halons can be collected and reused in equipment that still requires the gases and so it is likely that halon use for essential purposes will persist for some time. Some countries have also destroyed halon stocks though this is generally discouraged by

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HTOC as halons will continue to be needed to be used for essential use exemptions until viable alternatives can be found. There is also the possibility of the existing stocks being used up in other ways such as the large scale consumption of H-2402 in Russia as a chemical process agent during 2002–2003 when prices were low (HTOC, 2011).

Table 5 shows the banks of the halons at the end of 2010 estimated by HTOC (2011) to be 65 Gg, 42.5 Gg and 2.3 Gg for H-1211, H-1301 and H-2402, respectively. Table 5 also shows the banks for H-1211 and H-1301 calculated in this work by subtracting the cumulative emissions up to the end of 2010 derived in Sect. 4 from the cumulative production reported by HTOC (2011). This calculates a bank of 37 Gg for H-1211, 43 % lower than that reported by HTOC, and 43 Gg for H-1301, very similar to that reported by HTOC. The bank of H-1202 is estimated as 4 % of the H-1211 bank as described in Sect. 5. The bank of H-2402 cannot be calculated because HTOC does not report H-2402 production.

The emissions of H-1211, H-1301 and H-2402 derived in Sect. 4 would be altered by the revised lifetimes reported in Sect. 6. The decreased lifetimes of H-1211 and H-2402 compared to those reported in Montzka and Reimann et al. (2011) would require higher global emissions to fit the measurements. Likewise the increased lifetime of H-1301 would require lower emissions to fit the measurements. The model was run with the revised lifetimes and the cumulative emissions (1979–2009) derived for H-1211 increase by 26 Gg to 279 Gg, for H-1301 decrease by 4 Gg to 93 Gg and for H-2402 increase by 4 Gg to 39 Gg (Table 2).

These revised cumulative emissions have implications for the remaining banks of the halons. Calculating the banks, as described above, with the revised cumulative emissions would mean the H-1211 bank was 10 Gg, just 15 % of that estimated by HTOC, the H-1301 bank would be 49 Gg compared to 42.5 Gg estimated by HTOC (Table 5). The cumulative emissions of H-2402 would be 4 Gg higher but this cannot be directly compared to the bank reported by HTOC as they do not report production of H-2402 and their estimate of the bank is not a direct calculation of production less emissions.

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The estimate of the H-1211 bank being only 10 Gg seems unlikely given annual emissions in 2009 and 2010 of 5.7 and 5.0 Gg. This would suggest that at current annual emission rates the bank of H-1211 would be used up within 2–3 yr. Given the current rate of emissions it seems unlikely that the bank is so small and more likely that

5 production has been under-reported.

For H-1301 the calculation of a bank 15 % larger than that estimated by HTOC may be significant for the decline of tropospheric bromine contributed by the halons particularly because of the long lifetime of H-1301.

8 Total tropospheric bromine

10 The total bromine mixing ratio from methyl bromide and the halons in the troposphere peaked at 16–17 ppt around 1998 and by 2008 had declined to 15.7 ± 0.2 ppt (Montzka and Reimann, 2011). This decline has been attributed mainly to a decrease in the emissions of methyl bromide (Montzka and Reimann, 2011). The measurements from Cape Grim show that during the period 2002–2011 the H-1211 mixing ratio has fallen

15 slightly and that of H-1301 has risen slightly. Consequently there has been no change in the contribution to tropospheric bromine mixing ratios from the halons at Cape Grim between 2005 and mid-2011, remaining stable at 7.9 ppt.

Figure 4 shows the contribution of each of the halons to global mean tropospheric bromine mixing ratios, based on measurements at Cape Grim, extrapolated to 2060.

20 From 1978 to 2010 the emissions used to derive the halon mixing ratios are those derived in Sect. 4. Thereafter three scenarios are presented (Fig. 4b). Scenario 1 uses emissions based on the reported banks from HTOC (2011) and the bank release fraction (the proportion of the remaining bank released per year) reported in WMO 2010 (H-1211 – 0.075, H-1301 – 0.04, H-2402 – 0.08) (Daniel and Velders, 2011), this is

25 the same scenario presented in Fig. 4a. Scenario 2 uses emissions based on the banks calculated in this work using the atmospheric lifetimes of the halons reported in Montzka and Reimann et al. (2011) (Table 5). New bank release fractions are also

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used calculated for H-1211 and H-1301 by dividing emissions of the halon in 2010 by the calculated bank at the end of 2009 (H-1211 – 0.1, H-1301 – 0.038). Scenario 3 uses emissions based on the bank calculated in this work using the atmospheric lifetimes of the halons reported in this work (Table 5). It also uses new bank release fractions calculated in the same way as above (H-1211 – 0.3, H-1301 – 0.036). For H-2402 the same bank and bank release fractions are used for all three scenarios because a revised bank cannot be calculated in this work (see Sect. 7). H-1202 is not shown in Fig. 4 as its contribution is negligible due to low emissions and a short lifetime.

It is seen that for Scenario 1 (Fig. 4a), H-1211 mixing ratios fall rapidly after 2010 and H-1301 contributes more than 50 % of the total tropospheric bromine from halons after 2024 (compared to 39 % in 2010), this is because of its long atmospheric lifetime. For Scenario 2 H-1301 contributes 50 % earlier, in 2022, and for Scenario 3 in 2017. Figure 4b shows that if the H-1211 bank is smaller than estimated by HTOC, as suggested by this work, then the tropospheric bromine burden from the halons will fall more quickly in the coming decades but by 2060 all three scenarios converge. In 2060 H-1301 is contributing more than 80 % of the total 2.9 ppt of bromine from the halons in Scenario 1 (Fig. 4a). In Scenario 2 it is contributing about 85 % and in Scenario 3 it is contributing almost 95 % of the total bromine from the halons (Fig. 4b). Assuming that production has ceased, these predictions are an upper estimate of the future contribution of the halons to tropospheric bromine since, as stated in Sect. 7, they may be destroyed or consumed in alternative ways, preventing their release to the atmosphere.

9 Conclusions

The atmospheric mixing ratios of H-1202, H-1211 and H-2402 are all declining and are likely to continue to do so due to the cessation of all halon production in 2010. H-1301 mixing ratios are still growing and hence the total contribution of the halons to tropospheric bromine is not currently declining. H-1301 is likely to become the main

halon contributing to tropospheric bromine by 2025. The total contribution from the halons in 2060 is predicted to be 2.9 ppt, 37 % of that in 2010.

Emissions of all of the halons have declined since peaking in the late-1980s to mid-1990s but the decline has slowed in recent years with no significant changes in emissions of H-1301 and H-2402 between 2006 and 2010.

H-1202 emissions appear not to have declined to zero as would be expected if they occurred during H-1211 production, but instead they seem to be associated with H-1211 emissions. There could be a contamination of existing stocks of H-1211 of 4 % H-1202 or higher. Hence future emissions of H-1202 might be expected to follow the same trend of those of H-1211.

Revised lifetimes for the halons are discussed based on newly reported stratospheric lifetimes and high altitude balloon flights. These are 14 yr for H-1211, 75 yr for H-1301, 17 yr for H-2402 and 2.6 yr for H-1202. These new lifetimes could mean that the existing bank of H-1301 is 49 Gg, 15 % larger than presently believed and that the existing bank of H-1211 is 10 Gg, over 80 % smaller than presently believed. The discrepancy between the H-1211 bank calculated here and that reported by HTOC suggests considerable uncertainties in the H-1211 budget requiring further investigation.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/29289/2012/ acpd-12-29289-2012-supplement.pdf.

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Table 1. Mean mixing ratios of the halons at Cape Grim for January to June 2011, and mean growth rates for the periods 1985–1999, 1999–2005 and 2005–2011.

| | Mean mixing ratio Jan–Jun 2011 (ppt) | Mean growth rate (ppq yr^{-1}) | | |
		1985–1999	1999–2005	2005–2011
H-1211	3.98 ± 0.04	186 ± 14	67 ± 24	-42 ± 16
H-1301	3.15 ± 0.03	139 ± 7	54 ± 21	29 ± 17
H-2402	0.39 ± 0.01	16 ± 1.5	0 ± 1.7	-3.3 ± 2.5
H-1202	0.020 ± 0.001	2.2 ± 0.1	-1.7 ± 0.2	-2.6 ± 0.2

Table 2. Cumulative emissions of the halons between 1979 and 2009 reported by HTOC (bottom-up estimate), AGAGE (top-down estimate), and calculated in this work using firstly the reported lifetime of Montzka et al. (2011) and secondly the lifetime calculated in this work (Sect. 6).

Reference	H-1211 (Gg)	H-1301 (Gg)	H-2402 (Gg)	H-1202 (Gg)
HTOC	234	99	–	–
AGAGE	225	96	36	–
This Work				
Using τ_{atm}, WMO, 2010[a]	253	97	35	14
Using revised τ_{atm}^{b}	281	93	39	14
	(253–304)	(90–96)	(35–42)	(12–18)

[a] Except H-1202 (from this work).
[b] See Sects. 6 and 7 and Table 4.

Table 3. Tropospheric (τ_{trop}), stratospheric (τ_{strat}), and total atmospheric (τ_{atm}) lifetimes of the halons. Tropospheric lifetimes vary based on the defined height of the tropopause (Z_{trop}), with uncertainties due to ±20% photolysis rates also given at $Z_{trop} = 14$ km. Stratospheric lifetimes vary based on the diffusive loss from the top of the model which is determined by the ratio of the mixing ratio of the given molecule at 25 km to that in the top model box (23 km) (F). Uncertainties due to ±20% photolysis rates are given for representative values of F for each halon (see Sect. 6).

Model run	H-1211	H-1301	H-2402	H-1202
τ_{trop} (yr)				
$Z_{trop} = 12$ km	25.6	> 10 000	42.9	3.11
$Z_{trop} = 14$ km	25.0	> 10 000	40.7	3.00
($\sigma \pm 20\%$)	(21.0–30.9)	(–)	(34.0–50.8)	(2.51–3.72)
$Z_{trop} = 16$ km	24.6	> 10 000	39.1	2.92
τ_{strat} (yr)[a]				
$F = 1.0$	50.2	370	50.0	27.2
$F = 0.8$	39.5	75.9	39.3	24.4
($\sigma \pm 20\%$)	–	(74.0–78.0)	–	–
$F = 0.5$	33.6	47.5	33.4	22.3
$F = 0.2$	30.9	39.5	30.7	21.2
($\sigma \pm 20\%$)	–	–	(29.3–32.2)	(19.5–23.3)
$F = 0.0$	29.8	36.8	29.6	20.7
($\sigma \pm 20\%$)	(28.7–31.1)	–	–	–

[a] Stratospheric lifetimes are only calculated for $Z_{trop} = 14$ km (stratospheric lifetimes at $Z_{trop} = 12$ km and 16 km can be inferred using the total lifetime (Table 4) and the tropospheric lifetime).

Table 4. Reported tropospheric (τ_{trop}), stratospheric (τ_{strat}), and total atmospheric (τ_{atm}) lifetimes of the halons.

Reference	H-1211	H-1301	H-2402	H-1202
	τ_{trop} (yr)			
Burkholder et al. (1991)	23	> 397	< 34	3.2
This work[a]	25	> 10 000	41	3.0
	(21–31)	(–)	(34–51)	(2.5–3.7)
	τ_{strat} (yr)			
Volk et al. (1997)	24 ± 6	–	–	–
Laube et al. (2012b)[b]	25 ± 2	65 (+10, −7)	–	–
Laube et al. (2012b)[c]	30 ± 2	75 (+11, −8)	–	–
This work	30 ± 2[d]	75 (+11, −8)[d]	31[e]	21[e]
	(28–32)	(67–86)	(29–34)[f]	(19–23)[f]
	τ_{atm} (yr)			
Burkholder et al. (1991)[g]	16	65	< 20	3.3
Butler et al. (1998)	11[h]	–	–	–
This work[a,d]	14	75[i]	17	2.6
	(12–16)	(67–86)	(16–20)	(2.2–3.2)

[a] See Sect. 6 and Table 2 for further details.
[b] Based on a lifetime for CFC-11 of 45 yr.
[c] Based on a lifetime for CFC-11 of 53.6 yr.
[d] The lifetimes of H-1211 and H-1301 from Laube et al. (2012b) for a CFC-11 lifetime of 53.6 yr are used.
[e] For $F = 0.2$.
[f] Based on ±20 % photolysis rates and $F = 0.0$–0.5.
[g] These are the values reported in Montzka et al. (2011) with the exception of H-1202.
[h] A combination of the stratospheric lifetime (based on correlation with age) of Volk et al. (1997) and the tropospheric lifetime of Burkholder et al. (1991).
[i] The stratospheric lifetime from Laube et al. (2012b) is considered a total atmospheric lifetime as H-1301 has negligible loss in the troposphere.

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Table 5. Halon banks (Gg) at the end of 2010 reported by HTOC and calculated in this work using firstly the reported lifetime of Montzka et al. (2011) and secondly the lifetime calculated in this work (Sect. 6).

Reference	H-1211 (Gg)	H-1301 (Gg)	H-2402 (Gg)	H-1202 (Gg)
HTOC (2011)	65	42.5	2.3	–
This Work				
Using τ_{atm}, WMO, 2010[a]	37 (36)[b]	43	–	1.5[c]
Using revised τ_{atm}^{d}	10 (10)[b]	49	–	0.4[c]
	(−13–38)	(46–52)		

[a] Based on cumulative production reported by HTOC (2011) minus cumulative emissions derived in this work.
[b] Based on 4 % contamination with H-1202 (see Sect. 5).
[c] Based on the assumption that the remaining H-1211 bank is contaminated with at least 4 % H-1202 (see Sect. 5).
[d] See Table 4 for ranges of τ_{atm}.
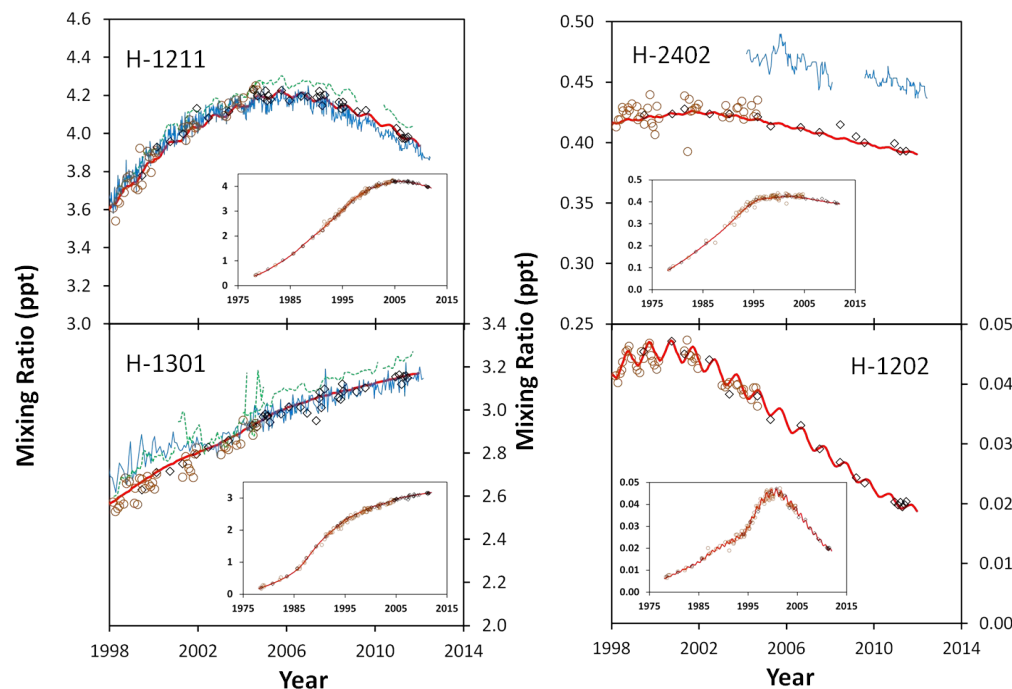
Fig. 1. Measured mixing ratios (ppt) of the halons from Cape Grim at UEA from 1978 to 2011 using the Al-PLOT column (brown circles) and the GasPro column (black diamonds). Solid red lines are the model runs used to derive emissions. Solid blue lines for H-1211, H-1301 and H-2402 are measured mixing ratios (ppt) from Cape Grim by NOAA (Montzka and Elkins, 2012). Dashed green lines for H-1211 and H-1301 are measured mixing ratios (ppt) from Cape Grim by AGAGE (http://agage.eas.gatech.edu/).

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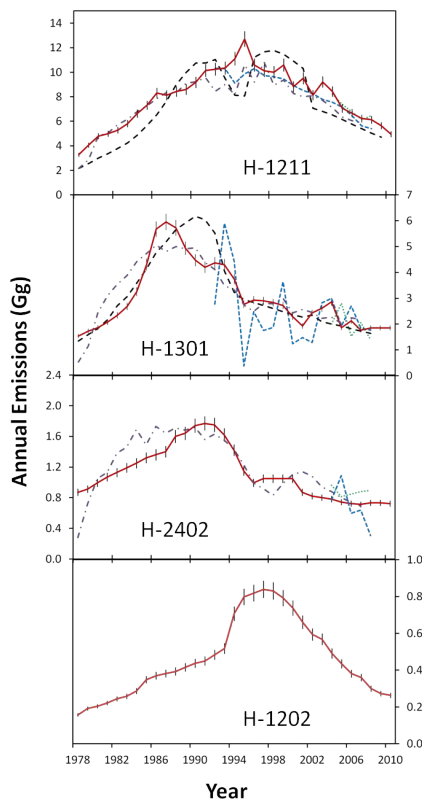
Fig. 2. Model derived global annual emissions (Gg) of the halons. Current work – red line; NOAA one box model (Montzka and Reimann, 2011) – blue short dashed line; AGAGE one box model (Montzka and Reimann, 2011) – green dotted line; AGAGE 12-box model (Montzka and Reimann, 2011) – purple dash-dot line; annual emissions reported by HTOC (2011) – black long dashed line. Uncertainty ranges, as defined in Sect. 4, are shown for each year.
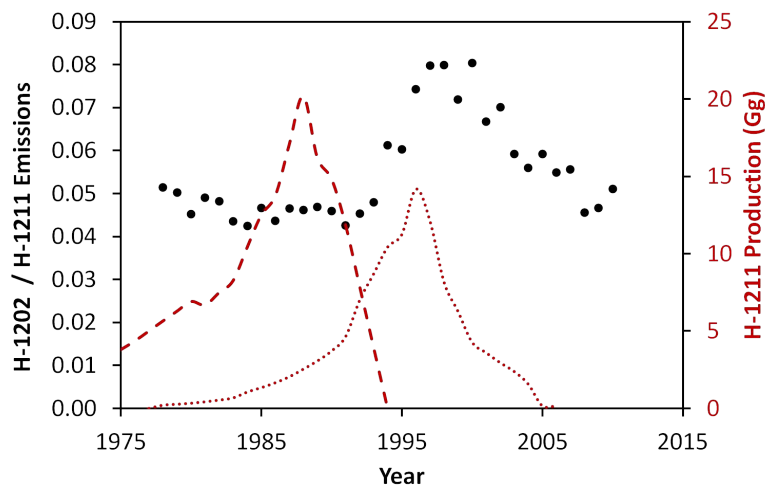
Fig. 3. The ratio of model derived emissions of H-1202 to H-1211 (see Fig. 2) (black circles). Also shown is production of H-1211 in non-Article 5 countries (red dashed line) and Article 5 countries (red dotted line).
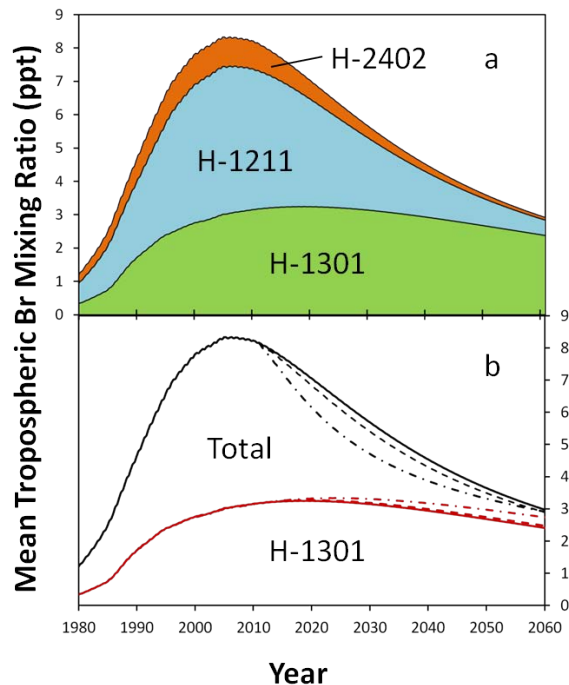
Fig. 4. Predicted contributions of the halons to mean global tropospheric bromine mixing ratios. Mixing ratios to the end of 2010 are based on the measurements at Cape Grim reported in Sect. 3. **(a)** Emissions after 2010 are based on banks from HTOC (2011) and bank release fractions from Daniel and Velders et al. (2011). **(b)** For emissions after 2010 as for Fig. 4a (solid line); for emissions after 2010 based on banks and bank release fractions calculated in this work using atmospheric lifetimes reported in Montzka et al. (2011) (dashed line); for emissions after 2010 based on banks and bank release fractions calculated in this work using the atmospheric lifetimes calculated in Sect. 6 (dash-dot line).