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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 #1

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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.

Major Comments:

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). For the Cape Grim archive, more details should be given supported by references. 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? For the firn air samples, either a detailed description of the sampling campaigns or citations to papers containing these descriptions need to be provided. Have tests been performed to ensure that the CFCs of interest are not affected by firn air sampling artifacts?

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.

pp. 31819 – 31823 The equations and derivations, as presented, are at times confusing and difficult to follow.

- 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)

- 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.

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

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

- 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)?

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

- P. 31822. After tuning J (the loss rate coefficient) in the manner described, are equations 4 – 6 then solved for Ys and P only?

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.

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

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.

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.

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 $\approx$1990), there seems to be a trend toward more negative isotopic values for all species, followed by an increasing trend after about 1990.

Minor Comments:

- The "dilution series" test is clear, valuable and well described – well done

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

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

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

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