Atmos. Chem. Phys. Discuss., 12, C9877–C9882, 2012
www.atmos-chem-phys-discuss.net/12/C9877/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Extreme ^{13}C depletion of CCl_2F_2 in firn air samples from NEEM, Greenland" *by* A. Zuiderweg et al.

A. Zuiderweg et al.

azuider@gmail.com

Received and published: 28 November 2012

We would like to thank the referees for their input. As a result there has been improvement to the manuscript and we are grateful for their efforts in this regard.

Response to Referee #3 Comment 1. The follow up on understanding the potential future magnitude of this influence is very cursory (0.29/mill/yr [sic] if emissions were zero... is this detectable? Likely to still be influenced by the source term at all points in the future?) Some additional discussion in this regard might be worthwhile.

Author Response: We have decided to deemphasize this point as it is not the main conclusion of this paper. Indeed, this increase is likely to be overshadowed by the remaining production contribution to atmospheric CFC-12 δ13C, and this has been

mentioned in section 3.3.

Comment 2. What are the potential magnitude of sampling artifacts that might affect 13C of CFC-12 with the compressor that was used? One would expect that the magnitude of these influences would increase in the lock-in zone where flow restrictions are larger. Could there be fractionation of CFC-12 through the emission process from compressors, foams, etc.?

Author Response: This is an unknown factor, however the firn-air studies done with similar technology, including Buizert et al., 2012 which used exactly the same equipment, have produced reliable samples for isotopic studies, though for CFC isotopes sample reliability has not been ascertained as this is the first time this aspect has been measured. On the other hand, the magnitude of the fractionation is such that it is hard to explain with potential artifacts. Also see our response to Referee #5, question 10.

Comment 3. Section 2.1 isn't that clear, were samples pressurized with the compressor on site in a single step?

Author Response: The samples were compressed on site. This has been added to the text.

Comment 4. How was the CFC-12 peak purity assessed throughout the firn?

Author Response: During analysis, peak purity was checked in two ways: 1) by using the quadrupole MS to examine the ion fragments and 2) by checking if the peak shape during integration departed from the ideal after subtracting the sloping background. Both methods indicated clean peaks for CFC-12. This information has been added now.

Comment 5. Although the authors have the data, they do not assess the CFC-12 history explicitly in the paper in a way that allows the reader to be sure that the time-inferred history is accurate (something more than what is given in section 3.1 seems worthwhile -how was the consistency with Buizert assessed?

Author Response: The mentioned consistency with Buizert et al., 2012 concerns a comparison between our measured data and the developed scenario in the referenced paper. These agree fairly well, please see the revised figure 3. We did not develop an independent scenario because of the relatively poor accuracy in mixing ratio measurement (+- 5%).

Comment 6. Although no independent CFC-12 history can be derived (p. 18509), the firn data could be used with the forward model to derive a history whose consistency could be check with the Walker et al history, for example).

Author Response: Unfortunately this is not possible because the forward model uses an atmospheric scenario as input, which does not exist for CFC-Â■12. So, the CFC-Â■12 firn measurements cannot be used at all in the modeling except to verify it afterwards. However, the aforementioned consistency of the firn measurements with that measured for Buizert et al., 2012 and its resultant scenarios assure the consistency of our data.

Comment 7. How is it known that the CFC-12 peaks "are free of artifacts"? Even if "all firn samples were treated identically [sic]", time - dependent errors could arise from a constant interference.

Author Response: As described in the text and the referenced method paper (Zuiderweg et al. 2011), we did not see any evidence of artifacts through the mentioned techniques. Also see our reply to comment 4.

Comment 8. on assessing the influence of induced fractionation within the firn. Does the model used in the present study adequately simulate these effects for those gases for which the effect is larger (p. 18511)? In other words, please demonstrate the skill of the model for accurately simulating isotopic effects for 13CH4, for example.

Author Response: This technique has already been verified to work for lighter species, specifically 13CH4 and CDH3 in Bräunlich et al. 2001.

Comment 9. The authors indicate that CFC-12 production methods have changed in the past, but there is no discussion as to whether or not these changes would/could/should/did have an impact on the 13C of CFC-12 produced. Without this evidence or discussion, the text needs some revision - e.g., though production changes have occurred over time, we do not have independent evidence that these changes actually influenced the isotopic abundance of CFC-12, though the results suggest they do...

Author Response: We agree. There is no direct evidence that the stated production changes have actually taken place, only we have model indications that they have done so. In this light we revised the statement to clarify.

Comment 10. Other points: Citations need improving... Assessment reports should be cited with chapter authors, not as WMO (2011) for example. The IPCC chapter (Forster et al.) has older info on halocarbon abundances that could be updated with the latest ozone assessment report. The ozone assessment also provides updated information about CFC-12 emissions (they remain 10% of peak levels; a improvement over "largely ceased" given on line 1 of p. 18504) and recent mixing ratios.

Author Response: Thank you for pointing this out. This has been addressed with the appropriate adjustments.

Comment 11. Stolarski and Cicerone (Canad. J. of Chem., 1974) were actually the first to describe the catalytic decomposition of ozone from Cl. Molina and Rowland proposed CFCs as being a potential source of that Cl.

Author Response: Thank you for the correction.

Comment 12. Chi-squared is likely a better indicator of goodness of fit than RMSD for the different scenarios because it accounts for the magnitude of a residual relative to the magnitude of uncertainty on a measurement, see work by Battle et al. (p. 18510).

Author Response: The Chi-squared test has been used in previous versions of the

Monte-Carlo model (e.g. Sowers et al., GBC, 2005, doi:10.1029/2004GB002408 and Bernard et al., ACP, 2006, www.atmos-chem-phys.org/acp/6/493/). It cannot be used in the case of a species with zero concentrations in the early XXth century because it involves a division by the species concentration, which leads to an unrealistically high weight of the early part of the record.

Comment 13. What sample volume was injected in making these measurements?

Author Response: 35 liters, this information has been added.

Comment 14. Lines 15-25 of p. 18514. What point is being made here that is relevant for this paper? Needs to be clearer.

Author Response: This was meant to indicate the complicated situation concerning time lags in leakage release to the atmosphere: it is not only the promptly produced and released CFC that influences the atmospheric production value, but rather that diverse leakage sources with differing rates are a going concern as well. We shortened the paragraph and trust that it is readable now.

Comment 15. Might mention CFC-12 in Table 1, Figure 7, and Figure 8. Might indicate "of CH3Cl and CFC-12 detected as CO2 at ions m/z=44..." in Figure 2 caption.

Author Response: These have been added.

Comment 16. What is the "ice-core trapped age"?

Author Response: This was meant to be age of air trapped in firn, and has been corrected as such.

Comment 17. No dates are given for the sampling dates associated with previous atmospheric measurements of 13C in (presumably, but not stated) CFC-12 (p. 18507).

Author Response: These have been added.

Comment 18. I presume the coefficients to the polynomials in the many scenarios were

randomly generated (line 26, p. 18509)?

Author Response: Yes, they were randomly generated. This information is already mentioned on p.18510 Line 3.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 18499, 2012.