

Interactive comment on “Establishing Long-term Measurements of Halocarbons at Taunus Observatory” by Tanja J. Schuck et al.

Anonymous Referee #2

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This is a valuable contribution to the European and global halocarbon measurements. It is also important because it is a long-term effort, complementary to the larger networks in this field, particularly because it uses different instrumentation. The manuscript is well written and structured, perhaps a bit lengthy in some of the sections. My comments are mainly minor.

General comments: In the abstract, I suggest to list more specifically what the key findings are and avoid vague descriptions like ‘differences’ without stating what the main differences are.

The description and interpretation of the results, in particular p. 11–16 are rather long and could benefit from shortening to the few main important features.

C1

Please publish the numerical results of the observations.

Specific comments:

p. 1, l. 2/3: I suggest to be more consistent with using the abbreviation ‘TO’ (introduced on line 2 but not used on line 3 and other places, or stick to the full name throughout.

While the beginning of the time series is clear (line 2), it is unclear when it ends, in particular in descriptions like p. 1, l. 15, where an understanding about the time frame is important.

p. 1, l. 3: Can you be more clear about the distinction ‘local’ vs ‘regional’. Are local emissions really assessed here (perhaps remove the expression ‘local’).

p. 1, l. 8: I suggest to be more clear here in the abstract that the measurement on the two instrument is a simultaneous one using a split system. Without reading the later descriptions, this is unclear in here.

p. 1, l. 12: ‘good agreement’. Can you be quantitative? Also, is the description ‘with a larger variability of mixing ratios at the continental site’ necessary/adding information?

p. 1, l. 14: Abbreviations like ‘CFC-11’, HYSPLIT etc should be spelled out the first time used both in the abstract and in the main text.

p. 1, l. 15: Rather than saying that there are ‘small expected differences’, could you write what these differences are? Also, I don’t understand the logic of that sentence, why should there be a similar decrease in atmospheric mixing ratios, there are different types of banks, functional releases and lifetimes of CFC-11 and CFC-12.

p. 1, l. 19: ‘can you be more specific than ‘occurrence’, perhaps mentioning frequency and/or magnitude of the pollution events over time.

p. 1, l. 20: Can you be more specific than just saying ‘differences’. What are the key differences.

C2

p. 2, l. 5: The term 'hydrochlorofluorocarbons' was introduced as the abbreviation 'HCFCs' one line above, yet here the full name is used. Check manuscript throughout for such inconsistencies. For example, the use of 'time-of-flight' and 'TOF' needs to be cleaned up also.

p. 2, l. 28: Is the factor 2.4 for Germany? Please be more specific.

p. 3, l. 6: Neither the term 'non-target' nor the 'time-of-flight mass spectrometer' have been introduced beforehand, this sentence appears to need more explanation or be removed.

p. 3, l. 6: Are the 50 compounds in addition to the selected compounds, or including them?

p. 3, l. 23: 'Additional' to what?

p. 3, l. 31: Please state the model/brand of the metal-bellows pump. Also, state what type of pump was used and how the flask samples are collected at MHD.

Figure 1: Can you make this a 2-panel figure with one of the panels zoomed in much more to see the area (e.g. 50 km radius) of the site? This would add important regional information.

p. 4, l. 6: 'ppt'. Spell out the first time used. . Also, if not done yet, specify whether this is a 'dry-air' mixing ratio or not.

p. 4, l. 10: I believe that the SI abbreviation for 'liter' is a capital 'L'. Same on next line.

p. 4, l. 20: Suggest to use 'downstream' instead of 'Behind'. Make clear, which fraction of the split refers to the TOF, and which to the Q-MS.

p. 5, l. 7: Suggest to change 'scales' to 'calibration scales' or 'primary calibration scales'. These calibration scales are SIO (Scripps Institution of Oceanography) calibration scales, and are preferably named that way, compared to 'AGAGE scales'.

C3

p. 5, l. 25: Drift in what?

p. 5, l. 28/29: Be consistent with spelling 'quadrupole MS' vs 'quadrupole-MS'.

p. 5, l. 30: Suggest to change 'TOF' to 'TOF-MS'.

p. 6, Table 1 caption: 'two primary standards'. Are these the same as the two 'target standards mentioned on p. 6, l. 14. If so, I suggest to use only one of the two terms. Please clarify.

Table 1: Are the precisions 1 sigma or 2 sigma, please specify in the caption. Please change 'AGAGE scales' to SIO calibration scales (see above) and spell out SIO somewhere. Check manuscript throughout and change to SIO.

p. 6, l. 16: Not clear to me what the author means with 'slopes'.

p. 7, eq. 1: Should there be a reference to this?

p. 8, l. 9: It is not sufficient if the calibration scales are 'typically' less than 3%, there would all need to be small differences. For example, observations of dichloromethane differ about by 10% between NOAA and AGAGE and are potentially due to calibration scale differences.

p. 8, l. 11: 'high quality' is a rather subjective statement. On what grounds do the authors base this?

p. 8, l. 15: Suggest to replace 'parallel' by 'simultaneous'.

p. 8, l. 21: The implication of the sentence 'The working standard used" is unclear to the reader. Note that the fact that the low mixing ratio in the standard does not create non-linearity per se, it would only create a factor offset. The key here and in Figure 4a is the non-unity slope between the two observational sets, the nonlinearity being created due to the large range of observations, regardless of the value for the standard. Is the nonlinearity in Fig 4a 'linear', i.e. is the solid fit line offset from 0/0 (how much)?

C4

- p. 8, l. 23: Was HFC-134a also among those substances in Hoker et al., 2015, and if so, was the nonlinearity there similar to the one mentioned in the present manuscript?
- p. 10, Figure 4a: The ca 6 data points, which clearly stick out from the remaining data points, are rather puzzling, particularly given the fact that they seem to be on a single slope. Are the Q-MS data produced with EI filaments? Over the last few years, Agilent EI filaments are known for their poor behavior towards the end of their lifetime. For the duration of about 10 days before ultimate failure, under continuous use, they create a 'bimodal' response, presumably due to some shifts in the coiled filament. Note that the bimodal behavior can change quickly such that while one compound is affected in a measurement, another compound may not. Figure 4a (and perhaps Fig 4b) reminds me of that. Both NOAA and AGAGE have therefore switched to using (straight) CI filaments (still running the MSs in EI mode). While signal response is slightly reduced, signal/noise is similar, lifetime and signal drift are better for the EI filaments.
- p. 10, l. 1ff: Without any interpretation, the purpose of the reporting of these low mixing ratios remains somewhat questionable. Are in-situ AGAGE data available from the internet for comparison for this time period?
- p. 10, l. 5: The wording 'measurements at Mace Head' is unfortunate and confusing, the measurements were not made at Mace Head (only the AGAGE in-situ measurements were made at the site). Samples were taken at Mace Head, but measurements were done at NOAA or Uni Frankfurt.
- p. 11, l. 26ff: Can you exclude seasonality in the emissions of these CFCs? It has been shown that emissions of other refrigerants are seasonally varying. For CFC-11, perhaps emissions from foam are seasonally dependent with enhanced emissions during warmer seasons?
- p. 12, l. 2: Suggest to change 'in Asia' to 'for Asia'.
- p. 14, l. 8: Please change 'first measured' to 'first reported'.

C5

- p. 14, l. 18: HFC-227ea is used in MDI, is there a possibility of large contamination in the lab by such device. Is lab air measured (should be mentioned in the methods). Is HFC-227ea use permitted in Germany (for applications other than MDI)?
- Fig 7: There are TOF-MS HFC-227ea results far below the baseline for 2014, presumably not explainable with measurement precisions. What is the cause of this?
- p. 15, l. 22: perhaps specify 'positive outliers', or 'above background' outliers.
- p. 15, l. 24: AND an enhance leakage rate during that time of the year.
- p. 16, l. 3: Why were higher harmonics tried? Perhaps because the fit was poor?
- p. 16, l. 4: 'outlier'. A positive outlier in MHD or a negative outlier in TO? p. 16, l. 8: Is there an interpretation/explanation for this?
- p. 16. In this paragraph (Dichloromethane) there is a lot of switching back and forth between observations from the data sets and published facts, making this part more difficult to read. Also, some of the facts are a repetition as they were already discussed in the introduction. Also some parts of individual sentences appear to be repetitions, e.g. the last sentence on p. 16.
- p. 17, l. 4: This interpretation appears to be a bit premature given that 2018 has not finished yet.
- p. 17, l. 6: Perhaps use a more convenient unit, i.e. 5 days.
- p. 17. Was wind speed also used as filter?
- p. 19 (trajectory analysis). Could this part be shortened? Perhaps only mention those observations, where a conclusion/interpretation is following, so that it is not heavily biased to a descriptive text.
- Please provide numerical results for the compounds discussed in this paper. This is probably best done in a supplement. The data should be listed in a way that also let

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the reader distinguish between background and non-background data. This could potentially be done in one single large supplementary table. Important details like which of the two instruments, which primary calibration scale and measurement precisions should be included. This is all very important for future users of these data independently on the availability through direct communication with UF.

Acknowledgments: If there are not many, why not mention the technical staff by their names.

References: Please make sure that subscripts of chemical formula are properly embedded. Please make sure that titles are consistently written with small initial letters in words other than names and the start of the title. Journal names should be abbreviated throughout.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-897>, 2018.