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Atmospheric Chemistry and Physics
Discussions

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 provide evidence, based on measurements, of chlorine-isotope fractionations in CFC-11 and CFC-113 in the stratosphere and confirm findings of fractionation of CFC-12. Based on these fractionations and some model calculations using emissions of these CFCs they predict long-term trends of delta(37Cl) in these CFCs over the past decades. These are compared to measured delta(37Cl) in tropospheric archived air samples (firn, flasks). The measurement-based findings of (expected) stratospheric fractionation for CFC-11 and CFC-113 is an important finding and appropriate for publication in this journal. The same is true for the tropospheric measurements despite the fact that not much can be said because of the relatively large uncertainties in the results compared to the expected signals. This paper should be published in ACP. However there are several issues that the authors need to take care of before publication. My major concern is about how the authors interpret the tropospheric results. There focus is given to the question of potential change in the delta(37Cl) in released CFCs over time and the magnitude of the change in d(37Cl) due to the stratospheric fractionation, and what the effect should be when mixed back into the troposphere. While I have no problem with the measurement results as such, as they are very convincing, the causal way these things are linked is not very convincing.

Referee comment 1

One of the major questions of this paper seems to be to understand if there had been chemical (isotope) changes in the production of the CFCs over time. I don't understand why this was not determined directly by measuring pure CFCs, which haven't cycled through the atmosphere. These CFCs must still be available in labs, old equipment etc. Obviously it would be a big task to approach this systematically but even with the analysis of a few pure CFC samples, a lot would be learnt. In fact, such samples might be readily available, for example from the group's effort to produce a primary calibration scale, which is presumably based on dilutions of pure CFCs. Often CFCs are used as boot-strap gases in the production of reference material for other compounds, and were probably already measured or readily available to be measured.

Author response

We would like to thank the reviewer for their comments, which we feel have improved our manuscript. We agree that an investigation of source materials would make for a very useful study. Our study uses a "top-down" approach to quantify long-term global isotopic changes rather than the suggested "bottom-up" investigation of source materials. A systematic investigation of source isotope deltas would require the measurement of a large variety of source materials, which is beyond the scope of our study.

Referee comment 2

Also, I suggest that the authors write a short paragraph on how these CFCs are produced, such that the reader will understand what the source chemicals are, and if isotope changes over time might be expected, or if there are various chemical reactions to produce these CFCs etc.

Author response

Zuiderweg et al. (2013) describe how the manufacturing processes used to synthesise chlorofluorocarbons have altered through industrial advances in the 20th century. The most significant change occurred in the production of the main feedstock (CCl4). Traditionally it was synthesised through the chlorination of CS2, but in the last 50 years CH4 has been used in this chlorination. Zuiderweg et al. (2013) cite these methodological changes as the most likely cause of the significant 13C enrichment of CFC-12, but there is no direct evidence to confirm that changes in production processes have changed the isotope signature of the resultant CFCs.

Referee comment 3

Abstract, l.2 ff. The study should referenced (probably full text citation depending on Copernicus rules).

Author response

This has been added.

Referee comment 4

Abstract, l. 13ff. This would read easier to me if you replaced ’estimate’ by ’calculate’ and ’due to’ by ’based on’.

Author response

This has been changed as suggested.

Referee comment 5

Abstract, l. 22: ’small’. Can you quantify, give a range or magnitude, is this ml or L the authors think of? This last sentence seems a bit lost anyway and I am not sure what the authors want to say with this.

Author response

This sentence highlights one of the main achievements of this work. Typically IRMS instruments use hundreds of litres of air to make measurements of isotope ratios in trace gases (e.g. Zuiderweg et al. 2013). We use approximately 200 ml of air in a single-detector system.

Referee comment 6

Abstract, l. 19: This sentence is confusing, perphaps replace ’changes’ by ’potential changes’. It seems like the causality should be reversed, by saying ’We find no evidence of changes in CFC manufacturing processes that would have potentially lead to chlorine isotope variations...’. In general I am not convinced about this statement at all, if at all, it should be accompanied with some limitations, e.g. within the uncertainty of xxx. Obviously if there were multiple production processes each creating different isotope ratios then there could be large variations which potentially cancel out.

Author response

By reversing the causality as suggested, greater emphasis is placed on the manufacturing processes and source material isotopic composition. In structuring the causality as we have, we aimed to emphasise the measurements we have made, rather than those that we have not. However, we agree that the sentence could be improved.

Referee comment 7

Figures 1, 3. Tick marks on x-axes seem to be missing. Generally improve figures, they are rather small, the text is hard to read,

Author response

Figures have been improved as suggested.

Referee comment 8

p. 31817, l. 21. Can you be a bit more concrete about 'reservor' (atmosphere?) and 'enrichement' (of what?).

Author response

Zuiderweg et al. (2013) measured δ(13C, CFC-12) on NEEM firn air and reported a relative 13C/12C enrichment of up to 80 ‰ from 1950 to the present-day.

Referee comment 9

p. 31820, line 11: Give a time frame for when 'all' sample measurements were bracketed by standards. Was this by daily calibration runs? If sample and standards were alternated, then perhaps replace 'all' by 'each'. As the sentence stands now, no information can be gained from it.

Author response

An alternating pattern was not used, so the word 'each' is not appropriate. We agree that this could be made clearer. Typically two sample measurements were made between standard runs.

Referee comment 10

p. 31821 l.15 ff. Did the rejected measurements coincide with poor measurement precisions? Did the rejected measurements in one compound coincide with those in another compound? Any ideas why these were anomolous? Without having to read Laube et al., 2013, can you add a summarizing sentence on the procedure, which also

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Interactive Discussion

Discussion Paper

explains if the '500 samplings' are actual measurement results. I presume that the rejected data are omitted from Fig. 1, it might be worth to mention that in the caption to Fig. 1. l. 21 Can you be more precise and say this per species?

Author response

Although some samples were rejected for multiple compounds, there is no discernible pattern. The individual measurement repeatability of rejected samples is worse than that of included samples for CFC-11 and CFC-113, but approximately the same for CFC-12. The εapp values were the same (within 1σ) before and after the exclusion of the rejected measurements.

A statistical "bootstrap" analysis technique was used to determine εapp values and their uncertainties (Volk et al., 1997). In this technique, a data pool is created by describing each sample with three values (the measured delta value and this value $\pm$ 1σ). The "bootstrap" tool draws 500 random samplings from the complete stratospheric data pool (including the possibility of drawing the same value repeatedly) to produce an overall εapp value and a robust associated uncertainty range.

No, rejected measurements are not included in Figure 1.

21 % (CFC-11), 10 % (CFC-12) and 7 % (CFC-113) of the stratospheric measurements were rejected through the bootstrap analysis.

Referee comment 11

p. 31822, F: be more clear about the flux. Between which compartments, and which direction is positive/negative.

Author response

All fluxes are always positive. 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

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Discussion Paper

to troposphere (in mol a-1)

Referee comment 12

P: ’trace gas production’. The term ’production’ is missleading here, replace something that denotes emission to the troposphere.

Author response

We are using the term "production" for any source to the atmosphere. However, given that this term could be understood to mean anthropogenic production, we agree that "emission" would be clearer.

Referee comment 13

p. 31824, l. 2ff: Why are there numbers in parentheses, and do the (1) and (2) relate to the following (1) and (2). Suggest to remove and describe differently.

Author response

Altered as suggested.

Referee comment 14

p. 31824, l. 5: The wording suggests that the age of air for an individual gas or isotopologue is unique. Aren’t these time distributions for individual gases?

Author response

Yes, this is correct and we agree that the original wording was misleading. Altered as suggested.

Referee comment 15

p. 31824, l. 7. Is the fractionation due to only the two processes mentioned a few lines up or other processes causing fractionation in the firn?

Author response

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Discussion Paper

These processes significantly affect the movement of gases in firn and are accounted for in the firn transport model. Other processes (e.g. thermal fractionation) are not thought to be significant and are therefore not included.

Referee comment 16

p. 31824, l. 26. Perhaps change to 'reconstructed scenario of the gas mole fraction (based on ...) if this is what the authors are trying to say. Can you give a rough estimate of the magnitudes of these processes for these compounds, something that lets the reader understand how important/significant these corrections are.

Author response

Altered as suggested. For within-firn isotope fractionation, a correction (of 1 – 2 ‰ is calculated using the reconstructed scenario of the gas mole fraction and assuming a constant atmospheric isotope delta.

Referee comment 17

p. 31825, l. 14: 'sink processes prefer ....' sounds jargon, can you rephrase.

Author response

Sink reactions discriminate against heavier isotopes, in other words, the heavier isotopologue is broken down more slowly.

Referee comment 18

Can you provide figures of dCl vs altitude similar to those in Laube et al., 2010. I find these findings of Cl isotope depletion a much stronger result than the temporal evolution of the tropospheric dCl

Author response

We chose to present the stratospheric data in Rayleigh plots (Figure 1 of the ACPD paper) because this allows us to show the reader how the εapp values where calculated (which are then used in the transport model). In our study the samples were collected at altitudes between 10 and 20 km, whereas the study by Laube et al. sampled between 14 and 34 km. The more limited sampling altitude range in our study means that plots of δ(37Cl) vs altitude do not provide a strong result. Plots of δ(37Cl) vs altitude are not used in our calculations and would not be an informative addition to our study.

Referee comment 19

p. 31841, Fig 3 caption line 6. Better say something along the lines of 'nonlinearities' as in this context the reader does not understand 'dilution series analysis'. 'relative to 2006 standard air'. It is a bit missleading to call a single air sample '2006 standard air'. Perhaps change to something like 'relative to an air samples collected in 2006'.

Author response

Changes made as suggested.

Referee comment 20

section 3.3 (p. 31827) is written in a rather confusing way and should be improved. The confusing parts are e.g. l. 6. 'This', meaning the present or the referenced study? perhaps replace by 'present'. 'include two additional species' why not name them? l. 14: '...such as theses'. l. 15: 'slightly higher'. In delta or mole fractions. 'slightly higher' is not very informative. I find these a lot higher. l. 19: '... and these measurements...?' should this say 'correction'?

Author response

Changes made as suggested.

Regarding the final suggestion, “correction” is not what is meant. However, we agree that the sentence could be made clearer. The oldest samples contain the lowest CFC mole fractions, producing higher than average analytical uncertainties. Also, a small correction was applied to 4 of them, introducing an additional error.

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Discussion Paper

Referee comment 21

When looking at Fig 3, it does not look like good agreement between firn and CGAA for CFC-113.

Author response

In the age range covered by both firn and Cape Grim samples they have mean values of -0.1 ± 2.4 ‰ and 2.1 ± 2.3 ‰ respectively.

Referee comment 22

When eye-balling in Fig 3, there seems to be an opposite trend for CFC-12 than what one would expect, by a few permil over the decades 1950 – 2000.

Author response

There are no statistically significant trends.

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 δT 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 R1.

Referee comment 23

l. 26. Shouldn't it be rather: '...isotopcially constant source signature based on the current understanding ....' You can't say that both (constant source and current understanding) are consistent, this could easily cancel out. Here again, if a constant source signature is consistent, then why wasn't there a single measurement done on a pure CFC sample to check if that is in agreement with the atmospheric observations?

Author response

Yes, our observations are consistent with an isotopically invariant source signature, but the high measurement uncertainty does not allow us to preclude the possibility that it has changed over time.

See response to comment 1.

Referee comment 24

p. 31828, lines 3ff. The CFC-12 system before the industrial release was very well balanced (zero). I don't think this has to do with a 'balanced' system alone, but primarily with the existance of pre-industrial N2O (and absence of CFC-12) per se.

Author response

We have already described the existence of pre-industrial N2O as the primary factor. The word "balanced" has been removed.

Referee comment 25

It appears that the entire Zuiderweg et al., 2013 story is based on 2 samples, were these analysed in the present study also? I am not very convinced about the line of argumentation, it appears very unlikely to have a large 13C variation without any concurrent change in Cl. Could a potential change in 13C mask/obscure some of the Cl measurements given that in the present study the measured fragments contain 'C'. Or is the 13C much less abundant in CFC-12 to affect the measured fragments?

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Discussion Paper

Author response

Yes, the two samples identified from the Zuiderweg et al. study were measured in our study. They agree with our other results; our δ(37Cl) measurements do not show any sign of the δ(13C) changes reported by Zuiderweg et al. (2013). It is difficult to speculate whether a change in one could occur without a concurrent change in the other, although we agree that it is unlikely. Investigating the influence of changes in source materials and manufacturing processes on δ(37Cl) and δ(13C) would make for a very interesting and useful study. However, these measurements are beyond the scope of our study. As stated in the ACPD paper, the instrument used for these measurements is run at a mass resolution of 1000 and we can therefore rule out interference from fragments containing 13C.

Referee comment 26

Please publish the major numerical results of the measurements (e.g. those that lead to Fig. 1 or 3), in an appropriate way (e.g. in the SI).

Author response

Tables containing details of the stratospheric and tropospheric samples have been added to the supplement.

Referee comment 27

Does ocean-atmosphere exchange play into this story particularly in the near future when CFCs are being release back to the atmosphere from the oceans, and some partical degradation (e.g. CFC-113 under suboxic conditions) might undergo large fractionations.

Author response

Oceanic sinks are negligible for the atmospheric budget of these compounds and are therefore very unlikely to alter their atmospheric isotope budgets. For this reason, we

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Discussion Paper

do not intend to include a discussion of ocean-atmosphere effects in this manuscript. Future studies of CFCs in the ocean interior may well want to look into processes such as degradation under suboxic conditions.

Referee comment 28

Supplement: Nonlinearity. These needs a few more information. Table S1. Is this one single sample (SX-0706077) that was diluted? What was it diluted with? What is SX-0706077, is this a real air sample or an artificial mixture? In the caption, mention that these are 'measured' mole fractions to clearly distinguish from the calculated mole fractions for this dilution series. Is there a reason why there are only mole fractions listed for this nonlinearity test, and not the delta values as well? Also, can you explain, which fragment is used for the calculation of the mole fractions. In the main text it is stated that C(35Cl)2F+ (m/z 101) and C35ClClF+ (m/z 103) and C(37Cl)2F+ are measured but it is not clear which is/are used for the mole fraction calculations. How was the non-linearity determined, was it against calculated dilutions or only by comparing the three compounds (in which case one would be vulnerable to simultaneous changes/errors in the three compounds towards lower mole fractions.

Author response

An air sample collected at Niwot Ridge in 2009 (SX-0706077) was diluted with nitrogen. Mole fractions for CFC-11, CFC-12 and CFC-113 were measured using the most abundant fragment ion (m/z 101).

These are all measured mole fractions.

The nonlinearities were calculated relative to the undiluted 2009 air sample (SX-0706077), which was used to make the dilutions. The dilution series measurements were made against the 2006 air standard used for all measurements in this manuscript, to ensure internal consistency.

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	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

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