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Atmospheric Chemistry and Physics
Discussions
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# *Interactive comment on* "Chlorine isotope composition in chlorofluorocarbons CFC-11, CFC-12 and CFC-113 in firn, stratospheric and tropospheric air" *by* S. J. Allin et al.

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General comments

Allin et al present analyses and interpretation of chlorine stable isotopes in CFC-12, CFC-11 and CFC-113 in tropospheric and stratospheric air samples, as well as in the Cape Grim air archive and in old air extracted from polar firn. This is an interesting data set in that it seems to present the first chlorine stable isotope measurements ever made on atmospheric CFC-11 and CFC-113. It also appears that the historical isotopic measurements (in the Cape Grim archive and in firn air) are a "first" for all species. The

authors are to be commended for tackling such challenging measurements successfully. Because of the novelty of the measurements, this manuscript should ultimately be publishable in ACP. However, at this stage there are several major components that in my opinion are underdeveloped and/or confusing and require further work before the manuscript can be accepted.

Referee comment 1

p.31818 (Methodology) Much more detail is needed on all the samples (these could go either in the main body of the paper or in the supplement). For the stratospheric samples, were all the samples collected in the cited von Hobe et al., 2013 study measured? If not, the relevant sample subset needs to be described (collection dates, sample type, altitude, lat-long, etc).

Author response

We would like to thank the reviewer for their comments, which we feel have improved our manuscript. Tables containing details of the stratospheric samples have been added to the supplement.

Referee comment 2

For the Cape Grim archive, more details should be given supported by references.

Author response

A table containing details of the Cape Grim samples has been added to the supplement. Details of the sampling procedure have been previously reported in Langenfelds et al. (1996), which is cited in Table 2 of the ACPD paper.

Referee comment 3

Have tests been performed to ensure that the species of interest are well preserved in the archive flasks over a long period of time, and are unaffected by artifacts at the times of archive creation and sub–sampling for this study?

Author response

The difference between sampling and analysis dates are highly variable, ranging from a few months to 34 years. In all cases, mole fractions for these species are consistent with previously reported time series (e.g. Martinerie et al., 2009), suggesting that they have not been altered by their storage environment. The measured delta values from both firn air and the Cape Grim archive agree within measurement uncertainties. In this way, the Cape Grim measurements confirm that the firn measurements represent the atmospheric composition and have not been influenced by unaccounted for fractionation processes (e.g. during sampling). Also, we see delta values of 0 ‰ in 2006, meaning that measurements of samples from 2006 contain 37Cl and 35Cl in approximately the same ratio as the laboratory standard (air collected in 2006 at Niwot Ridge). This again suggests that our data represent reproducible measurements of the atmospheric composition. Finally, several different sampling procedures were used to collect air at Cape Grim (e.g. cryogenic trapping and direct pumping of air). There are no statistical differences between measurements made on samples collected using these different procedures.

References: Martinerie, P., Nourtier-Mazauric, E., Barnola, J.-M., Sturges, W. T., Worton, D. R., Atlas, E., Gohar, L. K., Shine, K. P., and Brasseur, G. P.: Long-lived halocarbon trends and budgets from atmospheric chemistry modelling constrained with measurements in polar firn, Atmos. Chem. Phys., 9, 3911–3934, doi:10.5194/acp-9-3911-2009, 2009.

Referee comment 4

For the firn air samples, either a detailed description of the sampling campaigns or citations to papers containing these descriptions need to be provided.

Author response

Firn air was recovered from the NEEM ice core site in Greenland (NEEM Community

Members, 2013) and from the Fletcher Promontory ice core site in Antarctica (Mulvaney et al., 2014). In each case, shallow ice core drills progressively penetrated the firn column, stopping every few meters to allow recovery of the firn air. The firn air extraction technique (Schwander et al., 1993) uses a bladder inflated at the bottom of the borehole to seal off ambient air from above. Gas pumps draw sample air from the firn surrounding the lowest level of the borehole through continuous Dekabon tubes (internal diameter $\frac{1}{4}$ inch) passing through the bladder and its end caps, compressing the air into sample flasks at the surface. An infrared analyser (LI-COR LI-7000) continuously monitors the sample line CO2 and samples are only taken when the CO2 drops to a stable reading lower than modern ambient levels, indicating that uncontaminated air is being extracted from the borehole.

References: Mulvaney, R., Triest, J., and Alemany, O.: The James Ross Island and the Fletcher Promontory ice-core drilling projects, Ann. Glaciol., 55, 68, 179-188, doi: 10.3189/2014AoG68A044, 2014. NEEM Community Members: Eemian interglacial reconstructed from a Greenland folded ice core, Nature, 493, 7433, 489-494, doi: 10.1038/nature11789, 2013. Schwander, J., Barnola, J. M., Andrie, C., Leuenberger, M., Ludin, A., Raynaud, D., and Stauffer, B.: The age of the air in the firn and the ice at Summit, Greenland, J. Geophys. Res.-Atmos., 98, 2831–2838, doi:10.1029/92JD02383, 1993.

Referee comment 5

Have tests been performed to ensure that the CFCs of interest are not affected by firn air sampling artifacts?

Author response

See responses to comments 3 and 4.

Referee comment 6

p. 31819 (Sample Analysis) Is it possible that isotopic fractionation occurs during ionization and fragmentation in the MS ion source, affecting the measured values for CFC-11 and CFC-113? For both of those compounds, one of the Cl atoms is missing from the fragments that are actually measured. A discussion of this should be included.

Author response

Yes, the mass spectrometer is expected to cause isotopic fractionation. However, this fractionation is assumed to be identical for sample and standard and cancel out from the derived isotope delta since both are treated the same way (the "identical treatment principle"). This is standard practice for all relative isotope ratio measurements. The issue of delta linearity with respect to sample size is addressed in the discussion of the dilution series analysis in the supplement.

Referee comment 7

For equation 1, the authors need to justify why they use a non-standard definition of isotopic delta notation (without multiplying by the factor of 1000)

Author response

We are using the standard definition of delta (Eq. 1) and express the values in per mill, as stated in the ACPD paper. The factor of 1000 is included in the conversion to per mill, not in the definition of delta.

Referee comment 8

In equations 4 and 5, F seems to serve as both the magnitude of the trace gas flux as well as the bulk air flux – this should be clarified with subscripts.

Author response

Yes, more detailed definitions are needed. F: bulk air flux between troposphere and stratosphere and vice versa (in mol a-1) FTS: CFC flux from troposphere to stratosphere (in mol a-1) FST: CFC flux from stratosphere to troposphere (in mol a-1)

Referee comment 9

It is not clear to me that equation 8 follows from equation 7. Please present a more detailed derivation, in the supplement if necessary.

Author response

From Eq. 1 we have yT' = yT (1 + $\delta$T) Rstandard, yS' = yS (1 + $\delta$S) Rstandard and yP' = yP (1 + $\delta$P) Rstandard. Substituting this into Eq. (7) gives Eq. (8).

Referee comment 10

Same in regards to equations 9 & 10 following from 8 & 4

Author response

Eq. (4) is subtracted from Eq. (8) to give Eq. (9). Eq. (10) is derived in exactly the same fashion from Eq. (5), also using Eq. (11).

Referee comment 11

I don't understand the purpose of equation 12. Delta(st) is a measured quantity, whereas epsilon(app) is inferred (in part from delta(st)). So why use epsilon(app) to calculate delta(st)?

Author response

The ACPD paper refers to Röckmann et al. (2003) to explain this. $\delta$ST is a representative value of the stratospheric composition at the boundary of the 2-box model (just as yS is). It cannot be measured directly, but it is inferred from the ratio yS/yT and the empirically determined value for $\varepsilon$app.

Referee comment 12

I think it would be useful to discuss the meaning and purpose of and differences between epsilon(app) and epsilon(j) in detail

Author response

$\varepsilon$app is the apparent stratospheric isotope fractionation, which is empirically determined for the years 1999 to 2008 (reflecting the time of stratospheric sample collection and the age of stratospheric air). It depends on both chemistry and transport (Kaiser et al. 2006), which may have changed over the period of CFC emissions. $\varepsilon$J is a model parameter that is tuned to give $\varepsilon$app for the corresponding model years. It has no immediate physical interpretation and is only meaningful in the context of the chosen 2-box model.

Referee comment 13

After tuning J (the loss rate coefficient) in the manner described, are equations 4 – 6 then solved for Ys and P only?

Author response

Yes, that is correct.

Referee comment 14

Why is a larger suite of gases (than just CO2 and CH4) not used to constrain firn diffusivities for NEEM 2009? This should be done, unless the authors can demonstrate that this would make no significant difference to the firn modeling.

Author response

The firn modelling output has been re-calculated using SF6, HFC-134a, CH3CCl3, CFC-11, CFC-12 and CFC-113 as additional constraints. This did not make a significant difference to the results, although we agree that it was worth doing.

Referee comment 15

Table S4. The median age and age width are listed as preliminary. These need to be finalized.

Author response

This was an oversight and the numbers should not have been listed as preliminary. This has been changed.

Referee comment 16

I would recommend some chemical kinetics-based discussion of why epsilon(app) seems to be so much larger for CFC-12 than for CFC-11 and CFC-113 (and why the values appear to be similar for CFC-11 and CFC-113). To me, this seems like a somewhat surprising result.

Author response

$\varepsilon$app is affected by chemistry and transport, but the influence of transport is likely to be similar for these CFCs because of their similar lifetimes. Therefore, changes in $\varepsilon$app can directly be interpreted as changes in the intrinsic photochemical fractionation, which is dominated by photolysis. Theoretical quantum-chemical predictions of the photolytic isotope fractionations of these molecules are beyond the scope of this paper. However, we note that Zuiderweg et al. (2012) found that the 13C/12C fractionation during CFC-11 photolysis to be also of smaller magnitude to that of CFC-12, so the stronger fractionation of chlorine isotopes during CFC-12 photolysis is not entirely surprising.

Referee comment 17

The assumption of a constant Cl isotopic composition of the source for each of the gases is central to the box modeling. A discussion needs to be included justifying this assumption.

Author response

Without detailed information on isotopic fractionation during CFC production, changes in production processes or direct source gas measurements, this makes the fewest assumptions and is scientifically the most "economical" approach. In response to this comment, we show how the source $\delta$(37Cl) needs to change, assuming a constant tropospheric $\delta$(37Cl) (since there are no statistically significant trends in our tropospheric data). The results and a more detailed discussion can be found in the response to comment 18.

Referee comment 18

I am not convinced by the box model interpretation of the tropospheric history data. I agree that given the relatively large measurement uncertainties, the presented interpretations (along with their relatively narrow uncertainty bands) are possible. However, many other scenarios would be just as consistent with the data and need to be explored as well. I would specifically recommend exploring more data – driven (rather than model – driven) historical scenarios and removing the assumptions of constant isotopic composition of the source and possibly of constant sink fractionation. Just visually assessing the data in figure 3, two distinct trends in the isotopes seem apparent for all species. In the early part of the record (before 1990), there seems to be a trend toward more negative isotopic values for all species, followed by an increasing trend after about 1990.

Author response

The 2-box budget equations (section 2.3) can be solved for the isotope delta of the emissions ($\delta$E) (Röckmann et al. 2003), using the measured tropospheric isotope delta ($\delta$T). However, the tropospheric measurements have large uncertainties and no statistically significant trends over time (see ‘Trends analysis’ below). Assuming a constant $\delta$T at the mean measured value (“delta_T(flat)” in Figures R1-3), the resultant emissions deltas are shown (“delta_E(flat)” in Figures R1-3). The calculated decreases in $\delta$E are due to the stratospheric 37Cl enrichment (Figure 1 of the ACPD paper), which would have to be balanced by a decreasing $\delta$E to produce a constant $\delta$T value. The decreasing emissions from the late 1980s (Figure 2 of the ACPD paper) make the $\delta$E

decreases even more pronounced. These deviations from zero in the right hand panels do not indicate that the emissions have become significantly different from zero. These plots represent a cumulative effect over the whole time series, meaning that small tropospheric trends (hidden by the measurement uncertainties) would produce no change in the isotope delta of emissions (as shown in Figure 3 of the ACPD paper). Additional atmospheric $\delta$T scenarios have also been investigated. The “delta_T(low to high)” scenario in the left hand panels represent a change from the mean value minus the standard deviation at the beginning of the record to the mean value plus the standard deviation at the end. The “delta_T(high to low)” represents the inverse calculation. The resultant emissions deltas in the right hand panels show the large range of $\delta$E histories that are possible, based on the $\delta$T atmospheric scenarios presented here. None of these trends are robust and were used to illustrate the range of $\delta$E histories that could have produced our $\delta$T measurements. At present, these trends are not thought to be realistic, because we have no evidence of a changing source composition, degradation in the environment (other than the stratosphere), or isotope fractionation during their production, storage and measurement. In light of this and based on the evidence that we do have, we present a constant source isotope delta scenario in the paper but point out that this is just one of a range of scenarios that would fit our tropospheric data.

Trends analysis: Using linear regression, we have derived the following trends for the entire data series: CFC-11: (-0.044±0.023) ‰ a–1 (p = 0.065) CFC-12: (-0.031±0.023) ‰ a–1 (p = 0.19) CFC-113: (-0.063±0.030) ‰ a–1 (p = 0.042)

Except for CFC-113, these are not statistically significant at the 95 % confidence level. If the first point of the CFC-113 time series is omitted, the p value increases to 0.16; if the first two are omitted, the p value increases to 0.71. Therefore, we do not consider any of these trends to be statistically robust.

Furthermore, as suggested by the reviewer, we have split each time series into two periods and compared the mean $\delta$T values for each period. This reduces the effect of individual data points that may bias linear regression analyses (see above). We could not find any two periods with differences that were statistically significant at the 95 % confidence level. Using a t-test to compare the differences, the lowest p values were found for the periods shown in Figure R4.

Referee comment 19

Supplement, p.2. Please provide a reference for "the Matsunaga data series”

Author response

This has been added.

Referee comment 20

Figure S2. An equivalent plot for NEEM data should be provided for completeness

Author response

This is now included.

Referee comment 21

Table S3. For the caption, did you mean "median air age and the width of age distribution. . .”?

Author response

Yes, this has been changed.

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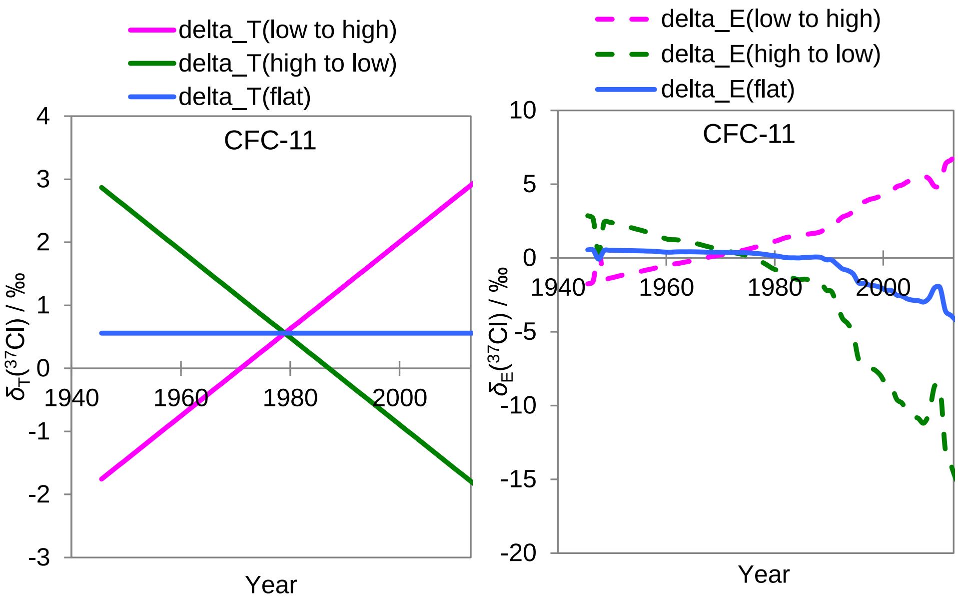
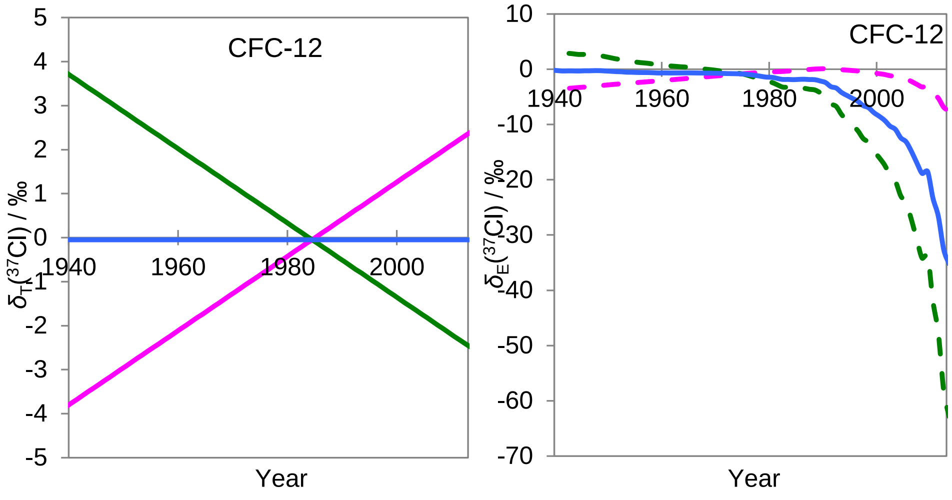
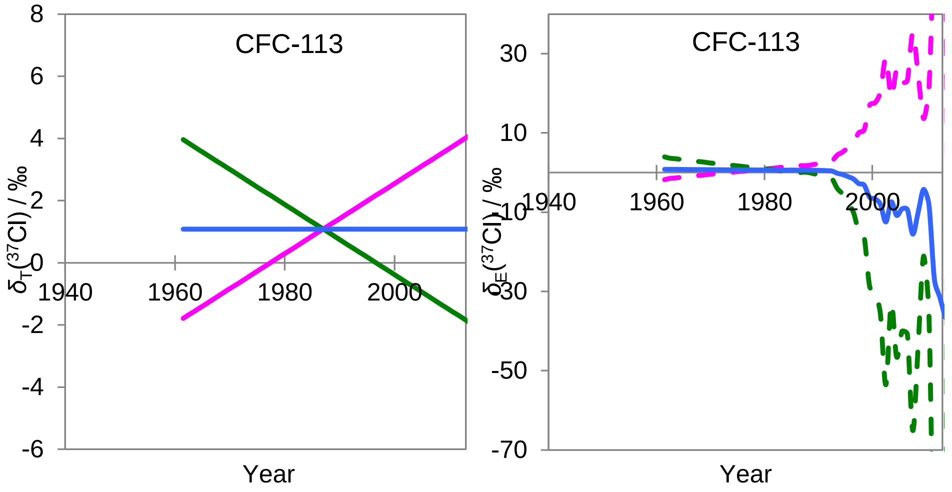
Interactive comment on Atmos. Chem. Phys. Discuss., 14, 31813, 2014.





C13132



C13133

|  | CFC-11 | CFC-12 | CFC-113 |
|---|---|---|---|
| Period 1 | 1946-1984 | 1955-1997 | 1962-1992 |
| mean | 2.1 ‰ | 0.7 ‰ | 2.4 ‰ |
| standard deviation | 3.2 ‰ | 3.3 ‰ | 3.3 ‰ |
| standard error | 1.1 ‰ | 0.7 ‰ | 0.8 ‰ |
| number of data points *n* | 9 | 24 | 15 |
| Period 2 | 1985-2012 | 1998-2012 | 1993-2012 |
| mean | 0.2 ‰ | –0.4 ‰ | 0.5 ‰ |
| standard deviation | 1.8 ‰ | 1.9 ‰ | 2.4 ‰ |
| standard error | 0.3 ‰ | 0.3 ‰ | 0.4 ‰ |
| number of data points *n* | 35 | 50 | 33 |
| Difference period 2 minus period 1 | –1.9 ‰ | –1.1 ‰ | –1.9 ‰ |
| standard error | 1.1 ‰ | 0.7 ‰ | 0.9 ‰ |
| *p* | 0.12 | 0.12 | 0.05 |