

## ***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 #2**

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Review of “Measurements of CFC-11, CFC-12, and HCFC-22 total columns in the atmosphere at the St. Petersburg site in 2009-2019”, A Polyakov, et al.

This article presents multi-year trends in CFC11 CFC12 and HCFC22 measured at St. Petersburg. It describes the retrieval of the vertical profiles from solar absorption spectra. Then goes on to analyze the trends and compare with other independent datasets.

While the final results and comparisons are reasonable the description of the spectral analysis and retrieval process is deeply limited and flawed and have be improved before acceptance for publication is conferred. Specific issues related to this are given in the

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‘Major’ section.

Major:

L 106: “The difficulties of the freons TCs retrievals are caused, first of all, by small values and a smoothed spectral dependency of the radiation absorption by these gases which lead to the low information content of the FTIR measurements with respect to the freons TCs.” This statement is vague, and poorly worded. While it may be colloquially expressing a practical opinion of someone doing retrievals it could be and would be more useful to readers if filled out more technically.

L128 – 136: “The analysis of the Inverse Problem Solution Process (IPSP)”, This apparent procedure is not described, therefor the methodology to determine the characteristics of the QHN, its full effect on spectra and subsequent retrievals, perhaps straight forward or perhaps more sophisticated is unknown. It likely would be of wide interest. Consequently the reader does not know how the author came to the exclusion of some 450 spectra.

L145-150: “the main criterion for choosing the optimal values of setup parameters was the stability of the target gas TCs during a day. More precisely, the root mean square value (RMS) over all days for SD of the gas TCs per a day was minimized. Along with the daily variability of the TCs, the mean value and the SD of the information content of measurements (degrees of freedom for signal, DFS) (Rodgers, 2000, p. 19) as well as the estimates of the systematic and random measurement errors and the spectral residual – the RMS difference between measured and calculated spectra for the retrieved state of the atmosphere ( $\chi^2$ )” Listing these does not explain how they are used. This section requires a thorough explanation.

L150: “Table 1 presents the main optimized parameters obtained in previous studies.” Table 1 does not specify any of the mention retrieval parameters.

L152 – 154: “Target gas absorption is calculated based on pseudo–lines (see

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mark4sun.jpl.nasa.gov/pesudo.html for pseudo-lines), interfering gases absorption is calculated based on spectroscopic information from the HITRAN database”, this is not true please see the list of interfering species.

L163: “The main factor that determines the shape of the SBL is the filter spectral transmission function (STF).” The spectral baseline is typically 0% transmission line. It typically is not affected by the optical filter transmission or envelope.

L163 – 169: Several points require more detail. Does the water vapor continuum effect the artificial light source spectra? The solar spectra? or both? “contribution in the considered spectral region under conditions of the St. Petersburg site can significantly exceed 50 %.” This 50% of what exactly?, “For a 30 cm<sup>-1</sup> window, the selectivity of continual uptake is sufficient to influence the IPSP results.” Completely unclear what this statement refers to. If this this continuum is a feature of the spectra and well modeled then some plot should be shown to prove it has been resolved.

L170 – 183: This paragraph tries to explain the process of modeling the ice. Its is still not clear where the ice is in the optical path. But the mention of LN2 assumes its at the detector. This should be made clear. Was the WV continuum modeling used in the retrieval? Appears not but its not clear. It appears the a simple quadratic background was used as is standard in many retrievals. The term cryo-sediment does not seem appropriate for the feature.

L205 – 214: The author should explain the large difference in the curves F12 versus F11 & F22

L215-239: and Fig’s 2-4: This section seems to compare a single (per species?) constraint called ‘OE’ with an alpha optimized T-P constraint. First the OE a priori (Sa) is not given or described. Further since it is only one of a large possible array of constraints the comparison is in no way of general significance or value to the reader as well as mis-labeled. This section is so lacking in information as to mis lead the reader. This section needs significant redress before re-submission. To wit the final statement

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regarding the contradicting conclusion found in Prignon is not explained.

Table 3 & 4: Table 3 and the upper section of table 4 should be combined into one table and the lower part of table 4 should stand alone as table 4 giving the uncertainties of the retrievals.

L245 – 250: Please add to the tables how many spectra were removed in each step to remove outliers. This would be instructive on ‘far’ versus ‘near’ outliers were removed & overall data quality.

L260: “spectral residuals vary from 0.34 to 0.52 % depending on the gas; it corresponds to the SNR values of 209,280, and 327” please explain (equation?) how these correspond?

L265 – 272: Earlier the authors state they have a modeled covariance. This could be a reasonable estimate and consequently the calculation could be performed and would be informative.

L293 – 297: There is no explanation of why or how the optical filter could have such an effect on the variability as it is a static or passive component. Some explanation is required to support this statement.

âĀĀ Minor:

L57 “Since Molina and Rowland (1974) have reported that CFCs accumulated in the Earth’s atmosphere lead to an increased rate of ozone depletion, the attention of both scientists and policymakers to the ozone hole problem has been increasing. “ This statement may have been true in the 1990’s but not so today.

L66 – Use of atmospheric content is not standard, often atmospheric burden when referring to the total column is used.

L73 & Amendments should be added after Montreal Protocol

L86-95 This review is not thorough. Certainly, any review of FTIR CFC efforts needs to

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include Rinsland 2010 and references therein.

L111: “the Tikhonov–Phillips (T–Ph) approach which is more suitable for long–lived gases with a pronounced trend.” – this statement is obvious or well known and requires a reference.

L124: “The observational system is based on a Bruker FS125HR Fourier spectrometer, but some of the equipment is non–standard.” Doe the author mean in an NDACC-IRWG sense?

L125: “a non–standard spectral filter F3 was used for measurements in the spectral region with considered freons absorption bands.” There is no reference for ‘F3’. If a local name it should be referenced as such.

L128 – 136: The author should also refer to this as ‘channeling’ its more common name and insert the in press [Blumenstock AMT 2021] for a reference.

L137: “For a preliminary assessment of the signal to noise ratio (SNR), the standard deviation (SD) of the signal”, Its not clear but presumably the SD of the SNR, Please clarify.

L146: “More precisely, the root mean square value (RMS) over all days for SD of the gas TCs per a day was minimized. “ This not clear at all, please re-phrase.

L150:  $\chi^2$  is within the nomenclature of SFIT is a normalized part of the convergence criteria. Is it being used here in that capacity or of simply renaming RM =  $\chi^2$ ? This needs clarification.

Table 2: Not readable needs to be reformatted with clear rows and columns

L190: “by a priori information of the Tikhonov–Phillips” T-P is an ad hoc constraint not actually a priori information.

L192: “Unlike the OE, the T–Ph approach does not “pull” the solution to the mean profile”, The OE does not pull, the retrieved profile retains the a priori value when there

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is no new information from the spectra. Also not to the 'mean' rather the a priori.

L195: "the OE approach requires the use of the covariance matrices for describing the variability of the target gases profiles," not so, an array of ad hoc constrains can be applied within the OE context.

L202: (sp) choice

L209: 'and the both' is awkward maybe should be 'and both'

L211: if the author is referring to a profile scaling procedure it should be clearly stated so e.g. "first guess profile multiplier."

L216: specify section and / or page of appropriate discussion in Rodgers & Connor 2003.

L251: "geographical latitude", is redundant.

L248: does "not provide a solution" mean not converge or other issues, or both?

L310: "which does not have a systematic component during a day, to the random error." This is not clear, What is a systematic component to a random error?

EQ2  $\sin()$

L406: 'belt' might better be 'range'

L418: "a noticeable seasonal variations" rather: "a noticeable seasonal variation"

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