Atmospheric Measurement Techniques Discussions

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Comment on amt-2020-488

Anonymous Referee #2

Referee comment on "An indirect-calibration method for non-target quantification of trace gases applied to a time series of fourth-generation synthetic halocarbons at the Taunus Observatory (Germany)" by Fides Lefrancois et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2020-488-RC2, 2021

The manuscript "Non-target analysis using gas chromatography with time-of-flight mass spectrometry: application to time series of fourth generation synthetic halocarbons at Taunus Observatory (Germany)" by Fides Lefrancois, Markus Jesswein, Markus Thoma, Andreas Engel, Kieran Stanley, and Tanja Schuck, is a well written account of their efforts to produce an alternative indirect calibration method for use in detecting short-lived compounds with large atmospheric trends in historical GC-TOF-MS data archives. This is a novel and interesting idea and presents a strong impetus for other research groups in this area of research to try out this kind of analytical approach. In short, the method circumvents the problem that arise when the calibration gas in use at the time of the air-sample analysis (canister or in-situ), did not have detectable amount of the target analyte or this amount in the calibration gas wasn't quantified. The method thus enables retrospective analysis of these kinds of datasets which can then be regarded as a type of digitized air archived. This method proves especially useful when considering several 4th generation CFC replacement compounds (HFOs/HCFO) which, up to recently, have only been present at very low mixing ratios in the atmosphere and with infrequent detections in the air archival data. The authors describe in detail the individual steps in their data evaluation for selecting data with good underlying quality predictors (based on relative response factors… i.e., extends standard analytical textbook internal standard GC-methods) and demonstrate the application to the detection of two common HFOs and one HCFO, in in-situ measurements and flask samples collected at the Taunus Observatory near Frankfurt am Main, Germany. These compounds have only become detectable in atmospheric samples over the last few years and thus the paper is of both timely and scientific importance. The manuscript is well apportioned and a delightful read with very few errors and a clear narrative. I have only trivial and minor comments that should be addressed before the paper can be accepted for publication.

General comment: The manuscript contains a large number of figures and perhaps one or two of those could be relegated to SI ?

Abstract – line 7: “thus” can be omitted in the sentence.

p. 2 line 36: Typo in spectrometry (spectrometry).

p.2, line 53: It is incorrect to say “TFA is known to cause negative environmental impacts”. Large concentrations of TFA will do that, but the authors should consult the references they cite themselves, especially Solomon et al., for a precise characteristic on this matter, what impact the current and predicted future levels of TFA in the environment will actually have.

P4. line 115. Mole should be capitalized ion the beginning of the sentence.

p.6 line 159-161: This sentence should be rewritten for clarity. It would benefit form some commas and perhaps start out with “Using equating 3, the rRF for the species of interest, which is not…..

p.6, line 165: replace “should” with “is assumed to”

p.7, line 173: I guess the selected compounds listed in table 1 could be termed “a training” set for the method. As such, the authors, and other researchers, will adopt similar or dissimilar training sets, for the technique to be “calibrated’ on for application to their datasets.

p.7, line 182: 10% - this this value arbitrarily chosen? Why not based on a statistical parameter such as sigma(s)?

Figure 4 caption: replace “used cylinders” with “used calibration gas”.

All figures could in general benefit from being made color “agnostic”. Several of them, e.g.

fig 6 and 8, are only legible in color print out, whereas there are no limitations on symbols shape that dictates the necessity of using colors.

P.15, line 254-255: Please comment on the fact that a larger fraction of data from the in-situ measurements than from the flask measurements were selected. Was this expected? Any predictable reason behind this outcome?

P.16, line 262: What does “partly different” mean here? Could a different description be used?

p. 16 line 275, Suggest replacing detectability with detection frequency.

p.16, line 278 and 281: inset “ weekly” before “mole fractions”.

p.18, line 285-287: How would this indirect retrospective method likely work out trained on a data set like that collected at Jungfraujoch – i.e., a setting with largely clean background air? Any ideas if it would work there as well?

p. 19, line 295-297: Does this mean that indirect values obtained from datasets involving flask measurements and in-situ measurements, respectively, shouldn’t really be directly compared? I.e., if the variability is quite unpredictable, which sample dataset is "generally” more likely to produce good indirect values.

p.21, line 311: “sufficiently” is probably a better word here than “rather”.

p.21, line 311-312: regarding “reference species with similar retention times” – has the sensitivity to the retention-times been tested? Is it just assumed “likely”- I’m not saying that this is not a good assumption , just wondering if the authors have tested this – if not, this should be an easy test within the GC-TOFMS data sets.

p.21, line 317: “… retainage a sufficient number of measurements”. Sufficient here means a very low number? Ref. Table 4 where e.g. 2018 has 3-6 observations?

p.22, line 325: These quoted different are much lower than what shows up for the annualized values in the tables. Is the large discrepancies for the annualized values not an issues since those are what are often cited?