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Trends in atmospheric halogen containing gases since 2004

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ABSTRACT

The changes in the atmospheric concentration of 16 halogenated gases in the atmosphere have been determined using measurements made by the Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS). ACE-FTS has been used to measure the change in concentration between 2004 and 2010 of CCl_4, CF_4, CCl_3F (CFC-11), CCl_2F_2 (CFC-12), $C_2Cl_3F_3$ (CFC-113), CH_3Cl, $ClONO_2$, COF_2, $COCl_2$, COClF, CHF_2Cl (HCFC-22), CH_3CCl_2F (HCFC-141b), CH_3CClF_2 (HCFC-142b), HCl, HF and SF_6 between 30°N and 30°S. ACE-FTS measurements were compared to surface measurements made by the AGAGE network and output from the SLIMCAT three-dimensional (3-D) chemical transport model, which is constrained by similar surface data. ACE-FTS measurements of CFCs show declining trends which agree with both AGAGE and SLIMCAT values. There are problems with the ACE-FTS retrievals of CFC-113 and HCFCs, with work currently ongoing to correct these problems. At lower altitudes the volume mixing ratio (VMR) of these species increase with altitude. This is due to problems with the retrievals at high beta angle (the angle between the orbital plane and the Earth–Sun vector). Although some of the retrievals have problems, we are confident that the trends are generally reliable. The concentrations of HCFCs appear to be increasing with ACE-FTS, SLIMCAT and AGAGE all showing positive trends. ACE-FTS measurements of the decomposition products (COFCl and $COCl_2$) do not show any significant trends. SLIMCAT data show a negative trend for COFCl which corresponds to the decrease in CFC-11, its assumed major source, during this time. COF_2 measurements from ACE-FTS show an increasing trend, while SLIMCAT shows a decreasing trend again linked to its assumed production from CFCs. $ClONO_2$ is highly photosensitive, thus the ACE-FTS occultations have been divided into local morning and evening occultations. Evening measurements of $ClONO_2$ show a decreasing trend in VMR, while morning measurements show an increasing trend. The reason for this difference is not understood at this time. The SLIMCAT output used in this study was not saved as local sunrise and sunset: therefore, only 24 h mean fields are available for $ClONO_2$. These SLIMCAT data show a decreasing trend. SLIMCAT and ACE-FTS both show an increasing trend in the VMR of HF and a decreasing trend in the VMR of HCl. These results illustrate the success of the Montreal Protocol in reducing ozone depleting substances. The reduction in anthropogenic chlorine emissions has led to a decrease in the VMR of stratospheric HCl.

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The replacement of CFCs with HCFCs has led to an increase in the VMR of HF in the stratosphere. As chlorine-containing compounds continue to be phased out and replaced by fluorine-containing molecules, it is likely that total atmospheric fluorine will continue increasing in the near future.

1. Introduction

In 1974 Molina and Rowland [1] suggested that chlorofluorocarbons (CFCs) would lead to the destruction of stratospheric ozone. It was the dramatic discovery of the Antarctic ‘ozone hole’ in 1985 [2] that illustrated the destructive power of long-lived halogenated gases. At this time, CFCs were widely used for a variety of applications such as in air conditioners and as foam blowing agents. The 1987 Montreal Protocol on substances that deplete the ozone layer and its subsequent amendments and adjustments [3] have phased out the production of CFCs and halons. As a temporary measure, CFCs have been replaced by hydrochlorofluorocarbons (HCFCs) that have shorter atmospheric lifetimes because they react with the OH radical. However, HCFCs still destroy stratospheric ozone and they are in turn being phased out and replaced by hydrofluorocarbons (HFCs). Because they contain no chlorine, HFCs have no direct chemical effect on stratospheric ozone. It is the UV photolysis of halogenated source gases in the stratosphere that releases reactive F, Cl and Br atoms, but F rapidly forms the very stable HF molecule so only Cl and Br atoms lead to ozone destruction. Iodine-containing gases would also destroy stratospheric ozone, but these molecules have such a short atmospheric lifetime that they do not reach the stratosphere [4].

Although HFCs do not destroy stratospheric ozone they are very powerful greenhouse gases, as are CFCs and HCFCs. Indeed, taken as a group, halocarbons are about equal to tropospheric ozone in terms of a positive anthropogenic radiative forcing, and only CO_2 and CH_4 are more important [5]. The Montreal Protocol has been successfully implemented since 1987 with the aim of eradicating the use of substances which are damaging to the ozone layer. It has fortuitously had a larger impact on reducing greenhouse gas emissions than the first commitment period of the Kyoto Protocol [6]. However, the Montreal Protocol has also led to rapidly increasing concentrations of HFCs that have serious implications for climate change. Velders et al. [7] predict that global-warming-potential-weighted HFC emissions in 2050 could be 9–19% of global CO_2 emissions.

It is crucial to assess the performance of the Montreal Protocol in reducing the concentrations of ozone depleting substances (ODSs) and to monitor the recovery of the ozone layer. Therefore, every 4 years the World Meteorological Organisation (WMO) and the United Nations Environmental Programme (UNEP) publish a report on the “Scientific Assessment of Ozone Depletion”, carried out by the Scientific Assessment Panel (SAP) of UNEP. The 2010 report was released in early January 2011 [4] and as usual relies heavily on high precision in-situ surface measurements of ODSs, with relatively modest contributions from satellite observations. High quality in situ measurements offer accurate and precise measurements of surface concentrations of ODS from a number of sites around the globe. Remote sensing from orbit allows the concentrations of these substances to be measured as a function of altitude, generally offering extensive spatial coverage, but with reduced accuracy and precision. Both spatial and temporal averaging of satellite data improves measurement precision, but often significant biases remain due to spectroscopic errors in the retrievals. Limb sounding satellite instruments such as MIPAS [8] and solar occultation instruments such as ACE-FTS [9,10] offer extensive four-dimensional (latitude, longitude, altitude and time) coverage of the atmosphere which is only possible from orbit. In particular, these satellite instruments make routine measurements of atmospheric composition in the stratosphere, where ozone depletion occurs.

2. The Atmospheric Chemistry Experiment

The Atmospheric Chemistry Experiment (ACE) Fourier transform spectrometer (FTS) was launched on board the satellite SCISAT-1 in August 2003. The main goal of the mission is to study ‘the chemical and dynamical processes that control the distribution of ozone in the stratosphere and upper troposphere’ [9]. SCISAT-1 is in a circular low earth orbit with an inclination of 74° [10], giving ACE almost global coverage from the Antarctic to the Arctic.

ACE builds on the legacy of the Atmospheric Trace Molecule Spectroscopy instrument (ATMOS) which was carried onboard NASA Space Shuttles on four different occasions (1985, 1991, 1992 and 1993). The pioneering observations of many halogenated gases (HF, HCl, HOCl, $ClONO_2$, CH_3Cl, CF_4, CFC-12, CFC-11, CCl_4, COF_2, HCFC-22 and SF_6) from orbit were made by ATMOS [11]. ACE’s primary instrument is a high-resolution ($0.02\,cm^{-1}$) FTS which operates between 750 and $4400\,cm^{-1}$. ACE-FTS operates in solar occultation mode, in which atmospheric absorption spectra are measured at a series of tangent heights during sunrise and sunset. Atmospheric profiles for more than 30 molecules are currently retrieved from ACE-FTS spectra with version 3.0 (http://www.ace.uwaterloo.ca), and the retrieval methodology is described by Boone et al. [12]. SCISAT-1 was launched by NASA in August, 2003 and the first routine data are available starting in February 2004. The ACE-FTS is in its eighth year of operation, so we are now in a position to observe long term trends in the VMRs of atmospheric gases. Some earlier halocarbon trend analyses were carried out by Rinsland et al. [13,14] by combining ACE-FTS and ATMOS measurements.

The ACE-FTS currently (v.3.0) measures 16 halogen-containing gases, CCl_4, CF_4, CCl_2F_2 (CFC-12), CCl_3F (CFC-11), $C_2Cl_3F_3$ (CFC-113), CH_3Cl, $ClONO_2$, COF_2, $COCl_2$, COClF, CHF_2Cl