The study of ozonosphere trace gases near St. Petersburg on the basis of FTIR solar spectra measurements

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Abstract

Direct solar spectra measured at St. Petersburg State University (59.88N, 29.82E) in 2009-2012 by ground-based FTIR spectrometer with high spectral resolution (0.005 cm^{-1}) have been analyzed.

Total columns of ozone and ozonosphere trace gases ($ClONO_2$, HCl, HNO_3) have been retrieved using PROFFIT 9.6 and SFIT v3.92 software.

Time series of the obtained for the first time in Russia $ClONO_2$ abundances have been compared to several NDACC stations data.

Evolution of changes in ozonosphere near St. Petersburg have been analyzed in complex through the dynamical (polar vortex intrusions) and chemical processes consideration on the example of winter 2009-2010.

Measurements

Table 1. Conditions of measurements

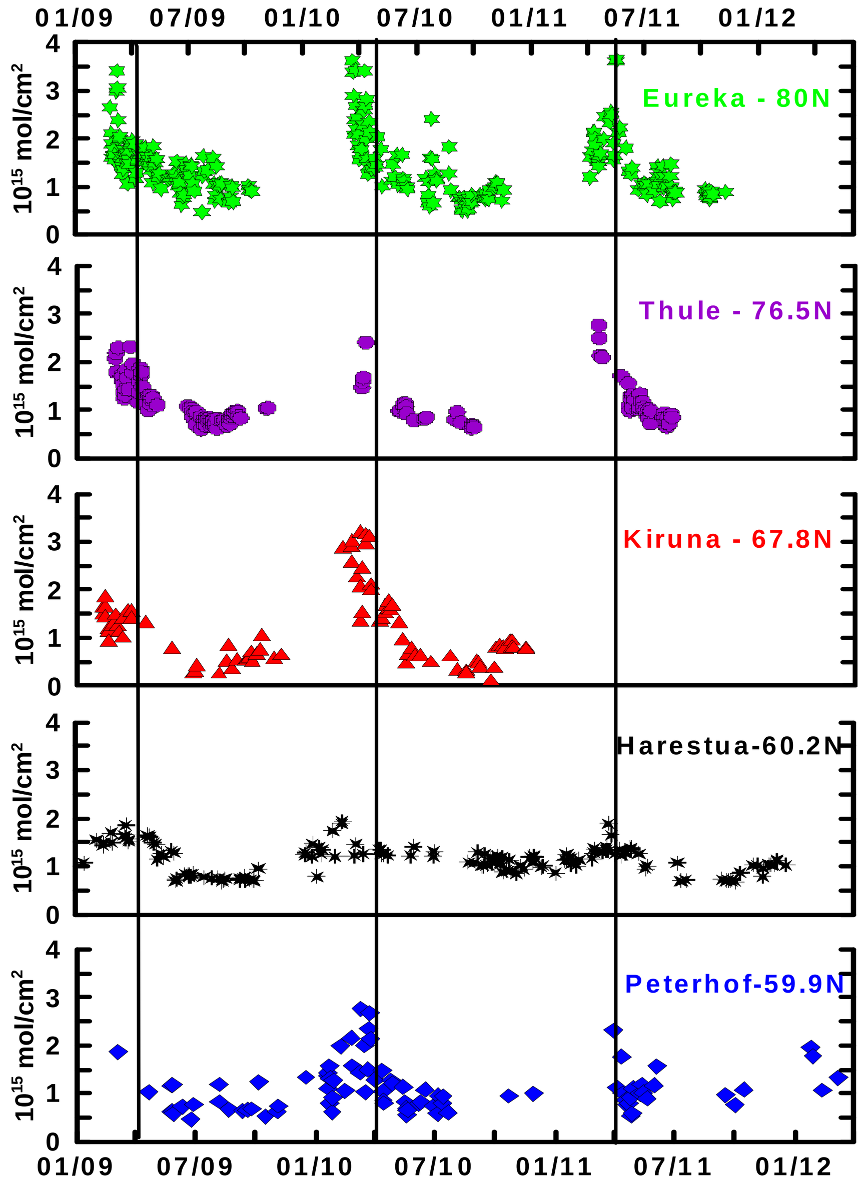
Instrumentation	FTIR-spectrometer Bruker 125HR
Spectral resolution	~0.005 cm^{-1}
Location	Peterhof - St. Petersburg (59.88N, 29.82E)
Time series	April 2009 - March 2012

Table 2. Retrieval features

Measured gases	Spectral windows, cm^{-1}	Random measurement error	Influenced gases	Software
O_3	991.25-993.80 1001.47-1003.04 1005.00-1006.90 1007.35-1009.00 1011.15-1013.55	1-2% [1]	H_2O, CO_2, C_2H_4	PROFFIT 9.6
HNO_3	867.00-869.60 872.80-875.20	1-2% [2]	H_2O, CO_2, C_2H_6	PROFFIT 9.6
$ClONO_2$	779.0-779.8 780.0-780.3 780.3-781.3	20-30%	H_2O, CO_2, O_3, HNO_3, C_2H_2	PROFFIT 9.6
HCl	2925.75-2926.00 2727.73-2727.83 2775.70-2775.80 2925.80-2926.00	2-5% [3]	CH_4, H_2O	SFIT2 v3.92

$ClONO_2$ column retrieval

Fig.1. $ClONO_2$ time series (01/2009-03/2012) at Peterhof and at several Northern Hemisphere NDACC stations.



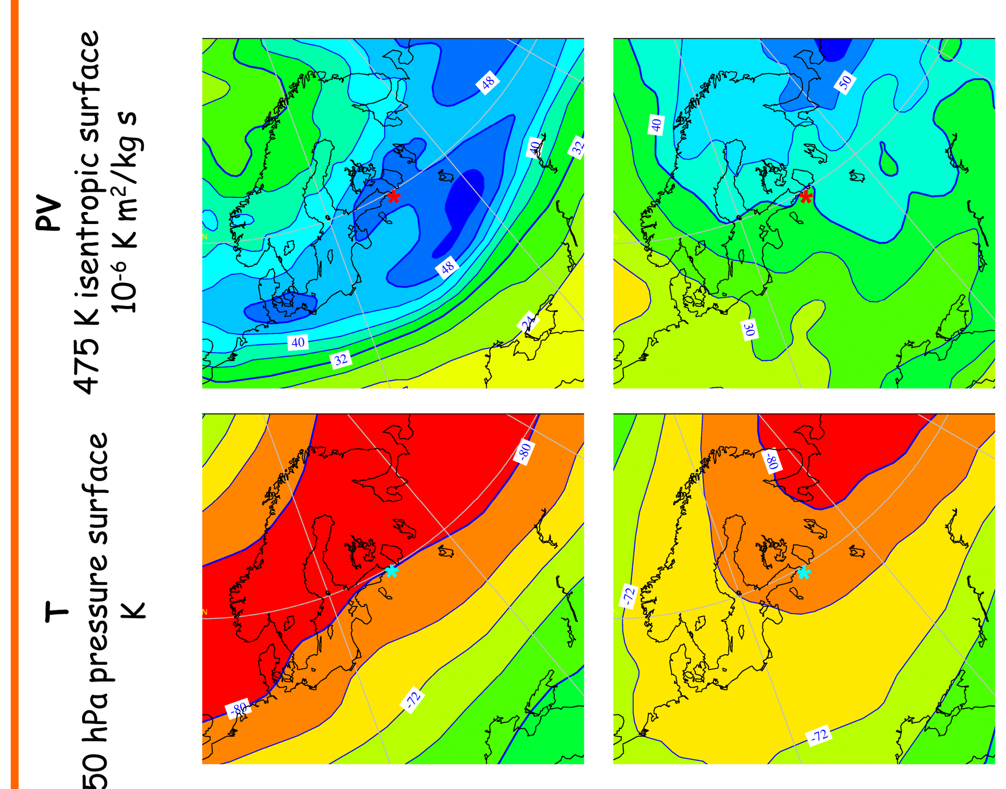
$ClONO_2$ column content have the same seasonal cycle with maximum in early spring at all stations. Amplitude of variability depends on the location of station.

Ozonosphere near St. Petersburg, winter 2009-2010

Changes in ozonosphere composition

- Dynamics –transportation of air masses (global circulation, polar vortex intrusion, etc.)
- Chemical reactions (Photolysis, heterogeneous reactions, catalytic cycles)

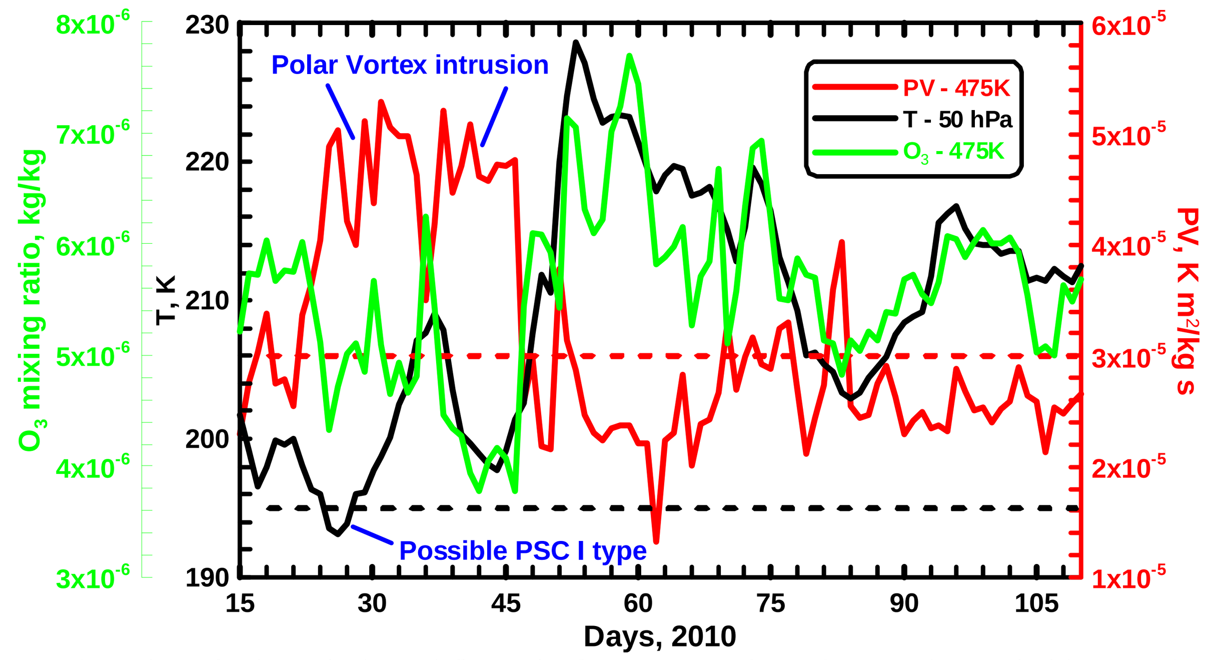
Fig. 2. ECMWF data: potential vorticity PV, temperature T (red or blue star on panels – location of Peterhof)



Day 26 (26.01.2010) Day 28 (28.01.2010)

PV – dark blue and T – red: higher values of a parameter

Fig. 3. PV, T and O_3 evolution during winter 2009-2010 near St. Petersburg-Peterhof (ECMWF data)



In days 15-20, 47-54, 68-86 Peterhof was near the edge, in days 21-46 - inside and other days – outside the polar vortex.

In days 25-27 there were conditions for PSC I type formation.

In days 47-54 – stratospheric warming was observed.

Strong correlations between T and O_3 mixing ratio were observed for most of the days except those with extremely low temperature in polar vortex (15-35).

Ozone loss in chemical reactions

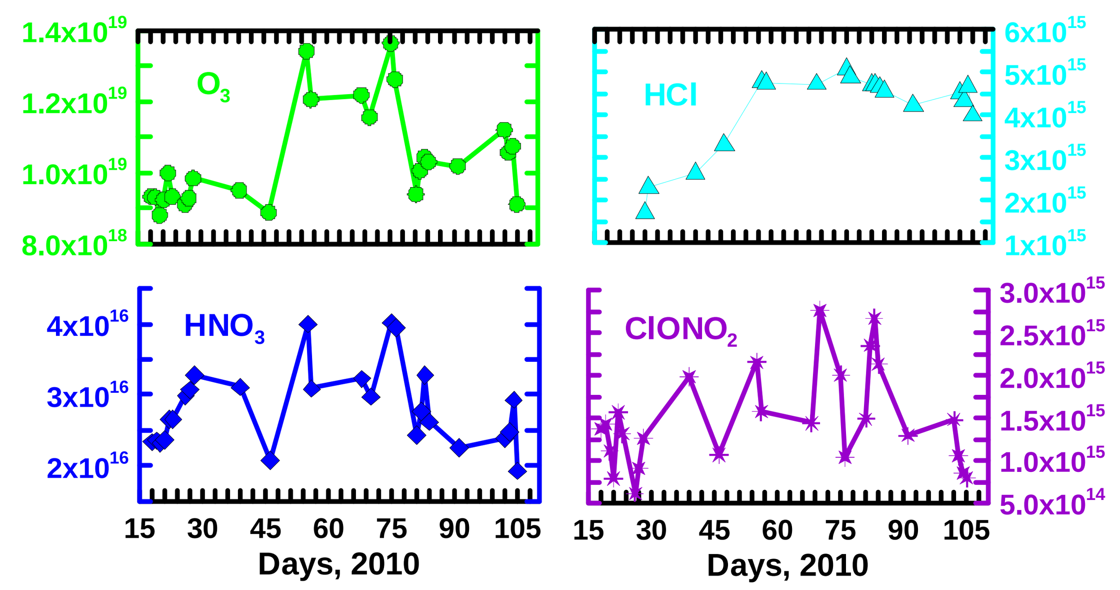
1. Chapman cycle
2. Catalytic cycles (X- free radicals, i.e. H, OH, NO, Cl or Br):
   $X+O_3 \rightarrow XO+O_2$
   $XO+O \rightarrow X+O_2$

Net: $O+O_3 \rightarrow O_2+O_2$

HCl and $ClONO_2$ are inactive reservoirs of inorganic chlorine, HNO_3 is a reservoir of nitrogen oxides. Gas-phase reactions inactive radicals. HCl and HNO3 can be removed to troposphere, $ClONO_2$ can be photo-dissociated back to active clorine.

Heterogeneous reactions on PSC or stratospheric aerosol particles convert reservoirs molecules back to radicals. Sunlight and low temperatures are required for these reactions [4].

Fig.4. Observed by ground-based FTIR spectrometer abundances of O_3, HNO_3, HCl and $ClONO_2$ (mol/cm²) in atmosphere near St. Petersburg



In days 15-45 low abundances of O_3 were observed together with low abundances of reservoir molecules. St. Petersburg these days was in polar vortex air masses. In 25-27 days lowest temperatures were observed and lowest $ClONO_2$ columns – chlorine activation may took place. After short warming on 46 day – low O_3 together with low HNO_3 columns were observed – denitrification of gaseous HNO_3 may took place. In stratospheric warming period 47-54 – abundances of all considered gases increased – this was a period of gas-phase reactions and inactivation of free radicals. The cooling of stratosphere in 78-86 days led to decrease of ozone and HNO_3 columns.

References:

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Acknowledgements:

ECMWF ERA-Interim data used in this study have been obtained from the ECMWF data server.

This work has been partly supported by grants of Russian Foundation for Basic Research 12-05-00596 and 12-05-00445 and SPbSU Scientific Research Projects 11.31.547.2010 and 11.37.28.2011.