Atmos. Chem. Phys. Discuss., 8, S4222–S4226, 2008
www.atmos-chem-phys-discuss.net/8/S4222/2008/

Atmospheric Chemistry and Physics Discussions

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

J. C. Laube and A. Engel

Received and published: 27 June 2008

The following efforts were undertaken in order to provide more evidence for the correct identification of the three CFCs:

1)The background subtraction of the averaged C2F3Cl scan spectrum was found to be an overcorrection as the nearby eluting CFC-12 signals were partially subtracted by accident. This affected mainly the ions with a mass/charge ratio of 50, 66, 85 and 87. A revised scan spectrum of the plume sample is now displayed in Figure 2 giving a better agreement with the NIST spectrum of C2F3Cl.

2)C2F3Cl could be obtained as pure substance. It was statically diluted to ppb levels and used to confirm the correct identification but also to calibrate the signals observed in the air samples.

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

3)The other two newly observed CFCs could not be obtained as pure compounds by now. To provide more evidence for the correct identification of these substances two Figures were added to the manuscript showing a comparison of the observed spectra from the plume sample and the corresponding NIST spectra.

Evidence for the correct prediction of mixing ratios is given in the text: "The relative sensitivity Si is then given by division of si with sCFC-12 (Eq. 2). Values of Si were between 0.10 and 1.20 and remained constant for each species within ś 6 % over a period of two years." This means, that the relative ionization efficiencies and ionization patterns did not vary highly for this instrument within the given time period. However, mixing ratios were derived for C2F3Cl and added to Table1. These mixing ratios were used for the evaluation of the relative sensitivity method and showed that the predicted mixing ratio range is too narrow. Nevertheless the predicted mixing ratio ranges came close to those calculated from the calibration, which is why we revised the corresponding statement and recommend the method as a first indication only (Thus, we use a relative sensitivity method to get a first indication of the observed atmospheric abundances.However, the estimates came very close and are thus useful to provide an indication of the other two substances mixing ratios.).

Specific comments

Referee comment(s): 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.

Author response: The paragraph is very brief as the ozone depletion process is considered as part of the general education of atmospheric scientists and can be looked up in most environmental textbooks.

Referee comment(s): 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

ACPD

8, S4222–S4226, 2008

should list the five CFC which are increasing.

Author response: The manuscript was adapted as requested (Five of them - CF_2Cl_2 (CFC-12), $CFCl_3$ (CFC-11), CF_2ClCF_2Cl (CFC-114), CF_3CFCl_2 (CFC-114a) and $CF_2ClCFCl_2$ (CFC-113) - are decreasing in the global background atmosphere due to their regulation under the Montreal Protocol.).

Referee comment(s): 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.

Author response: The used sampling consisted of stainless steel. Furthermore the same sampling line was used for the sample taken at the air conditioning system which contained none of the newly observed substances. Both details were added to the manuscript.

Referee comment(s): 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, line 24: How were these trajectories calculated? Which program was used? What meteorological data was used?

Author response: All requested details were added to the manuscript.

Referee comment(s): Page 6688, lines 22 -24: This conclusion seems rather far fetched.

Author response: The sentence was slightly changed in order to make clear that it contains not a conclusion but a speculation.

ACPD

8, S4222–S4226, 2008

Referee comment(s): 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.

Author response: Each of the three substances was measured on two mass fragments (one was used as a quantifier and one for confirmation) and this additional information was added to the manuscript.

Referee comment(s): 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.

Author response: We can exclude this as no pressure regulators were used for the sample measurements. Furthermore three different blanks (vacuum injection and preconcentration of ultra-pure Helium and Nitrogen) were carried out and none of them showed a CFC signal. These details were added to the analytical procedure section.

Referee comment(s): Page 6690, lines 10 and 11: This statement is rather speculative.

Author response: It is, but we consider it as a reasonable speculation due to the presence of characteristic fragments and the high ECD sensitivity towards these substances.

Referee comment(s): 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?

Author response: It is unlikely. The statement was replaced by another: But although their contribution to ozone depletion can be expected to be rather small it is important to find out more about their sinks and sources and their ability to reach the stratosphere.

ACPD

8, S4222–S4226, 2008

Interactive Comment

Referee comment(s): 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".

Author response: The explanations of the abbreviations were added and the Montreal Protocol cited as requested. From our view the aim and relevance of the manuscript was already made clear as "we report the first atmospheric observations of three CFCs" and "although their ozone depletion potential might be small, the newly observed short-lived CFCs are potential contributors to stratospheric chlorine".

Referee comment(s): 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 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"

Author response: All requested corrections were applied to the manuscript

---

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

ACPD

8, S4222–S4226, 2008

Interactive Comment