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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.

Anonymous Referee #2

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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.

Comments in more detail.

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. 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.

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

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

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.

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.

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,

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

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.

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 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?

p. 31822, F: be more clear about the flux. Between which compartments, and which direction is positive/negative. P: 'trace gas production'. The term 'production' is missleading here, replace something that denotes emission to the troposphere.

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.

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?

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?

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.

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

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

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'.

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

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.

p. 31828, l. 10: It might be better to replace 'cite' by 'suspect' or similar.

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?

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).

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.

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 nonlinearity 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.

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