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Ground-Based Measurements of HF Total Column Abundances in the Stratosphere near St. Petersburg (2009–2013)

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Abstract—An analysis of ground-based spectroscopic measurements of hydrogen fluoride total column abundances (HF TCAs) near St. Petersburg for a 4-year period (2009–2013) is performed. The average HF TCA is 1.93×10^{15} cm^{-2}, and the RMS variation (natural variability) for the measurement ensemble is about 20%. The data are in good agreement with measurements collected at the NDACC stations (Bremen and Harestua), taking into account the differences in latitude. The monthly average HF TCAs show seasonal variation with peaks in late winter and early spring and troughs in the period from November to January. The variability of the monthly averages is at a maximum in winter and spring. A comparison of the HF TCAs from ground-based measurements with those from ACE-FTS solar occultation measurements shows that the total abundances from the ground-based data are 12% lower than those from the ACE-FTS data, and the RMS differences depend on the version of the satellite data processing system, being 13 and 16% for versions 2.2 and 3.0, respectively. The calculated ratio between HCl and HF total column abundances is significantly lower in late winter and spring. The linear trend of this ratio is 2.5% per year. Although the trend statistics is insufficient due to the short observation period, the pattern is explained both by the decrease in the stratospheric HCl content and the small increase in HF TCAs over the studied period and is consistent with literature data.

Keywords: atmospheric gaseous constituents, anthropogenic pollution, ozone-depleting gases, infrared spectroscopy

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INTRODUCTION

In the stratosphere, hydrogen fluoride occurs mainly as a product of the photodissociation of human-induced hydrogen fluoride compounds, and therefore its column abundance is a convenient measure of human impact on the atmosphere [1]. HF does not participate actively in ozone photochemistry, but, due to its considerably long lifetime in the stratosphere (over 10 years), it can be used as a measure of dynamic processes in the atmosphere [2]. Also, the HCl/HF column abundance ratio characterizes the intensity of heterogeneous processes on polar stratospheric cloud particles [2].

The presence of HF in the atmosphere was first detected in ground-based spectroscopic measurements in 1975 [3]. Subsequently, regular measurements of the HF total column abundances (HF TCAs) were made by various research groups and, in recent years, at the NDACC (Network for the Detection of Atmospheric Composition Change) stations. In addition, balloon and aircraft measurements were carried out for the vertical and latitudinal distributions of HF abundances (see, e.g., [4]). Satellite measurements of HF profiles were obtained using the ATMOS instrument [5], and, in the period from September 1991 to November 2005, using the HALOE instrument [6]. These data allowed researchers to create a global climatology of HF abundances in the Earth's stratosphere [7]. Currently, satellite data are obtained using the ACE-FTS instrument, which measures HF profiles by solar occultation [8].

Ground-based measurements at the NDACC stations allowed researchers to find long-term trends in HF abundances. In the 1970s–1980s, there was a rapid growth in HF TCAs, which reached 10.9 ± 1.1% per year above Kitt Peak [9]. The further increase in HF TCAs above this station was much slower: the rate in 1977–2001 was 4.3 ± 0.15% per year [10]. According to the 1996–2009 trend estimates obtained from measurements above Kiruna (Sweden), the increase in HF TCAs during this period was close to zero (0.65 ± 0.25% per year) [11]. Similar results were obtained in [12], where measurements were analyzed for 17 stations located from 80.05° N to 77.88° S.

In this paper we analyze 4-year measurements of HF TCAs near St. Petersburg, in particular, their seasonal variations, and compare these data with ground-based measurements obtained at the nearest NDACC stations and with satellite measurements. In our previ-

Comparison of HF TCAs from ground-based measurements in Peterhof and ACE-FTS data (for two processing versions, 2.2 and 3.0) in 10^{15} cm^{-2} and in %

ACE version	N	Mean		Mean difference	RMS difference	Standard deviation of the difference	Variability amplitude	
		Peterhof	ACE				Peterhof	ACE
2.2	8	1.70	1.90	0.20 (12%)	0.22 (13%)	0.11 (6%)	0.13 (8%)	0.20 (11%)
3.0	7	1.83	2.06	0.23 (12%)	0.28 (16%)	0.20 (11%)	0.56 (30%)	0.48 (23%)

N is the number of comparisons.

ous paper, we reported a similar study covering 2 years of measurements [13].

MEASUREMENT DETAILS AND DATA INTERPRETATIONS

High-resolution IR spectra of direct solar radiation were measured using a spectral complex created at the Physics Department of St. Petersburg State University on the basis of a Bruker IFS125 FTIR spectrometer [14] from January 2009 to April 2013. One to fifteen spectra (most often five or six) were measured per day. In this paper we analyze the results of determining the average daily HF TCAs.

Solar radiation measurements were made with a path difference of 180 cm^{-1} from spectra obtained using a Norton–Beer medium apodization function at a resolution of 0.008 cm^{-1}. The signal-to-noise ratio determined from the noise path of the "zero" signal fluctuated between 400 and 1600, with a typical value being about 1200. The measurements were interpreted using the SFIT2 ver. 3.92 software by first recovering the vertical profile of the gas abundances and then integrating the mentioned profile to obtain the total column abundances. Most of the NDACC stations use this software. In interpreting the data, we used the NDACC recommended spectral intervals for HF TCAs: 4000.86–4001.10, 4038.81–4039.07, and 4109.77–4110.07 cm^{-1}. We also note that, in interpreting the ground-based measurements, we used data on the atmospheric temperature profile and (as an initial approximation in the refinement) on the profile of the mixing ratio of water vapor from the radiosonde data collected at the Voeikovo weather station (26063 ULLI; the distance to the spectral measurement site was 50 km). Above the uppermost radiosonde level or in the absence of measurements, the Voeikovo data were supplemented with those from the AQUA satellite (the AIRS and AMSU-A instruments) [15]. The results of simulation by the WACCM model [16, 17], version 6 for St. Petersburg, were examined to select the following profiles: as an a priori HF profile, we took the average profile and, as an initial approximation for interfering gases apart from the already mentioned water vapor (CH_4 and O_3), we used their monthly averages for the respective month.

According to our estimates for the random component of the TCA determination error, which were based on both calculating an error matrix in solving the inverse problem and on (the lower bound estimate) the TCA variability during periods when the atmosphere and the instrument operation were stable, this component was ~2–3%. Note that the various sources of error in the FTIR spectrometer determinations of HF TCAs were studied in [18]. According to the estimates in [18], the random component of the TCA determination error (given similar signal-to-noise ratios) is 2.7%, and the main contribution to the systematic error comes from the error of the HF absorption line intensity (4.3%). The similar estimates in [19] yielded a total random error component of 6% and a systematic error of ~5% (mainly due to errors in the intensity of the HF absorption line). The estimates [20] gave a random component of 2% and a total systematic error of 6%. Note that the small variations in the error estimates reported in different studies are explained by the use of different spectral intervals and the differences in the instrument parameters, measurement conditions (solar zenith angles, etc.), and the state of the atmosphere at the time of the measurements. Other details of measurements and data interpretation which remained unchanged during the last two years of measurements are described in our paper [13].

HF TCA MEASUREMENTS: RESULTS AND ANALYSIS

The main characteristics of the solar spectra and HF TCA ensemble are shown in the table. During the study period, the total number of solar spectra that were accepted for processing was 2110. The analysis of these spectra gave 1832 HF TCAs (some of the spectra did not allow acceptable values to be obtained for the RMS differences between the calculated and measured spectra and were discarded for this or other technical reasons). The resulting values were averaged to obtain the daily average HF TCAs for 303 days of the 4-year period. Due to weather conditions, most of the measurements were carried out in spring and summer.

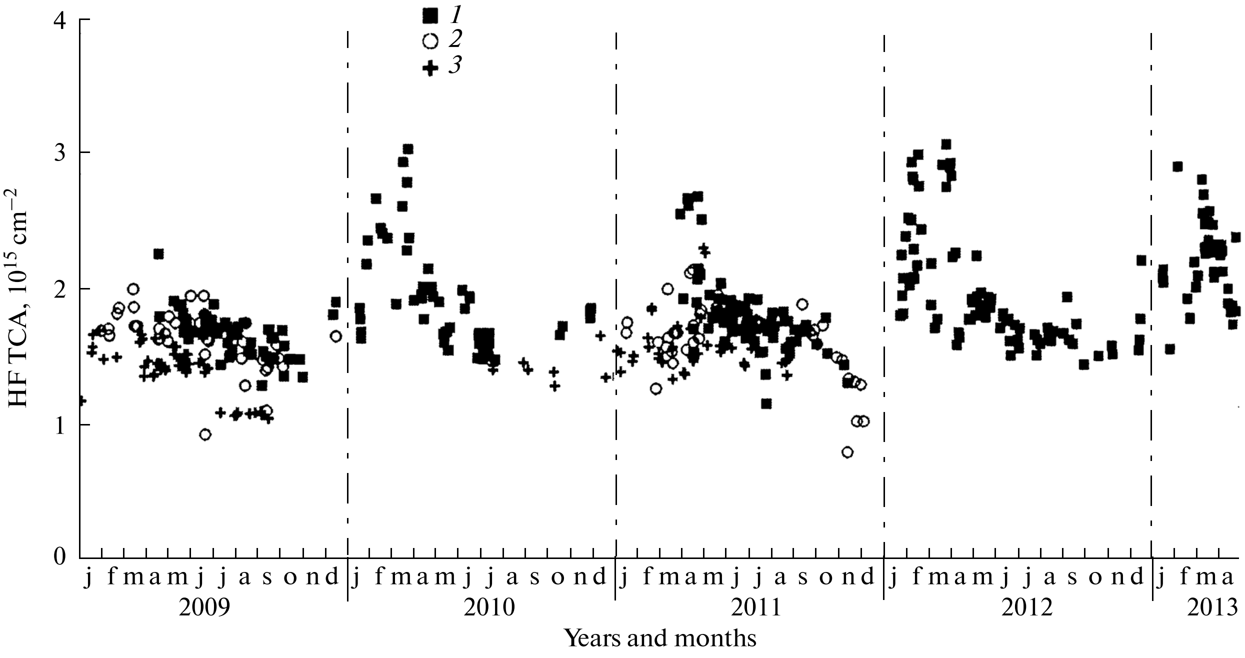

Fig. 1. Daily average HF TCAs for Peterhof (*1*), Harestua (*2*), and Bremen (*3*).

There were also sizable gaps in the measurements due to instrument malfunction (e.g., a little less than 4 months from December 2010 to March 2011).

The average HF TCA in the neighborhoods of St. Petersburg (2009–2013) was 1.93 × 10^{15} cm^{-2}. The average TCA variability throughout the day was 0.082 × 10^{15} cm^{-2}, or 4.3%. This value can be considered an upper-bound estimate for the random error in the TCA measurements. The RMS variation (natural variability) for the whole measurement ensemble was 0.38 × 10^{15} cm^{-2} (around 20%).

Figure 1 shows the results of ground-based spectroscopic measurements of HF TCAs carried out in Peterhof during the 4-year period. The daily average HF TCAs are in the range 1.5–3.0 × 10^{15} cm^{-2}, with a pronounced peak in January to March. HF TCAs are observed to decrease in summer and spring. Figure 1 also presents the available NDACC measurements for Bremen (2009–2011) and Harestua (2009 and 2011). The HF TCAs above Bremen (53.1° N) were lower than above Peterhof (59.9° N) and Harestua (60.2° S), which is consistent with the overall latitudinal pattern of HF TCAs (see, e.g., [13]).

The photodissociation of chlorofluorocarbons (CFCs) in the tropics and the stratospheric transport are the main factors underlying the latitudinal distribution of HF, which is in general characterized by a minimum in the tropical region and maxima in the polar regions. The seasonal variations in HF TCAs differ considerably in different latitudes. They are very small in the tropics and considerably higher in polar regions. In middle and high latitudes, maxima are observed in winter and early spring and minima are recorded in summer. The intensity of the downward movements of air masses determines the seasonal variation of TCAs in the polar regions. They are typically ~1.0–1.5 × 10^{15} cm^{-2} in summer and can be as high as 1.5–2.0 × 10^{15} cm^{-2} or more in winter, i.e., increase by 50–100% or more. In middle latitudes, TCAs are observed to vary substantially; in particular, the abundances increase markedly in winter and spring due to the penetration of polar air to middle latitudes, which is caused by the disruption of winter polar vortices. In this case TCAs can be as high as ~3 × 10^{15} cm^{-2}.

The monthly average HF TCAs and their variations throughout the month for the same period are shown in Fig. 2. These values demonstrate a complex seasonal pattern with peaks in late winter and early spring and troughs in summer and in November and December. The variability of the monthly average HF TCAs is at a maximum in winter and spring, which is due to the dynamic characteristics of the polar vortex. For comparison, the figure also shows the monthly averages for Harestua, which are in most cases close to those for Peterhof (recall that Peterhof and Harestua are located at almost the same latitude, but the distance between these sites is about 1000 km). It may be noted that in 2012 there was maximum variability of the monthly average HF TCAs for Peterhof.

Figure 3 shows the four-year averages of monthly HF TCA values and their standard errors. For comparison, the figure also shows the average monthly averages for Harestua (from the available data; for 2009 and 2011). In the period from May to December, there is a very good agreement between the monthly averages in Peterhof and Harestua. In winter and early

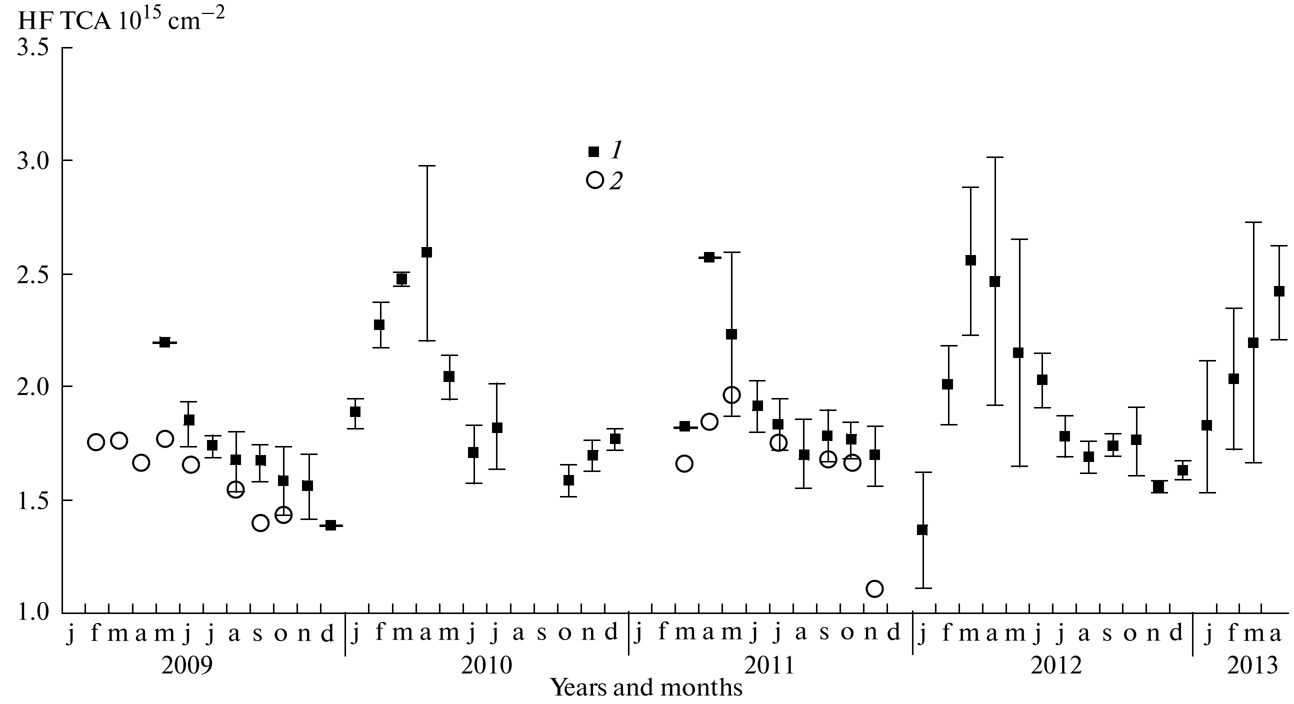

Fig. 2. Monthly average HF TCAs for Peterhof (*1*) and Harestua (*2*). The vertical segments show the variability of the Peterhof data over a month.

spring, there are noticeable differences in TCAs between the two observation sites. Thus, the Peterhof data has a spring peak, which is absent in the Harestua data. The observed differences can be explained by the features of the location of the polar vortex in winter and spring. The noticeable excesses in TCAs for Peterhof are due to the penetration of polar vortex air masses into the area.

The ground-based measurements of HF TCAs were compared with the satellite data (ACE-FTS) for measurements carried out on the same day, provided that the spatial displacement was less than 500 km. The ACE research team grants access to two versions (2.2 and 3.0) of ACE-FTS datasets (http://www.ace.uwaterloo.ca/data.html). Different measurement data ensembles are presented for the different versions.

Both ACE-FTS data-processing versions (table) give higher TCAs when compared with the ground-based measurements. The percentagewise systematic differences are 12% for both versions. The RMS differences are lower for version 2.2. The considerable difference between the amplitudes of the HF TCA variability both for the two processing versions (11 and 23%) and for the data of the corresponding observation arrays in Peterhof is noteworthy (8 and 30%). The difference is due to a very small amount of synchronous satellite and ground-based measurements and their nonuniform seasonal distribution. Namely, unlike version 2.2, the recorded version 3 measurements include an abnormally high value detected on February 18, 2012, which exceeds 2.8×10^{15} cm^{-2} from observations of both types (given that the average values are 1.7 and 1.8×10^{15} cm^{-2}), which explains the abovementioned variability levels.

Important information about the state of the stratosphere can be derived from the ratio of HCl and HF TCAs because (dynamics being eliminated due to the chemical inertness of HF) this approach allows the variation in the stratospheric composition to be analyzed on the basis of chemical processes alone [2]. HCl TCA determinations were also obtained by interpreting solar spectra in a different spectral region and will be discussed in greater detail in a separate paper. In the study period, these were 283 days with simultaneous measurements of HF and HCl TCAs.

Figure 4 shows the pattern of the seasonal variation: a typical minimum of the HCl/HF TCA ratios is observed from December to March and is due to the passage of a polar vortex with lower HCl abundances in the stratosphere. Maximum ratios are observed in summer. The presence of a polar vortex above Peterhof is characterized in the figure by potential vorticity values at the level of a potential temperature of 475 K (the data were obtained from the web site http://www.ecmwf.int). An analysis of Fig. 4 reveals a connection between the HCl/HF TCA ratio and potential vorticity. Indeed, calculations show a noticeable negative correlation (the correlation coefficient is -0.72 ± 0.04) between these values. In other words, low values of the mentioned ratio correspond to the passage of a polar vortex above the observation site.

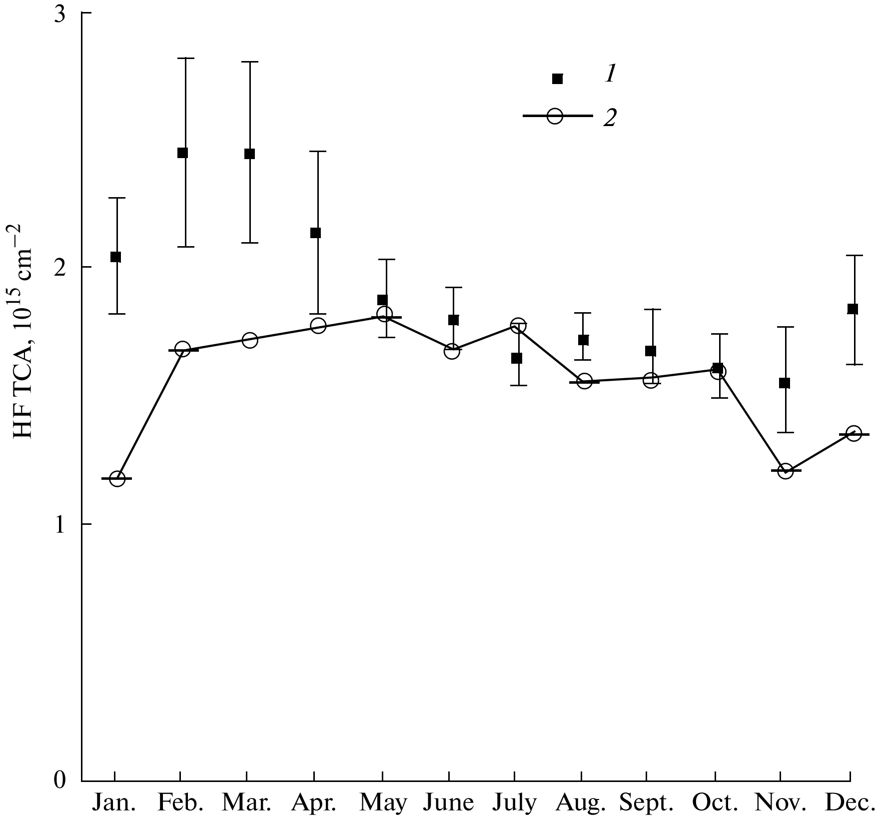

Fig. 3. Monthly average HF TCAs averaged over four years for Peterhof (*1*) and Harestua (*2*) (for 2 years). The vertical segments show the standard errors of the monthly averages.

Figure 5 presents the monthly average values of HCl and HF TCAs. The vertical segments show the RMSEs of these values during each month. The minimum of the HCl/HF ratios is observed in winter and spring and characterizes the minimum values of HCl in the stratosphere, which are due to the photolysis of HCl molecules. The pattern of the average monthly ratios in Fig. 5 is even more conclusive than the ratio of the daily average values, because it consists of fewer dots, retaining, nonetheless, all the main features of the seasonal variation, except for the fluctuations in the winter of 2012–2013. One of these features is the presence of a negative linear trend in the HCl/HF TCA ratio. It is estimated at ~2.5%/yr, given a large estimation error due to the short measurement period. The determination coefficient of the trend is 0.089, which is evidence that the trend estimate is nonsignificant due to a short observation period. Nevertheless, the presence of the trend in Figs. 4 and 5 is supported by the fact that, according to independent research results, HCl TCAs are decreasing, albeit slowly (e.g., according to [11, 12], the trend is approximately –1%/yr), while HF TCAs are increasing very slightly [21].

CONCLUSIONS

High-resolution ground-based spectroscopic measurements of solar infrared radiation yielded hydrogen fluoride total column abundances (HF TCAs) near St. Petersburg during a 4-year period (2009–2013). The data were analyzed to make the following conclusions:

(1) The monthly average HF TCA near St. Petersburg (2009–2013) was 1.93×10^{15} cm^{-2}, and the RMS variation (natural variability) for the whole measurement ensemble was around 20%. The measurement data for Peterhof are in good agreement with NDACC measurements (Bremen and Harestua), taking into account the differences in latitude.

(2) The monthly average HF TCAs show seasonal variation with peaks in late winter and early spring and troughs in summer and in the period from November to January. The variability of the monthly averages is at a maximum in winter and spring. In 2012, the variability of monthly average HF TCAs in Peterhof was observed to be at a maximum.

(3) A comparison of the HF TCAs from ground-based measurements with those from ACE-FTS solar occultation measurements showed that the total abundances from the ground-based data are 12% less than

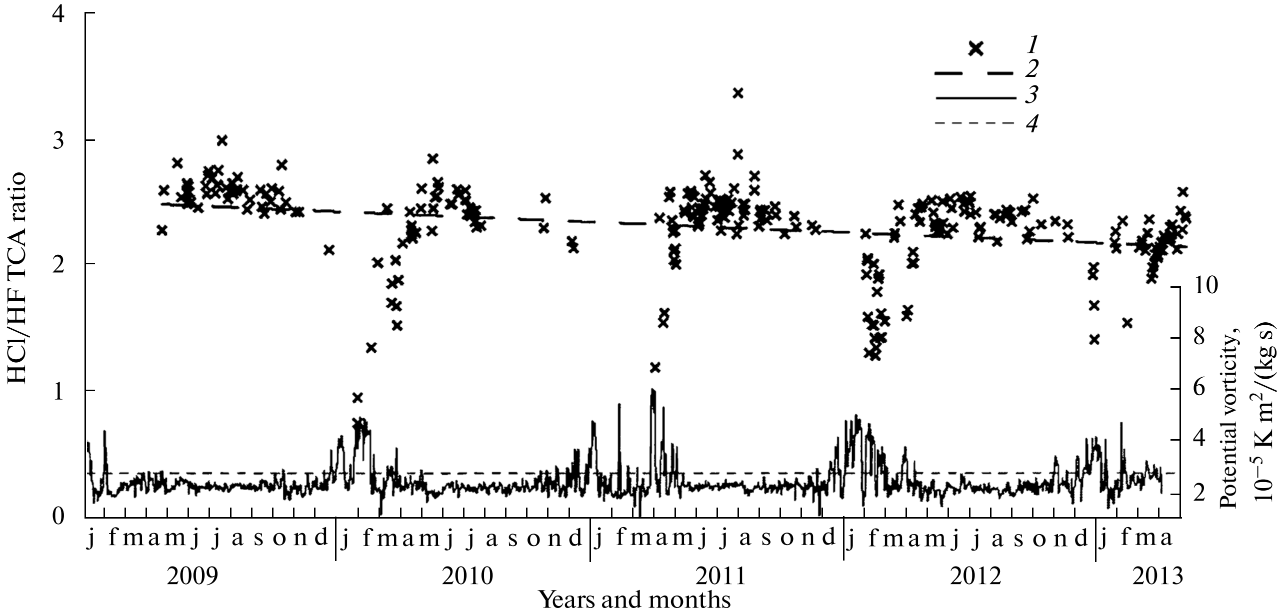

Fig. 4. Ratio between the daily average HCl and HF TCAs for the whole measurement period and potential vorticity. (*1*) Ratio of the daily average total column abundances; (*2*) a linear approximation of the ratio; (*3*) potential vorticity; and (*4*) critical value of potential vorticity, the exceeding of which indicates the presence of a polar vortex.

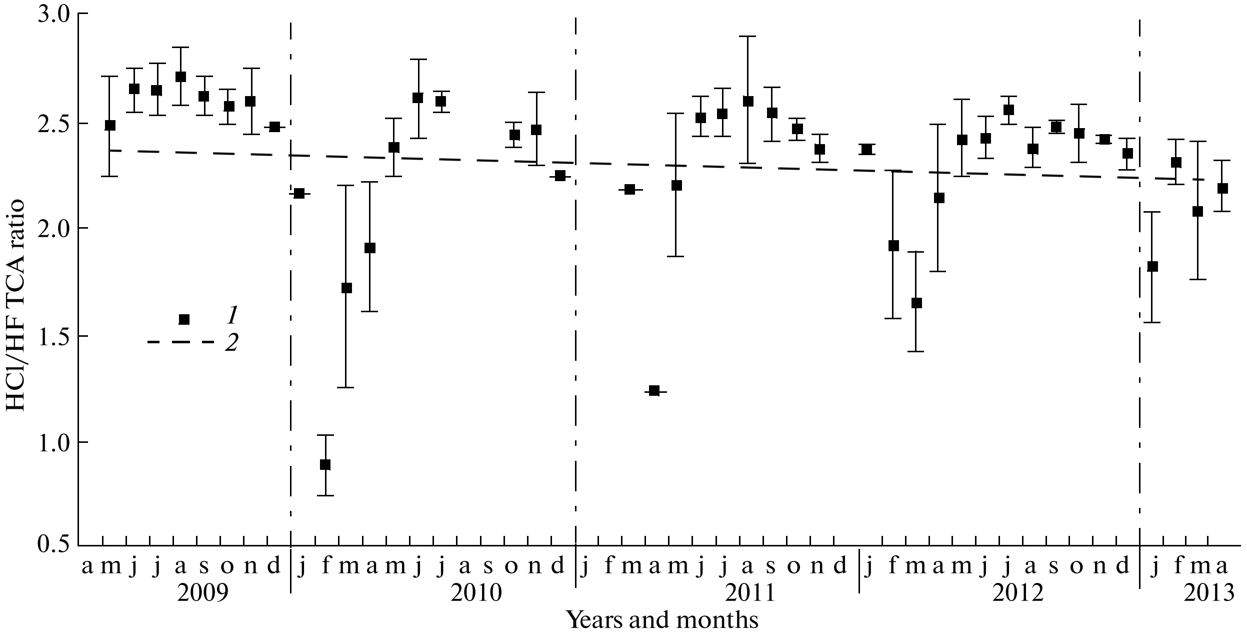

Fig. 5. Daily average HCl/HF TCA ratios for the whole measurement period. The vertical lines characterize the RMS variability of the ratio. (*1*) Monthly average ratios of the daily average TCAs; (*2*) linear approximation.

those from the ACE-FTS data, and the RMS differences depend on the satellite data processing version, being 13 and 16% for versions 2.2 and 3.0, respectively. However, it would be premature to infer about the quality of the different satellite data processing versions due to the small number of comparisons between the satellite and ground-based measurements.

(4) An analysis of the HCl/HF TCA ratio showed that it decreases in late winter and in spring, which indicates a considerable decrease in HCl abundances due to photodissociation. This minimum correlates with the passage of a polar vortex above Peterhof (the measurement site), which is evidenced by a negative correlation (–0.72 ± 0.04) between the HCl/HF TCA

ratio and potential vorticity. The TCA ratios show a linear trend (a preliminary estimate is 2.5%/yr). Although this trend is not statistically significant enough, it is consistent with independent data and indicates a decrease in stratospheric HCl during the study period and a slight growth in HF TCAs.

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