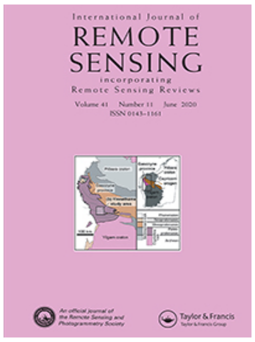

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Atmospheric HCFC-22 total columns near St. Petersburg: stabilization with start of a decrease

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ABSTRACT
We study the changes in the growth rate of atmospheric HCFC-22 ($CHClF_2$, or chlorodifluoromethane) total column (TC) in the vicinity of St. Petersburg, Russia (60° N). Although HCFC-22 surface concentrations at the two nearest sites of the Halocarbons and other Atmospheric Trace Species group (HATS) (53.3° N and 71.3° N) and mean HCFC-22 mixing ratios in the upper troposphere measured by the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE FTS) in the latitude range of 55–65° N continue to increase, their growth rate is slowing down, especially in the last three years. Analysis of the temporal variability of HCFC-22 TCs measured at the St. Petersburg site of Network for the Detection of Atmospheric Composition Change (NDACC) shows that its total atmospheric abundancy reached a maximum in 2016–2017 and is currently decreasing. Thus, the measurements in the atmosphere above St. Petersburg have detected a local decrease of the HCFC-22 content, which demonstrates the effectiveness of restrictions on the production of HCFC-22.

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1. Introduction

Since Molina and Rowland (1974) reported that chlorofluorocarbons (CFCs) accumulated in the Earth's atmosphere led to an increased rate of ozone depletion, the attention of scientists and policymakers to the ozone hole problem has been increasing. Detecting and monitoring of ozone and other stratospheric gases as well as the ozone depleting substances, including CFCs, was crucial for testing the theories of the ozone hole formation mechanism (Cracknell and Varotsos, 2009). As the result of the Montreal Protocol and its amendments and adjustments, which restricted the emission of CFCs (WMO 2018), industry moved away from CFCs to less ozone-depleting hydrochlorofluorocarbons (HCFCs), especially chlorodifluoromethane HCFC-22, or $CHClF_2$.

As HCFCs were 'transitional substances' for the replacement of CFCs, their production increased rapidly in developed countries in the 1990s and peaked in the mid-1990s. This continued up to the 2000s, when the production and consumption of HCFCs in developed countries decreased as a response to the Montreal Protocol. Meanwhile, in the developing countries the production and consumption of HCFCs increased rapidly in the 2000s and

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was not controlled until 2016. Although the ozone depletion potential of HCFC-22 is much lower than that of CFCs (Hurwitz et al. 2015), it too is an ozone-depleting substance. Besides, HCFC-22 is a greenhouse gas (Siegemund et al. 2002). The Kigali Amendment to the Montreal Protocol on Substances that Deplete the Ozone Layer entered into force on 1 January 2019, following ratification by 65 countries. Under the Amendment, all countries will gradually phase down HCFCs by more than 80 percent over the next 30 years and replace them with more environmentally friendly alternatives.

Thus, for example, in the USA the production and import of HCFC-22 was banned on 1 January 2010, except to service and maintain existing equipment. HCFC-22 air conditioners were banned from production by the Environmental Protection Agency (EPA) (https://www.epa.gov/ods-phaseout/phaseout-class-ii-ozone-depleting-substances) as well, starting in 2010. The production and import of HCFC-22 will be decreased gradually to zero by 2020, at which point equipment can only be serviced with recycled or stockpiled HCFC-22. In 2010, HCFC-22 was banned for import into Russia, and in 2013, into the Eurasian Customs Union as a whole. According to http://www.ozoneprogram.ru/biblioteka/publikacii/rekomendacii_konferencii/), the production of HCFC-22 in Russia began to be cut from 2013. Therefore, a gradual slowdown in the growth of HCFC-22 in the atmosphere and, in the future, its decrease should be expected.

Considering all the above-mentioned facts, monitoring the concentration of HCFC-22 in the atmosphere is an important task. The global network AGAGE (Advanced Global Atmospheric Gases Experiment), equipped with in situ gas sensors, was founded to observe the variability of CFCs and HCFCs concentrations. AGAGE started HCFC-22 measurements in 1990 (Dunse et al. 2005). National Oceanic and Atmospheric Administration's (NOAA's) Halocarbons & other Atmospheric Trace Species (HATS) group sampling network started monitoring HCFC-22 concentrations in 1992 (Montzka et al. 1993); data are regularly updated at ftp://ftp.cmdl.noaa.gov/hats/hcfcs/hcfc22/flasks/(Montzka et al. 2015). Besides the measurements of surface concentrations, observations of HCFCs have been made using space-borne infrared spectroscopy techniques. Since 2003, HCFC-22 has been measured with the ACE-FTS (Atmospheric Chemistry Experiment Fourier Transform Spectrometer) instrument (Bernath 2017), and with MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) in the period 2002–2012 (Kellmann et al. 2012).

While the above-mentioned ground-based measurements allow only near-surface concentrations of HCFC-22 to be obtained, satellite experiments provide information on profiles higher than 5–6 km. Recently, some results of FTIR ground-based measurements were obtained at several NDACC (Network for the Detection of Atmospheric Composition Change) stations. Total columns (TCs) of HCFC-22 were measured at the Saint-Denis and Maïdo NDACC sites at Réunion Island (Zhou et al. 2016), and some results were presented at conferences (Zander et al. 2005; Mahieu et al. 2010, 2013) and at InfraRed Working Group (IRWG) NDACC workshop meetings. Lastly, Prignon et al. (2019) discussed in detail the HCFC-22 ground-based FTIR measurements at the Jungfraujoch site. It should be stressed that ground-based IR solar radiation measurements allow the TCs of the gas to be determined, i.e. its content in a whole atmosphere, contrary to the local or satellite occultation measurements.

HCFC-22 is not a gas that it is mandatory to measure at NDACC stations, so no standard technique is available for its retrieval from solar spectra. We use a technique developed by Polyakov, Virolainen, and Makarova (2019) for HCFC-22 retrieval near St. Petersburg. The average systematic uncertainty of the retrieved HCFC-22 TCs is

4.8%, while the random uncertainty is 3.7%. Our results demonstrate that the HCFC-22 TC growth rate has slowed down, and in the last two or three years it has stopped, and moreover started to decrease. This is the fact to which we want to draw the attention of readers in this short paper.

2. The measurements

The St. Petersburg NDACC site is located in a suburb of St. Petersburg, Russia (Peterhof), approximately 30 km west of the city centre at 59°53′ N, 29°50′ E, 20 m a.s.l. Although the site joined the IRWG NDACC community with its FTIR (Fourier transform infrared) system only in 2016, the spectral measurements in fact started earlier; a spectra data set has been accumulated since 2009. The spectra are registered with a Bruker 125 HR spectrometer with a spectral resolution of about 0.005 cm^{-1}. The description of the site and the spectral measurements are given in detail by Timofeyev et al. (2016). Spectra are processed with the SFIT4 code (Hase et al. 2004) in an 828.75–829.4 cm^{-1} micro-window, using the technique described by Polyakov, Virolainen, and Makarova (2019). Here we analyse the data measured between March 2009 and July 2019. From our estimates, the systematic error of the HCFC-22 TCs equals 4.8%; the random error equals 3.7%. The daily mean values of the HCFC-22 TCs are shown in Figure 1. The mean daily variability of the HCFC-22 TCs totals 0.9%: this comprises 1.0% for measurements before 2016 and 0.8% for measurements after 2016, when an optical filter was changed (for details, see Polyakov, Virolainen, and Makarova 2019). The daily means demonstrate a slow growth of HCFC-22 TCs approximately up to 2016, then some stabilization, with a slight decrease after 2017.

3. Discussion

To analyse and evaluate our results, we consider the independent data. As mentioned above, besides FTIR ground-based measurements, there are two main principally different

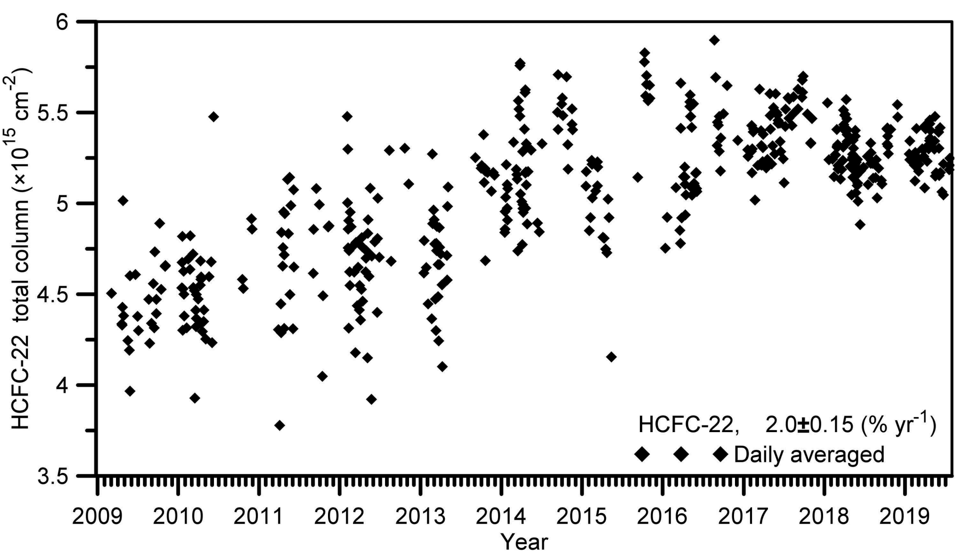

Figure 1. Daily averaged HCFC-22 TCs.

sources of data on HCFC-22 concentrations: local measurements near the Earth's surface and satellite sun occultation measurements. We use the data of two sites of the NOAA HATS project (Montzka et al. 1993) – the data are regularly updated at ftp://ftp.cmdl.noaa.gov/hats/hcfcs/hcfc22/flasks/, and the ACE-FTS satellite experiment data version 4.0 (Boone et al. In preparation; Bernath et al. 2019). All data are presented in Figure 2.

In the figure, MHD denotes the *Mace Head, Ireland* site, 53.3°N, 9.9°W and BRW denotes the *Barrow, USA* site, 71.3°N, 156.6°W. The ACE-FTS instrument provides mixing ratio profiles above a certain altitude. The lower bound can be different, but not less than 5 km. For comparison, we calculate the mean molar fraction values of HCFC-22 from ACE-FTS data between 8 and 10 km. Due to its long life time – 12 years (WMO 2018) – HCFC-22 is well mixed in the troposphere, and these values can be used for comparison versus the mean molar fraction. Figure 2 depicts a noticeable decrease of HCFC-22 TCs after 2017, as obtained by ground-based FTIR measurements. At the same time, the HATS surface data show a continuing increase and no decrease. Besides, Prignon et al. (2019) show that the accumulation rate of HCFC-22 TCs seems to have slowed down in the time period 2008–2017; it is estimated at the Jungfraujoch NDACC site to be 2.57 ± 0.09% yr^{-1}. Estimates for the previous period show a higher growth rate of HCFC-22 TCs.

Therefore, only the measurements taken above St. Petersburg are detecting a decrease in HCFC-22 TCs, whereas the measurements at other places do not indicate any decrease. The possible reason for this different behaviour may come from the different localizations of the measured gas volume. There are two types of localization mismatch: 1) Vertical (altitude of the measured gas volume); 2) Horizontal (geographical location, i.e. longitude of the measured gas volume). To study the dominant factor in the different behaviour of HCFC-22, we calculate and show in Figure 2 (purple curve) the running average of the ACE-FTS

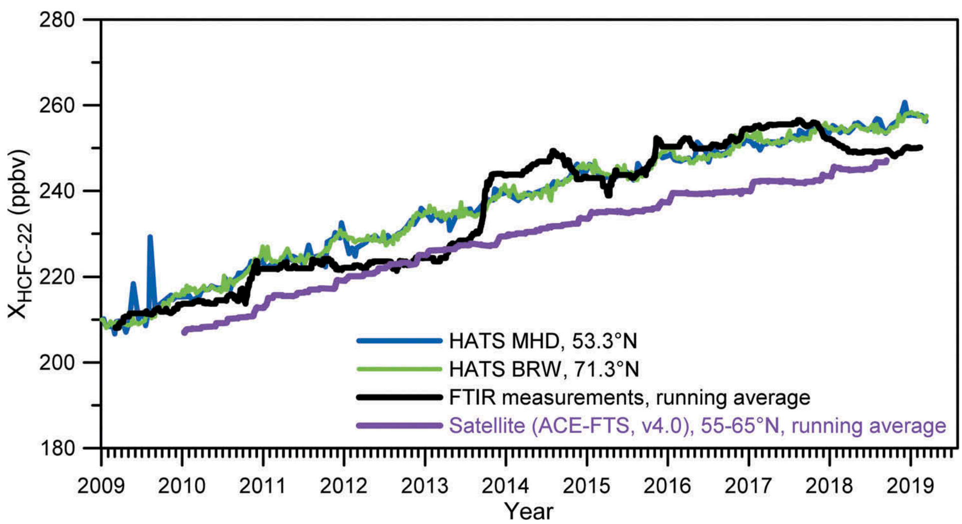

Figure 2. Mean molar fraction of HCFC-22, $X_{HCFC\text{-}22}$. Approximately weekly flask measurements of the HATS sites nearest to the latitude of St. Petersburg: MHD and BRW sites (blue and green curves; data obtained from ftp://ftp.cmdl.noaa.gov/hats/hcfcs/hcfc22/flasks/), a running average (one year) of daily mean mole fractions of HCFC-22 FTIR measurements at St. Petersburg site (black curve) and ACE-FTS data in 55–65° N latitude range (purple curve).

Table 1. Growth rate of HCFC-22 obtained by ground-based FTIR measurements over St. Petersburg, by ACE-FTS observations in the 55–65° N latitude range, and at the HATS stations MHD and BRW in the 3-year period. HW – half width of confidence interval for 95% probability.

	Growth rate ± HW, (% yr^{-1})			
Period (summer to summer)	St. Petersburg	ACE-FTS	HATS MHD	HATS BRW
2016 – 2019	−0.66 ± 0.49	0.20 ± 1.39	1.25 ± 0.11	0.91 ± 0.07
2013 – 2016	1.19 ± 0.81	1.06 ± 1.28	1.87 ± 0.12	1.82 ± 0.07
2010 – 2013	2.06 ± 1.30	3.13 ± 1.21	2.33 ± 0.16	2.32 ± 0.07

measurements in the 55–65° N latitude range for all longitudes. The curve demonstrates the continuous slowing down of the HCFC-22 increase, while ground-based FTIR data show a decrease of the HCFC-22 content in the atmosphere in the vicinity of St. Petersburg. We assume that the reason for the different behaviour of the HCFC-22 time series is due to the different geographical locations of the compared measurement data.

Furthermore, we numerically estimate the rate of HCFC-22 changes above St. Petersburg for all considered measurements and for different observation periods. First, we exclude the seasonal variations of HCFC-22 according to a simple approach suggested by Timofeyev et al. (2020, in print): we calculate the monthly averages for the considered period and subtract them from the individual measurements. This method is reliable for HCFC-22 as its seasonable variability is small enough. Then we estimate the growth rate value for the minimum possible time period. The time period, in which the estimate of a confidence interval width of 95% probability does not exceed the trend value itself for the St. Petersburg measurements, is 3 years. To estimate the slope of an approximating line, we use the mean-squared minimization (Santer et al. 2000). The results are shown in Table 1.

As can be seen from the table, the growth rate of the HCFC-22 TCs above St. Petersburg is decreasing; and in the last 3 years it has become negative, i.e. a decrease of the HCFC-22 TCs is observed. The growth rate of the HCFC-22 surface concentrations at both of the HATS stations demonstrates a significant decrease over time, although a substantial increase of HCFC-22 still persists over the past 3 years. For the ACE-FTS data, a decrease in the growth rate leads to the fact that in the last 3 years (2016–2019) the growth of HCFC-22 is no longer reliable. Since the ground-based FTIR measurements make it possible to observe the HCFC-22 TCs, HATS measurements are localized in the surface layer, and ACE-FTS data are localized in the upper troposphere, we may assume that the main decrease in the growth rate of HCFC-22 occurs in the middle and upper troposphere, and is most pronounced up to the start of the decrease in the vicinity of St. Petersburg.

4. Conclusions

The time series of the HCFC-22 content based on satellite and ground-based measurements have been analysed. It has been shown that in recent years in the latitudes of 55–65° N, on average, a gradual slowdown in the growth rate of its concentrations both at the surface and in the upper troposphere is observed. At the same time, in the vicinity of St. Petersburg (at a latitude of 60° N), the slowdown in the growth rate of HCFC-22 TCs is more significantly pronounced, to the extent that the increase of TCs has turned to its decrease in the last 3 years.

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Disclosure statement

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