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# Chlorine Nitrate in the Atmosphere over St. Petersburg

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**Abstract**—Ground-based measurements of the total chlorine nitrate ($ClONO_2$) in the atmosphere have been taken for the first time in Russia using the Bruker IFS-125HR infrared (IR) Fourier spectrometer (FS). The average error of the total $ClONO_2$ measurements, performed in 2009–2012 in Peterhof, is (25 ± 10)%. The results have been compared with measurements performed using similar devices at the NDACC network, Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) satellite measurements, and the total $ClONO_2$ numerical simulation (performed using the EMAC chemical climatic model). The total $ClONO_2$ seasonal variations are similar for three considered observation stations (Peterhof, Kiruna, and Eureka) with the maximum in February–March, which is more pronounced at higher latitudes. High correlations ($R$ = 0.7–0.9) between the MIPAS satellite data, ground-based measurements near St. Petersburg, and the values calculated using the EMAC model have been revealed. The modeling data are on average smaller than the data of the ground-based and satellite measurements. An analysis of the seasonal variations in the total $ClONO_2$ monthly average values in the St. Petersburg region indicated that this difference is caused by the fact that the model underestimated the maximal total $ClONO_2$ values in the atmosphere.

*Keywords*: ozone-depleting gases, chlorine nitrate, Fourier spectroscopy
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## 1. INTRODUCTION

Chlorine nitrate ($ClONO_2$), together with chlorine hydride (HCl), is the main reservoir of active chlorine compounds in the stratosphere. $ClONO_2$ molecules play a key role in the ozone catalytic depletion processes [1, 2]. The amount of ozone depleted in the reactions with the participation of chlorine compounds depends on the relationship between active (ozone-depleting) gases, such as Cl and ClO, and inactive gases—reservoirs ($ClONO_2$ and HCl). Therefore, it is necessary to regularly measure the content of both active chlorine gases-reservoirs in order to understand the processes proceeding in the ozonosphere.

The data on $ClONO_2$ in the stratosphere were obtained for the first time using balloon spectroscopic measurements of the direct solar radiation in the IR region [3] and the Atmospheric Trace Molecule Spectroscopy (ATMOS) satellite device [4]. In the following years, the ATMOS, ILAs, MIPAS, and ACE satellite devices were used to measure $ClONO_2$ (see, e.g., [5–8]). The ground-based $ClONO_2$ measurements were performed for the first time at Jungfraujoch [9] and McMurdo [10] stations. Subsequently, $ClONO_2$ was measured at many stations of the Network for the Detection of Atmospheric Composition Change (NDACC) international measurement network [11].

This work presents the results of the first Russian measurements of total $ClONO_2$, performed using Bruker IFS-125HR IR FS with a high spectral resolution near St. Petersburg in 2009–2012 [12]. The paper compares the results with the ground-based total $ClONO_2$ measurements at the nearest NDACC stations, Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) satellite measurements [13], and the results of the total $ClONO_2$ numerical simulation for St. Petersburg (performed using the EMAC chemical climatic model) [14].

## 2. GROUND-BASED TOTAL $ClONO_2$ MEASUREMENTS

The PROFFIT software system [15], which was designed at the Institute of Technology, Karlsruhe University (Germany), and is used at several NDACC stations, was used to interpret the solar radiation IR measurements in the present work. The National Center for Environmental Prediction (NCEP) pressure and temperature profiles, based on the satellite and radiosonde measurements [16], and a priori information about the profiles of $ClONO_2$ and influence gases (see Table 1) based on the Whole Atmosphere Community Climate Model (WACCM) data [17] were

**Table 1.** Bruker FS measurement characteristics and data for interpreting spectra

| Parameter | Characteristic |
|---|---|
| Spectroscopy | HITRAN 2008 |
| Temperature profiles $T$(p) | NCEP daytime profiles |
| Used spectral windows, $cm^{-1}$ | 779.0–779.8<br>780.0–780.3<br>780.3–781.3 |
| Used climatology (a priori profiles) | WACCM (one for all seasons) |
| Influence gases | $H_2O$, $CO_2$, $O_3$, $HNO_3$, $C_2H_2$ |
| Spectral resolution | ~0.008 $cm^{-1}$ at Norton–Beer medium apodization [20] |
| Site of measurements | Peterhof (59.88° N 29.82° E) |
| Period of measurements | Apr. 2009–Mar. 2012 (89 days) |

specified in order to calculate total $ClONO_2$ for each day of spectrometric measurements. The algorithm based on the Tikhonov–Phillips regularization method [18, 19] was used to solve the inverse problem.

The main information about the specific features of the Bruker FS measurements and the interpretation of the obtained spectra are presented in Table 1.

The vertical profile of the studied gas content, which was subsequently integrated in order to obtain the total content (TC), was initially recovered when the spectra were interpreted. Note that the daily number of measurement varied from 1 to 18 spectra (typical values were five to six spectra).

The present paper analyzes the determinations of the daily average total $ClONO_2$ values; i.e., the individual TC measurements were averaged over a day. The solar radiation was measured with a path length difference of 180 $cm^{-1}$ and the Norton–Beer medium apodizing function, which is widely used in Fourier spectroscopy, was used for conversion; the spectral resolution was 0.008 $cm^{-1}$ in this case. Since the absorption was slightly selective, the smooth systematic measurement errors over the spectrum strongly affect the total $ClONO_2$ recovery result; therefore, all measured spectra were subjected to rigorous selection concerning the absence of substantial systematic errors in them. As a result, 374 spectra for 89 measurement days were selected in order to determine total $ClONO_2$ during the entire period of measurements.

We should note that the $ClONO_2$ absorption lines are rather weak, and the transmission function in these lines is 0.98–0.99; therefore, the TC determination error is rather raw. To estimate the accumulated total $ClONO_2$ measurement error, we considered the following error types:

(i) instrumental errors (random measurement noise, instrument function specification errors, zero signal level position error, and tracing system pointing accuracy);

(ii) methodical errors (quality of spectroscopic information of different gases, solar line attachment, and amplitude specification accuracy);

(iii) specification uncertainty of measurement conditions (temperature vertical profiles).

The specified errors of the main parameters shown above affecting the total $ClONO_2$ determination accuracy, their relative contribution to the systematic and random measurement errors, and resulting errors (systematic, random, and total) for one of the typical measurement days are listed in Table 2. The contribution of other error sources to the TC measurement accumulated error is smaller by several orders of magnitude.

Note that the systematic error magnitude is presented. This error can make both positive and negative contributions to the accumulated systematic error. For example, the contribution can be positive for the instrument function specification errors and negative for the spectroscopic information errors, and the sign of the temperature profile specification errors can also depend on altitude [21].

Table 2 demonstrates that the total $ClONO_2$ measurement error (both systematic and random) mainly depends on the signal zero level specification error. This error source includes all continual sources, including spectral supports, specification of continual absorption, sinusoidal additions to the spectrum due to the ray path in the device optical scheme, etc. The contribution of these errors increases with the decreasing content of the studied gas in the atmosphere on the emission propagation path. Measurement noise, which can be decreased by averaging the results of the larger number of successive observations, also substantially contributes to the random error. When we calculate the systematic error, we cannot neglect the spectroscopic information specification error, which as a rule decreases with each following version of the base of registered atmospheric gas spectral lines [22].

Summarizing an analysis of the Bruker FS total $ClONO_2$ determination errors in Peterhof, we should note that the average measurement error is (25 ± 10)% for the entire ensemble, and the error random and sys-

**Table 2.** Characteristics of the errors introduced by different total $ClONO_2$ measurement error sources.

| Source | Value | $\psi_{syst}$ | $\psi_{rand}$ | $\lvert\sigma_{syst}\rvert$ | $\sigma_{rand}$ | $\Sigma$ |
|---|---|---|---|---|---|---|
| Spectral zero line shift | 0.5% | 0.5 | 0.5 | 1.48 (12%) | 1.48 (12%) | 2.09 (17%) |
| Modulation effectiveness | 1% | 0.5 | 0.5 | 0.12 (1%) | 0.12 (1%) | 0.17 (1.4%) |
| Phase error | 0.01 rad | | | | | |
| Temperature profile | 1K (<9 km)<br>2K (9–35 km)<br>5K (>35 km) | 0.3 | 0.7 | 0.02 (0.2%) | 0.16 (1.3%) | 0.16 (1.3%) |
| Spectral line intensity | 10% | 1.0 | 0.0 | 1.13 (9%) | 0 | 1.13 (9%) |
| Spectral line half-width | 5% | | | | | |
| Measurement noise | From residual | 0.0 | 1.0 | 0 | 1.17 (10%) | 1.17 (10%) |
| Contribution of all errors | | | | 1.87 (15%) | 1.90 (16%) | 2.67 (22%) |

$\psi_{syst}$ and $\psi_{rand}$ are the weights of the systematic and random error components, respectively; $\sigma_{syst}$ and $\sigma_{rand}$ are the values of the systematic and random errors, respectively; $\Sigma$ is the total error in $10^{14}$ $cm^{-2}$.

tematic components are (18.7 ± 7.3) and (17.6 ± 7.3)%, respectively. In the winter and spring time, the relative error is smaller because the TC values are larger. The relative error is larger in summer, when $ClONO_2$ molecules actively break down under the action of photolysis. For comparison, we indicate that the error of the total $ClONO_2$ measurement error is 29% for Bruker FS at Kiruna station (67.84° N, 20.41° E) in [23] and 23% (with random and systematic components of 15 and 8%, respectively) for Bruker FS at Thule station (76.53° N, 68.74° W).

Total $ClONO_2$ is determined at a number of NDACC stations equipped with Bruker 120M, 120HR, and 125HR FS with a high spectral resolution (the last FS modification functions at the St. Petersburg State University station in Peterhof). To illustrate the possibilities of ground FS, we present in Fig. 1 the time variations in total $ClONO_2$ obtained at Peterhof station and two NDACC stations in the Northern Hemisphere, where information about total $ClONO_2$ was available on the NDACC server during the studied period (2009–2012) [11]. The data are presented for Eureka station in Canada (80.05° N, 86.42° W) and Kiruna station in Sweden. Kiruna, which is the closest station to Peterhof, is located at a distance of 1000 km north-northwestward, and Eureka is located at a distance of 4000 km in the same direction. On the whole, analyzing Fig. 1, we can see that the TC seasonal variations are identical for all considered stations. At higher latitudes, the total $ClONO_2$ absolute maximum is larger, and its variability is stronger. This is caused by the photochemical and dynamic processes in the stratosphere related to the circumpolar vortex formation and decay and to spring solar activity.

## 3. GROUND-BASED TOTAL $ClONO_2$ MEASUREMENTS AS COMPARED TO MIPAS SATELLITE DATA AND EMAC SIMULATION RESULTS

Comparisons were performed based on the calculations of the correlation coefficient (*R*) and three ensemble discrepancy characteristics (at the level of daily average values):

(i) rms discrepancy $S = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - y_i)^2}$,

(ii) mean discrepancy $M = \frac{1}{N}\sum_{i=1}^{N}(x_i - y_i)$,

(iii) standard deviation from the mean discrepancy

$$\sigma = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - y_i - M)^2}. \quad (1)$$

The MIPAS device performed limb measurements of the noise radiation from the atmosphere in the 685–2410 $cm^{-1}$ region on the Envisat satellite from March 2002 to April 2012 [13]. To make a comparison with the total $ClONO_2$ ground-based measurements in Peterhof, we used the IMK data of the V5R+CLONO2_220 MIPAS version [25]. The data were selected at a radial distance of 500 km from Peterhof station. The total $ClONO_2$ trends beginning from 2004 were studied in [26]. The authors indicated that different $ClONO_2$ values are observed for the morning and evening (daytime and nighttime) measurements since $ClONO_2$ molecule breaks down in daytime under the action of the solar light and the $ClONO_2$ concentration increases again at night. At a concentration maximum (28–32 km), the $ClONO_2$ mixture ratio for the evening and morning values differs by up to 10%. Thus, to make a comparison with the daily average ground-based $ClONO_2$ measurements, we selected only daytime MIPAS measure-

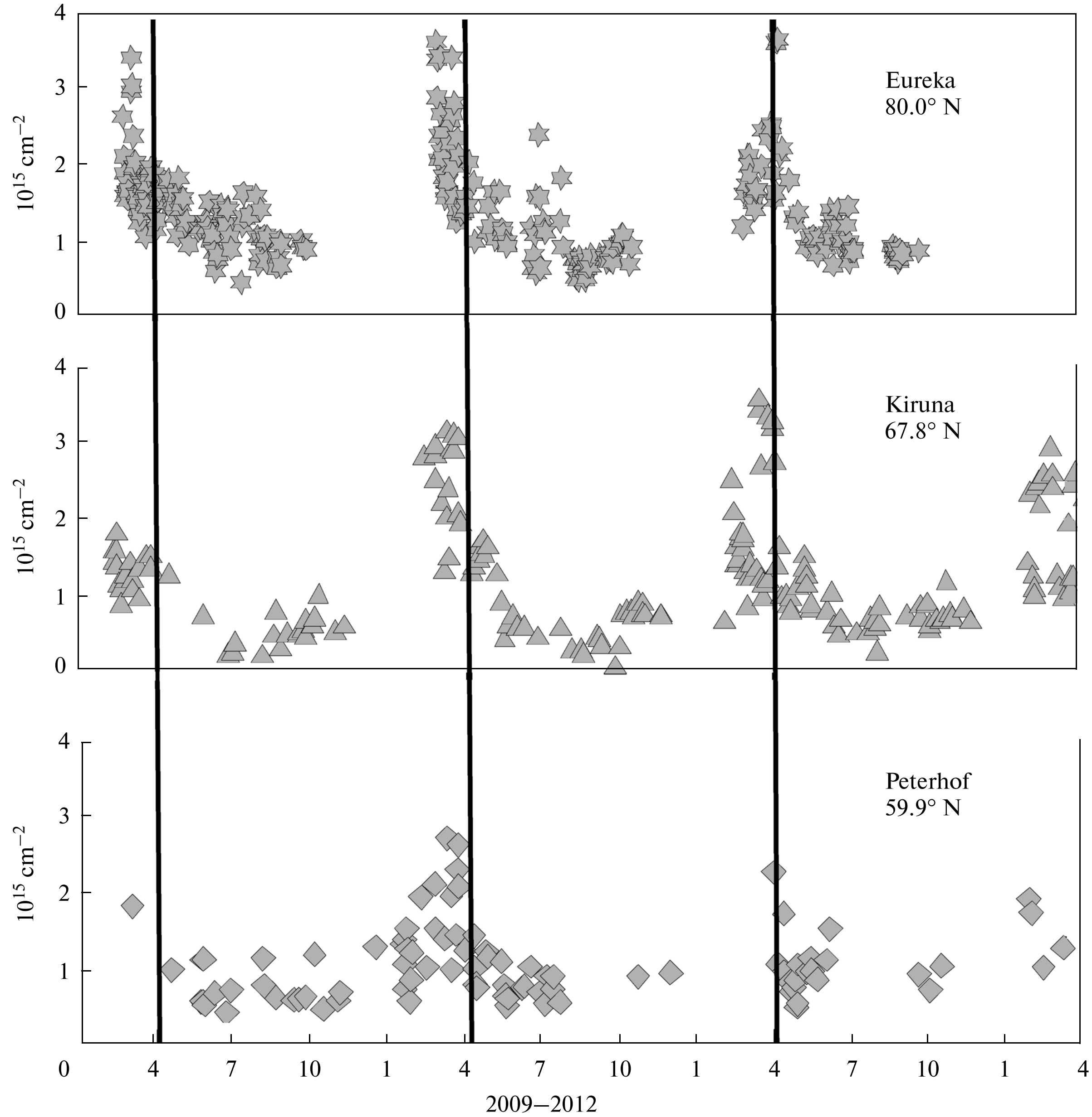

**Fig. 1.** Time variations in total $ClONO_2$ at Peterhof and NDACC stations in 2009–2012.

ments (near local noon). If several satellite measurements of the mixture ratio profiles were performed at a radial distance of 500 km from the ground station, these measurements were averaged. Then, the profiles were integrated over altitude with regard to the measured temperature and pressure profiles. Note that the MIPAS data recommended for the usage correspond to altitudes of 13 to 45 km; i.e., the integration is performed over the larger part of the stratosphere, and the troposphere is eliminated from the calculations in this case.

The average values over the ensemble including 43 days, when the ground-based total $ClONO_2$ measurements were performed in Peterhof, and statistical characteristics (1) of comparing this ensemble with the coordinated ensemble of the MIPAS satellite measurements are given in the second line of Table 3. Hereafter, the relative values are reduced to the absolute values of the first of the listed ensembles.

First, we note that the correlations between the satellite and ground data (the last column in Table 3) are high ($R = 0.8$). In addition, it is clear that systematic differences between two ensembles are almost not observed, and the excess of the ground-based measurements over the satellite ones within 1% can result from the fact that tropospheric $ClONO_2$ is ignored in

**Table 3.** Statistical characteristics of the compared total $ClONO_2$ ensembles

| Ensemble | Average over ensemble, $10^{15}$ cm$^{-2}$ | Comparison | $S$, % | $M$, % | $\sigma$, % | $R$ |
|---|---|---|---|---|---|---|
| Bruker | 1.19 ± 0.56 | Bruker – MIPAS | 29 | +0.8 | 29 | 0.80 ± 0.06 |
| EMAC | 1.12 ± 0.39 | Bruker – EMAC | 32 | +6.6 | 32 | 0.73 ± 0.07 |
| MIPAS | 1.18 ± 0.53 | MIPAS – EMAC | 22 | +5.8 | 21 | 0.88 ± 0.03 |

(Bruker ground and MIPAS satellite measurements and the EMAC simulation data): 43 implementations.

the satellite data. In [7] the tropospheric content varies from 1 to 3%, depending on the observation station. On the WACCM profiles [16] taken as an initial approximation and climatological information for St. Petersburg, tropospheric $ClONO_2$ accounts for about 2% of TC. The rms deviation from the mean discrepancy is 29% and can be caused by the measurement errors of both devices. Recall that the Bruker FS total $ClONO_2$ measurement error is on average 25%, and the error of the $ClONO_2$ mixture ratio vertical profile measurement, performed using the MIPAS device, is 8–14% when the vertical resolution is 2.5–9 km for layers lower than 40 km [24]. The better rms agreement between the MIPAS and EMAC data is probably explained by the fact that the MIPAS measurement accuracy is higher.

In [7] the total $ClONO_2$ measurements are compared with the MIPAS Bruker FS ground-based measurements for several NDACC stations. The following values were obtained for the stations in the Northern Hemisphere that are located at latitudes of 60° to 80°: (–0.9 ± 26.4)% for Spitsbergen (78.92° N, 11.93° E), (–6.9 ± 24.0)% for Thule, (–8.3 ± 20.1)% for Kiruna, and (10.8 ± 24.3)% for Harestua (60.21° N, 10.75° E). These data were obtained when the MIPAS data were taken at a distance of no more than 400 km from the ground station and at a time difference not more than 4 h. Thus, the discrepancies with the satellite measurements for Peterhof station (0.8 ± 29)% fit well into the general statistics of comparisons between the Bruker FS ground-based measurements and the MIPAS satellite measurements and confirm the previously made conclusions on the MIPAS measurement quality.

To consider the correlations between the ground and satellite data in more detail, we present Fig. 2a, which shows the spread in the data of measurements performed with both devices. It is evident that the points are compactly located around the "zero" curve when the total $ClONO_2$ values are small (background) (mainly summertime measurements). The TC values obtained using Bruker FS are much smaller than the MIPAS values only on two days. Larger values are measured on the ground when the TC values are larger, which can result from the fact that tropospheric (below 13 km) $ClONO_2$ is insufficiently taken into account in the satellite measurements.

In addition to the comparison of the Bruker FS data with the satellite measurements, we also compared our measurements with the simulation data. The EMAC (ECHAM/MESSy Atmospheric Chemistry model) chemical climatic model, to which total $ClONO_2$ values measured in Peterhof were compared, was developed at the Max Planck Institute of Chemistry in Mainz and was described in detail in [14]. This model was used to analyze the meteorological data in [27].

The data on total $ClONO_2$, delivered to us by the IMC scientific team (Karlsruhe), were obtained from the EMAC simulation with a horizontal resolution of 2.8° × 2.8° (T42) on 39 vertical layers from 0 to 80 km and have a time step of 11 h. To make a comparison with the daily average values of the total $ClONO_2$ spectrometric measurements, we took only the TC model values corresponding to the daylight hours (as a rule, from 9 to 19 h). Two ensembles are compared in line 3 of Table 3 and in Fig. 2b. The days for comparison were taken as in the case when a comparison with the MIPAS data was performed. These days were specially selected provided that all data are available in order to uniformly analyze three ensembles. Table 3 indicates that significant correlations ($R = 0.73$) are observed between the $ClONO_2$ ground-based measurements and the simulation data; at the same time, mean TC according to the ground-based measurements is higher by (6.6 ± 32)%. The same situation is correspondingly observed when the simulation data are compared with the satellite measurements: the measured values are larger by (5.8 ± 21)%. The correlation coefficient between two ensembles is higher in the latter case (0.88). Analyzing Fig. 2, we can see that the points are concentrated along the straight line differently than along the "zero" line; i.e., for larger total $ClONO_2$ values, the model underestimates $ClONO_2$ when compared to ground-based measurements. A similar pattern is also observed when the simulation data are compared with satellite measurements (Fig. 2c).

In [28] the data of measurements at different ground stations are compared with the simulation results, and it was indicated that the model total $ClONO_2$ calculations on average exceed the ground-based measurements by (30.1 ± 90.6)% for all stations (12 stations at different latitudes in the Northern and Southern hemispheres) during 2000–2009. In this case the simulation data for winter and early spring are underestimated and the background values for sum-

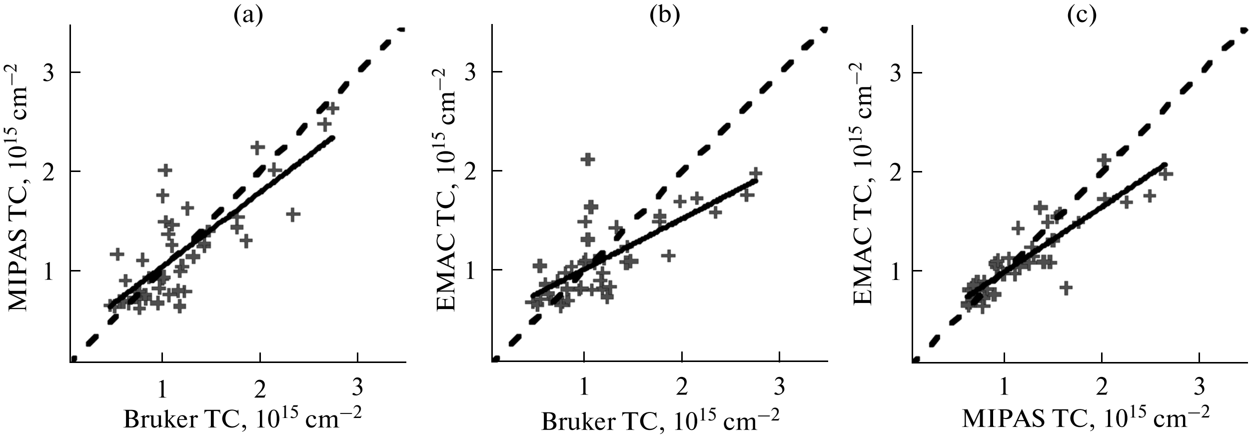

**Fig. 2.** Comparison of the data on $ClONO_2$ obtained using the Bruker ground-based measurements, MIPAS satellite measurements, and EMAC simulation data.

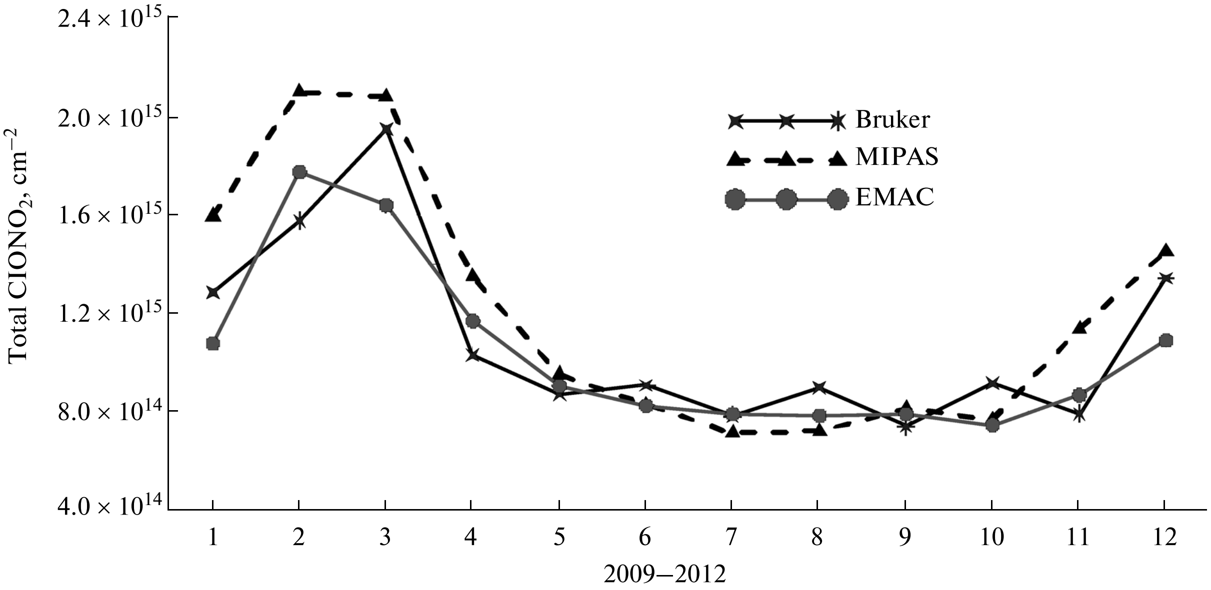

**Fig. 3.** Seasonal variations in the monthly average total $ClONO_2$ values in the St. Petersburg region based on the data for 2009–2012 (43 implementations) obtained using the ground-based (Bruker) and satellite (MIPAS) measurements and the simulation data (EMAC).

mer and spring are overestimated for three stations at latitudes of 60°–80° in the Northern Hemisphere. For Eureka, the EMAC simulation data are overestimated during the entire year and are more significant in winter and in spring. Note that a comparison was performed only for monthly average total $ClONO_2$.

Figure 3 shows the seasonal variations in the total $ClONO_2$ monthly average values in the St. Petersburg region according to the data of all three ensembles (43 implementations). Note that all data correspond to the 2009–2012 period. As for the majority of the midlatitude and high-latitude stations in the Northern Hemisphere [28], the simulation results for St. Petersburg are underestimated when compared to the ground-based and satellite in situ measurements during the period when $ClONO_2$ was maximal in the atmosphere. At the same time, the simulation data are in good agreement with the ground-based measurements in the remaining months (except for August).

We should note that the performed comparison of the ground, satellite, and model ensembles is preliminary, since the sample is small (only 43 implementations for three years of measurements); however, this comparison adequately reflects general tendencies observed at different NDACC stations.

## 4. MAIN RESULTS AND CONCLUSIONS

We presented the results of the first total $ClONO_2$ measurements performed in 2009–2012 based on the high-resolution IR Bruker IFS-125HR FS solar radiation spectra near St. Petersburg. We compared these data with the ground-based measurements at the nearest NDACC stations, MIPAS satellite measurements, and the results of a numerical simulation performed using the EMAC chemical climatic model.

(1) The lines of the $ClONO_2$ absorption in the Earth's atmosphere are rather weak; therefore, the total $ClONO_2$ determination error is high. The average error of the Bruker FS total $ClONO_2$ measurements in Peterhof is (25 ± 10)% and the error random and systematic components are (18.7 ± 7.3)% and (17.6 ± 7.3)%, respectively. These error values are in good agreement with the data of other NDACC stations.

(2) The total $ClONO_2$ seasonal variations are identical for the three considered observation stations (Peterhof, Kiruna, and Eureka) and have maximums in February–March. At higher latitudes, the total $ClONO_2$ absolute maximum is larger and its variability increases from year to year.

(3) High correlations ($R = 0.8$) are observed between the MIPAS satellite measurements and the ground data (Peterhof). Systematic differences between two ensembles are not observed. The rms discrepancies with the satellite measurements for Peterhof (±29%) fit well into the general statistics of comparisons of the Bruker FS ground data and the MIPAS satellite measurements and confirm the conclusions on the MIPAS measurement quality.

(4) Significant correlations ($R = 0.73$) are observed between the total $ClONO_2$ ground-based measurements and the values calculated using the EMAC model. In this case the simulated values are on average smaller than the ground-based and satellite total $ClONO_2$ measurements by (6.6 ± 32)% and (5.8 ± 21)%, respectively. The correlation coefficient between the simulation ensemble and MIPAS measurements is 0.88.

(5) A comparison of the seasonal variations in the total $ClONO_2$ monthly average values in the St. Petersburg region during the period when $ClONO_2$ was maximal in the atmosphere indicates that the simulated values are smaller than the ground-based and satellite in situ measurements. The same situation is also observed for most midlatitude and high-latitude stations in the Northern Hemisphere [28]. At the same time, the simulation data are in good agreement with the ground-based measurements for most months (except August).

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