Chapter 14
Measurements of Trace Gases at Saint-Petersburg State University (SPbSU) in the Vicinity of Saint-Petersburg, Russia

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Abstract An overview of atmospheric trace gas measurements made using various spectroscopic ground-based instrumentation and measurement techniques at the Department of Physics of Atmosphere, St. Petersburg State University is given. The SPbSU trace-gas retrievals have been compared to independent ground-based and satellite measurements as well as to models. Temporal variations (from diurnal cycles to long-term trends) of trace-gases have been studied on the basis of experimental data.

Keywords Ground-based measurements • Atmospheric trace gases • Fourier-spectrometer Bruker

14.1 Introduction

Atmospheric trace gases play an important role in forming the radiative characteristics of the atmosphere and ozonosphere and accordingly effect global climate [20]. Therefore measurements of the variability of climate influencing atmospheric gases by different local and remote methods are performed very intensively and continuously all over the world. At St. Petersburg State University (Atmospheric Physics Department) ground-based spectroscopic measurements of trace gases started in the early 1990s at Old Peterhof, approximately 35 km southwest from the center of St.-Petersburg (59°88′ N, 29°83′S, 20 m asl.). Measurements of IR solar radiation spectra by SIRS-spectrometer with middle resolution [3] were first performed at SPbSU but have subsequently been augmented by other remote methods for measuring the atmospheric trace gases.

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14.2 Instrumentation and Measurement Techniques

At first stage of the investigation (beginning in 1991), ground-based spectroscopic measurements of CH_4 and CO total column amounts (TCA) have been performed using a Solar IR Spectrometer (SIRS). SIRS is a low resolution (0.4−0.6 cm^{-1}) grating spectrometer which was designed at the Department for observations of solar IR radiation in the 3.15−4.55 μm wave-range. The gas TCA retrieval algorithm is based on the optimal estimation method [17]. CH_4 and CO TCA time series have been analyzed to reveal variability of different time scales (long-term trends, annual and interannual variability etc.) of the gases for the St. Petersburg region [4, 5].

Trace gas remote determinations have been carried out also by measurements of zenith scattered solar radiation in the UV and visible spectral ranges. For performing the measurements, an automated spectral complex based on a grating spectrometer (KSVU instrument) developed at SPbSU which allowed registration of a spectrum of scattered radiation in the range of 428−515 nm with 1.3 nm resolution has been used [11]. The NO_2 vertical column amount has been retrieved from twilight solar scattered visible radiation measurements using the DOAS (Differential Optical Absorption Spectroscopy) method [9]. Beginning with 2004, the measurements have been carried out by means of the KSVU instrument (later, since 2008 – by an OceanOptics spectrometer). The interpretation of this kind of ground-based measurements is performed using the standard techniques developed for the international network of stations NDACC (formerly NDSC) (http://www.ndacc.org) and SAOZ [15] (WinDOAS, [1]). Since 2008, determination of the ozone vertical profiles at the 20−80 km altitude region have begun using measurements of downward thermal radiation in the microwave ozone absorption lines [2].

Since January 2009, combined determination of atmospheric gas composition has been started using ground-based measurements of IR direct solar radiation by Fourier-spectrometer Bruker IFS-125 with a high spectral resolution (up to 0.002 cm^{-1}). An original sun-tracking system for the Bruker IFS125 HR was designed at the Atmospheric Physics Dept. of Saint-Petersburg State University. It makes possible the measurement of more than 20 greenhouse and reactive gases in the atmosphere over St. Petersburg [6, 7, 10, 12–14, 18, 19, 21]. In Table 14.1 short descriptions of the ground-based devices and measurement methods used at SPbSU are given.

14.3 Trace Gases Measurements Near St. Petersburg

Simultaneous measurements which were performed by SIRS (original retrieval algorithm [8]) and Bruker (SFIT2 retrieval algorithm [16]) during 2009–2010 allowed us to harmonize the CH_4 time series obtained by two spectrometers (Fig. 14.1). The systematic difference between the Bruker IFS125 HR and SIRS measurements totals 1.8%.

Long-term trends in the CH_4 TCA were estimated using SIRS and Bruker IFS125 HR observations (Fig. 14.2). The increase rate for 2005−2010 is

Table 14.1 Instruments and measurement techniques used by SPbSU for trace gases measurements

Device	Start	Retrieval algorithm	Method and spectral range	Measured gases	Comments
Spectrometer SIRS-2	1991	Original code (optimal estimation) [8]	Direct Sun radiation 3.15–4.55 μm	CO, CH_4, H_2O	Spectral resolution 0.2–0.5 cm^{-1}
Fourier-spectrometer Bruker IFS-125	2009	SFIT2 v. 3.9× (optimal estimation) [16]	Direct Sun radiation 1–16 μm	~20 gases	Spectral resolution – up to 0.002 cm^{-1}
UV-VIS-NIR spectrometers		WinDOAS [1]	Zenith scattered solar radiation	O_3, NO_2, O_2-O_2	Spectral resolution:
Visible-NIR-KSVU	2004		420–520 nm		1.3 nm
OCEAN OPTICS HR4000 UV HR4000 visible	2008		280–420 nm 400–610 nm		0.4 nm 0.6 nm
MW-ozonometer	2008	Original code (optimal estimation) [2]	MW atmospheric radiation 110 GHz	O_3	Vertical profile (25–60 km)

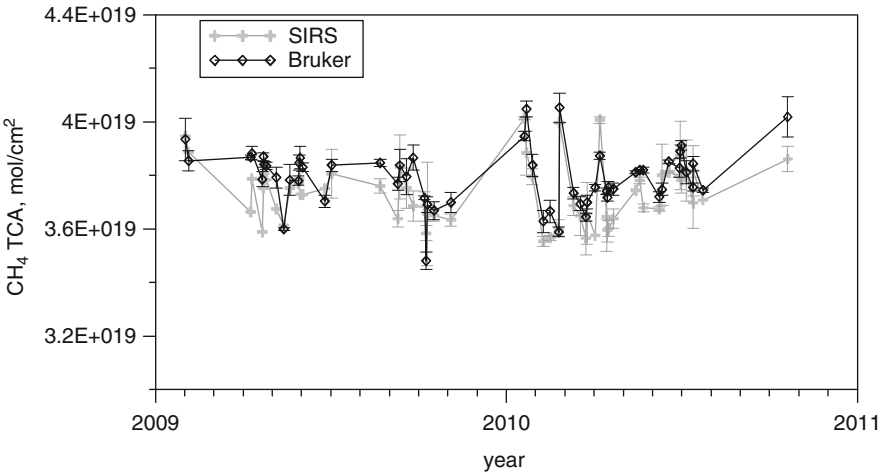

Fig. 14.1 Results of simultaneous measurements of the CH_4 TCA

(1.0 ± 0.4)% per year. The linear trend of CH_4 (near Saint-Petersburg) for the whole measurement period (1991−2010) amounts to (0.16 ± 0.1)% per year.

In Fig. 14.3 data on the stratospheric O_3 column retrieved from ground-based OceanOptics UV (top) and stratospheric NO_2 column retrieved from ground-based KSVU and OceanOptics VIS (bottom) measurements near Saint-Petersburg are compared with collocated satellite (Aura OMI instrument) and Envisat SCIAMACHY

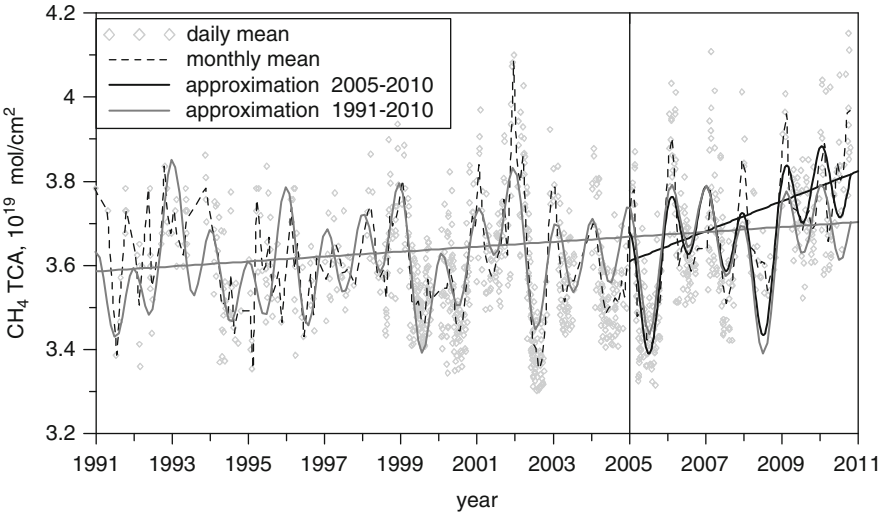

Fig. 14.2 Long-term trends in the CH_4 TCA near Saint-Petersburg

measurements, respectively. Reasonable agreement between the two types of data for both measurements is evident – the relative difference is +2.4 ± 4.3% for O_3 and 2 ± 48% for NO_2.

In Fig. 14.4 ground-based measurements of the NO_2 tropospheric column (KSVU) are compared with calculations using the HYSPLIT dispersion model and the correlative satellite OMI data in winter–spring 2006. There is qualitative agreement between the simulated (HYSPLIT) and measured (KSVU, OMI) tropospheric NO_2 variations. Currently, NO_2 can also be measured with a DOAS mobile device.

14.4 Combined Measurements of Atmospheric Trace Gases with a High Spectral Resolution

Since 2009 combined measurements of atmospheric trace gases have been performed using the Fourier-spectrometer Bruker IFS-125 with a high spectral resolution. In Table 14.2 the spectral windows used for the retrieved TCA of different gases and retrieval errors are given.

The spectral intervals used for trace gas retrieval are obtained from the recommendations of NDACC stations for such kinds of measurements as well as from preliminary analysis of measured and calculated spectra (e.g., Virolainen et al. [19]).

In Table 14.3 the annual-average N_2O TCA near Saint-Petersburg measured by a Fourier spectrometer (SPbSU) is compared with the same values for a number of NDACC stations.

One can see that the mean values and annual variability of N_2O TCA is very similar for all of the listed stations (mid and high latitudes).

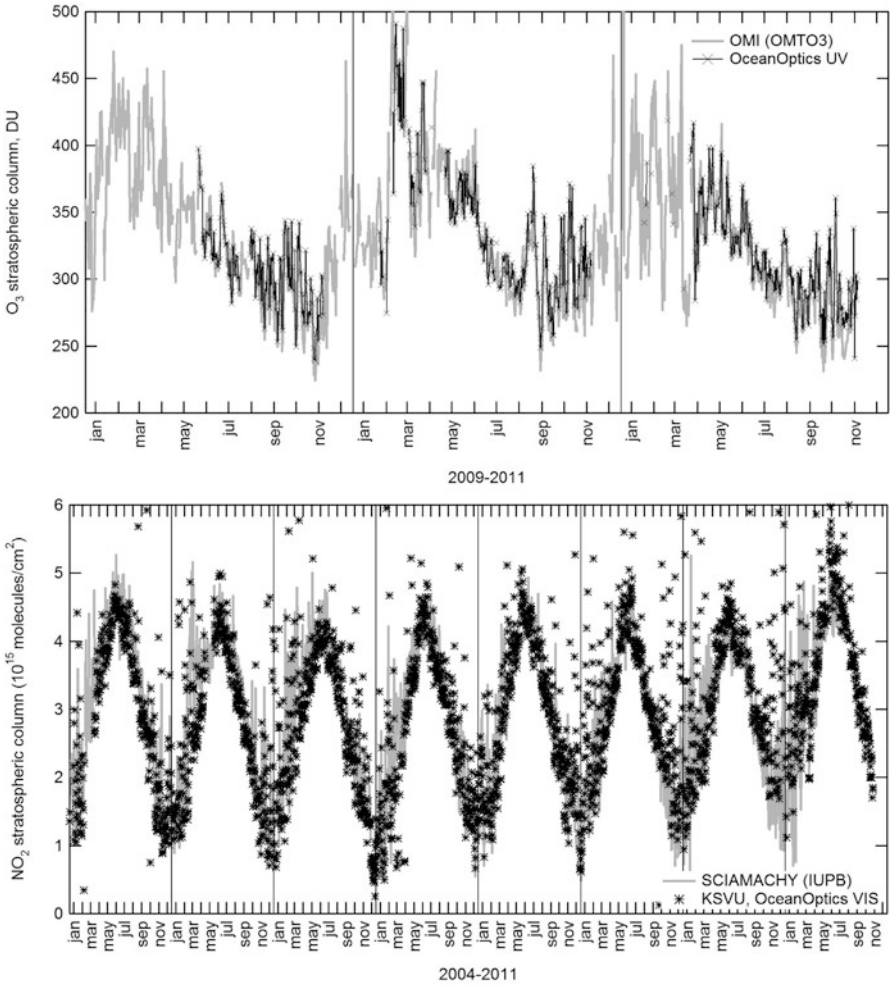

Fig. 14.3 Comparison of ground-based and satellite stratospheric O_3 (*top*) and NO_2 (*bottom*) column measurements

The results of ozone TCA ground-based measurements by Fourier spectrometer, Dobson spectrometer, ozonometer M-124 and satellite OMI measurements near Saint-Petersburg are compared in Fig. 14.5. Measurements by the Dobson spectrophotometer and M-124 filter ozonometer were carried out at the Main Geophysical Observatory in Voeikovo (50 km to the north-east of Peterhof), satellite measurements are collocated in space to ground-based measurements within about 100 km.

It is clearly evident that the different types of measurements are in good qualitative coincidence. The amplitude of ozone TCA changes obtained by Bruker spectrometer data are slightly less than by the OMI or M-124 data, especially in the early spring period of measurements, when the TCA values are sufficiently large (around 400 DU). In addition, one can see that the Bruker spectrometer data for August 2009 at small TCA values (less than 300 DU) are somewhat overestimated in comparison with the other probes.

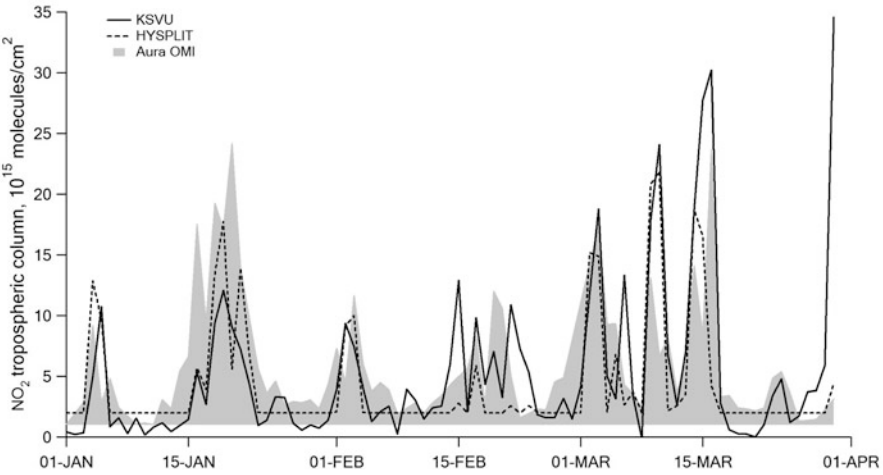

Fig. 14.4 NO_2 tropospheric column measurements at St. Petersburg compared to HYSPLIT dispersion model and satellite OMI data in winter–spring 2006

Table 14.2 Measured gases and random retrieval errors

Measured gases	Spectral windows, cm^{-1}	Random error for single measurement, %	Influenced gases
CO_2	2,626.3–2,627.0	1.0	CH_4, HDO
CH_4	2,613.70–2,615.40	1.0	HDO, CO_2, NO_2
	2,650.60–2,651.30		
	2,835.50–2,835.80		
	2,903.60–2,904.03		
CO	2,057.70–2,058.00	1.5	O_3, CO_2, OCS, N_2O, H_2O
	2,069.56–2,069.76		
	2,157.50–2,159.15		
HF	4,038.0–4,039.7	1–5	H_2O, CH_4
N_2O	2,551.435–2,552.400	1.1	CH_4
NO_2	2,914.590–2,914.707	8.2	CH_4, HDO
C_2H_6	2,976.6–2,977.1	4.0	O_3, H_2O, CH_4
HCl	2,925.75–2,926.0	1.7	CH_4, H_2O
O_3	six windows in 773–1,044	1	H_2O, CO_2
CCl_3F	830–870	13	H_2O, HNO_3, O_3
HNO_3	867.5–870.1	1–9	H_2O, CO_2, OCS

The results of numerical pair-wise comparison of different O_3 TCA measurements are given in Table 14.4. The period of comparison dates to 2009, from early spring to late fall, 52 sunny days of simultaneous measurements in total. The measurements under consideration use a F3 filter allocating the spectral range from 650 to 1,400 cm^{-1}. The spectral resolution of the measurements in the chosen spectral ensemble was 0.005–0.008 cm^{-1}. The average and rms errors, as well as the

Table 14.3 Comparison of N_2O TCA near Saint-Petersburg with that from NDACC stations

Station	Annual N_2O TCA, 10^{-18} mol/cm^2	Annual variability, %
SPbSU	6.53	12
Bremen	6.46	9
Toronto	6.49	17
Harestua	6.58	16
St. Danis	6.6	6

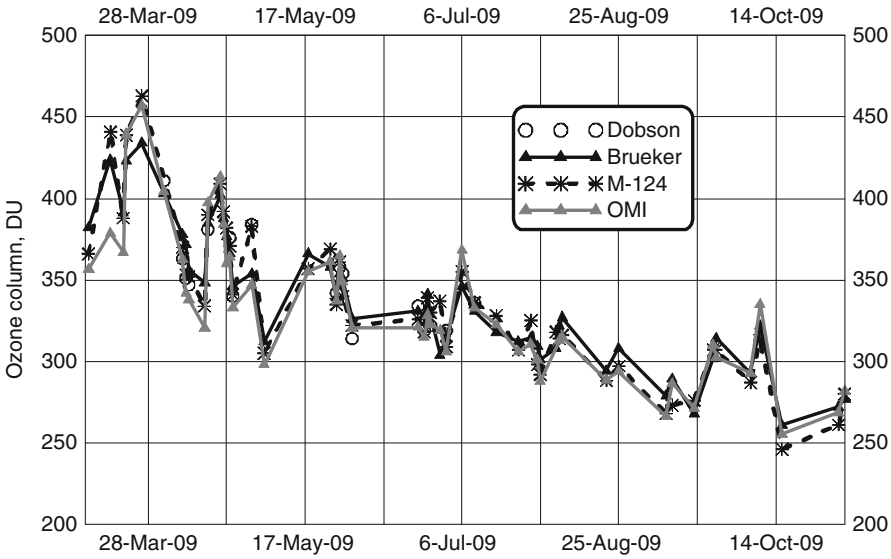

Fig. 14.5 Comparison of ground-based and satellite ozone TCA (in DU) measurements near Saint-Petersburg

Table 14.4 Comparison of O_3 TCA measurements

Measuring devices	Number of comparisons	Mean difference	RMS difference	Correlation coefficient
Bruker−Dobson	17	0.7 DU (0.3 %)	11.4 DU (3.2 %)	0.90
Bruker−OMI	51	5.3 DU (1.7 %)	14.2 DU (4.1 %)	0.95
Bruker−M124	51	0.6 DU (0.4 %)	11,7 DU (3.4 %)	0.97
M124−Dobson	16	−0.2 DU (−0.06 %)	6.8 DU (2.0 %)	0.99
M124−OMI	50	4.6 DU (1.3 %)	13.5 DU (3.8 %)	0.96
OMI−Dobson	17	−5.5 DU (−1.7 %)	12.2 DU (3.5 %)	0.91

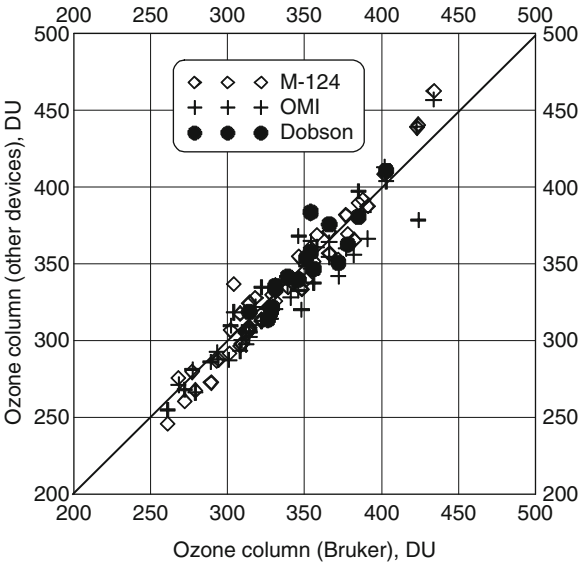

Fig. 14.6 Correlation between the ozone TCA obtained from different devices (mean: 0.3–1.7 %, RMS: 3–4 %) near Saint-Petersburg

coefficients of correlation between measurements by different probes, are presented. The correlation coefficients are close to unity with a maximum value of 0.97 for the Bruker–M-124 pair.

Analyzing the rms error, it can be seen that the maximum (4%) is observed between the ground-based measurements by the Bruker spectrometer and the results of the OMI satellite measurements. The rms between TOC measurements with the help of OMI and M_124 probes is also close to 4%. The rms error between the Peterhof and Voeikovo measurements is 3–3.5%. These errors can be explained by both the errors of the measurements themselves and the spatial and temporal variations of ozone.

In addition to the correlations shown in Table 14.4, Fig. 14.6 demonstrates the rate of consistency between the measurement results depending on the ozone TCA value. The average TCA value over all ensembles is around 330 DU; the rms value is around 45 DU (around 15%). It can be seen from Fig. 14.6 that the M-124 and Dobson spectrophotometer data are very linear (this is also because there are no shifts between these data); at the same time, the comparison between OMI and Bruker spectrometer data reveals that the TCA values for OMI are slightly higher. This is more apparent for ozone TCA values of around 340–400 DU (i.e., above average).

Measured monthly average values of the CO_2 TCA near Saint-Petersburg in 2009−2011 and their variations are given in Table 14.5.

It is seen that the maximum in CO_2 variability is observed in April 2009–2010, in July 2009 and during the summer months ion 2011 (more than 10 ppm and, consequently, more than 3% of mean values). The observed means of CO_2 TCA refer to 2010.

Ground-based measurements of the HF TCA by Fourier-spectrometer Bruker IFS-125 were carried out during April 2009−April 2010. The random and

Table 14.5 Monthly average values (in ppm) of CO_2 TCA and its variations (Δ) in 2009–2011

Year/month	2009	Δ	N	2010	Δ	N	2011	Δ	N
April	397.0	14.6	9	393.4	10.5	9	390.7	6.7	11
May	390.5	8.2	7	395.7	4.8	7	391.3	8.7	10
June	389.3	3.9	6	390.8	6.2	7	392.8	12.6	13
July	387.6	11.3	9	395.9	7.1	9	393.6	11.4	12
August	387.0	5.0	6	–	–	–	388.3	10.9	10
September	389.0	8.8	3	–	–	–	390.1	2.6	4

N – number of measurement days

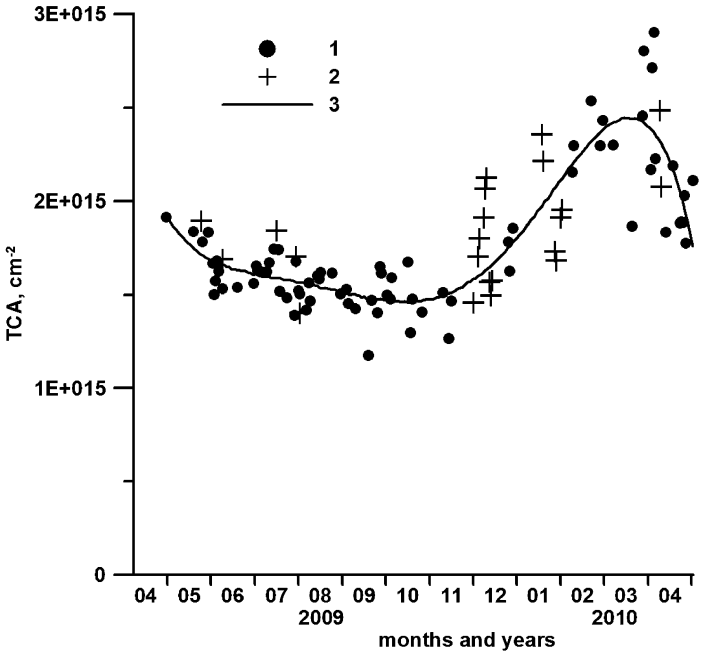

Fig. 14.7 Comparison of SPbSU ground-based (1) and satellite (calculated using profiles of HF mixing ratio measured by ACE-FTS) (2) HF TCA measurements for April 2009–April 2010 (3) – an approximation of HF TCA by a fifth-degree polynomial

systematical errors of the HF TCA measurement are 1–5% and 5–6%, respectively. The mean values and rms variations of the HF TCA are 1.77×10^{15} cm^{-2} and 21%, respectively. The results are in good agreement with other ground-based (NDACC data) and satellite (ACE-FTS) measurements (Fig. 14.7).

The numerical values of this comparison of ground-based (Bruker) and satellite (ACE experiment) measurements are presented in Table 14.6. The columns refer to 500 and 1,000 km distance coincidence of the considered measurements. One can see that the mean difference in both ensembles totals 8%, rms – 11 and 15% for 500 and 1,000 km, respectively.

Table 14.6 Statistical characteristics for a comparison of satellite and ground-based HF TCA measurements

Distance, km	500	1,000
Number of comparisons	9	43
Mean for Saint-Petersburg (SP), mol/cm^2	1.62×10^{15}	1.70×10^{15}
Mean for ACE-FTS	1.75×10^{15}	1.84×10^{15}
RMS HF for SP, % of the natural variability	16	16
RMS HF for ACE-FTS, % of the natural variability	8	13
Mean difference, %	8	8
RMS difference, %	11	15
Standard deviation, %	7	13

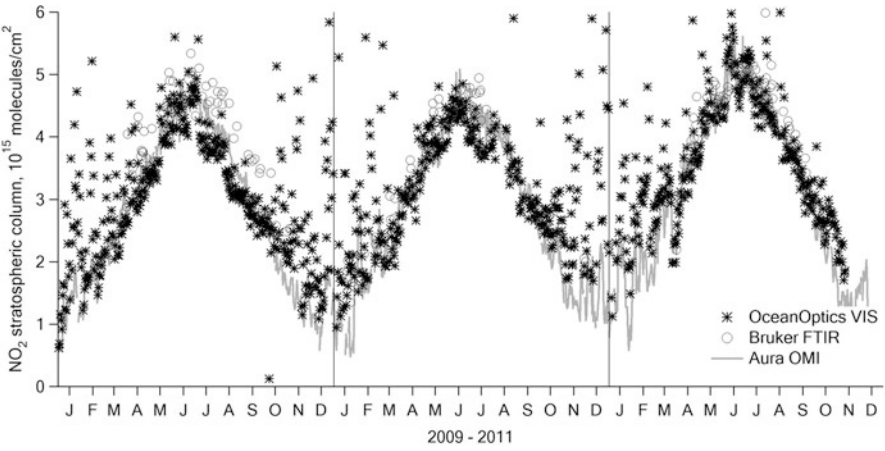

Fig. 14.8 Bruker NO_2 TCA measurements compared to ground-based (OceanOptics VIS and IR Bruker) and satellite data (OMI)

Results from a comparison of the NO_2 TCA ground-based (using DOAS method to zenith scattered solar radiation measurements and measurements of direct Sun spectra by Fourier-spectrometer Bruker IFS-125) and satellite measurements (Aura OMI instrument) are shown in Fig. 14.8.

One can see that the Bruker measurements of the NO_2 TCA are in good quantitative agreement with the OMI data (a little bit higher in summer maximum). The OceanOptics results have a larger spread of measurement values.

14.5 Summary

1. A large number of atmospheric trace gases are being measured since the early 1990s by different ground-based devices using different interpretation methods at SPbSU.

2. Currently, NO_2 is measured with a DOAS mobile device. In the near future other gases will be measured with the mobile FTIR spectrometer.
3. Temporal variations (from diurnal cycles to long-term trends) of trace gases are studied on the basis of experimental data.
4. Trace gases measurements are being used for validation of satellite data.
5. Further development of techniques for retrieving profiles of trace gases and increasing the number of retrieved trace gases are planned.

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