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Total columns of freons retrieved from ground-based IR solar spectra measurements near Saint Petersburg, Russia

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Measurements of the atmospheric total columns (TCs) of trichlorofluoromethane CCl_3F (CFC-11), dichlorodifluoromethane CCl_2F_2 (CFC-12), and chlorodifluoromethane CHClF_2 (HCFC-22) at the NDACC station St. Petersburg are considered. These gases are the most common representatives of a group of aliphatic organic compounds often called by the DuPont brandname "Freons". Since the 30-ies of the last century, they have been used in industrial applications as refrigerants and propellants. Due to their destructive effect on the ozone layer the production of CFC-11 and CFC-12 has been phased out under the Montreal Protocol entered into force in 1989, which led to the beginning of a decrease in their content. Nevertheless, they are still one of the major anthropogenic sources of active chlorine that destroys ozone in the stratosphere. HCFC-22 became a replacement for the most dangerous for ozone layer freons, but later it was also recognized as a dangerous compound for stratospheric ozone. Nowadays, the production and consumption of HCFC-22 are reduced and it is planned to be completely phased out. Therefore, the monitoring the content of freons in the atmosphere is very important.

Although the content of freons is measured by satellite methods and the sampling method, only the ground-based IR method based on the measurement of IR solar radiation allows obtaining TCs of freons.

A technique for ground-based measurements of the TCs of CFC-11, CFC-12, and HCFH-22 has been developed. The technique is based on the ground-based measurements of solar IR spectra by IFS125HR instrument. For the processing of spectra, the SFIT4 software is used. The analyzed spectral windows are: $1160 - 1162 \text{ cm}^{-1}$ for CFC-12, $828.75 - 829.4 \text{ cm}^{-1}$ for HCFC-22, and $830 - 860 \text{ cm}^{-1}$ for CFC-11. Due to the wide spectral interval for CFC-11 retrieval, the preliminary measured spectral transmission function of the instrument filter, the water vapor continuum, and the absorption of radiation by an ice on the MCT detector are taken into account as well. Systematic and random errors of TCs retrieval are estimated as 7.4% and 2.9% for the CFC-11 TCs, 5.0% and 3.7% for the CFC-12 TCs, and 2.0% and 2.7% for the HCFH -22 TCs.

Estimates of TCs above Saint Petersburg have been obtained using the developed technique for the period of 2009 – 2019. The variability during a day is of 0.8, 0.9, and 3.7 %, the total variability for 2009 – 2019 is of 3.7, 2.4 and 5.6%, for CFC-11, CFC-12 and HCFC-22, respectively. Trend estimates of CFC-11, CFC-12 and HCFC-22 for 2009 –2019 are $-0.31 \pm 0.07\%$, $-0.45 \pm 0.06\%$ and $+2.2 \pm 0.14\%$, respectively, which are consistent with data from other authors.

In recent years, a tendency toward a decrease of HCFC-22 TCs in the atmosphere above St. Petersburg has been observed, that can be associated with the restriction of HCFC-22 production and use.

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