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Atmospheric Chemistry and Physics Discussions

Interactive comment on "First atmospheric observations of three chlorofluorocarbons" *by* J. C. Laube and A. Engel

Anonymous Referee #1

Received and published: 6 May 2008

The authors report the detection of three previously unobserved unsaturated CFCs in an atmospheric plume at ppb levels and in the background atmosphere at ppt levels. They conclude that these compounds might play a role in stratospheric ozone depletion and/or act as greenhouse gases and thus need to be monitored and possibly regulated. The first observation of a new class of halogenated compounds in the atmosphere would indeed by highly interesting, but the methods for identification and quantification of the new compounds presented by the authors are not convincing. Also the analytical method is not adequately described and several sections of the manuscript are not well written. The authors need to provide more evidence for their conclusions and improve the manuscript in order to be acceptable for publication.

Specific comments:

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The author's identification of the three unsaturated CFCs is solely based on relative retention time (deduced from boiling points) and the comparison of a SCAN mass spectrum obtained during the plume with the NIST mass spectral library. In Figure 2 the authors show a mass spectrum from this plume and list the relative abundances of mass/charge ratios for C2F3Cl from the NIST mass spectral library in the figure caption. Most fragments are found in the plume and the NIST mass spectrum; however the relative mass/charge ratios are not in good agreement. This might be due to different fragmentation patterns of C2F3Cl in the mass spectrometers used by the authors compared to the mass spectrometers used for the NIST mass spectral library (as often observed), but this might also indicate that the authors did not observe C2F3Cl. No data is shown for the other two compounds. To be convincing the authors should obtain or prepare a dilution of the three compounds to ppb (better ppt) levels in order to properly verify retention times and mass spectra.

As the authors have no calibration or dilution for the discussed unsaturated CFCs, they try to estimate the mixing ratios based on relative mass spectrometric sensitivities of the main ion compared to CFC-12 corrected by a "fragmentation correction factor" based on the fragmentation patterns of the compounds. This is a very unusual way of estimating the mixing ratio of a compound, as ionization efficiencies and ionization patterns vary highly and are very difficult to predict. The authors do not present evidence that this method actually predicts reasonable mixing ratios for compounds for which calibrations are available or for which background mixing ratios are known, e.g. for the listed compounds CFC-11, CFC-113, HCFC-22, Halon-1211, and CHCl3. To be convincing the authors have to provide this evidence - or follow the classical route and obtain or prepare a dilution of the three compounds to ppb or ppt levels and calibrate their measurements.

Due to the discussed issues many conclusions of the manuscript seem rather farfetched unless the authors can provide stronger evidence for the identification and quantification of the new compounds.

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Interactive Comment

Page 6684, lines 20 - 26: This paragraph should be improved, e.g. key phrases such as Ozone Depletion Potential are missing and the process of halogen activation is not explained.

Page 6685, line 1: The "Scientific Assessment of Ozone Depletion: 2006" is available and should be cited. Also the authors should list the discussed CFCs (11, 12, 13, 113, 114/114a, and 115).

Page 6685, lines 2 and 3: The author should list the five CFC which are increasing.

Page 6685, line 23: How did the authors verify that the used sampling line did not outgas the discussed unsaturated CFCs? From research on CFCs in groundwater it is known that certain polymers outgas certain CFCs.

Many important details of the analytical procedure are missing, such as dimensions of the analytical column and the pre-concentration trap; amount, weight, mesh size, manufacturer, ... of packing materials for analytical column and pre-concentrations trap; pressure or flow conditions of the analytical procedure; carrier gas quality, origin, and type; bulk gas (oxygen, nitrogen, carbon dioxide, ...) handling, ...

Page 6685, line 27: The authors should explain how the two detectors are operated simultaneously. Are they in parallel or in series? What are the flow rates?

Page 6688, lines 22 -24: This conclusion seems rather far fetched.

Page 6688, line 24: How were these trajectories calculated? Which program was used? What meteorological data was used?

Page 6688, line 29 and page 6689, line 1: Did the authors measure the new compounds only on one mass/charge ratio per compound in those samples? After retention time and mass spectrum of a compound are clearly verified it is better to use at least two characteristic mass/charge ratios for each compound to minimize the possibility of bias due to coeluting compounds.

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Interactive Comment

Page 6689, line 15: Can the authors exclude that C2F3Cl (which is a Kel-F monomer) and/or the other unsaturated CFCs are not degradation products from polymers used in the analytical system? Many regulators contain Kel-F.

Page 6690, lines 10 and 11: This statement is rather speculative.

Page 6690, lines 20 and 21: Assuming that the compounds are of anthropogenic origin and that most anthropogenic emissions occur outside of the tropics and that the discussed compounds have short lifetimes, how likely is that significant amounts are emitted in the tropics and reach the stratosphere?

Technical comments:

Although known to many readers, abbreviations such as MS and ppt should be defined.

Page 6685, lines 6 - 14: This paragraph should be improved. The aim and relevance of the manuscript are not clearly stated. Also use "Montreal Protocol on Substances That Deplete the Ozone Layer".

Page 6685, line 17: Use "Frankfurt (Main), Germany"

Page 6685, line 23: The authors state that 500 ml of air were pre-concentrated, but the figure caption for figure 1 states that 1000 ml were pre-concentrated.

Page 6685, line 24: "at liquid nitrogen temperature"

Page 6685, line 26: Use "Porasil C/n-Octane"

Page 6686, lines 6 - 8: Poor language/laboratory jargon: "some large additional signals".

Page 6686, lines 8 - 9: Use generally accepted terms such as "background air" or "unpolluted air". Write for example "In Figure 1 the ECD chromatograms of the plume (in red) and a background air sample (in blue) are shown".

Page 6686, lines 12 - 15: Instead of "Our" and "to get enhanced detection limits" write

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e.g. "The MSD is" and "to achieve".

Page 6686, lines 18 - 19: Although familiar to many readers the acronym NIST should be defined and a reference for the NIST mass spectral library should be provided.

Page 6686, line 23: Write "As the used chromatographic column" instead of "As the chromatographic system".

Page 6689, line 6: "Data is too sparse"

Page 6690, line 1: Poor language/laboratory jargon: "nice overview on that topic"

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 6683, 2008.