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Atmospheric Measurement Techniques Discussions

Interactive comment on "Measurements of CFC-11, CFC-12, and HCFC-22 total columns in the atmosphere at the St. Petersburg site in 2009–2019" *by* Alexander Polyakov et al.

Anonymous Referee #1

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Summary

This manuscript presents time series of three major long-lived halocarbons (CFC-11, CFC-12 and HCFC-22), as derived from ground-based Fourier Transform Infrared measurements performed at the high latitude low altitude site of Peterhof, in the vicinity of St Petersburg (SPB), Russia. A Tikhonov –Phillips regularization is adopted and the alpha parameter is selected for each gas such as to minimize intraday variability. A complete detailed uncertainty budget for the systematic and random components is carefully established and discussed.

The resulting decadal time series (2009-2019) are investigated in terms of absolute

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atmospheric content, trend and seasonality. Comparisons with WACCM model data, satellite and surface in situ measurements are presented, and the authors conclude that a reasonable agreement is observed between all data sets.

This is a relevant contribution to AMT, and these time series will contribute to the verification of the success of the Montreal Protocol. This has been shown to be very important, even for species showing a decreasing trend, for which prohibited production has taken place recently (e.g., Montzka et al., 2018; Rigby et al., 2019).

However, some of the conclusions dealing with the regularization are not supported by the material currently presented, and as such, they could be seen as overstatements. Moreover, these conclusions are formulated as of general application. While the conclusions reached are almost certainly relevant for the SPB site, different situations might be encountered at other FTIR stations. Related concerns are detailed below.

I would recommend publication after careful revision of the corresponding sections, or removal of some of the discussions which are currently part of section 2.3 (and related sentences in the summary and conclusion sections).

Major concerns

As indicated above, the major concern with this contribution is that some of the conclusions are presented as universal truth while they are not backed by the material presented. These conclusions are all related to the choice of a Tikhonov-Phillips (T-Ph) regularization that would be more appropriate than OE, e.g.:

– T-Ph regularization it is more suitable for long-lived gases with a pronounced trend
– the profiles retrieved by the OE method are less reliable, showing distorted profile shapes when compared to T-Ph results

Although the T-Ph approach and its tuning are discussed in length in the manuscript, important information is missing regarding the OEM retrievals. No details are given

(or even summarized) on the choice of the many OEM parameters, on the resulting information content (DFS), on the error budgets. And what about the efforts deployed and the indicators used to validate the definition of the OEM a priori states for the three targets? A paper by the same authors listed in the references (Polyakov at al., 2018) might provide these details, but unfortunately this work is not freely available to me. If we miss this kind of information, we cannot be convinced that T-Ph is necessarily a better option than OEM. It might well be that non-optimum OEM results are compared with carefully tuned T-Ph products. Then it is potentially comparing apples and pears in Figures 2 to 4.

Regarding these figures, it is also important to keep in mind that total columns are retrieved, or a single piece of information (DFS is merely larger than 1). Then the shape of the retrieved profiles is not very relevant, especially because the computed error bars affecting each single (and meaningless taken alone) mixing ratio are so large that they define a broad range of possible solutions with an identical total column. A profile with a more realistic form could likely be drawn without exceeding the resulting uncertainty ranges.

Another reason given by the authors for selecting T-Ph against OEM regularization is the lack of supporting geophysical information needed to build a covariance matrix: ”it should be taken into account that the OE approach requires the use of the covariance matrices for describing the variability of the target gases profiles, preferably the real covariance matrices, that are unavailable for the considered freons”. However, 16 years of ACE profiles are available, they could be used (and consistently extrapolated down to SPB altitude) to construct it, including for the extra diagonal elements. MIPAS data products are also available to the community (see Chirkov et al., 2016). Then at least two multi-year data sets with global coverage. Second, OEM regularization could make use of ad hoc parameters such as to determine the a priori states. This might sound as artificial, but it is not that different than setting up the alpha for T-Ph. It is true however that it could be trickier, because several parameters are available: the per-layer a priori

covariance, the type of inter-layer correlation (Gaussian, exponential), the correlation length. Note by the way that for long-lived and well-mixed gases, it could be relevant to set up a length of several kilometers in order to avoid oscillations in the retrieved profiles.

Finally, it should be noted that the gases involved in the present study do not present "pronounced trends". CFC-11 and CFC-12 will have only changed by about 5% after 10 years. Even if it is larger for HCFC-22 ($\sim$25% over 2009-2019), this remains less than the changes observed for some other FTIR products over a single year. For example, ethane presents total columns varying on average by more than a factor two over a season, and still OEM regularization is fully and successfully applicable.

Addressing the concerns detailed above could in my opinion be done in two ways. First, provide some information on how the OEM regularization was optimized, and supply elements allowing the reader to evaluate and compare on more solid grounds the data products, in terms of uncertainty, daily scatter, DFS... Or to significantly reduce section 2.3 and to give focus on the valuable derived time series and the comparisons with other data sets. In any case, one should not be left with the message that T-Ph regularization is necessarily the good option for the retrievals of CFCs or HCFCs. Such conclusions cannot be reached with a single site study, especially when involving challenging conditions. It remains to be demonstrated that it would also be the case for other FTIR stations. So adding “for our site”, “in our case” at some selected places in the text could be appropriate to temper the argumentation and make it more specific.

Second order issues and minor comments

Page 2

I think the one-sentence description (starting line 42) of the impact of halogenated source gases on the formation of the ozone hole is a bit oversimplified and may deserve an additional statement informing about the roles of the stratospheric reservoirs of chlorine and of the heterogeneous reactions in chlorine activation. The gas phase

chemistry does not explain the massive polar ozone depletion, and the photolysis of CFCs does not happen in the Polar Regions since there is no high-energy UV photon available there. Another option is to identify and include a good reference.

Line 45: the Montreal Protocol does not act directly on the halocarbons emissions. Instead, the production of the relevant gases are limited and then banned. I suggest replacing “emission” by “production” on line 45.

Page 3

Line 61: this sentence is somewhat misleading: the phase-out (100%) of the CFCs was decided in 1992, for a complete implementation by the end of 1995 (Copenhagen Amendment). In 1989, only a reduction was enforced by the initial treaty.

Line 62: Brown et al. 2011 is a good reference, but more recent trends have been published by the ACE team, considering now 16 years of measurement and improved versions of the data. I strongly suggest considering here and each time it is relevant these updated results (see Bernath et al., 2020), also for the trend comparisons.

Lines 63-66: it also depends on the evolution of the bromine and nitrogen stratospheric loadings!

Line 74: to my knowledge, the HFCs are targeted by the Kigali Agreement, not the HCFCs. HCFCs regulation is under the earlier amendments or adjustments. Please check and amend if needed.

Line 83: do you mean down to the Earth surface?

Line 86: it might be true that the publications on the subject were rather episodic, but not the measurements which were continuously performed and exploited at some of the NDACC sites. For example, halocarbon FTIR time series have been systematically included in the successive editions of the WMO assessments on ozone depletion.

Line 89: note that “freon” is a registered trademark.

Page 4

Lines 93-94: this is not correct, Prignon et al. (2019) proposed an approach for the determination of total *and* partial columns, for the 1988-2017 time period (three decades), not only for 1999-2018.

Lines 106-108: I somewhat disagree with the arguments on the situation as to the absorptions and spectral signatures (quoted as low and smoothed). In my opinion, this discussion as presented misses the fact that the situation is very different for the three target gases: CFC-11 is likely the more difficult with a broad feature perturbed by strong water vapor lines; CFC-12 has a stronger and more isolated signature peaking at more than 10% and HCFC-22 presents a narrower feature quite free of interferences (HWHM probably on the order of $\sim$0.05 cm-1), resulting in the possibility to select a less wider micro-window. Of course, the spectral scenes will also be influenced by the latitude and altitude of the station.

Page 5

Line 126: I guess QHN is another description of channeling? Note the relevant discussion paper on AMTD by Blumenstock et al. (2020). Harmonizing the designations could be helpful.

Line 163: the discussion on the spectral transmission function is interesting and original. If I understand correctly, the selection of the relevant parameters is conducted such as to limit the CFC-11 intraday variability. In the end, do you see any correlation between the water vapor and the CFC-11 total columns?

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Lines 236-239: the statements regarding the Prignon et al (2019) paper are not correct. These authors also used a T-Ph regularization with alpha=9, minimizing the smoothing and measurement errors as per Steck (2002). Please amend your text accordingly.

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Line 268: regarding the smoothing error, Prignon et al. (2019) have indeed evaluated it to be small (see Table 1 in their paper).

Line 297: is the mean molar fraction (or MMF) another name for the dry air mole fraction (often denoted xTARGET, see e.g., section 2.4 in Barthlott et al., 2015), as used by the NDACC and TCCON communities? If yes, it might be good here also to harmonize the designations.

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Table 4 reports much higher daily SD for HCFC-22 than for other gases. Is this a filter 3 effect (before 02/2016)? Or is this just because intraday variability for an unregulated gas might be affected by polluted episodes (excursion above the baseline in in situ surface time series)? Also and with the exception of HCFC-22, the random errors quoted on line 18 are significantly larger than the intraday SD on line 4. Shouldn't they be commensurate?

Page 18

Trends on Table 5: it is more and more clear that the uncertainties affecting trends are often underestimated because the methods used do not account for the auto-correlation present in the time series (see e.g., Santer et al., 2000). This is particularly critical and becomes problematic for species with small rates of change. And one can certainly expect significant auto-correlation for long-lived gases. Did you account for auto-correlation in your uncertainty estimates reported in Table 5? They appear rather small in both cases (using the Gardiner or Timofeev methods) and your comment on lines 354-355 puzzles me.

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Figure 8: the seasonal modulations for the various data sets are presented, and it is immediately obvious that surface measurements are much more flat than the others. But do you think that a direct comparison is meaningful? Unlike remote-sensing

measurements, surface sampling is unaffected by atmospheric dynamics (tropopause height changes, pressure variation...) and the include very high frequency measurements, leading to very robust averages. It might be useful to alert the readers of these specific and different situations.

Typos

Typos were not systematically searched for. I just spotted a few ones. See below. And the list of references was not thoroughly checked.

Line 32: replace FS1125HR by IFS125HR

Line 120: replace FS1125HR by IFS125HR

Line 316: replace HCFH-22 by HCFC-22

Line 319: replace Analisys by Analysis

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