

Comparing Data Obtained from Ground-Based Measurements of the Total Contents of O₃, HNO₃, HCl, and NO₂ and from Their Numerical Simulation

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Abstract—Chemistry climate models of the gas composition of the atmosphere make it possible to simulate both space and time variations in atmospheric trace-gas components (TGCs) and predict their changes. Both verification and improvement of such models on the basis of a comparison with experimental data are of great importance. Data obtained from the 2009–2012 ground-based spectrometric measurements of the total contents (TCs) of a number of TGCs (ozone, HNO₃, HCl, and NO₂) in the atmosphere over the St. Petersburg region (Petergof station, St. Petersburg State University) have been compared to analogous EMAC model data. Both daily and monthly means of their TCs for this period have been analyzed in detail. The seasonal dependences of the TCs of the gases under study are shown to be adequately reproduced by the EMAC model. At the same time, a number of disagreements (including systematic ones) have been revealed between model and measurement data. Thus, for example, the EMAC model underestimates the TCs of NO₂, HCl, and HNO₃, when compared to measurement data, on average, by 14%, 22%, and 35%, respectively. However, the TC of ozone is overestimated by the EMAC model (on average, by 12%) when compared to measurement data. In order to reveal the reasons for such disagreements between simulated and measured data on the TCs of TGCs, it is necessary to continue studies on comparisons of the contents of TGCs in different atmospheric layers.

Keywords: trace gas components, simulation, gas composition, Fourier transform spectroscopy

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1. INTRODUCTION

The Earth's climate changes and a decrease in the ozone-layer thickness in both middle and high latitudes have been observed since the early 1980s. Therefore, the Montreal Protocol, designed to phase out the production of chemical compounds that are responsible for stratospheric ozone depletion—first and foremost, halons and chlorofluorocarbons—was adopted in 1987 [1]. This, in turn, gave impetus to extensive experimental and model studies of spatiotemporal variations in the characteristics of the gas composition of the atmosphere. Climatically important gases are measured using different local and remote sensing methods and different (ground-based, aircraft, aerostat, and satellite) observation platforms. Ground-based remote sensing methods, including those based on measurements of direct solar IR radiation with Fourier spectrometers of high resolution (NDACC and TCCON networks), are of great importance.

Different three-dimensional numerical models of the gas composition of the atmosphere—chemistry climate models (CCMs)—making it possible to simulate

spatiotemporal variations in the atmospheric contents of climatically important trace gas components (TGCs) and predict their changes (see, for example, [2]) have been developed and widely used in recent decades. Such models are used, in particular, to estimate the time of recovery of the ozone layer, and they often yield completely different results [3, 4]. In connection with this, both validation and improvement of such models on the basis of comparisons between their results and measurement data obtained in different regions of the globe are of great importance. In particular, a special international project was devoted to the validation of a number of developed models [4, 5].

This work, which may be considered an extended study [4] conducted for a new measurement site and time period (2009–2012), gives the results of a comparison between data obtained from ground-based spectroscopic measurements of the total contents (TCs) of ozone, HNO₃, and HCl and the stratospheric content (SC) of NO₂ in the atmosphere over Petergof (St. Petersburg, 59.88° N, 29.82° E) and those obtained from simulations with the EMAC model [6].

Table 1. Features of solving the inverse problem

TGC	Spectral windows, cm^{-1}	Random measurement errors	Influencing gases	Software
O_3	991.25–993.80 1001.47–1003.04 1005.00–1006.90 1007.35–1009.00 1011.15–1013.55	1–3% [19]	H_2O , CO_2 , C_2H_4	PROFFIT
NO_2	2914.590–2914.707	8–18% [20]	CH_4 , HDO, H_2O	SFIT2
HNO_3	867.00–869.60 872.80–875.20	2–7%	H_2O , CO_2 , NO_2	PROFFIT
HCl	2727.73–2727.83 2775.70–2775.80 2925.80–2926.00	2–5% [21]	CH_4 , H_2O	SFIT2

Earlier, measurement and simulation data on the TC of ClONO_2 were similarly compared in [7], and a joint analysis of the TC and column-average concentration of methane was made in [8].

The TGCs under consideration in this work— HNO_3 , HCl, and NO_2 —play an important role in the chemistry of stratospheric ozone; they participate in ozone-depleting catalytic cycles [9] and heterogenic reactions on the surface of aerosols [10]. Active chlorine and nitrogen oxides are responsible for significant ozone depletion in the middle stratosphere. Along with ClONO_2 , HCl is a reservoir of active chlorine, and nitrogen oxides, including NO_2 , are generated during HNO_3 photolysis; therefore, determining quantitative ratios between active gases and gas reservoirs is of importance in understanding and simulating ozone-depleting processes.

2. DETAILS OF GROUND-BASED MEASUREMENTS AND INTERPRETATION

Data of ground-based spectrometric measurements were obtained in Petergof in 2009–2012. Solar-radiation spectra were measured with a ground system based on a Bruker IFS 125HR Fourier-transform spectrometer [11]. These measurements were performed under the conditions of clear sky or sufficiently large breaks in clouds. On average, the number of days with such conditions is 70–90 per year. The interferometer path-length difference was 180 cm, which, if the Norton–Beer medium apodization is used [12], corresponds to a spectral resolution of 0.008 cm^{-1} . The TCs of the gases under study were determined using the SFIT2 and PROFFIT software tools used at the NDACC and TCCON stations [13]. Some examples of time variations in the contents of different gases are given in [14].

Table 1 shows the features of the solution of inverse problem (spectral channels (windows), measurement errors, etc.). Table 1 also gives the references to the papers, in which the entire scheme of determining the contents of HCl, O_3 , and NO_2 is described in detail. Here, we only note that a relatively low accuracy in determining the TC of NO_2 is due to its low absorption in the spectral lines under consideration. For the same reason, the ground-based measurements of solar radiation with a Bruker IFS 125HR Fourier-transform spectrometer are low-sensitive to variations in the tropospheric content of NO_2 ; therefore, below, we will consider only its stratospheric content.

Since data (used in this work) on HNO_3 have not been published yet, we will note the features of determining its TC. The PROFFIT software was used to interpret the results of measurements of IR solar radiation. In order to calculate the TC of HNO_3 , for each day of spectrometric measurements, both pressure and temperature profiles were specified on the basis of both satellite and radiosonde data obtained at the National Center for Environmental Prediction (NCEP) [15], and a priori information on the profiles of the contents of HNO_3 and influencing gases (see Table 1) according to Whole Atmosphere Community Climate Model (WACCM) data was used [16]. To solve the inverse problem, an algorithm based on the Tikhonov–Phillips regularization method was used [17, 18]. In interpreting spectra, first the vertical profile of the HNO_2 content was retrieved and then it was integrated to obtain TC.

For HNO_3 , like for ozone and HCl, the results obtained from individual measurements were averaged daily. For NO_2 , the results of individual measurements were first brought to the local noon [20] and then were averaged.

Table 2. Statistical characteristic of the data ensembles and their comparisons

TGC (days)	Ensemble	Mean, cm^{-2}	Rms deviation, cm^{-2}	Disagreement, %	Correlation coefficient
O ₃ (189)	Measurements	9.25×10^{18}	1.24×10^{18}	-12 ± 8	0.91 ± 0.01
	Model	10.4×10^{18}	1.7×10^{18}		
HNO ₃ (191)	Measurements	2.38×10^{16}	0.56×10^{16}	$+36 \pm 18$	0.63 ± 0.04
	Model	1.51×10^{16}	0.42×10^{16}		
HCl (309)	Measurements	4.36×10^{15}	0.60×10^{15}	$+22 \pm 8$	0.81 ± 0.02
	Model	3.40×10^{15}	0.44×10^{15}		
NO ₂ (233)	Measurements	3.32×10^{15}	1.10×10^{15}	$+14 \pm 13$	0.92 ± 0.01
	Model	2.85×10^{15}	1.05×10^{15}		

3. NUMERICAL MODEL

The TCs of different gases over the 2009–2012 period were calculated using the EMAC model developed at the Max Planck Institute for Chemistry [6]. The EMAC model is a combination of the ECHAM5 atmospheric general circulation model [22] and different submodels that are combined by the Modular Earth Submodel System (MESSy) interface [23]. The EMAC model simulates both chemical and dynamic processes occurring from the troposphere to the lower mesosphere (39 layers along the vertical, up to ~80 km from the surface) with a horizontal resolution of $2.8^\circ \times 2.8^\circ$. An example of using such a model in analyzing long-term variations in the contents of gases is given in [24], where data obtained from ground-based measurements of the TCs of HCl, HF, and ClONO₂ at 17 NDACC stations were compared with those obtained using five different models, including the EMAC model.

The EMAC array of data on the contents of different gases is a time series with an 11-h step. For comparison with daily averaged spectrometric data on the TCs of gases, we used their TC model data corresponding only to daylight hours (as a rule, from 9:00 to 19:00). For NO₂, because of significant daily variations, all data (including measured ones) were brought to the local noon. And, since spectrometric measurements are sensitive only to the stratospheric content of NO₂ [20], we considered model data only on its stratospheric content (for heights over 10 km).

4. COMPARISON RESULTS

Spectrometric data on the TCs of ozone and HNO₃ available up to March 2012 inclusive, on the SC of NO₂ available through May 2012, and on the TC of HCl available through 2012 were used for comparison. Thus, for all the TGCs under consideration, their samples contained data collected over three and more years; therefore, their analysis and comparison make it possible to analyze also seasonal variations in their

contents and disagreements between the model and measurement data ensembles under consideration.

For a general analysis of the two measured and simulated data ensembles, we estimated the following statistical characteristics given in Table 2: ensemble averages and their variability (rms deviation), mean differences between measured and calculated values and their variability given in the Disagreement column, and correlation coefficients. In the first column of Table 2, the number of days used for comparison between model and measurement results is given in brackets.

It follows from Table 2 (averages and disagreements) that, for all TGCs (except for ozone), the model underestimates their atmospheric contents, when compared to measurement data. For the TC of ozone, on the contrary, the model yields higher values when compared to measured ones. Note that, earlier [19], when comparing the TC of ozone with independent measurements, data obtained from ground-based spectrometric measurements, in a varying degree, exceeded those obtained from other measurements; i.e., one can state with certainty that the model overestimates the TC of ozone in the atmosphere over the St. Petersburg region. One can also see that the EMAC model yields higher values for the natural variability of the ozone TC and lower values for the variability of the TCs of the rest of the gases, when compared to experimental data. The coefficient of correlation between the two data ensembles for the contents of TGCs is significant for all the gases under consideration, and this coefficient is maximal for NO₂ and ozone. For the SC of NO₂, high correlations are due to a strong natural variability of this gas (the rms deviation is over 30%). Seasonal cycles are clearly pronounced for both gases. For HCl, the coefficient of correlation is also sufficiently high. Correlations are minimal for HNO₃, which is caused by the relatively low accuracy in its determining. Table 1 gives mean errors in determining the TC of HNO₃ due to random measurement noise; however, the total error in determining this gas with

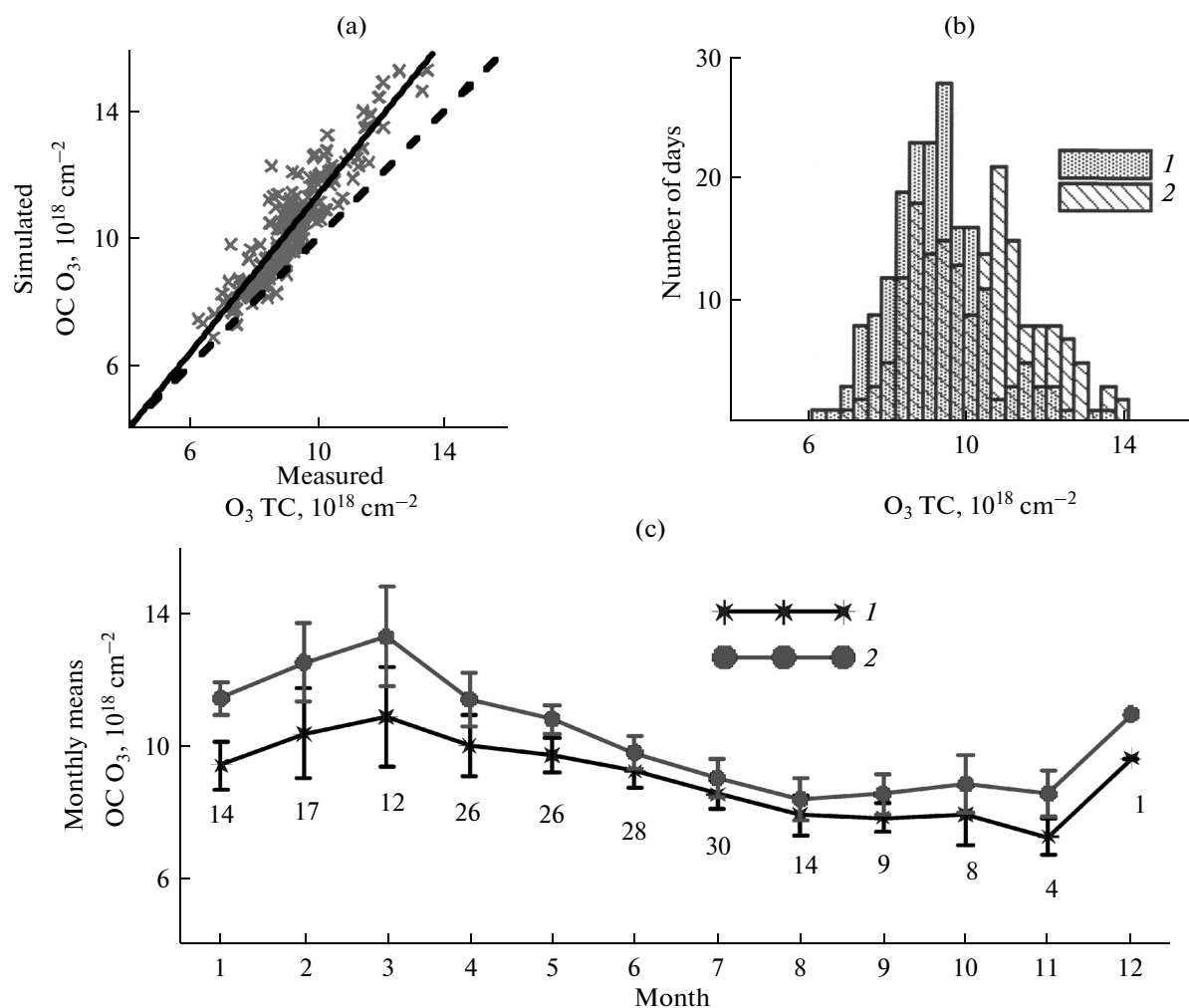


Fig. 1. Comparison between measurement and simulation data ensembles for the TC of ozone (*1* and *2* correspond to measurements and simulation, respectively): (a) data scattering for the TC of ozone, (b) distribution of its TC variations, and (c) monthly means of its TC and their rms deviations (figures under the curves indicate the number of days used for comparison).

the IR method may reach 10% due to contributions made by other error sources.

It is easily seen that, for HCl, O_3 , and HNO_3 , the main disagreements between their measured and calculated TCs are due to systematic error (for example, the disagreement for HCl is 22% and the rms deviation in this case is 8%). At the same time, for the SC of NO_2 , the contributions of both systematic and random errors to the disagreement are almost equal.

Let us analyze in more detail the comparison between the two data ensembles obtained from ground-based spectrometric measurements and on the basis of the EMAC model.

4.1. Ozone

Figure 1a shows the data scattering for the ozone TC obtained from measurements and simulations, and Fig. 1b shows the distribution of the ranges of variations in the ozone TC values obtained from the mea-

surements and simulations. It follows from Fig. 1 that, almost in all cases, the ozone TC values obtained from simulations exceed those obtained from measurements. In addition, at almost the same total range of variations in the TC of ozone, the distribution of its TC has a more pronounced maximum shifted towards lower values in the measurement data ensemble when compared to the simulation data ensemble. The model is characterized by a wider scattering of ozone TC data when compared to the measurements.

The results of comparison of time variations in the ozone TC between data obtained from simulations and from its averaged measured values showed that the model overestimates the TC of ozone (when compared to measurements), especially for the winter–early spring period. For summer and early autumn, against the background of a decrease in absolute ozone TC values (seasonal variations), a decrease in relative disagreements between the two data ensembles is observed. Figure 1c (monthly means) shows that the

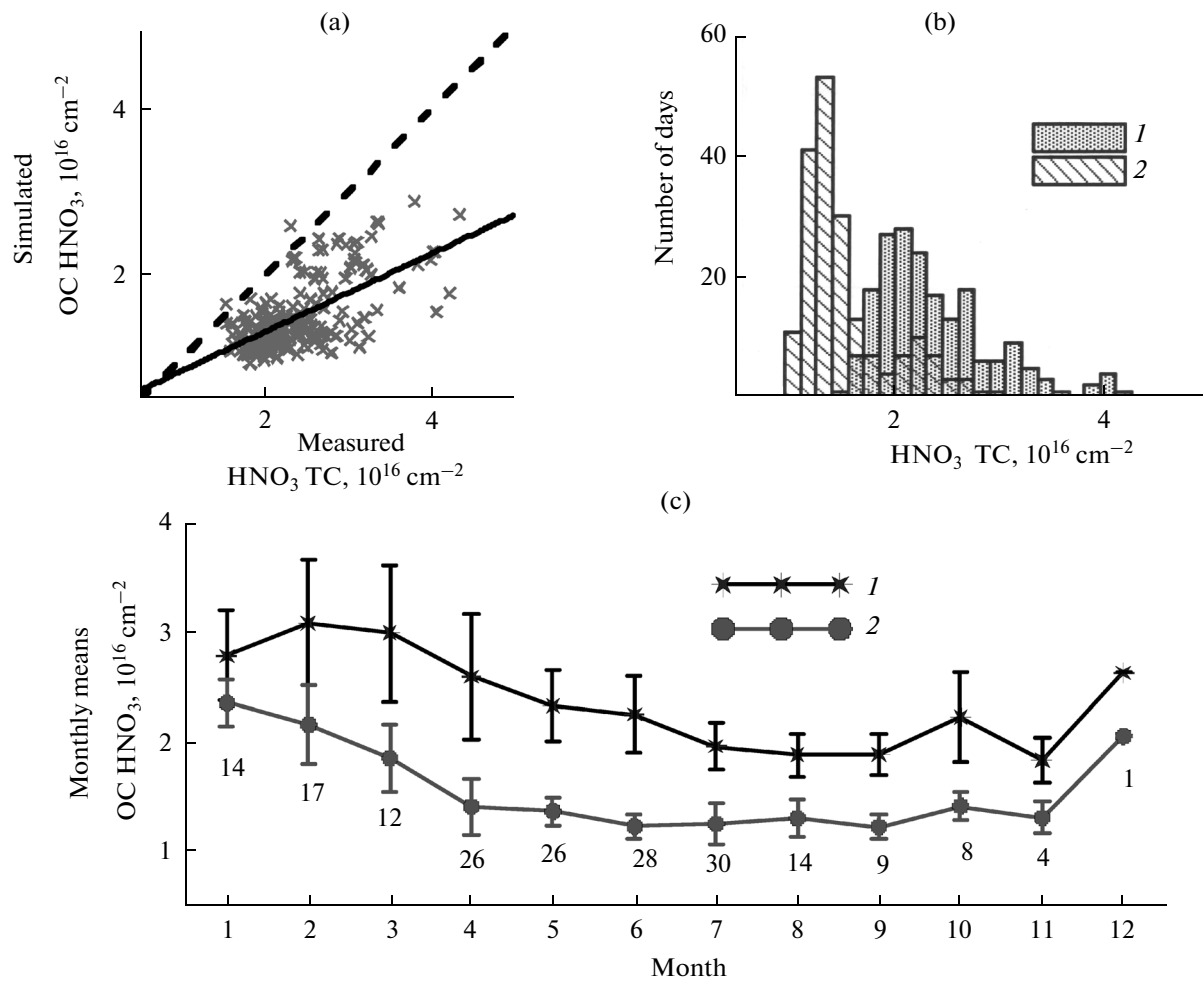


Fig. 2. Same as in Fig. 1, but for the TC of HNO_3 .

model yields higher TC values for the first 3 months of the year when compared to measurements (the difference is about 20%) and, in the rest of the months, the disagreement does not exceed 5–15%. As a result, the model yields a somewhat larger amplitude of seasonal ozone variations for the St. Petersburg region.

4.2. HNO_3

It follows from Fig. 2a that, for almost all days, the model underestimates the content of HNO_3 when compared to its measured values; this underestimation is more pronounced for high measured values of its TC, and the variability of its measured values is significantly higher than that of its model values.

It follows from Fig. 2b that the distributions of the $\text{HNO}_3 \text{ TC}$ variation ranges for the two data ensembles are shifted with respect to each other (measurements yield higher values of the $\text{HNO}_3 \text{ TC}$); in this case, the distributions for model data are narrower than those for measured ones (i.e., the model incompletely

reflects the variability of the $\text{HNO}_3 \text{ TC}$ when compared to measurements).

Comparisons between daily means of the $\text{HNO}_3 \text{ TC}$ showed that, for all seasons, the model yields significantly lower values when compared to measurements. Analyzing its monthly means over the three years (Fig. 2c), one can see that both the model and measurements yield the seasonal variations in the $\text{HNO}_3 \text{ TC}$, with its maximum within the winter period (December–January for the model and February–March for the measurements). For February–October, the difference between the seasonal cycles amounts to 30–45%; the model underestimates the TC of HNO_3 when compared to measurements. Moreover, in both model and measurement data, the secondary maximum is observed in October. This maximum is most likely random, because, over 3 years, the number of days with coinciding data is only 8 for October and 4 for November. The highest number of days with coinciding data is noted for April–July. It should also be noted that there are no

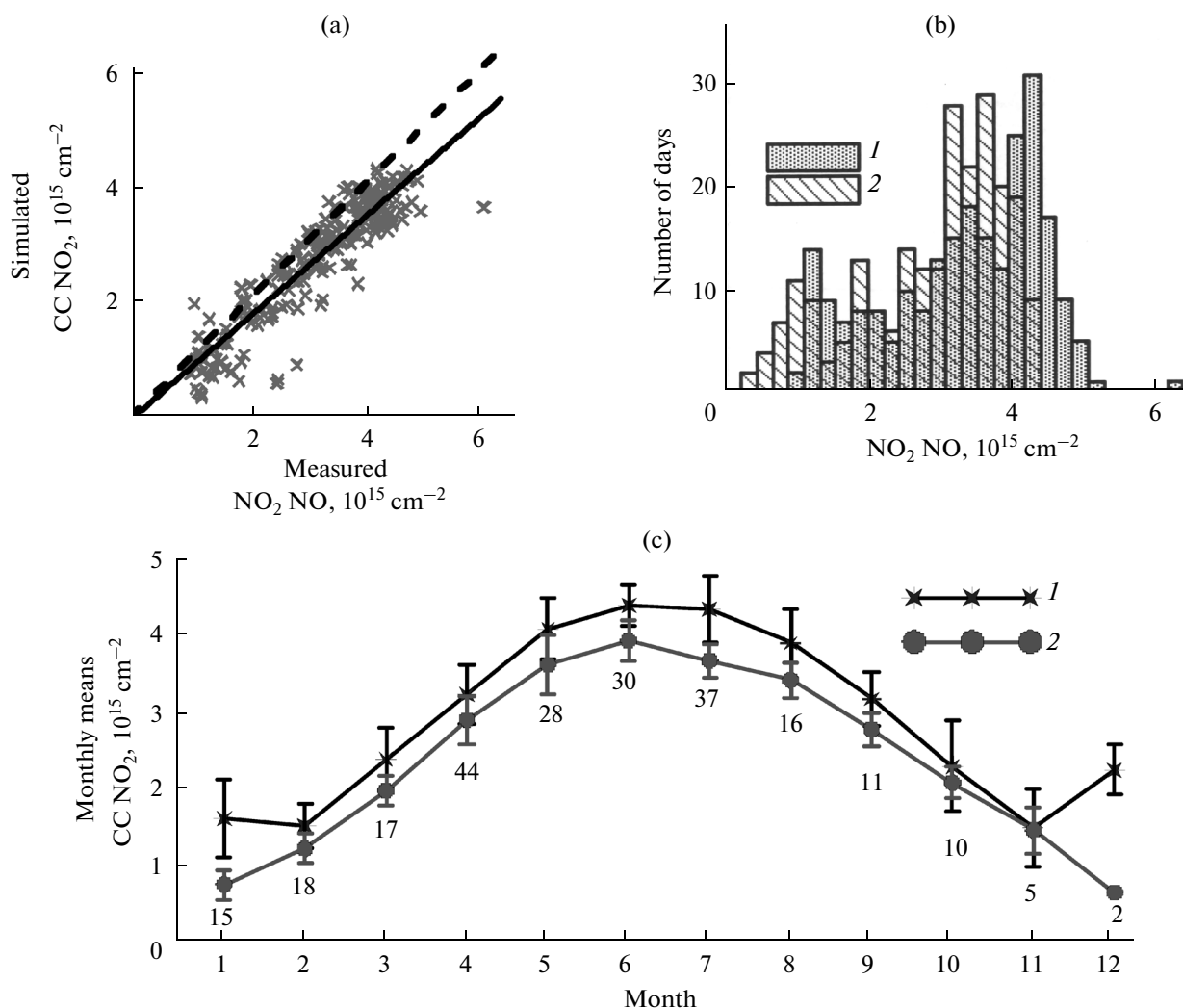


Fig. 3. Same as in Fig. 1, but for the SC of NO_2 .

clear seasonal variations in disagreements between model and measurement data.

4.3. NO_2

It follows from Fig. 3, in which the model and measurement data on the SC of NO_2 in the St. Petersburg region are compared, that the straight line in the scatter diagram (Fig. 3a) passes almost diagonally; i.e., the measurement and model data on the SC of NO_2 are in good qualitative and quantitative agreements. The boundaries of the ranges of variations in the SC of NO_2 (Fig. 3b) are almost the same; however, the distribution for lower NO_2 SC values is wider for the model than that for measurements. The distributions for measurement data are narrower and have maxima for slightly higher (than mean) values.

An analysis of the time variability of the NO_2 SC shows that the model adequately reproduces the known seasonal cycle of the stratospheric component

of the NO_2 TC, which is mainly determined by daylight hours (and their related duration of N_2O_5 photolysis reactions). In both model and measurement data, the minimum SC of NO_2 is observed in winter and its maximum SC is observed in summer (Fig. 3c). The NO_2 content calculated using the model proves lower than that obtained from measurements throughout the year, and these disagreements may reach high relative values (over 100%) in the winter months (December and January). Such strong differences are due to a significant increase in the errors of spectrometric measurements under the conditions of a low NO_2 content in winter (and, in addition, the absorption of infrared radiation in the used spectral line is weak). It should be noted that, according to results obtained in [20], our data obtained from spectrometric measurements systematically exceed data obtained from other independent measurements of the SC of NO_2 (on average, by 8%). If this correction to spectrometric measurements and the contribution of erroneously high winter con-

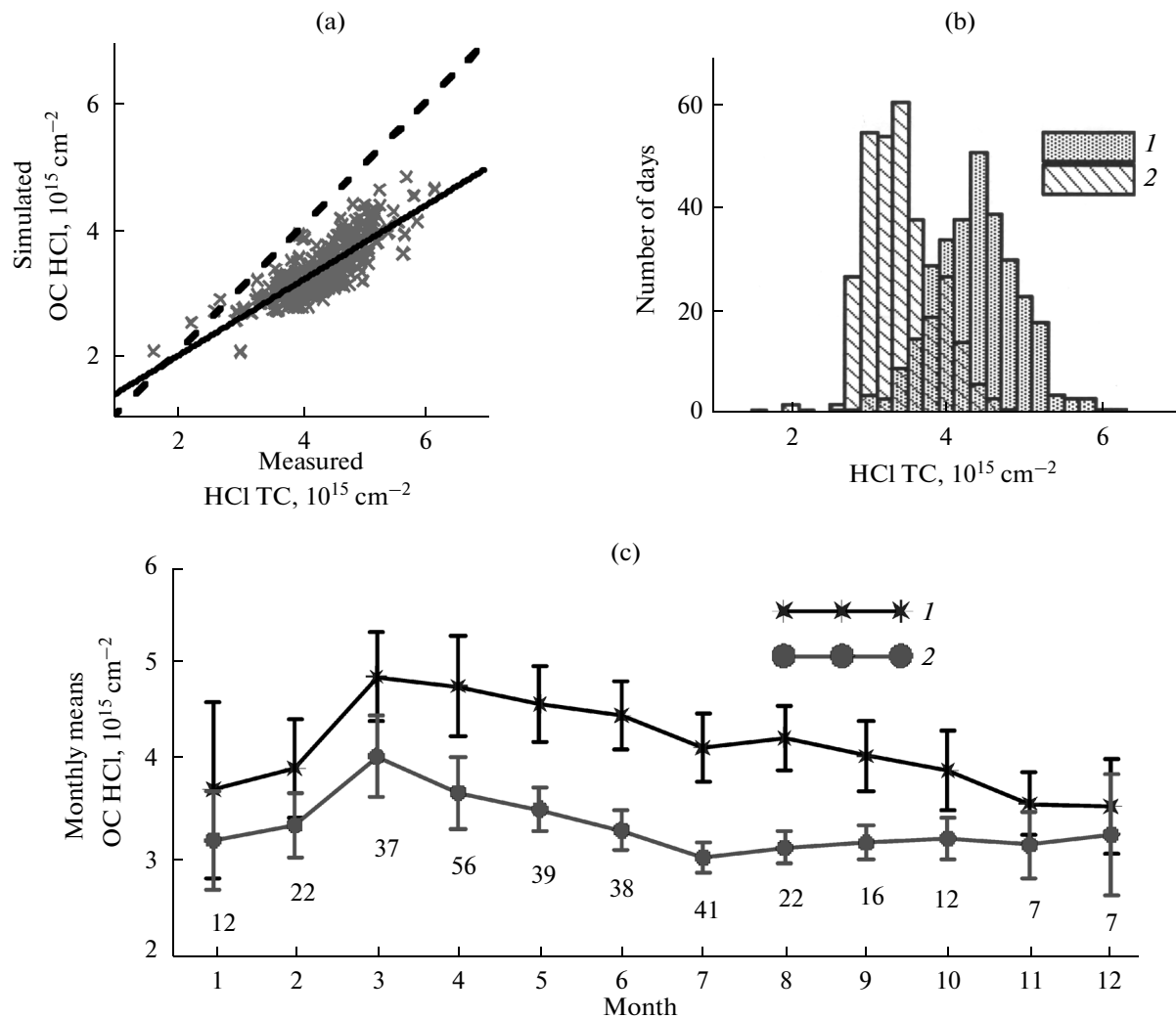


Fig. 4. Same as in Fig. 1, but for the TC of HCl.

tents are taken into account, the estimate obtained in this work for the mean disagreement between spectrometric and model data ($\sim 14\%$) may imply that the quality of the results of the NO_2 SC simulation is good.

4.4. HCl

It follows from the scattering of the HCl TC data ensembles shown in Fig. 4a that the points lie along the straight line inclined towards measured values; i.e., the model underestimates the HCl TC in the atmosphere over St. Petersburg, and the higher measured HCl TC values are, the stronger is their underestimation by the model. It follows from the HCl TC variation ranges shown in Fig. 4b for the two data ensembles that the distributions of the HCl TC values, as in the case of the HNO_3 TC, are shifted with respect to each other (measurements yield higher values); the distribution for model data is narrower than that for measured ones (i.e., the model incompletely describes

the variability of the TC of HCl when compared to measurements).

The time variations in the daily mean TC of HCl showed that, for all days except one (January 27, 2010), when measurements were performed under the conditions of a polar stratospheric vortex [21], the model underestimates the TC of HCl when compared to measurements.

It follows from the seasonal variations in the monthly mean TC of HCl (Fig. 4c) that, without consideration for such a systematic disagreement, the model and measurement data are in good agreement. Such disagreements increase during the warm months. However, as in the case of the TC of HNO_3 , there are also some differences: maximum HCl concentrations are observed in March for the EMAC model and in March–April for ground-based spectrometric measurements. The same situation with such a shift in maximum concentrations was also observed for the TC of ClONO_2 [7]. Taking into account the fact that

both photochemical and dynamic processes in the ozonosphere cause the maximum concentration of HCl to lag by 1 month when compared to that of ClONO₂, one can trace the similar time shift between the model and measured maxima for both gases.

Comparing our results with measurement data [24], one can note that, in both cases, the EMAC model underestimates the TC of HCl (on average, by 24% in [24] and 22% in our case). The results of comparisons between data obtained with the KASIMA model [25] and from measurements taken at the Kiruna station (Sweden) showed that the model TC of HCl is, on average, noticeably lower than its measured TC.

5. CONCLUSIONS

The results of comparisons between data on the TCs of ozone, NO₂, HCl, and HNO₃ obtained from the 2009–2012 ground-based spectroscopic measurements in Petergof and simulations using the EMAC model showed the following:

1. For NO₂, HCl, and HNO₃, the model underestimates their TCs, when compared to measurement data (on average, by 14% for NO₂, 22% for HCl, and 36% for HNO₃). For ozone, on the contrary, the model yields its higher (by 12%) mean TC when compared to measurement data.

2. When compared to measurement data, the model yields a stronger natural variability for the TC of ozone and a weaker variability for the TCs of the rest of the gases.

3. The coefficient of correlation between the two measurement and simulation data ensembles is significant for all the gases under consideration, and this coefficient is maximum for NO₂ (0.92), O₃ (0.91), and HCl (0.85) and minimum for HNO₃ (0.63).

4. The basic disagreements between the measurement and simulation data on the TCs of HCl, O₃, and HNO₃ are caused by the systematic component. At the same time, for the SC of NO₂, the contributions of both systematic and random errors to the disagreement between the two data ensembles are almost the same.

5. Mean seasonal dependences of the TCs of the gases under study are adequately simulated by the EMAC model.

However, the model overestimates the TC of ozone (when compared to measurement data), especially for the winter–early spring period, and yields a slightly larger amplitude of its seasonal variations for the St. Petersburg region.

The model adequately simulates seasonal variations in the TC of HNO₃ with its maximum in winter. It should be noted that its maximum is observed in December–January for the model and in February–March for measurements. For February–October, the difference between its model and measured seasonal variations stably amounts to 30–45% (model data are underestimated when compared to measurement data).

The model adequately reproduces seasonal variations in the stratospheric component of the NO₂ TC. According to both model and measurement data, the minimum SC of NO₂ is observed in winter and its maximum SC is observed in summer. The NO₂ contents calculated using the model prove lower than those measured throughout the year, and this difference reaches higher relative values in December and January.

The model underestimates the TC of HCl when compared to measurement results. Seasonal variations in the monthly means of the HCl TC according to measurement data (without consideration for the systematic disagreement) are in good agreement to those according to model data. Disagreements increase during the warm period of the year.

6. In order to specify the reasons for such disagreements between model and measurement data, it is necessary to compare not only the TCs of the TGCs under consideration, but also their contents in different atmospheric layers.

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