Total columns of freons retrieved from ground-based IR solar spectra measurements near Saint Petersburg, Russia

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Our subjects are:

- Trichlorofluoromethane CCl_3F (R-11, CFC-11)
- Dichlorodifluoromethane CCl_2F_2 (R-12, CFC-12)
- Chlorodifluoromethane CHF_2Cl (R-22, HCFC-22)

Due to the use of CFCs as propellants and refrigerants in the 1980s, measurements at that time show rapid growth in CFC-11 and CFC-12. In order to reduce ozone-depleting substances, including CFCs, 27 countries signed a global environmental treaty - the Montreal Protocol - in September 1987.
Hydrochlorofluorocarbons (HCFCs) have been used to replace CFCs after the Montreal Protocol.

As a result, the growth of HCFC-22 has been observed since 2004, But it also destroys ozone and is a greenhouse gas, so its use is reduced and its content decreases.

The concentrations of CFC-11, -12 in the troposphere reached their maxima in 1992 and 2003, respectively, and since then there has been a decrease.

1) CFC-11 and CFC-12 are the dominant sources of chlorine in the stratosphere
2) They are responsible to ozone depletion.
3) They absorb infrared radiation, contribute to the greenhouse effect.
4) Due to the long lifetime (60, 120, 12 years) they are indicators of transport and mixing in the lower stratosphere and upper troposphere.

Until recently, data on local and satellite sun occultation measurements were mainly used to study the content of the gases.
Methods of ground-based spectroscopy, in contrast to the satellite method, are sensitive to gas concentrations up to the Earth’s surface.
Within the network NDACC (Network for the Detection of Atmospheric Composition Change), measurements are performed using IR Fourier interferometers. These measurements allow to obtain the total content (TC) of CFC-11, CFC-12, HCFC-22, and some other freons.
The work (Zhou et al, 2016) presents the results of CFC-11, CFC-12, HCFC-22 TC measurements at two NDACC stations of Re-Union Island.

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The archive of ground-based spectral measurements of solar radiation, accumulated at the NDACC St. Petersburg station since 2009, can be used to obtain data on the TC of freons.
For the inversion of spectroscopic measurements, we use the widely distributed SFIT-4 code widely used in the NDACC network.
The code is universal, and setting its numerous parameters for solving problems of determining the content of various gases is nontrivial.

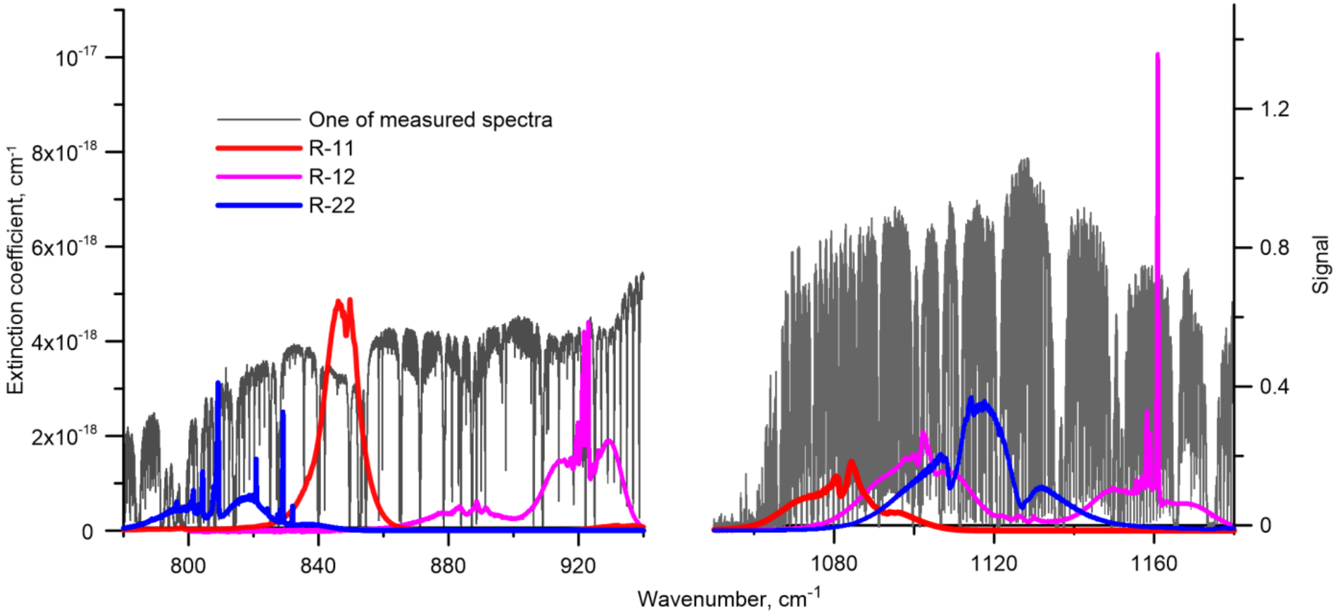

Figure 1. Extinction coefficients of the freons (link axe) and one of measured spectra (right axe)

The presence in the infrared region of the spectrum of the absorption bands of the freons under consideration (Figure 1) makes it possible to record their content in the atmosphere by analyzing the spectra of solar radiation transmitted through the atmosphere.

Table 1. Retrieval techniques

gas	Microwindow, cm^{-1}	Curvature	Beam freq, cm^{-1})[2]	H_2O lines HITRAN	H_2O profile or TC
HCFC-22	828.75 – 829.4	no	1.1 / no	2009	TC
CFC-11)[1]	830 – 860	10^{-6}	1.1 /no	2016	profile
CFC-12	1160 – 1162	no	1.26 /no	2009	TC

)[1] ice film 0.3 / 0.9 um, water vapor continuum preliminary calculated, the value of curvature a priori uncertainty was chosen to model ice film variability.
)[2] before / after 2016.

As a priori profiles of target gases, the mean profiles of the WACCM v6 model for the period 2009-2019 were used.

As a priori profile of water vapor, the PROFITT result was used.
Optimal Estimation technique was used.

Whole description of the retrieval techniques you can found in J Appl Spectrosc
87(1), 2020, 92–98. DOI 10.1007/s10812-020-00968-6 (CFC-11)
86(3), 2019, 449-456, DOI 10.1007/s10812-019-00840-2 (CFC-12)
85(6), 2019, 1085-1093. DOI 10.1007/s10812-019-00763-y (HCFC-22)

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Table 2. Error budgets: Mean systematic and random uncertainties (%) for CFC-11, CFC-12 and HCFC-22. SD is shown after sign ± . «Sb» represents the relative uncertainties (absolute value) of the non-retrieved parameters (also in %). When a relative uncertainty is smaller than 0.01 %, it is considered negligible and represented as “–”. Last line of the table shows mean DOFS with SD.

		CFC-11		**CFC-12**		**HCFC-22**	
Error	Sb	Systematic	Random	Systematic	Random	Systematic	Random
Smoothing	–	0.16±0.06		0.15±0.03		1.40±0.51	
Measurement noise	–	–	0.29±0.13	–	0.28±0.04	–	1.94±0.61
Retrieval parameters	–	–	1.6±0.07	–	0.02±0.01	–	0.18±0.06
Interfering species	–	–	0.04±0.04	–	0.03±0.01	–	0.11±0.12
Temperature	–	1.92±0.03	2.13±0.33	1.54±0.13	1.71±0.15	–	1.56±0.11
Sun Zenith Angle	0.1±0.5	0.25±0.27	1.25±1.33	0.21±0.17	1.06±0.85	0.27±0.22	1.36±1.13
Target line intensity	7/1/5	7.01±0.24	–	0.99±0.03	–	4.88±0.42	–
Target air-broadening of line width	7/1/5	0.01±0.01	–	0.18±0.10	–	1.36±0.34	–
H2O spectroscopy	10	0.92±0.50	–	0.44±0.42	–	0.48±0.50	–
Total	–	**7.43±0.13**	**2.93±0.86**	**1.99±0.12**	**2.21±0.54**	**5.32±0.09**	**3.08±0.61**
Daily SD, %		0.82		0.82		3.03	
DOFS		1.35±0.23		1.73±0.07		1.33±0.24	

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Two samples (high Sun in summer and low Sun in winter) of TC sensitivity and a priori and retrieved profiles of analyzed freons.

Table 3. Smoothing errors and DOFS

	CFC-11	CFC-12	HCFC-22
Smoothing error	0.16±0.06	0.15±0.03	1.40±0.51
DOFS	1.35±0.23	1.73±0.07	1.33±0.24

As a priori profiles of target gases, the mean profiles of the WACCM v6 model for the period 2009-2019 were used.

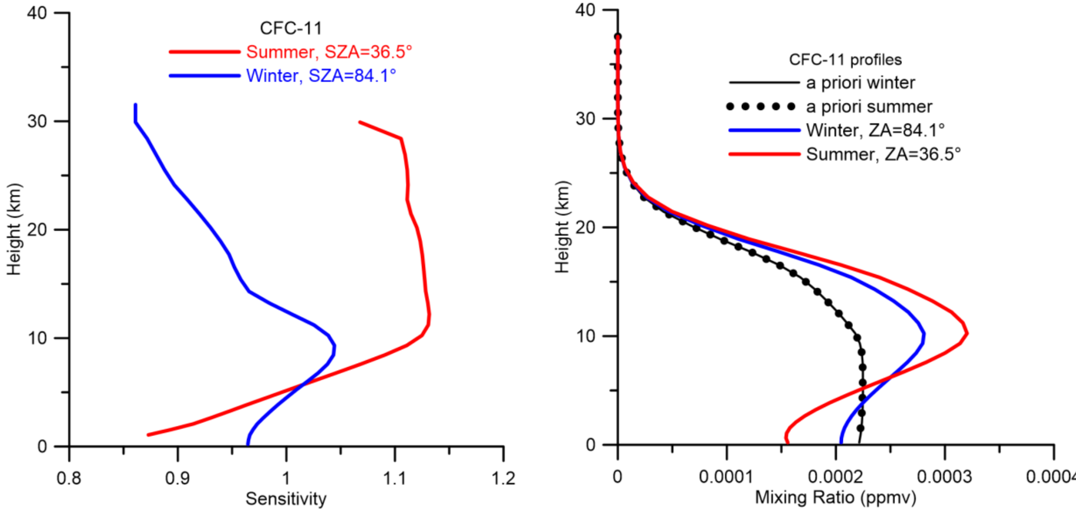


Figure 2. The sensitivity of the CFC-11 TC wrt its mixing ratio profile and a priori and restored profiles 06/16/2018 09:54 and 10/14/2018 13:57

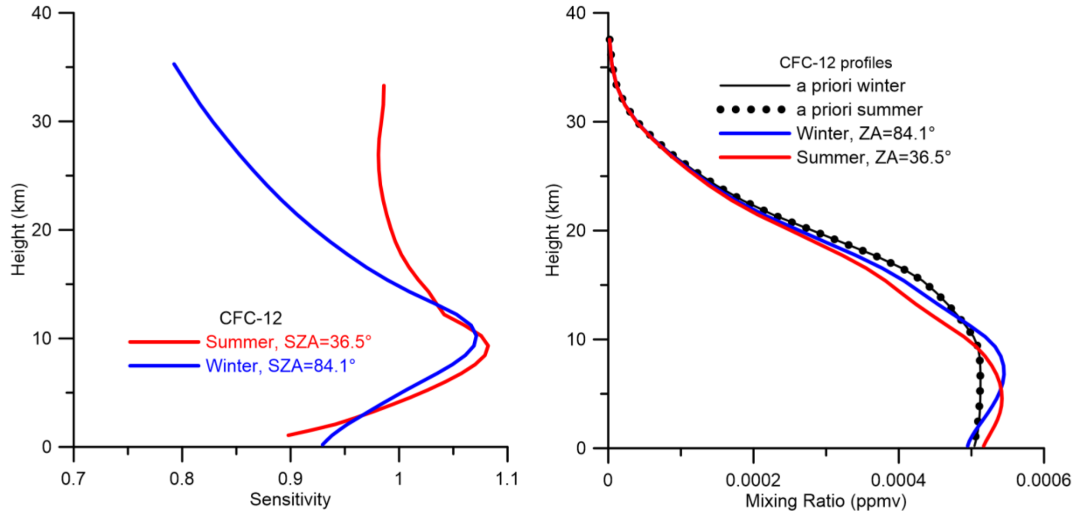


Figure 3. The sensitivity of the CFC-12 TC wrt its mixing ratio profile and a priori and restored profiles 06/16/2018 09:54 and 10/14/2018 13:57

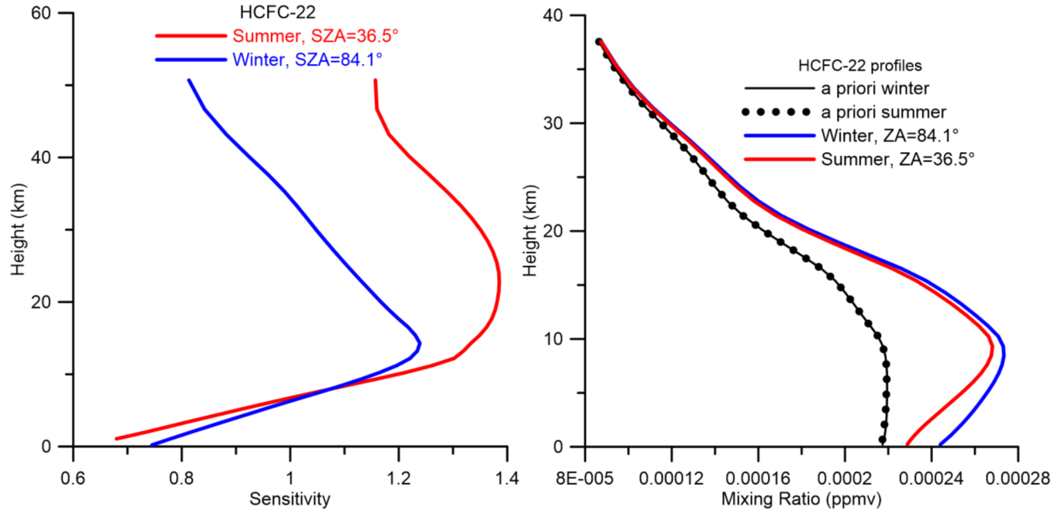


Figure 4. The sensitivity of the HCFC-22 TC wrt its mixing ratio profile and a priori and restored profiles 06/16/2018 09:54 and 10/14/2018 13:57

Total columns of freons retrieved from ground-based IR solar spectra measurements near Saint Petersburg, Russia

Figure 5. Measurement results: Total column amount and mean molar fraction

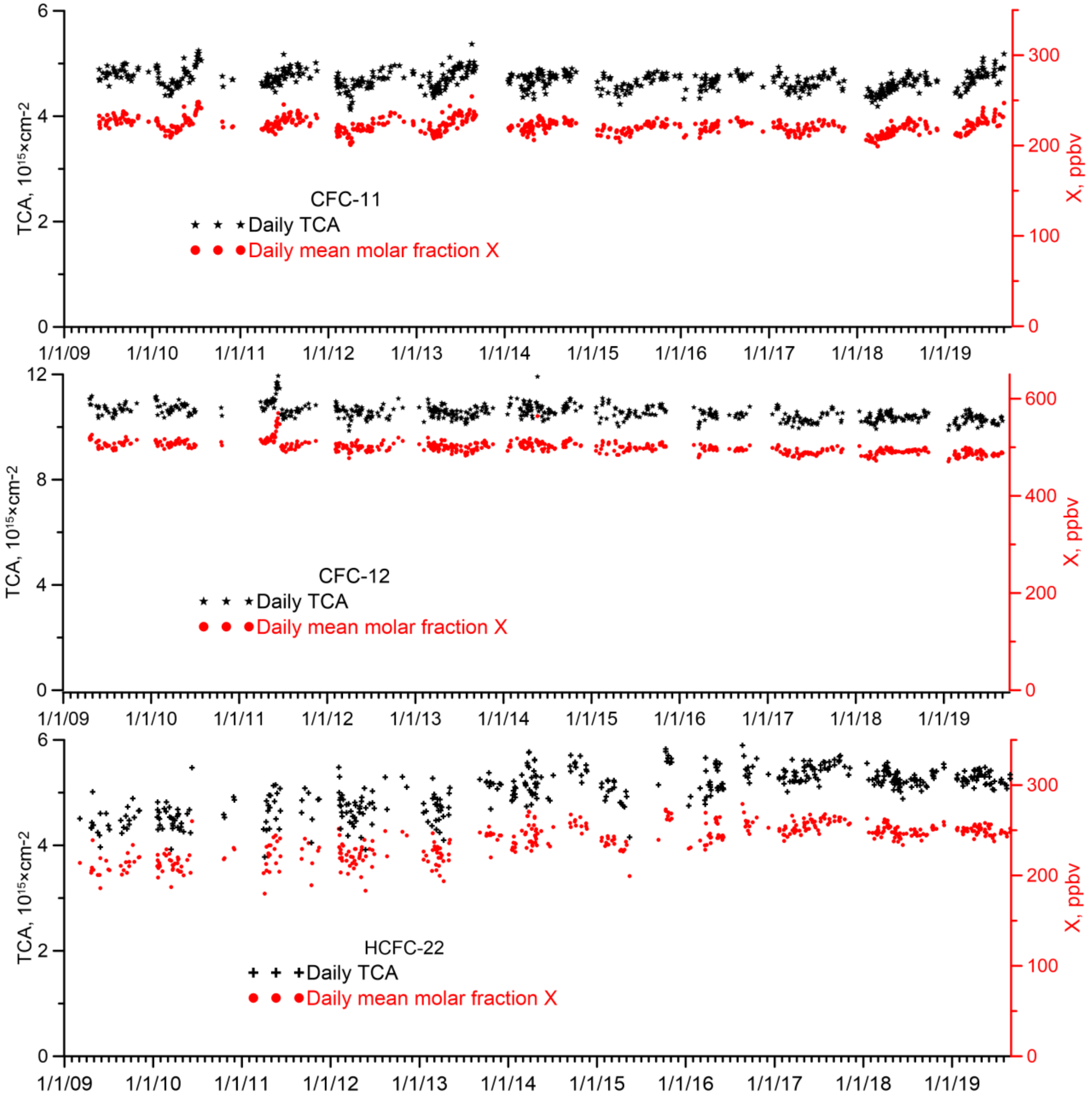
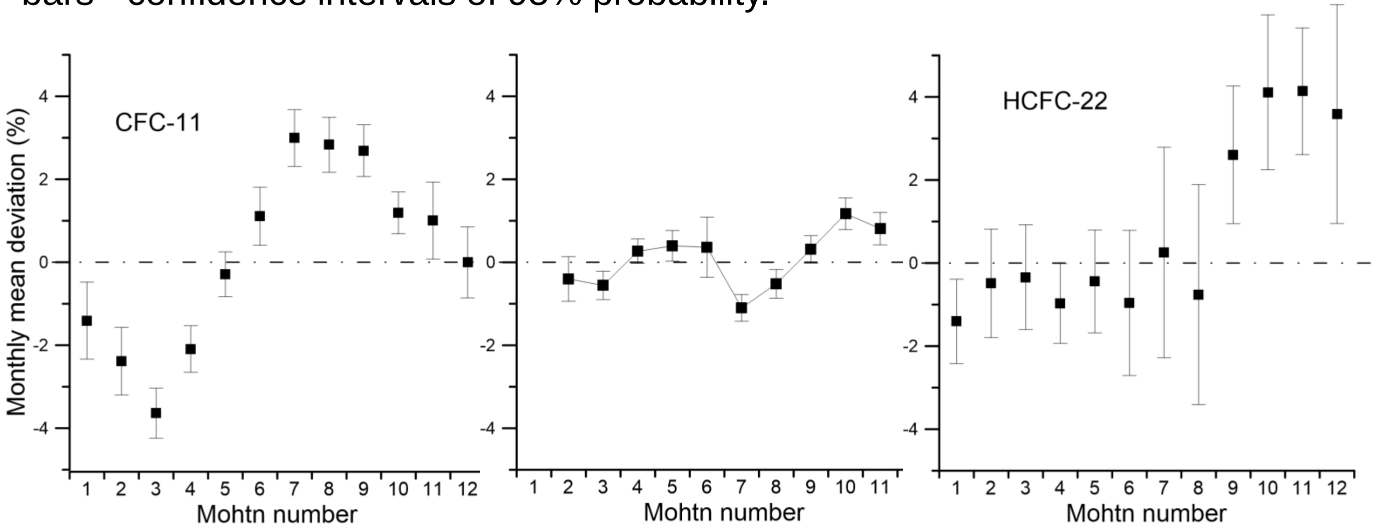


Figure 6. The seasonal variation of the monthly average deviations of X minus the trend according to ground-based measurements at St. Petersburg station. Vertical bars - confidence intervals of 95% probability.



As we can see from fig. 2 and 4, and - to a lesser extent, from fig. 3, due to the low sensitivity of the technique in the lower part of the troposphere, the resulting profiles have some altitudinal dependence. But due to the long lifetime and the absence of intensive sources and sinks, the mixing ratio of the gases in the troposphere is expected to be independent of altitude. Fig. 2 and 4 show the dependence of the profile shape on the season, which can lead to season variations. To get rid of this dependence, we plan to continue working on the technique, in particular, consider Tikhonov-Phillips regularization instead of Optimal Estimation, before analyzing season variability of the gases.

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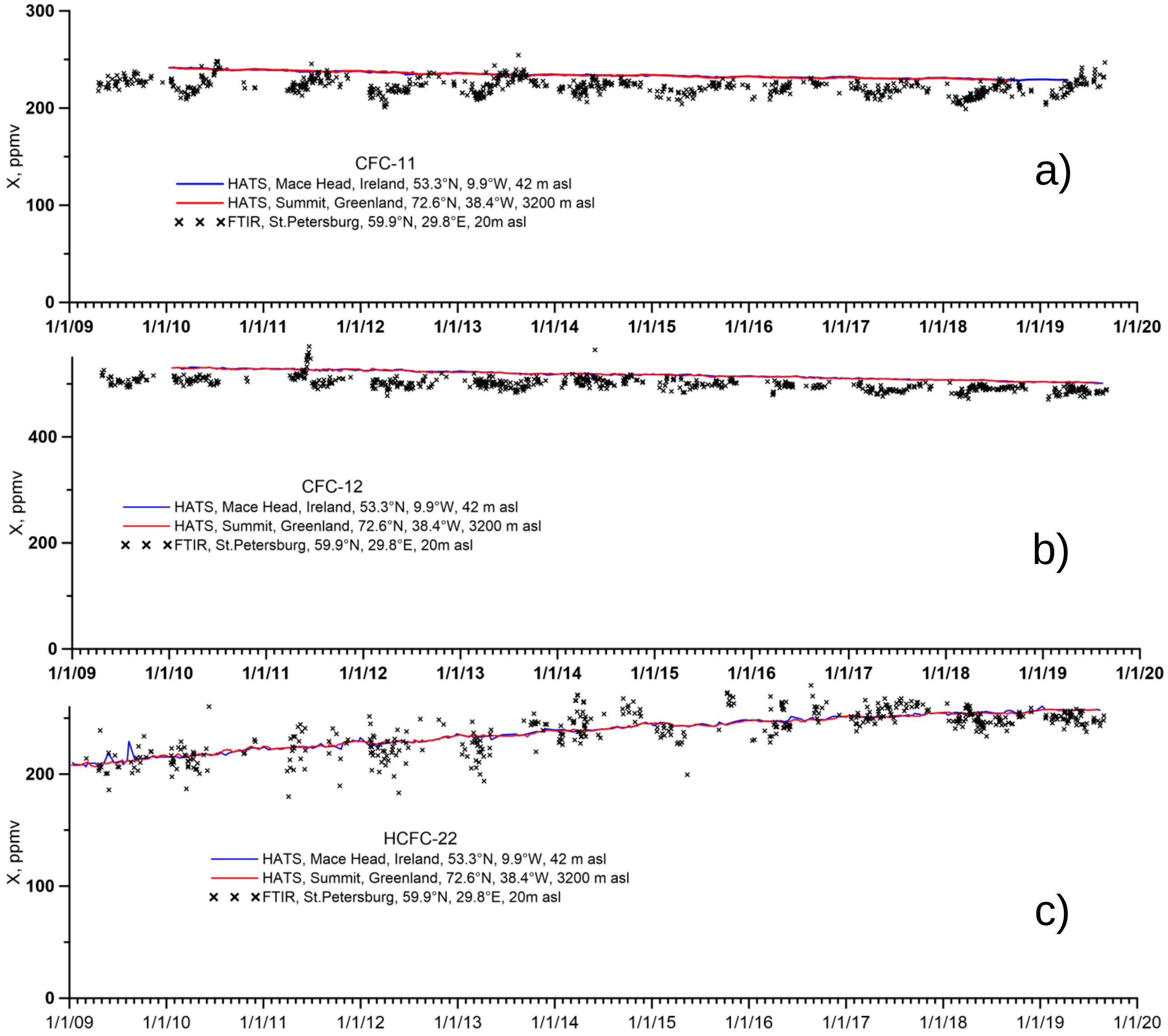
Fig 7. FTIR data of St.Petersburg NDACC station and in situ HATS measurements



We compare our results with the in situ (flask) data obtained by Halocarbons & other Atmospheric Trace Species (HATS) group (Montzka et al. 1993); data are regularly updated at ftp://ftp.cmdl.noaa.gov/hats/hcfcs/hcfc22/flasks/(Montzka et al. 2015). Fig. 7a-7c show mean molar fraction by FTIR TC data and HATS measured molar fraction near surface by different stations (latitude is shown in the picture). CFC-11 and CFC-12 profiles quickly decreases in the stratosphere (see fig. 2,3), that is the reason why our mean molar fraction data are less then HATS local ground-based molar fraction, see fig. a), b). HCFC-22 has more high profile, and our results are varying around HATS measurements in close latitudes. In general, the agreement of our results with the results of the HATS group should be considered as satisfactory.

Table 4: Trend estimations, (% / year)

gase	St. Petersburg, MMF	Zhou et al, TC		WMO, MMF
	2009-2019	2004-2016	2009-2016	2010-2016
CFC-11	-0.31±-0.07	–0.86 ±0.12	-	-0.70+-0.17
CFC-12	-0.45±0.06	-	–0:76±0.05	-0.47+-0.08
HCFC-22	+2.2±0.14	2.84±0.06	-	2.54+-0.14

MMF – Mean Molar Fraction, TC – Total Column.
Technique of a trend estimation: Timofeyev at al, IZVESTIYA. ATMOSPHERIC AND OCEANIC PHYSICS 56(1) 79–84, 2020

In the Table 4 some trends estimations are shown. We can see an excellent agreement for CFC-12 by St. Petersburg vs WMO. For CFC-11 our decrease speed is much less then this one by both Zhou et al and WMO. The reason is increase of global emissions of CFC-11 (Montzka et al., 2018). Our estimate of the HCFC-22 increase value is less than that obtained by Zhou et al. (2016) and WMO due to the slowing down of the increase, see Polyakov et al., 2020.

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Conclusions

1) Techniques for assessment the Total Column values of CFC-11, CFC-12, HCFC-22 by spectral measurements of solar radiation at the NDACC station St. Petersburg were proposed.
2) The series of CFC-11, CFC-12, HCFC-22 TCs in the atmosphere above the station at station Petersburg were obtained for the period 2009-2019.
3) Satisfactory agreement of the obtained results with in situ measurements of the HATS group is shown.
4) The analysis of the obtained vertical profiles (an intermediate result of solving the inverse problem) showed the feasibility of further improving the methods, which may affect the resulting seasonal variation.
5) Using the existing methods, the seasonal variation of CFC-11 was obtained with a minimum of -4% in March and a maximum of 3% in July-September, HCFC-22 with a maximum of 4% in late autumn and early winter.
6) Estimates of the trends of the considered gases are obtained (-0.31±-0.07, -0.45±0.06, 2.2±0.14 (%/y) for CFC-11, CFC-12, HCFC-22), their satisfactory agreement with independent data is shown.

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