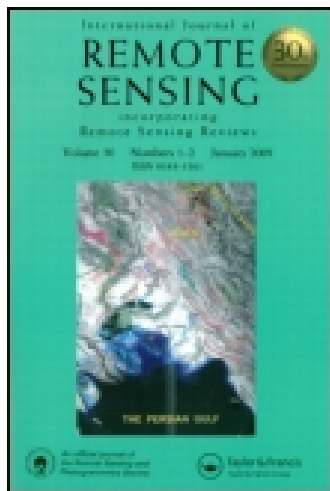


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International Journal of Remote Sensing

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tres20>

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Published online: 28 Aug 2014.

To cite this article: Yana Virolainen, Yury Timofeyev, Alexander Polyakov, Dmitry Ionov & Anatoly Poberovsky (2014) Intercomparison of satellite and ground-based measurements of ozone, NO₂, HF, and HCl near Saint Petersburg, Russia, *International Journal of Remote Sensing*, 35:15, 5677-5697

To link to this article: <http://dx.doi.org/10.1080/01431161.2014.945009>

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Intercomparison of satellite and ground-based measurements of ozone, NO₂, HF, and HCl near Saint Petersburg, Russia

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(Received 31 July 2013; accepted 7 April 2014)

Regular intercomparison of different observing systems is a part of their testing and validation protocol, which gives the estimates of real measurement errors. The main objective of our study is the comparison of satellite and ground-based measurements of atmospheric composition near Saint Petersburg, Russia. Since early 2009, high-resolution Fourier Transform Infrared (FTIR) solar absorption spectra have been recorded at Peterhof station (59.82° N, 29.88° E), located in the suburbs of Saint Petersburg. We derived column amounts of O₃, HCl, HF, and NO₂ from these spectra using the retrieval codes SFIT2 and PROFFIT. We compared the data retrieved from Bruker 125 HR FTIR measurements with coincident satellite observations of the Microwave Limb Sounding (MLS), Ozone Monitoring Instrument (OMI), Fourier Transform Spectrometer from Atmospheric Chemistry Experiment (ACE-FTS), Global Ozone Monitoring Experiment (GOME and GOME-2), and Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) instruments. The relative differences in ozone columns of FTIR from OMI-TOMS amount within (+3.4 ± 2.9)%, from GOME-2 are (+2.2 ± 3.0)%. The comparison of FTIR and MLS measurements of stratospheric ozone columns gives no mean and 5% of the RMS differences. Measurements of NO₂ columns agree with the mean difference of +9% and the RMS differences within 14–16% for FTIR vs. GOME-2, SCIAMACHY, and OMI. FTIR vs. GOME comparison gives (+6 ± 31)%. HCl columns comparison for FTIR vs. MLS shows –4.5% in the mean and 12% in the RMS differences. FTIR vs. ACE-FTS comparison (nine cases) gives –8% and 10% for the mean and the RMS relative differences, respectively. Comparison of HF columns shows (–12 ± 6)% and (–12 ± 11)% for FTIR vs. ACE data v.2.2 and v.3.0, respectively. These figures show that the Peterhof ground-based FTIR measuring system can be used to support the validation of satellite data in the monitoring of stratospheric gases.

1. Introduction

Changes in climate and the strong decrease of ozone column abundances in high and mid-latitudes observed in recent decades had led to the restriction of the emission of CFCs and HCFCs by the Montreal Protocol in 1987 and later to its amendments and adjustments (WMO 2007). Since then, stratospheric ozone has been monitored closely by many different measurement techniques (satellite, ground-based, airborne, etc.) (Solomon et al. 2007). In addition to ozone observation, it is very important to know the concentration of the substances involved in the ozone depletion cycle to monitor the effectiveness of the Montreal Protocol and to predict the development of the ozone layer.

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As the number of observation systems increases from year to year, the problem of testing and validation of them all becomes very important. The data obtained must be verified to confirm that the retrieved quantities are as accurate as possible. Intercomparison of different observing systems is one of the stages in the validation process, which gives the understanding of how theoretical error analysis actually represents the real properties of various remote-sensing measurements (Rodgers 2000). The validation of satellite observations is a routine procedure during the entire operation time of space-borne instruments. The more locations of ground-based stations are involved in these intercomparisons, the higher the accuracy of the observed data that can be obtained.

The department of Physics of Atmosphere at Saint Petersburg State University (SPbSU) has performed regular ground-based measurements of various atmospheric constituents at Peterhof station (59.82° N, 29.88° E) since the early 1990s. Ground-based measurements of CH₄, H₂O, and CO total column amounts with the low resolution (0.4–0.6 cm⁻¹) Solar Infra-Red Grating Spectrometer (SIRS) designed at the department (Makarova, Poberovskii, and Timofeev 2004; Makarova et al. 2009) were used for validation of satellite instruments (see, e.g. De Laat et al. 2010 on this subject).

Since the beginning of 2009, the SPbSU Peterhof station observing system has been recording solar spectra using the Bruker IFS 125 HR Fourier Transform Infra-Red (FTIR) instrument at spectral resolutions of 0.01–0.005 cm⁻¹ in a spectral region 3–16 μm (Poberovskii 2010). The specified spectral region and resolution of the SPbSU FTIR observing system allow the retrieving of a wide range of various atmospheric species (Poberovskii et al. 2010; Polyakov et al. 2011; Virolainen et al. 2011; Yagovkina et al. 2011; Kshevetskaya, Poberovsky, and Timofeev 2012; Timofeyev et al. 2013; Polyakov, Timofeev, and Poberovskii 2013; Rakitin et al. 2013; Semakin, Poberovskii, and Timofeyev 2013; Ionov et al. 2013; Virolainen, Timofeyev, and Poberovsky 2013).

The present research focuses on the measurements of ozone and several stratospheric constituents (HCl, HF, and NO₂), which play an important role in the stratospheric ozone chemistry. HCl and NO₂ are involved in the ozone-destroying catalytic cycles (Crutzen 1970; Molina and Rowland 1974) and in heterogeneous reactions on solid surfaces (see, e.g. Peter 1997 for detailed analysis). Active chlorine and nitrogen oxides are responsible for significant ozone destruction in the middle stratosphere. Active chlorine is released from reservoir gases such as HCl and ClONO₂ by heterogeneous reactions on the surfaces of the polar stratospheric clouds (PSCs) (Crutzen and Arnold 1986), which are formed at very low temperatures. After the disappearance of PSCs, chlorine is deactivated by the reaction with NO₂ forming ClONO₂ (Oelhaf et al. 1994). Thus, the quantity relation between active and reservoirs gases is very important in understanding the ozone-destroying processes. In the Arctic stratosphere, the planetary wave activity usually disturbs the polar vortex. This effect makes it difficult to separate chemical ozone loss from dynamic processes. At the same time, HF is not involved in the catalytic ozone destruction and has a long lifetime. Therefore, HF is often used as a tracer for stratospheric dynamics and transport, and hence, as a reference for chemically more active trace gases such as HCl (Chipperfield et al. 1997).

As ozone and many ozone-related gases have absorption bands in the infrared region, FTIR spectrometers are highly suited for measuring the atmospheric constituents related to stratospheric ozone. In particular, many stratospheric minor species have been monitored using ground-based FTIR observing systems within the framework for the Network for the Detection of Atmospheric Composition Change (NDACC). Similar FTIR spectrometers are used by the special monitoring network TCCON (Total Carbon Column Observing Network) for regular accurate and precise measurements of column contents of CO₂, CH₄, and other climate-forming gases (Wunch et al. 2011).

In this paper, we consider the series of measurements of vertical columns of ozone, HCl, HF, and NO₂ performed with a high-resolution FTIR spectrometer near Saint Petersburg in 2009–2013. We compare them with the results of coincident satellite observations with Microwave Limb Sounder (MLS), Ozone Monitoring Instrument (OMI), Fourier Transform Spectrometer from Atmospheric Chemistry Experiment (ACE-FTS), Global Ozone Monitoring Experiment (GOME and GOME-2), and Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) instruments.

2. FTIR data

In this paper, we analyse the observational data obtained from ground-based direct solar absorption measurements with the high spectral-resolution FTIR spectrometer Bruker 125 HR at Peterhof station. The spectrometer considered has a maximum optical path difference of 180 cm, yielding a spectral resolution of unapodized spectra up to 0.005 cm⁻¹ (0.008 cm⁻¹ after Norton–Beer medium apodization). Two detectors, MCT (mercury–cadmium–telluride) and InSb (indium–antimonide), cover the spectral range between 650 and 5400 cm⁻¹. In order to improve the signal-to-noise ratio, we record spectra within limited spectral bands using a set of appropriate optical bandpass filters and co-add them for up to 12 min measurement interval. The filter set allows the selection of three wide spectral bands: 650–1350, 1700–3400, and 2600–5400 cm⁻¹ (Poberovskii 2010). The averaged signal-to-noise ratio in the line-free continuum amounts from hundreds to thousands (depending on the band considered).

2.1. Retrieval parameters

High-resolution spectra include many distinct and overlapping absorption lines of a large number of atmospheric constituents. To derive the total column abundance of the target absorber gas from measured spectra, we selected one or a few microwindows, in which radiances are more sensitive to changes in target gas abundance and less sensitive to changes in interfering gases (Table 1).

The retrieval of atmospheric constituents' column amounts from recorded spectra in our research is based on two inversion codes, which are commonly used within the NDACC

Table 1. Characteristics of the retrieval.

Gas	Microwindows (cm ⁻¹)	Random error of measurement (%)	Influenced gases	Retrieval code
O ₃	991.25–993.80 1001.47–1003.04 1005.00–1006.90 1007.35–1009.00 1011.15–1013.55	1–2 (Virolainen et al. 2011)	H ₂ O, CO ₂ , C ₂ H ₄	PROFFIT 9.6
NO ₂	2914.590–2914.707	8–18 (Ionov et al. 2013)	CH ₄ , HDO	SFIT2 v3.93
HF	4000.86–4001.10 4038.81–4039.07 4109.77–4110.07	1–5 (Polyakov et al. 2011)	H ₂ O, CH ₄	SFIT2 v3.93
HCl	2727.73–2727.83 2775.70–2775.80 2925.80–2926.00	2–5 (Polyakov, Timofeev, and Poberovskii 2013)	CH ₄ , H ₂ O	SFIT2 v3.93

infrared community: SFIT2 and PROFFIT. SFIT2 was developed jointly at the National Aeronautics and Space Administration (NASA) Langley Research Center, Hampton, VA, USA, the National Center for Atmospheric Research (NCAR) at Boulder, CO, USA, and the National Institute of Water and Atmospheric Research (NIWA) at Lauder, New Zealand (Rinsland et al. 1998). PROFFIT was developed at the Institute for Meteorology and Climate Research of the Karlsruhe Institute of Technology (KIT). Hase et al. (2004) and Duchatelet et al. (2010) showed that when similar constraints are applied, the results of PROFFIT retrievals are in excellent agreement with those derived with SFIT2.

We applied the SFIT2 inversion code using the Optimal Estimation Method (see, e.g. Turchin, Kozlov, and Malkevich 1971; Rodgers 2000) to measured spectra for HF, HCl, and NO₂ total columns retrieval. For ozone columns retrieval, we used the PROFFIT inversion code in a mode of Phillips–Tikhonov approach (Phillips 1962; Tikhonov 1963). Depending on target gas, we took the corresponding pressure and temperature profiles daily from the following sources:

- National Center for Environmental Prediction (NCEP) (Lait, Newman, and Schoeberl 2005) for Peterhof location;
- Local nearby radiosounding data at Voeykovo station (59.95° N, 30.71° E) (Upper Air Database 2013); and
- Aqua satellite instrument – Atmospheric Infrared Sounder (AIRS) (AIRS data products 2013).

The *a priori* profiles of other atmospheric constituents were taken from The Whole Atmosphere Community Climate Model (WACCM) data – the same climatology for all seasons for Peterhof location (see, e.g. Park et al. 2013). For spectroscopic parameters of the absorption lines, we used the HITRAN database (Rothman et al. 2009).

The time series analysed in the paper consist of daily mean total columns of the retrieved gases. The days of measurements for each target gas differ slightly because not every spectral filter region can be measured every day, depending on the season or rapid changes in the weather conditions. Moreover, the dependence on direct sunlight leads to an irregular sampling of the measurements, with considerable gaps, especially during autumn and wintertime. The mean relative statistical error of a single measurement totals 1–2% for ozone, 8–18% for NO₂, 1–5% for HF, and 2–5% for HCl depending on measurements conditions (see Table 1).

2.2. Error analysis

Theoretical error estimation is usually based on the analytic method suggested by Rodgers (2000), which identifies three error classes: (1) smoothing error, (2) errors due to uncertainties in forward model parameters (instrumental characteristics, spectroscopic data, conditions of experiment, etc.), and (3) error due to measurement noise. If we have no information on the fine vertical structure of the target atmospheric parameter, it is better to abandon the estimation of the smoothing error and consider the observation as an estimate of a state smoothed by the averaging kernels. In any case, the smoothing errors can be substantial in comparing the vertical profiles of the target parameter measured by different device, but not the column contents of the retrieved gases. Errors are traditionally divided into systematic and random, depending on whether they are constant in a series of measurements or vary randomly with the time. Sometimes it is difficult to distinguish one from another because some error sources can be random in one time scale and systematic in

Table 2. Estimated errors for ozone retrieval.

Error source	Uncertainty	Column		9–41 km/9–20 km/20–41 km	
		Random (%)	Systematic (%)	Random (%)	Systematic (%)
Zero baseline offset	0.5%	0.1	0.2	0.2/0.1/0.1	0.2/0.5/0.4
Temperature profile	1 K (<10 km) 2 K (10–35 km) 5 K (>35 km)	1.7	1.0	2.3/0.4/3.4	1.0/0.6/1.1
Line intensity	2%	–	1.9	–	2.0/2.4/3.3
Pressure broadening coefficient	5%				
Measurement noise	From residuals	0.1	–	0.1/0.1/0.1	–
Total		1.8	2.1	2.3/0.5/3.4	2.2/3.1/3.8

another (e.g. instrumental characteristics). In the opposite, the measurement noise is always random error; the uncertainty of spectroscopic data is systematic and unchanged in time. In the assessment of the measurement accuracy of definite device for understanding its quality, it is more essential to analyse the random errors of the retrieval.

The PROFFIT software allows studying the errors from different sources – instrumental (zero baseline offset, modulation efficiency, phase error of instrumental line shape, measurement noise, line of sight, etc.), spectroscopic (line intensity uncertainty, pressure broadening coefficient), and measurement conditions (temperature uncertainty, solar angle, etc.). We retrieve water vapour, as interfering gas preliminary; that is why we do not include water vapour uncertainty in error budget analysis.

Table 2 demonstrates the estimated errors (random and systematic) of ozone retrieval for total and stratospheric partial columns for a number of the most substantial error sources (for more details, see Virolainen et al. forthcoming). One can see that the major source of systematic error is spectroscopic lines uncertainty. Temperature is the second major source of systematic errors, in particular, in the middle stratosphere. At the same time, temperature uncertainty plays a major role in the random error budget. Schneider and Hase (2008) showed that simultaneous retrieval of temperature and ozone profiles could decrease the random errors of the total ozone retrieval by several times. Thus, we can achieve higher precision of our instrument in ozone retrieval using another measurement scheme.

Table 3 summarizes the results of error budget assessments for the Peterhof FTIR device (Polyakov et al. 2011; Virolainen et al. 2011; Polyakov, Timofeev, and Poberovskii 2013; Ionov et al. 2013) and the error analysis given by other researchers for FTIR devices of the same type (Rinsland et al. 2002, 2003; Wiacek et al. 2007; Mahieu et al. 2008; Hannigan, Coffey, and Goldman 2009). The results of self-calculations are in good

Table 3. Estimated errors of FTIR total columns retrievals of different gases.

Errors (%)	O ₃	HCl	HF	NO ₂
Random	1–2	2–3	2–3	8–18
Systematic	2–3	1–2	1–2	10–30
Total	2–5	2–4	2–4	15–30

agreement with independent error estimations, which confirm the quality of Peterhof FTIR measurements. Further details of FTIR measurements and their errors for different target gases we will discuss later.

3. Satellite data

At the present time, various satellite methods, spectral bands from ultraviolet to radio-waves and a great number of different space-borne instruments are used for global monitoring of the atmosphere and the Earth's surface. Methods differ in accordance with the observing geometry (nadir, limb), with radiance–atmosphere interaction (scattering, emission, absorption, refraction), with radiance source (the Earth's atmosphere, the Sun, the Moon), and so on. Below, the basic characteristics of satellite instruments that we used for the comparison with FTIR ground-based measurements are briefly described.

3.1. ACE

ACE is a Canadian-led mission for atmospheric remote sensing launched on 13 August 2003 into a 74° inclined orbit at 650 km altitude (Bernath et al. 2005). ACE-FTS records solar spectra below 150 km altitude at 0.02 cm⁻¹ spectral resolution (maximum optical path difference of ±25 cm) from 750 to 4400 cm⁻¹. Full resolution spectra are recorded in 2 s with an altitude spacing determined by the scan time, typically 3–4 km. The ACE-FTS instrument has a circular field of view with 1.25 mrad diameter (Boone et al. 2005) and is self-calibrating as linear response photovoltaic detectors are used and low Sun solar occultation spectra are divided by exo-atmospheric solar spectra from the same occultation. The ACE orbit yields solar occultation measurements (85° N–85° S latitude).

3.2. Microwave Limb Sounder (MLS)

MLS is one of the four instruments aboard the Aura satellite, launched on 15 July 2004 into a near polar sun-synchronous orbit at an altitude of 705 km. It measures millimetre and submillimetre emission by scanning the Earth's atmospheric limb every 24.7 s with ~13:45 LT ascending equatorial crossing time, thus providing retrievals of daytime and night-time profiles roughly every 165 km along the suborbital track (Waters et al. 2006). Vertical scans are synchronized to the Aura orbit, leading to retrieved profiles at the same latitude every orbit, with a spacing of 1.5° great circle angle along the suborbital track; the 240 limb scans per orbit provide close to 3500 profiles per day. The vertical retrieval is on a pressure grid with six levels (or pressure surfaces) per decade change in pressure in the stratosphere and with three levels per decade for pressures smaller than 0.1 hPa. MLS data products & data access (2012) from version 2.2 (v2.2) and the recent versions 3.3/3.4 are available from the NASA Goddard Earth Sciences (GES) Data and Information Services Center (DISC).

3.3 Ozone Monitoring Instrument (OMI)

OMI is the other sensor aboard the Earth Observing System (EOS) Aura satellite. It is a nadir-viewing spectrometer which measures the solar radiation backscattered by the Earth's atmosphere and surface in three channels covering the 270–500 nm wavelength range (UV-1: 270–314 nm, UV-2: 306–380 nm, visible: 350–500 nm) with a spectral resolution of about 0.5 nm (Levelt et al. 2006). More details about the instrument and its

scientific objectives can be found in the Science Requirements Document for OMI EOS (<http://aura.gsfc.nasa.gov/>).

3.4. *Global Ozone Monitoring Experiment (GOME)*

GOME is an instrument aboard the European Space Agency's (ESA's) Second European Remote Sensing Satellite (ERS-2), which was launched in April 1995. The main scientific objective of the GOME mission was to determine the global distribution of ozone and several other trace gases (Burrows et al. 1999). GOME was measuring the sunlight scattered from the Earth's atmosphere and/or reflected by the surface in nadir viewing mode in the spectral region 240–790 nm at a moderate spectral resolution of between 0.2 and 0.4 nm. Using the maximum 960 km across-track swath width, the spatial resolution of a GOME ground pixel is $40 \times 320 \text{ km}^2$ for the majority of the orbit and global coverage is achieved in 3 days after 43 orbits.

3.5. *GOME-2*

GOME-2 aboard the MetOp-A satellite, launched in October 2006, is a scanning spectrometer that captures light reflected from the Earth's surface and backscattered by the atmosphere. MetOp-A is flying in a sun-synchronous orbit with ~9:30 LT descending equatorial crossing time and a repeat cycle of 29 days. GOME-2 is a nadir-scanning UV/VIS spectrometer with four main optical channels covering the region from 240 to 790 nm with a resolution between 0.26 and 0.51 nm. The default swath width of the GOME-2 scan is 1920 km, which enables global coverage within 1.5 days (Valks et al. 2009).

3.6. *Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY)*

The SCIAMACHY spectrometer is an atmospheric sensor aboard the European satellite ENVISAT. It was launched in March 2002 as a joint project of Germany, The Netherlands and Belgium. SCIAMACHY was designed to measure sunlight transmitted, reflected, and scattered by the Earth's atmosphere or surface in the ultraviolet, visible, and near-infrared wavelength region (240–2380 nm) at a moderate spectral resolution (0.2–1.5 nm, $\lambda/\Delta\lambda \approx 1000\text{--}10,000$) (Bovensmann et al. 1999). SCIAMACHY was measuring the earthshine radiance in limb and nadir viewing geometries and the solar or lunar light transmitted through the atmosphere observed in occultation. Inversion of the ratio of earthshine radiance and solar irradiance yields information about the amounts and distribution of ozone and many important atmospheric constituents.

4. Results and discussion

For comparing the series of measurements of different remote-sensing systems, we investigated the following statistical characteristics: the mean difference M , the root-mean-square (RMS) difference S , and the standard deviation from the means σ (Equations (1)–(3), respectively).

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

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

$$\sigma = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - y_i - M)^2}, \quad (3)$$

where x_i and y_i are the coincident individual measurements of compared instruments, and N is a number of the coincident days of measurements.

We compared the average daily values of column contents using the individual criteria of spatial and temporal coincidence for each target gas, which depended on the availability of remote-sensing measurements. The obtained differences between data sets are caused by measurement errors of separate instruments as well as by spatial and temporal variabilities of target gas abundances. We can approximate these differences as the measurement error upper bound of considered instruments.

4.1. Ozone, O_3

In this paper, we analyse ozone vertical columns derived from 1190 measured spectra, corresponding to 189 clear-sky days, from April 2009 to March 2012 (Virolainen, Timofeyev, and Poberovsky 2013). For each day, we retrieved ozone columns from individual spectral measurements using the PROFFIT code in several spectral microwindows from 991 to 1013 cm^{-1} (see Table 1), then averaged them, and compared with independent data.

4.1.1. Ozone total column

On the first stage of study, we compared the FTIR measurements of the total ozone column – with the data derived from the standard instrument – Dobson spectrophotometer (Dobson 1957) operating at the closest to FTIR location Voeykovo station (see, e.g. Virolainen et al. 2011 for a detailed analysis). The total ozone measurement errors of Dobson spectrophotometers do not exceed 0.5–1.5%; measurements can be found at WOUDC data centre (World Ozone and Ultraviolet Radiation Data Centre 2012). Due to the participation of Dobson spectrophotometer in a field validation campaign during the considered time period and the requirements of clear-sky conditions for measurements, only 74 coincident days in 2009–2011 are available for comparison of two ground-based devices (see Table 2). The mean relative difference FTIR vs. Dobson amounts +1.4%, standard deviation from mean is less than 3.5%. Taking into account the different locations of two observing stations (opposite sides of Saint Petersburg within a distance of ~50 km), the coincidence of two series of ozone measurements allows estimating FTIR ozone column measurement errors within 1–2%.

Further in this section, we compare ground-based FTIR measurements of ozone columns with satellite measurements. The ozone columns for GOME-2 used here are the overpass Level 2 data (Ozone overpass data based on GOME 2012), where the nearest satellite measurement is indicated, if it is closer than 200 km to Peterhof station. The ozone algorithm retrieval is based on the Differential Optical Absorption Spectroscopy (DOAS) method. Total ozone columns derived from this algorithm have been validated

Table 4. Statistical characteristics of ozone total column comparison.

Devices	Number of days	RMS (%)	Mean (%)	Standard deviation (%)	Correlation coefficient
FTIR-OMI	178	4.5	+3.4	2.9	0.98 ± 0.01
FTIR – GOME-2	95	3.7	+2.2	3.0	0.97 ± 0.01
FTIR-Dobson	74	3.7	+1.4	3.4	0.95 ± 0.01

using ground-based networks (Balis et al. 2007). Error analysis indicates an accuracy and precision of ozone total columns of 3.6–4.3% (Van Roozendael et al. 2004). OMI ozone column data, measured from ground to approximately 80 km, are retrieved using the Total Ozone Mapping Spectrometer (TOMS) algorithm (developed by NASA). The ozone products used in the present study are from the overpass Level 2 Aura/OMI OMTO3 (v8.5) data (DATA/AURA/OMTO3 dataset 2012). The same as for GOME-2, we took for comparison OMI measurements within 200 km from Peterhof station for each day. The ozone total column uncertainty from OMI is estimated to be 3% (Bhartia and Wellemeyer 2002). Furthermore, recent validations of OMI ozone products have been performed (Balis et al. 2007; McPeters et al. 2008).

Table 4 compares the ozone columns from FTIR and OMI/GOME-2 satellite measurements. FTIR vs. OMI (TOMS version 8) data are related to measurements series in 2009–2012, FTIR vs. GOME-2 to 2009–2011. Correlations between ground-based and spaceborne series of ozone column measurements are also depicted in Figure 1 (FTIR vs. OMI – Figure 1(a), FTIR vs. GOME-2 – Figure 1(b)). The mean relative differences of FTIR data are $(+3.4 \pm 2.9)\%$ with OMI and $(+2.2 \pm 3.0)\%$ with GOME-2. Positive signs of mean relative differences, appearing in the comparison between FTIR and UV satellite instruments (GOME-2 and OMI), suggest that the IR ground-based measurements overestimate the ozone total column. This trend confirms the systematic difference between IR and UV measurements, already seen in other papers (see, e.g. Kagawa et al. 2007; Viatte et al. 2011). One can see in Table 4 the strong correlations between FTIR and satellite data for the corresponding measurement period: 0.98 and 0.97 for OMI and GOME-2. The slopes of the linear regressions (see Figure 1) are 0.90 for OMI and 0.93 for GOME-2

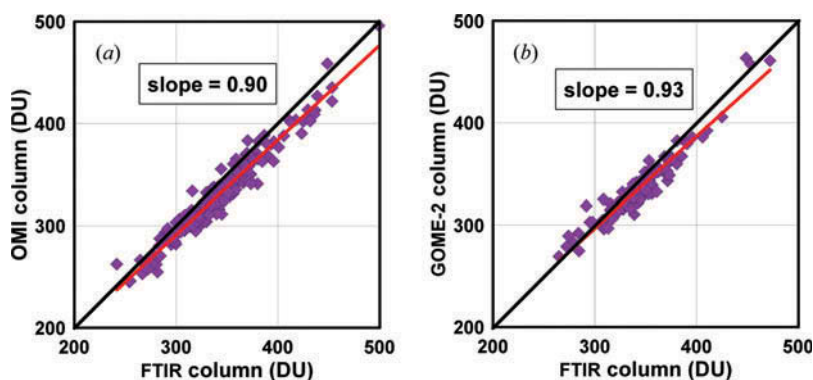


Figure 1. Scatter plot of ozone total columns measured by ground-based FTIR vs. observed OMI (TOMS v.8) (a) and GOME-2 (DOAS) (b).

concerning the comparisons with FTIR, which reflect the overestimation of FTIR ground-based measurements compared to UV satellite, which is larger for larger absolute values of ozone columns.

The differences from linear regression for the considered series of FTIR vs. OMI ozone column measurements are within 5%; for FTIR vs. GOME-2, several cases of satellite ozone column overestimation (up to -9% for ozone column around 300 DU) are observed for the considered period. To conclude, except observed bias, ozone column data derived from FTIR measurements are in good agreement with satellite measurements within the measurement errors of the instrumentation considered.

4.1.2. Ozone stratospheric column

To study vertical resolution of the FTIR ozone retrieval method, averaging kernels (Rodgers 2000) have been analysed (Virolainen and Timofeyev 2008). The full width at half maximum of the rows of the averaging kernel gives the vertical resolution, which is in the order of 9–15 km for the retrieved ozone in this study. Furthermore, the trace of the averaging kernel matrix, the so-called degree of freedom for signals (DOFS), provides another useful measure of retrieval quality of target species. The independent pieces of information retrieved from the observed spectra in the ozone spectral microwindows under the given retrieval strategy (see Table 1) contain from 2.9 up to 4.1 DOFS depending on the conditions of measurements. This provides a minimum of three independent layers on average, which approximately covers the troposphere and two altitude ranges in the stratosphere.

For comparison of the stratospheric column derived from ground-based FTIR, we use MLS satellite ozone VMR profiles (Level 2 Version 3.3 Standard Atmospheric Products). We selected satellite profiles within 500 km radius with the centre in Peterhof station, averaged and integrated by the height to get stratospheric column amounts. For more details on the accuracy of MLS ozone measurements, see the MLS validation papers (e.g. Froidevaux et al. 2008) as well as references therein. Table 5 presents the statistical characteristics of the comparison of FTIR ozone column daily series for the stratospheric layer 9–41 km and collocated MLS data (overall and for four seasons independently). The largest value of relative mean difference between both types of measurements of $(3.2 \pm 5.3)\%$ (overestimation of the FTIR stratospheric columns) is observed only for winter conditions. This bias can be explained by the different air masses in the field of

Table 5. Statistical characteristics of ozone stratospheric column (9–41 km) comparison (FTIR vs. MLS).

Season (days)	Device	Mean/variability, DU	RMS (%)	Mean (%)	Standard deviation (%)	Correlation coefficient
Winter (30)	FTIR	338 ± 45	6.1	+3.2	5.3	0.92 ± 0.03
	MLS	327 ± 44				
Spring (58)	FTIR	341 ± 34	5.2	-1.0	5.1	0.87 ± 0.03
	MLS	344 ± 35				
Summer (72)	FTIR	287 ± 24	3.6	-0.4	3.6	0.90 ± 0.02
	MLS	288 ± 23				
Autumn (21)	FTIR	261 ± 25	5.6	0.0	5.6	0.82 ± 0.07
	MLS	261 ± 24				
All (181)	FTIR	310 ± 44	5.0	+0.1	5.0	0.94 ± 0.01
	MLS	310 ± 43				

view of two instruments in winter time when the sun is often located near the horizon. In other seasons, no statistically significant biases are observed. RMS difference for FTIR vs. MLS for all seasons amounts within 3.6–6.1% (smaller values for summer, larger for winter series). The correlations between FTIR and MLS data for the corresponding measurement period vary from 0.82 (for autumn) up to 0.92 (for winter).

Figure 2 depicts the comparisons of daily time series of ozone columns in two stratospheric layers 9–20 km (Figure 2(b)) and 20–41 km (Figure 2(a)) of FTIR and MLS instruments. There is no statistically significant mean difference observed for time series measured by different instruments for both layers. Total mean difference for FTIR vs. MLS equals $(-0.3 \pm 12.9)\%$ and $(+0.3 \pm 6.0)\%$ for 9–20 km and 20–41 km layers, respectively. The correlation coefficients of 0.90 (for 9–20 km) and 0.82 (for 20–55 km) suggest a strong relationship between two considered data sets. One can see in Figure 2 the seasonal dependence of the relative difference: for winter months, FTIR overestimates ozone columns in the upper stratosphere and underestimates those in summer months. The opposite situation is observed for the lower stratosphere. It can be explained by the seasonal changes in ozone vertical. Overall, the comparison of ground-based and satellite

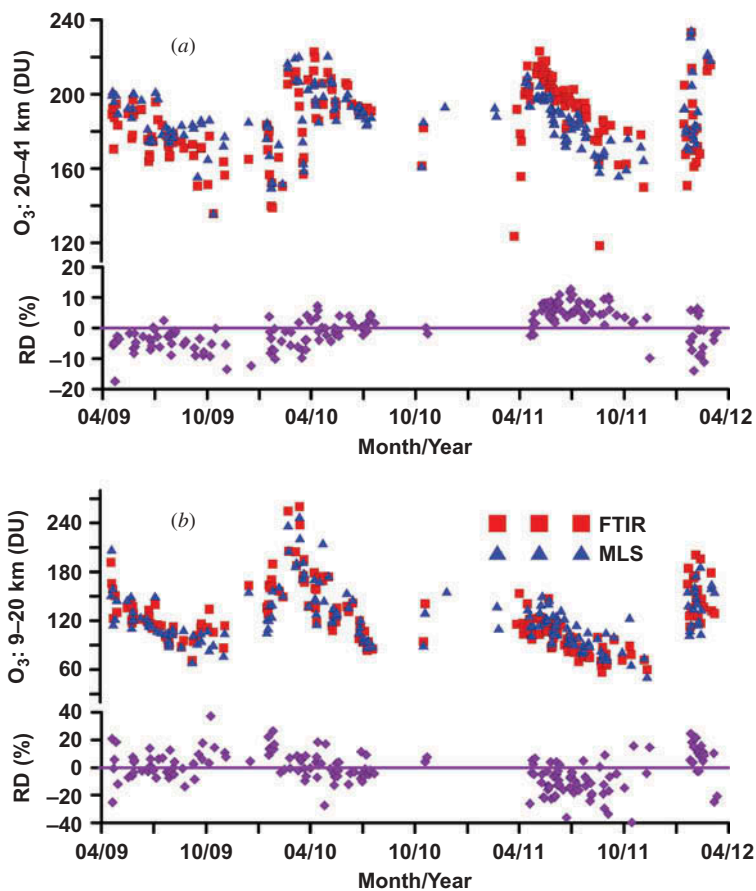


Figure 2. Time series of ozone columns in two stratospheric layers 9–20 km (b) and 20–41 km (a) derived from FTIR (red squares) and from MLS (blue triangles). Relative differences (RD) in % (purple diamonds) are also indicated.

measurements demonstrates the larger overestimation of FTIR retrievals vs. satellite data for larger absolute values of ozone columns.

To summarize the discussion in general, good agreement is observed for collocated FTIR and satellite ozone columns measurements; in most cases, the mean and RMS differences amount within measurement errors of the instruments compared. Some of the differences between FTIR and satellite observations may be caused by ozone spatial and temporal variations, even though there is no large difference in space and time for the criteria used to determine coincident measurements. Furthermore, different spectroscopic windows used by FTIR and other instruments might also have some contribution to the observed differences.

4.2. NO₂

Ionov et al. (2013) considered the FTIR ground-based measurements of NO₂ columns at Peterhof station between April 2009 and October 2011. This paper extends the analysis up to May 2012. We applied SFIT2 software to 1493 solar absorption spectra (recorded during 233 days of observation) in a 2914.59–2914.71 cm⁻¹ microwindow (see Table 1). Due to the weak absorption of NO₂ in the IR spectral range, statistical errors of NO₂ column measurement are large, varying from 8 up to 18%, in averaged amount within ~8%. Systematic errors of FTIR NO₂ measurement may reach 30% and be caused by the uncertainty of the NO₂ vertical profile (Rinsland et al. 2003). Daily averaged NO₂ values are calculated with the weights related to random errors of individual measurements. To avoid the influence of diurnal variations of NO₂ stratospheric column on the averaged values, individual measurements are adjusted to the local noon time before averaging by means of the photochemical model as described by Ionov et al. (2008). Standard deviations of the daily means amount within (4.1 ± 1.6)% on average.

NO₂ total columns derived from FTIR measurements are compared with those retrieved from the coincident ground-based and satellite visible (VIS) scattered radiation spectra. In these measurements, NO₂ columns are retrieved from spectra recorded in the 400–450 nm range with resolution better than ~1 nm using the traditional DOAS algorithm (Platt and Stutz 2008). Thus, daily averaged FTIR data are compared with ground-based VIS twilight measurements (Poberovskii et al. 2007) and satellite data obtained from GOME, SCIAMACHY, OMI, and GOME-2 instruments. SCIAMACHY and GOME-2 columns are taken within 200 km radius from Peterhof station, OMI – 30 km radius, GOME measurements, due to its low horizontal resolution, may present information on the air masses of hundreds of kilometres away from Peterhof. The series of independent retrievals selected for the comparison are also normalized to local noon measurements as FTIR data. Statistical characteristics of NO₂ total columns comparison are given in Table 6.

Table 6. Statistical characteristics of NO₂ total columns comparison of FTIR retrieval vs. other instruments.

Device	Mean (%)	σ (%)	Correlation coefficient
VIS ground-based	+9	15	0.82 ± 0.02
ERS*2 GOME	+6	31	0.41 ± 0.07
Envisat SCIAMACHY	+9	16	0.82 ± 0.02
Aura OMI	+9	14	0.90 ± 0.01
MetOp GOME-2	+8	14	0.82 ± 0.02

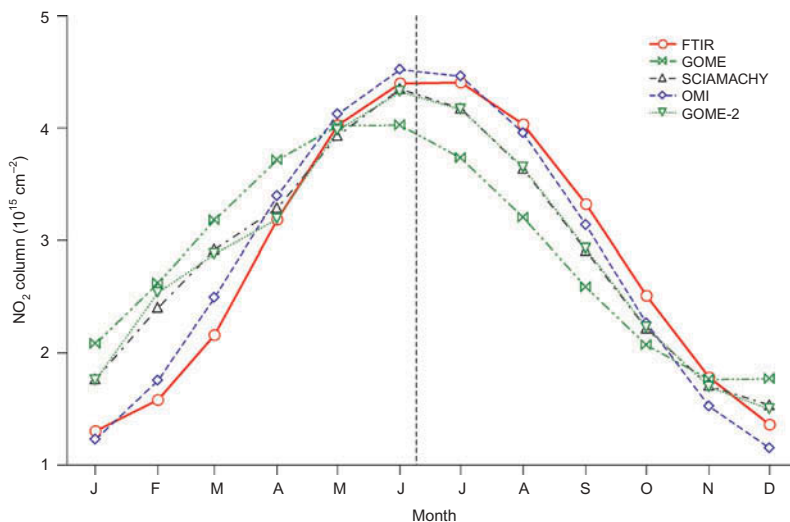


Figure 3. Seasonal cycle of NO_2 monthly means column measurements. FTIR data are corrected on NO_2 tropospheric column amount ($0.4 \times 10^{15} \text{ cm}^{-2}$).

All measurements except GOME are in good coincidence with FTIR data: mean differences equal +9%, standard deviation from mean (σ) amounts within 14–16%. Systematic overestimation of FTIR measurements may be caused by different sensitivity of remote-sensing instruments to variations in vertical profiles of NO_2 and incorrect *a priori* profiles taken in the retrieval algorithms. Comparison of FTIR vs. GOME for NO_2 column retrievals gives +6% of relative mean difference and up to 31% of σ difference. The large values of σ are mainly due to the low spatial resolution of GOME measurements.

The comparison of monthly means (Figure 3) demonstrates good coincidence of different types of retrievals. Bias of $0.4 \times 10^{15} \text{ cm}^{-2}$ related to tropospheric column amount is subtracted from FTIR measurements. In general, all presented curves can be approximated by the sinusoid with maximum amplitude on 22 of June (except GOME with maximum in May), which corresponds to the maximum daylength.

4.3. HF

In this section, the results of 4-year HF column retrievals from FTIR measured spectra at Peterhof station are analysed and compared with time series of ACE-FTS measurements. The whole number of FTIR spectra recorded from April 2009 up to April 2013 totals 2110. SFTI2 code is applied to derive HF columns using the Optimal Estimation Method in several microwindows of $4000.8\text{--}4110.1 \text{ cm}^{-1}$ spectral range (see Table 1). The errors of single HF column measurement vary from 1% to 5% (Polyakov et al. 2011). Derived columns are averaged for each day, which performs 303 daily averaged measurements. Mean daily variability for considered series amounts to 4.3%. This value can be considered as an upper bound of random measurement error. The standard deviation for the whole series of HF measurements totals 20% with a strong maximum in early spring caused by the dynamical processes in the stratosphere in that period – intrusion of polar stratospheric air masses. The experimental and model estimations of this quantity vary from ~10–15% to 30–40% at different latitudes (see, e.g. Rinsland et al. 2002; Mahieu et al. 2008).

Table 7. Statistical characteristics of HF total columns comparison of coincident FTIR retrievals vs. two versions of ACE-FTS data (absolute values are in $\times 10^{15} \text{ cm}^{-2}$ units).

ACE version	Mean FTIR	Mean ACE	Mean difference	RMS difference	Standard deviation
2.2	1.70 ± 0.13	1.90 ± 0.20	-0.20 (12%)	0.22 (13%)	0.11 (6%)
3.0	1.83 ± 0.56	2.06 ± 0.48	-0.23 (12%)	0.28 (16%)	0.20 (11%)

The ACE-FTS instrument measuring the gas composition of the atmosphere is based on the sun occultation method (Wolff et al. 2008). This method permits ~ 28 measurements per day, the latitude of which slowly changes during the year. Due to specific features of the occultation method and the orbital parameters of the ACE satellite, the number of coincident days of measurements within 500 km distance from Peterhof is very few.

The results of comparison of FTIR HF columns vs. ACE-FTS HF columns (two versions of the retrieval algorithm) for coincident days of measurements in the whole period of FTIR observations are shown in Table 7. It should be noted that for ACE-FTS data version 2.2 and 3.0 sets of coincident days are different (8 days for v.2.2 and 7 days for v.3.0). It is well seen that both versions of ACE data overestimate FTIR retrievals with a bias of 12%. RMS difference FTIR vs ACE amounts within 13% and 16% for v.2.2 and v.3.0, respectively. The variability of the derived HF columns from ACE measurements is larger for v.3.0 (23%) vs v.2.2 (11%). The same increase is observed in FTIR HF column variability (30% vs. 8%). This feature may be caused by the difference in selected sets of measurements. Mahieu et al. (2008) demonstrated that for five considered NDACC stations in the northern hemisphere, ACE HF columns overestimate FTIR data by 6.5–12.3%.

4.4. HCl

HCl columns shown in this paper are derived from 1141 spectra recorded in 214 clear-sky days, from April 2009 to March 2012, at Peterhof station (Polyakov, Timofeev, and Poberovskii 2013). HCl columns are obtained with SFIT2 code in several spectral microwindows from 2727 up to 2926 cm^{-1} recommended for HCl retrievals by the NDACC society (see Table 1). For each day of measurements, single retrievals are averaged and compared with MLS and ACE-FTS satellite data. The optimal estimation method is used for the retrieval of HCl profiles with given *a priori* variability of 20% of VMR in each atmospheric level. Derived profiles are integrated to receive HCl column amounts. The estimated random and systematic errors for single HCl column retrieval do not exceed 3.8% and 4.5%, respectively.

The selection of HCl column measurements, performed with the ACE-FTS instrument within a radius of 500 km from Peterhof, provides a sample of 63 retrievals for the duration of FTIR observations. The ACE-FTS measurements, generally, are stopped at heights below 10–15 km due to the presence of clouds and high optical depth along tangent paths. Estimates show that the contribution of the HCl profile at heights below 10–15 km to column content is quite high and reaches $1.5 \times 10^{15} \text{ cm}^{-2}$. Therefore, to get HCl columns from ACE-FTS measurements, the vertical profiles are additionally constructed from below using the climatically mean WACCM profile for Saint Petersburg.

Comparing FTIR and ACE measurements, we found that FTIR data slightly overestimate those of ACE data for the period; means total $(4.29 \pm 0.53) \times 10^{15} \text{ cm}^{-2}$ vs. $(4.15 \pm 0.37) \times 10^{15} \text{ cm}^{-2}$, respectively. The difference in the variability may be due to the different data sets of satellite and ground-based measurements as well as due to the large-

scale horizontal averaging of satellite data. The comparison of the data for 9 coincident days of measurement gives relative mean difference in FTIR vs. ACE of -8% and RMS of 10.4% . The correlation coefficient of (0.78 ± 0.14) suggests a strong relationship between two data sets. As was shown by Mahieu et al. (2008), the mean difference of ACE vs. FTIR (seven NDACC stations in northern hemisphere) varies from 2.2% to 15.5% in HCl column contents.

The MLS instrument determines the vertical profiles of HCl VMR from the microwave measurements of the thermal emission of the horizon of Earth and performs several orders of magnitude more measurements during the day than the ACE-FTS instrument (Waters et al. 2006). In particular, analysis of MLS data shows that for the period of observation considered, 4049 measurements were performed during daytime within the same radius of 500 km from Peterhof. MLS HCl column mean equals $(4.42 \pm 0.55) \times 10^{15} \text{ cm}^{-2}$, which is higher than FTIR and ACE means by 3% and 6.3% , respectively. It should be noted that the seasonal cycle for both types of measurements is the same, but MLS measurements overestimate HCl columns in the second half of each year. A statistical analysis of 141 cases of coincident measurements shows relative mean difference of -4.5% for FTIR vs. MLS retrievals. The RMS difference for this comparison amounts 11.9% . The bias found in the comparison of these methods may be caused by using the constant HCl VMR tropospheric profiles in MLS retrievals.

5. Conclusions

In this study, we compared the ground-based FTIR measurements performed at Peterhof station (59.82° N , 29.88° E) with high-resolution Bruker 125 HR spectrometer with O_3 , NO_2 , HF, and HCl columns derived from various satellite instruments. We analysed the FTIR spectra with the SFIT2 inversion code using OEM for HF, HCl, and NO_2 total columns retrieval and PROFFIT inversion code using the Phillips–Tikhonov approach for ozone content retrievals. The mean relative statistical errors of FTIR single measurement total $1\text{--}2\%$ for ozone, $8\text{--}18\%$ for NO_2 , $1\text{--}5\%$ for HF, and $2\text{--}5\%$ for HCl depending on the measurements conditions.

We derived the ozone columns for 189 days, from April 2009 to March 2012, and showed that FTIR data overestimate satellite measurements with mean relative differences of $(+3.4 \pm 2.9)\%$ vs. OMI and of $(+2.2 \pm 3.0)\%$ vs. GOME-2 data for the days of measurements considered. We observed the strong correlations between FTIR and satellite data: 0.98 and 0.97 for OMI and GOME-2, respectively. We compared the stratospheric ozone columns with MLS data and obtained no statistically significant bias between two series of measurements. RMS differences for FTIR vs. MLS measurements amount to within $3.6\text{--}6.1\%$ (smaller values for summer, larger for winter series). Mean differences for FTIR vs. MLS equal $(-0.3 \pm 12.9)\%$ and $(+0.3 \pm 6.0)\%$ for $9\text{--}20 \text{ km}$ and $20\text{--}41 \text{ km}$ layers, respectively. The correlation coefficients of 0.90 (for $9\text{--}20 \text{ km}$) and 0.82 (for $20\text{--}55 \text{ km}$) suggest a strong relationship between the two data sets considered.

We retrieved NO_2 stratospheric columns from FTIR spectra for 233 days of observation, from April 2009 to May 2012, and compared them with satellite data obtained from GOME, SCIAMACHY, OMI and GOME-2 instruments. All measurements except GOME are in good coincidence with FTIR data: mean differences equal $+9\%$, standard deviation from mean amounts within $14\text{--}16\%$. Systematic overestimation of FTIR measurements may be caused by different sensitivity of remote-sensing instruments to variations in vertical profiles of NO_2 . Comparison of FTIR vs. GOME for NO_2 column retrievals gives

+6% of relative mean difference and up to 31% of standard deviation (σ). The large values of σ are mainly due to the low spatial resolution of GOME measurements.

We derived HF total columns for 303 days from April 2009 to April 2013 and compared them with ACE-FTS columns (two versions of the retrieval algorithm) for coincident days of measurements (8 days for v.2.2 and 7 days for v.3.0). Both versions of ACE data overestimate FTIR retrievals with a bias of 12%. RMS difference FTIR vs. ACE amounts within 13% and 16% for v.2.2 and v.3.0, respectively.

HCl total columns retrieved for 214 days, from April 2009 to March 2012, were compared with ACE-FTS and MLS data. The comparison of the data for 9 coincident days of measurement gives relative mean difference in FTIR vs. ACE of -8% and RMS of 10.4% . The correlation coefficient of (0.78 ± 0.14) suggests strong relationship between the two data sets. The statistical analysis of 141 cases of coincident FTIR-MLS measurements shows a relative mean difference of -4.5% for FTIR vs. MLS retrievals. RMS difference for this comparison amounts 11.9% . The bias found in the comparison of these methods may be caused by using the constant HCl VMR tropospheric profiles in MLS retrievals.

Resuming the discussion, we can say that at Peterhof station satellite measurements of ozone and NO_2 column amounts underestimate those obtained from FTIR ground-based measurements (OMI and GOME-2 for ozone; OMI, GOME, GOME-2, and SCIAMACHY for NO_2). At the same time, for HF and HCl column retrievals satellite measurements overestimate ground-based measurements (ACE for HF; ACE and MLS for HCl). For stratospheric ozone columns (9–41 km), there is no observed mean difference between MLS and FTIR measurements.

Based on the current study, we conclude that the FTIR observing system of Peterhof station is well suited for the monitoring of stratospheric gaseous composition and can be very useful for validating and complementing satellite data in the Saint Petersburg region.

Acknowledgement

Used devices for ground-based FTIR measurements belong to the SPBU Resource Centre 'Geomodel'.

Funding

The experimental part of this study was fulfilled with the partial financial support of Saint Petersburg State University [grant 11.37.28.2011], as well as of Russian Foundation for Basic Research [grant 05–12–00596]. The processing and analysis of data were performed with financial support of Russian Science Foundation [grant number 14-17-00096].

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