Contents lists available at ScienceDirect



Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Sixteen-year trends in atmospheric trace gases from orbit



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ARTICLE INFO

Article history: Received 3 April 2020 Revised 16 June 2020 Accepted 18 June 2020 Available online 19 June 2020

ABSTRACT

The composition of the Earth's atmosphere is changing. The Atmospheric Chemistry Experiment (ACE) satellite measures infrared transmission spectra of the atmosphere using the Sun as a light source. ACE provides a global view of atmospheric composition from altitude composition profiles for 44 molecules starting in February 2004. Altitude-latitude abundance distributions and composition trends for more than 16 years are presented and briefly discussed. The ACE trends provide a quantitative state-of-the-atmosphere report.

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1. Introduction

Satellite remote sensing of the Earth's atmosphere offers a global perspective that is not available from ground-based or airborne instruments. The Atmospheric Chemistry Experiment (ACE) satellite [1] (a.k.a. SCISAT) measures the composition of the atmosphere by recording the absorption of 44 molecules plus 24 isotopologues [2] by using the solar occultation method. During sunrise and sunset, the centre of the solar radiance is tracked, and its attenuation is measured with a high-resolution infrared spectrometer as well as with a visible-near infrared spectrophotometer (not discussed in this paper).

These solar occultation spectra are processed on the ground and yield altitude profiles of volume mixing ratios (VMRs or mole fractions) with a typical vertical resolution of about 3 km from an altitude of 5 km (or the cloud tops) in the troposphere up to about 120 km in the lower thermosphere for CO_2 . The long horizontal pathlength associated with the limb-viewing geometry of ACE improves the detection limits compared to nadir-viewing satellites. Although nadir-viewing satellite instruments such as IASI (Infrared Atmospheric Sounding Interferometer) on MetOp-A [3] offer exceptional global coverage and relatively high horizontal resolution (e.g., 12 km at nadir), they lack the vertical resolution of limb sounders and typically provide total column densities for trace gases rather than profiles.

The Canadian ACE satellite was launched by NASA in August 2003 and was designed for a two-year operational lifetime. Now in its 17th year, ACE still works well and has a time series of

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https://doi.org/10.1016/j.jqsrt.2020.107178 0022-4073/© 2020 Elsevier Ltd. All rights reserved. data starting in February 2004. ACE's longevity provides an opportunity to measure the change in atmospheric composition of 44 gases as a function of latitude, longitude and altitude for more than 16 years. Anthropogenic chlorofluorocarbons (CFCs) and related gases are responsible for the destruction of stratospheric ozone which protects us from deleterious ultraviolet radiation. ACE monitors the progress of the Montreal Protocol, which controls the production of these long-lived halogen-containing gases [4]. Noncondensable greenhouse gases such as CO₂, CH₄ and N₂O are the "control knob governing Earth's temperature" [5]. Air quality is affected by the oxidation of organic molecules [6] such as C_2H_6 (ethane), CH₃OH (methanol) and CH₃C(O)CH₃ (acetone) catalysed by nitrogen oxides (NO and NO₂). ACE has a global data set for 16+ years for H₂O, O₃, N₂O, NO, NO₂, HNO₃, N₂O₅, H₂O₂, HO₂NO₂, O₂, N₂, SO₂, HCl, HF, ClO, ClONO₂, CFC-11, CFC-12, CFC-113, COF₂, COCl₂, COFCl, CF₄, SF₆, CH₃Cl, CCl₄, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, HFC-23, CO, CH₄, CH₃OH, H₂CO, HCOOH, C₂H₂, C₂H₆, OCS, HCN, CH₃C(O)CH₃, CH₃CN, PAN (CH₃C(O)OONO₂), high and low altitude CO_2 as well as pressure and temperature, http: //www.ace.uwaterloo.ca/molecules.php.

In this paper we will present an overview of altitude-latitude distributions for all ACE molecules as well as VMR trend values from 2004 to the present. The goal is not an exhaustive review or extensive comparison with other datasets, but a broad survey of the latest ACE-FTS results.

2. Methods

The ACE-FTS data used are the v4.0 Level 2 ACE data products [2] available via signup online (https://databace.scisat.ca/l2signup.php). The first step was to remove outliers. The median average deviation (MAD) was calculated on the 1 km ACE altitude grid.



Fig. 1. Altitude-latitude distribution for CFC-11 (CCl₃F) (left), and trends for ACE-FTS and from Montzka et al. [8] (right). The ACE-FTS VMR trend values are the average of data from 60°S to 60°N latitude and 5.5 to 10.5 km in altitude.

The MAD is the average of the absolute values of the differences between the median and the data points. All points that deviated more than 6 MADs above or below the median were discarded. After filtering, data were binned into years and quarters for trend analysis, and 5° latitude and 1 km altitude bins for distributions. The quarters used were December, January, February (DJF); March, April, May (MAM); June, July, August (JJA); and September, October, November (SON). Averages were calculated for each bin and plotted for each molecule to obtain trends and distributions. Altitude-latitude VMR distributions presented in this work are averaged over the entire ACE mission (March 2004 – February 2020).

Trends were calculated using a linear regression least-squares model. In the cases for which two lines were used to fit the trends, the break point was chosen by plotting the graph and estimating the intersection of the two lines to get the break point. Although there are more sophisticated methods for change point detection in geophysical times series, we found that this simple method works well (see CFC-11 and OCS below). Although a linear trend analysis is not always completely appropriate, it is a reasonable approximation for most ACE data. Seasonal variations were removed by fitting and subtracting sine waves using periods of half a year and a year. The portion of the global distribution used to create each trend value is provided in the figure and noted in the caption. All VMRs in the selected region were included in the trend analysis without weighting. One standard deviation on the trend value is quoted and trends are considered significant if the value exceeds two standard deviations.

The choice of the atmospheric region to include for trend analysis was based on several factors. Primarily tropospheric molecules such as CFCs and organic molecules were restricted to the troposphere typically for latitude ranges of 60°S to 60°N and 5.5/6.5 km to 10.5 km in altitude, except if the distributions looked unusual near the poles, typically because of atmospheric dynamics, then 30°S to 30°N (tropical and subtropical) was used. In the case of the 30°S to 30°N latitude range, the upper troposphere was often used, 11.5 km to 17.5 km because retrievals of tropospheric molecules with low abundances become increasingly difficult as the altitude decreases due to spectroscopic interference from other molecules. For primarily stratospheric molecules, the latitude range was either 60°S to 60°N or 30°S to 30°N, depending on whether the distribution peaked near the equator. The altitude range was also selected to cover the main part of the distribution. In some cases, such as H₂O, a particular atmospheric region such as the stratosphere was selected because of the importance of stratospheric H₂O in changing the climate. In general, small changes in the choice of atmospheric region did not change the trends significantly, but no attempt was made to study this.

Note that the satellite orbit is such that ACE-FTS measurements feature global coverage but are weighted strongly toward higher latitudes [1]. Thus, data points employed for trend calculations contain an implicit weighting toward the outer limits of the latitude range, as a consequence of larger numbers of occultations contributing to the average.

3. Results and discussion

Long-lived CFCs (chlorofluorocarbons) such as CFC-11 (CCl₃F) are stable in the troposphere but are dissociated by UV radiation in the stratosphere to release Cl atoms which lead to the catalytic destruction of ozone [7]. The production of CFC-11 has been prohibited by the Montreal Protocol since 2010, and its tropospheric abundance was decreasing as expected until 2012 [8]. Montzka et al. [8] found that the decrease in CFC-11 abundances on the ground was slower than expected after 2012 because of illegal production. ACE-FTS provides a global altitude-latitude distribution and upper tropospheric trends that are comparable to surface values of Montzka et al. [8] (Fig. 1), although the ACE-FTS VMRs are biased low by 5%. The ACE-FTS VMR trend values are the average of data from 60°S to 60°N latitude and 5.5 to 10.5 km in altitude (Fig. 1). ACE-FTS VMRs have a break at 2012 with trends of -1.81 ± 0.05 ppt/year (2004–2012) and -1.16 ± 0.04 ppt/year (2012– 2020).

In addition to CFC-11, ACE measures CFC-12 (Fig. 2) and CFC-113 (Fig. 3), which are also decreasing in abundance. As the CFCs were phased out, the Montreal Protocol allowed transitional HCFCs (hydrochlorofluorocarbons) such as HCFC-22 (Fig. 4), HCFC-141b (Fig. 5) and HCFC-142b (Fig. 6) to be used. HCFCs have shorter atmospheric lifetimes than CFCs because they react with OH in the troposphere and therefore destroy less stratospheric ozone [9]. HCFC production is now essentially phased out in developed countries and will be phased out entirely by 2040 in developing countries. The rate of increase of these 3 HCFCs has slowed since 2012 (Figs. 4-6). The ACE-FTS distributions for HCFC-141b (Fig. 5) and HCFC-142b (Fig. 6) are peculiar because of spectroscopic interference by other molecules in the retrieval; however, the ACE-FTS trend values are in reasonable agreement with independent measurements (e.g., [9]), although the VMRs are biased. For HCFC-141b, the NOAA flask values range from about 15 to 25 ppt for 2004-2020 (https://www.esrl.noaa.gov/gmd/hats/gases/ HCFC141b.html) and the trends look similar to the ACE-FTS trends,



Fig. 2. CFC-12 (CCl₂F₂) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 60°S to 60°N latitude and 5.5 to 10.5 km in altitude.



Fig. 3. CFC-113 (CCl₂FCClF₂) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 60°S to 60°N latitude and 6.5 to 11.5 km in altitude.

so the high values near the top of the distribution plot are clearly retrieval artifacts.

HCFCs are being replaced by HFCs (hydrofluorocarbons) such as HFC-134a which have a negligible effect on stratospheric ozone because they contain no chlorine. The production of long-lived HFCs such as HFC-134a is also being phased out under the Kigali amendment to the Montreal Protocol in favour of short-lived species such as HFOs (hydrofluoroolefins) because of their large global warming potential [9]. ACE-FTS measures HFC-134a (Fig. 7) as well as HFC-23 (CHF₃) (Fig. 8) which is released as a byproduct of HCFC-



Fig. 4. HCFC-22 (CHClF₂) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 60°S to 60°N latitude and 5.5 to 10.5 km in altitude.



Fig. 5. HCFC-141b (CH₃CCl₂F) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 60°S to 60°N latitude and 6.5 to 10.5 km in altitude.



Fig. 6. HCFC-142b (CH₃CCIF₂) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 60°S to 60°N latitude and 6.5 to 10.5 km in altitude.

22 (CHClF₂) manufacture [9,10] and CF₄ (PFC-14) (Fig. 9) released during aluminium production [9]. HFC-134a and HFC-23 are increasing rapidly (Figs. 7, 8) as is CF₄ (Fig. 9). HFC-23 and HFC-134a are increasing more rapidly (0.79±0.01 ppt/year, 5.4 ± 0.1 ppt/year, respectively) since 2012 as is CF₄ (0.85±0.01 ppt/year) since 2014.

ACE-FTS measures 3 additional halogen-containing source gases: CCl_4 (Fig. 10), CH_3Cl (Fig. 11) and SF_6 (Fig. 12). CCl_4 production is controlled by the Montreal Protocol, but has been declining more slowly than expected likely because of byproduct emissions from sources not included in the inventories [9]. CH_3Cl is the only significant source of chlorine in the stratosphere that is not



Fig. 7. 1,1,1,2-Tetrafluoroethane (HFC-134a, CH₂FCF₃) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 30°S to 30°N latitude and 11.5 to 17.5 km in altitude.



Fig. 8. Fluoroform (HFC-23, CHF₃) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 60°S to 60°N latitude and 6.5 to 10.5 km in altitude.



Fig. 9. Carbon tetrafluoride (CF₄, PFC-14) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 60°S to 60°N latitude and 25.5 to 40.5 km in altitude.

due to human activity and hence is not governed by the Montreal Protocol. ACE-FTS shows a small upward CH₃Cl trend (Fig. 11) of 1.1 \pm 0.2 ppt/year in the upper troposphere of the tropics. SF₆ is used primarily for electrical insulation [9] and shows an increasing trend (Fig. 12). The altitude-latitude distribution of SF₆ is typical for a long-lived trace gas.

The photolysis of the organic source gases, CFCs, HCFCs and HFCs, leads to the formation of several halogen-containing intermediate species such as COF_2 (Fig. 13), COCIF (Fig. 14) and $COCl_2$ (Fig. 15). Although the total column of COF_2 has been measured from the ground at NDACC (Network for the Detection of Atmospheric Composition Change) sites [9, 11], these stratospheric prod-



Fig. 10. Carbon tetrachloride (CCl₄) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 30°S to 30°N latitude and 8.5 to 10.5 km in altitude.



Fig. 11. Methyl chloride (CH₃Cl) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 30°S to 30°N latitude and 12.5 to 17.5 km in altitude.



Fig. 12. Sulfur hexafluoride (SF₆) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 30°S to 30°N latitude and 12.5 to 17.5 km in altitude.

uct gases are best measured from orbit. As discussed by Harrison et al. [12], the main sources of COF_2 are CFC-12, HCFC-22 and CFC-113, and although CFC-12 (Fig. 2) and CFC-113 (Fig. 3) are decreasing, HCFC-22 (Fig. 4) and HFCs are increasing, leading to a net slow increase in COF_2 abundance (Fig. 13). COFCl is declining (Fig. 14)

because the main source gas, CFC-11 (Fig. 1), is decreasing. The main source of COCl₂ in the stratosphere is CCl₄ [13], and its decline (Fig. 10) has led to the observed decrease in Fig. 15. In the upper troposphere, there has been a small positive trend (not shown)



Fig. 13. Altitude-latitude distribution for carbonyl fluoride, COF₂ (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 30°S to 30°N latitude and 29.5 to 41.5 km in altitude.



Fig. 14. COCIF altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 30°S to 30°N latitude and 22.5 to 28.5 km in altitude.



Fig. 15. COCl₂ altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 30°S to 30°N latitude and 23.5 to 28.5 km in altitude.

in the $COCl_2$ abundance [4, 13] attributed to an increase in CH_2Cl_2 emissions (not measured by ACE).

The remaining halogen-containing product gases measured by ACE-FTS are $CIONO_2$ (Fig. 16), CIO (Fig. 17), HCI (Fig. 18) and HF (Fig. 19). Stratospheric CIO (Fig. 17) forms from the reaction of CI

atoms (originating from CFCs and HCFCs) with ozone. Additionally, Fig. 17 shows ClO production in the polar regions, particularly for the Antarctic, from HCl and ClONO₂ reservoir molecules, catalysed by polar stratospheric clouds [14]. ClO is involved in a catalytic cycle that destroys stratospheric O₃ [7]. ClO and NO₂



Fig. 16. Altitude-latitude distribution for chlorine nitrate, CIONO₂ (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 60°S to 60°N latitude and 25.5 to 32.5 km in altitude.



Fig. 17. Chlorine monoxide (CIO) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 90°S to 60°S latitude and 16.5 to 25.5 km in altitude.



Fig. 18. Hydrochloric acid (HCl) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 60°S to 60°S latitude and 28.5 to 48.5 km in altitude.

can combine to form $CIONO_2$ (Fig. 16); HCl (Fig. 18) and HF (Fig. 19) are the end products of CFC, HCFC and HFC oxidation. $CIONO_2$ VMRs are declining (Fig. 16) as stratospheric chlorine loading decreases as a result of the Montreal Protocol. Measuring stratospheric HCl trends [9] from the ground [11] or from orbit [15] monitors the success of the Montreal Protocol (Fig. 18). The stratospheric HCl VMR is decreasing more slowly since 2012 (Fig. 18), when the VMRs of short-lived Cl-containing molecules such as CH₃CCl₃ were reduced to negligible values [15]. Similarly, stratospheric HF [16] is the result of anthropogenic production of



Fig. 19. Hydrofluoric acid (HF) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 60°S to 60°S latitude and 45.5 to 55.5 km in altitude.



Fig. 20. Altitude-latitude distribution for carbon dioxide, CO₂ (left), and trends from ACE-FTS and NOAA [21] (right). The ACE-FTS VMR trend values are the average of data from 90°S to 90°N latitude and 7.5 to 17.5 km in altitude.

CFCs, HCFCs and HFCs; in contrast to HCl, HF VMRs are still increasing (Fig. 19). HF VMRs are still increasing because although CFCs are decreasing, HCFCs (e.g., Figs. 4-6) and HFCs (Figs. 7-8) are increasing.

In terms of radiative forcing, the 3 most important greenhouse gases are CO₂, CH₄ and N₂O [17]. Although H₂O vapour has the largest greenhouse effect, it is the noncondensing greenhouse gases that control the Earth's surface temperature [5]. The v.4.0 CO₂ retrieval from ACE-FTS is a special case because CO₂ is also used to determine temperature, pressure and instrument pointing. At low altitude, from 5.5-17.5 km, temperature and pressure are taken from the Canadian weather service model, the tangent height is determined from the N₂ collision-induced absorption spectrum, and the CO₂ VMR is freely determined [18]. From 18 km to about 60 km, the CO₂ VMRs are from a phenomenological model due to G. Toon [18] and temperature, pressure and pointing are retrieved using CO₂ lines. Above about 60 km, ACE-FTS relative pointing is known from geometry (no refraction) and the CO₂ VMR is retrieved again. The ACE satellite is uniquely able to retrieve low altitude CO₂ VMR profiles [19] to complement nadir viewing satellites such as OCO-2 that retrieve column densities [20]. Global distribution and global trend are presented in Fig. 20; good agreement is observed between ACE-FTS and NOAA global values [21], https://www.esrl.noaa.gov/gmd/ccgg/trends/global.html.

The altitude-latitude distributions and global trends for CH₄ and N₂O are presented in Figs. 21 and 22, respectively. The ACE-FTS upper tropospheric VMRs have a low bias of about 8% for CH₄ compared to surface values but the trends (Fig. 20) are similar to NOAA for 2004–2006 and for 2006–2014; however, the more rapid recent increase in the NOAA VMRs since 2015 is less pronounced in the ACE-FTS data (e.g., [22]). The low altitude ACE-FTS and surface trend values agree for N₂O (Fig. 22), although, as is often the case for ACE-FTS, there are biases relative to the ground-based values (e.g., https://www.esrl.noaa.gov/gmd/hats/combined/N2O.html). Although most N₂O is produced by microbial activity at the surface of the Earth, ACE-FTS discovered that auroral activity can produce N₂O in the upper atmosphere (seen faintly in Fig. 22) [23].

Fig. 23 shows ACE-FTS H₂O vapour and the stratospheric trend of 22 \pm 2 ppb/year caused by increasing injection of water across the tropical tropopause [24]. The main source of water in the stratosphere is the oxidation of CH₄, but the increase in CH₄ VMR (Fig. 21) is too small to account for the increase in stratospheric H₂O abundance. Increases in stratospheric water vapour have the effect of increasing surface temperatures (e.g., [25]) so these trends are of interest because of their effect on climate. The region chosen for trend analysis (from 60°S to 60°N latitude and 20.5 to 48.5 km in altitude) covers the stratosphere but misses the mesospheric maximum. The increase in stratospheric H₂O is not monotonic but



Fig. 21. Methane (CH₄) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 60°S to 60°N latitude and 5.5 to 10.5 km in altitude.



Fig. 22. Nitrous oxide (N_2O) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 60°S to 60°N latitude and 5.5 to 10.5 km in altitude.



Fig. 23. Water vapour (H₂O) altitude-latitude distribution (left), and stratospheric trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 60°S to 60°N latitude and 20.5 to 48.5 km in altitude.

displays a positive bump peaking in 2013 and a negative bump peaking in 2015 [24].

In addition to CH₄, ACE-FTS measures many organic molecules in the troposphere, such as the hydrocarbons ethane (C_2H_6) and ethyne (acetylene, C_2H_2). The primary source of ethane is fugitive emissions from oil and natural gas production, which is concentrated in the Northern Hemisphere (e.g., [26]). The relatively short atmospheric lifetime of C_2H_6 of 2 months leads to the large abundance in the Northern Hemisphere (NH) as shown in the ACE-FTS altitude-latitude distribution (Fig. 24). The positive NH trend of 8 \pm 2 ppt/year is consistent with the increase in oil and gas production in North America [26]. In contrast to ethane, ethyne's primary sources are biomass burning and combustion, and the ACE-FTS altitude-latitude distribution (Fig. 25) reflects these



Fig. 24. Altitude-latitude distribution for ethane, C₂H₆ (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 30°N to 90°N latitude and 5.5 to 10.5 km in altitude.



Fig. 25. Ethyne (acetylene, C₂H₂) altitude-latitude distribution (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 30°N to 90°N latitude and 7.5 to 10.5 km in altitude.

sources [27]. In the NH, there is a slight downward trend of -0.9 ± 0.2 ppt/year (Fig. 25). The surprisingly high VMRs of ethane and ethyne near the Arctic circle are due to the transport of emissions from lower latitudes and the reduced destruction by OH at high latitudes.

CO has similar tropospheric emission sources as ethyne so has a similar low altitude distribution (Fig. 26). There is a small negative trend for global upper tropospheric CO (Fig. 26). In the SH (Southern Hemisphere) the tropospheric CO trend is not significant (not shown) but the NH (Northern Hemisphere) troposphere has a trend of -0.28 ± 0.11 ppb/year. At high altitudes in the upper mesosphere and lower thermosphere, the source of CO is UV photolysis of CO₂. This CO can occasionally descend to lower altitudes and even into the stratosphere during polar winter/spring (Fig. 26). The ACE-FTS distribution shows this increase in VMR with increasing altitude in the mesosphere and lower thermosphere (not shown), and the upper atmospheric VMR reflects the 11-year solar cycle (e.g., [28]).

ACE also retrieves 6 oxygen-containing organic molecules: CH₃OH, H₂CO, HCOOH, OCS, CH₃C(O)CH₃ and CH₃C(O)OONO₂ (PAN). CH₃OH (methanol) originates primarily from biogenic sources (plant emissions) and the ACE-FTS distribution (Fig. 27) shows a peak for the boreal forest [29]; there is no VMR trend. H₂CO (formaldehyde) is produced by the oxidation of numerous organic molecules [30], notably methane and isoprene, and the ACE-FTS distribution (Fig. 28) shows a stratospheric peak near 40 km in the tropics due to the oxidation of CH₄ [31]. The slight increasing trend for this feature is not statistically significant. However, the tropospheric formaldehyde trend in the tropics ($30^{\circ}S$ to $30^{\circ}N$, 5.5–10.5 km) has a positive value of 0.37 ± 0.11 ppt/year. HCOOH (formic acid) and acetone (CH₃C(O)CH₃) are produced by oxidation of biogenic emissions as well as by biomass burning [32, 33]. The ACE-FTS distributions in Figs. 29 (formic acid) and 30 (acetone) reflect these sources and acetone, in contrast to formic acid which has a slight non-significant negative trend, has a significant positive trend.

PAN (CH₃C(O)OONO₂) is produced by the oxidation of biogenic and anthropogenic organic molecules and biomass burning [34] that form the peroxyacetyl radical (CH₃C(O)O₂) which combines with nitrogen dioxide (NO₂). PAN thermally dissociates in a few hours near room temperature but is stable for months in the cold upper troposphere. The pollutant NO₂ can therefore be transported over large distances in the troposphere by PAN. The ACE-FTS distribution of PAN (Fig. 31) resembles that of acetone and formic acid, but has a negative trend since 2012. The trends in the NH and SH (not shown) are different: both show a break point at 2012, but the NH has no significant trend before 2012, while SH has a value of -1.4 ± 0.6 ppt/year. After 2012, the NH trend for PAN is -6.5 ± 1.0 ppt/year and -3.7 ± 0.5 ppt/year for the SH.

Carbonyl sulfide (OCS) is the most abundant sulfur containing molecule in the atmosphere and has a relatively long lifetime (compared to the other oxygenated organics) of about 2.5 years [35]. OCS can reach the stratosphere where it forms sulfate aerosols that cool the climate. The ACE-FTS distribution reflects the



Fig. 26. Carbon monoxide (CO) low altitude-latitude distribution (left), and upper tropospheric VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 5.5 to 10.5 km in altitude.



Fig. 27. Methanol (CH₃OH) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 6.5 to 10.5 km in altitude.



Fig. 28. Altitude-latitude distribution for formaldehyde, H₂CO (left), and trends from ACE-FTS (right). The ACE-FTS VMR trend values are the average of data from 30°S to 30°N latitude and 32.5 to 45.5 km in altitude.



Fig. 29. Formic acid (HCOOH) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 6.5 to 10.5 km in altitude.

long lifetime, and shows a positive trend to 2016 and a negative trend from 2016 to the present (Fig. 32). The NOAA flask measurements show a similar trend pattern with a decline since 2016 (https://www.esrl.noaa.gov/gmd/hats/gases/OCS.html).

The other sulfur-containing molecule retrieved by ACE-FTS is SO_2 . Although there was an SO_2 research product earlier [36], it is now a routine data product in version 4.0. ACE-FTS is sensitive

enough to observe background SO_2 levels (Fig. 32) of 10–15 ppt in the lower stratosphere. Enhanced values of 1–2 ppb are seen in volcanic eruptions, but they have been filtered out in Fig. 32. There is no significant background stratospheric SO_2 trend.

Two nitrogen-containing organic molecules, HCN and CH₃CN, are retrieved by the ACE-FTS. Hydrogen cyanide (HCN) and ace-tonitrile (CH₃CN) are produced almost entirely by biomass burning



Fig. 30. Acetone (CH₃C(O)CH₃) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 6.5 to 10.5 km in altitude.



Fig. 31. PAN (CH₃C(O)OONO₂) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 7.5 to 10.5 km in altitude.

[37, 38]. The ACE-FTS distributions of HCN and CH₃CN are in Figs. 34 and 35 and there are no significant trends. Notice the increase in HCN and CH₃CN abundance in 2016 from fires associated with an unusually strong El Niño [37].

Five inorganic nitrogen-containing species NO, NO_2 , HNO_3 , N_2O_5 , $HOONO_2$ (ClONO₂ has already been discussed) that are the

main components of the reactive nitrogen family (NO_y) are retrieved by ACE. With the exception of NO at high altitudes, the VMRs of these molecules all peak in the stratosphere because they originate from N₂O. N₂O is inert in the troposphere with an atmospheric lifetime of about 120 years but reacts with O(¹D) atoms in the stratosphere to produce NO [39], which leads to the chem-



Fig. 32. Carbonyl sulfide (OCS) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 8.5 to 10.5 km in altitude.



Fig. 33. Sulfur dioxide (SO₂) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 18.5 to 24.5 km in altitude.



Fig. 34. Hydrogen cyanide (HCN) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 8.5 to 11.5 km in altitude.

ical production of the other NO_y molecules. NO is also produced in the upper atmosphere by the reaction of N atoms with O_2 [40] and occasionally can descend to the stratosphere (e.g., [41]), where it is able to destroy ozone. The stratospheric peak and the upper mesosphere-lower thermosphere production of NO is seen in Fig. 36. NO and NO₂ (NO_x) destroy stratospheric ozone in a catalytic cycle [6]; the altitude-latitude distribution of NO₂ is presented in Fig. 37. There are no significant trends for NO and NO₂. The recombination reaction of OH with NO₂ produces HNO₃, an NO_x reservoir that releases NO₂ by photolysis. HNO₃ VMRs peak



Fig. 35. Acetonitrile (methyl cyanide, CH₃CN) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 30°S to 30°N latitude and 13.5 to 17.5 km in altitude.



Fig. 36. Nitric oxide (NO) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 35.5 to 51.5 km in altitude.



Fig. 37. Nitrogen dioxide (NO₂) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 28.5 to 40.5 km in altitude.

in the cold polar stratosphere (Fig. 38) and there is a small positive trend in the stratosphere of the Northern Hemisphere. NO_2 is oxidized by O_3 to produce NO_3 , which is particularly important at night when rapid photolysis of NO_3 is suppressed. NO_3 combines with NO₂ to form N₂O₅, another NO_x reservoir. The ACE-FTS distribution of N₂O₅ is shown in Fig. 39. ACE-FTS N₂O₅ VMRs are very variable and a reasonable plot (Fig. 39) was obtained by using only sunrise data with 10° latitude binning and no filtering.



Fig. 38. Nitric acid (HNO₃) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 30°N to 60°N latitude and 18.5 to 28.5 km in altitude.



Fig. 39. Dinitrogen pentoxide (N₂O₅) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 30°N to 60°N latitude and 26.5 to 40.5 km in altitude.



Fig. 40. Peroxynitric acid (HOONO₂) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 25.5 to 33.5 km in altitude.

 $HOONO_2$ is formed by recombination of the HO_2 radical and NO_2 [42]; the ACE-FTS distribution is provided in Fig. 40 and there is a slight non-significant positive stratospheric trend.

Considering all of its roles in atmospheric chemistry and radiative transfer, O₃ is arguably the most important trace gas. The ACE-FTS trend (Fig. 41) for upper stratospheric O₃ (60°S-60°N from 25.5–45.5 km) is $+9 \pm 3$ ppb/year, reasonably consistent with recent measurements from limb sounders (e.g., [43]). The polar stratosphere (60°S-90°S or 60°N-90°N, 25.5–45.5 km) is very variable and does not have a statistically significant ozone trend (not shown). However, if only the summer months are used then the NH polar trend is 7.5 \pm 3 ppb/year and the SH polar trend is 9.0 \pm 3.9 ppb/year. Nadir sounders such as IASI (Infrared Atmospheric Sounding Interferometer) have also been used to measure ozone trends [44] and the values for the middle to upper stratosphere are similar to ACE-FTS trend values.



Fig. 41. Ozone (O₃) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 25.5 to 40.5 km in altitude.



Fig. 42. Hydrogen peroxide (H₂O₂) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 5.5 to 10.5 km in altitude.



Fig. 43. Nitrogen (N₂) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 28.5 to 32.5 km in altitude.

The NO_x, ClO_x and HO_x catalytic cycles limit the abundance of stratospheric O₃ [6]. Although ACE-FTS does not measure H, OH or HO₂ (HO_x), it retrieves the associated H₂O₂ reservoir molecule [45]. H₂O₂ forms by the self-reaction of HO₂ and photolyzes to release two OH radicals. The oxidation of anthropogenic and biogenic hydrocarbons in the troposphere creates HO₂ as a byprod-

uct and the H_2O_2 distribution (Fig. 42) reflects this source. H_2O_2 also has a VMR that increases with altitude in the upper stratosphere (Fig. 42). There is no significant tropospheric trend for H_2O_2 (Fig. 42).

Finally, ACE-FTS detects the weak dipole-forbidden lines of the vibration-rotation bands of N_2 and O_2 from 15 to 48 km for N_2



Fig. 44. Oxygen (O₂) altitude-latitude distribution (left), and VMR trends from ACE-FTS (right). The ACE-FTS VMR values are the average of data from 60°S to 60°N latitude and 21.5 to 33.5 km in altitude.

Linear trend values for the 44 ACE-FTS molecules in%/year and ppt/year associated with Figs. 1-44. One standard deviation in the last digits is quoted in parentheses. For those molecules for which two linear trends were used, the most recent trend is in the table and the earlier trend is given in a footnote.

Molecule	Trend,%/year (error)	Trend, ppt/year (error)	Molecule	Trend,%/year (error)	Trend, ppt/year (error)
COCIF	-0.88(11)	-0.389(0.057)	HCN	-0.13(28)	-0.31(66)
H ₂ O	0.237(30)	$12.7(1.5) \times 10^3$	НСООН	-0.51(28)	-0.22(13)
H_2O_2	0.30(24)	0.64(49)	HF	0.864(47)	17.44(82)
HCFC-22	1.758(51) ^a	4.012(81) ^b	HFC-134a	6.73(37) ^c	5.45(11) ^d
HCFC-141b	0.54(20) ^e	0.145(49) ^f	HNO ₃	0.60(17)	49(12)
HCFC-142b	0.90(14) ^g	0.145(18) ^h	HO_2NO_2	0.21(13)	0.47(28)
HCl	-0.314(26) ⁱ	-8.21(73) ^j	N ₂	-0.0051(51)	-32(30) x10 ⁶
N_2O	0.2559(80)	799(24)	PAN	$-11.7(2.3)^{k}$	$-5.87(62)^{l}$
N_2O_5	0.20(17)	2.2(1.7)	CFC-11	$-0.526(17)^{m}$	$-1.162(44)^{n}$
NO	0.13(16)	10(12)	COF ₂	0.34(11)	0.96(28)
NO ₂	-0.01(11)	-0.7(5.0)	CIONO ₂	-0.546(85)	-4.53(78)
02	0.0000(47)	$-4.6(13.5) \times 10^{6}$	CO ₂	0.550(10)	2149(37) x10 ³
O ₃	0.126(43)	9.4(3.2) x10 ³	C_2H_6	1.26(30)	8.1(1.6)
OCS	-1.387(56)°	$-6.03(40)^{p}$	H_2CO	0.18(18)	0.19(19)
$(CH_3)_2CO$	2.40(37)	7.94(86)	C_2H_2	-1.29(38)	-0.89(22)
CCl ₄	-1.228(41)	-0.983(42)	CF ₄	1.036(20) ^q	0.853(13) ^r
CFC-12	$-0.611(14)^{s}$	$-3.051(84)^{t}$	CFC-113	-1.466(20)	-1.015(19)
CH₃Cl	0.176(42)	1.06(24)	CH₃CN	-0.24(16)	-0.62(43)
CH₃OH	0.02(19)	0.1(1.0)	CH ₄	0.343(17) ^u	5.84(27) ^v x10 ³
CHF ₃	3.438(88) ^w	0.793(11) ^x	ClO	0.23(43)	0.53(96)
CO	-0.51(14)	-0.35(10) x10 ³	COCl ₂	-0.70(13)	-0.079(17)
SF ₆	4.26(16) ^y	0.322(6) ^z	SO ₂	0.34(43)	0.030(36)

 ${}^{a}\;\; 3.737(89)\;{}^{b}6.83(12)\;{}^{c}10.57(33)\;{}^{d}4.477(72)\;{}^{e}1.51(22)\;{}^{f}0.348(46)\;{}^{g}6.76(30)\;{}^{h}0.821(23)\;{}^{i}-0.539(44)\;{}^{j}-14.5(1.3).$

and 15 to 40 km for O₂. The fractional abundances of N₂ and O₂ have known constant values of 0.78 and 0.21 in this altitude range. Note that ACE VMRs make no "correction" for H₂O vapour; they are not dry air values as is customary to report for surface measurements. The altitude-latitude and trend plots of N₂ (Fig. 43) and O₂ (Fig. 44) are therefore a test of the retrieval accuracy. The retrieval accuracy is about 5% for both molecules and there are regions, for example a horizontal band near 30 km, that display systematic errors. There are no trends for either N₂ or O₂ for version 4.0 retrievals. The VMRs for each molecule are a special case with errors from geophysical variability, statistical errors from the signal-to-noise ratio of spectral features, systematic errors from the spectroscopic parameters and temperature/pressure. Nevertheless, the N₂ and O₂ retrievals provide a general estimate of the retrieval accuracy of about 5% for systematic errors.

4. Conclusions

The ACE 2004-2020 trends in atmospheric composition highlight changes and provide a quantitative "state-of-the-atmosphere" report (Table 1). The success of the Montreal Protocol is illustrated by the decreasing abundances of CFC-11, CFC-12, CFC-113, CCl₄, and the recent slowing of the rate of increase of their transitional replacements, HCFC-22, HCFC-141b and HCFC-142b. The naturally occurring CH₃Cl source gas, however, shows a small increase of 0.18±0.04%/year. The chlorine-containing intermediate species $COCl_2$ (-0.70±0.13%/year), COFCl (-0.88±0.11%/year) and $CIONO_2$ (-0.54±0.09%/year) are decreasing in the stratosphere as is the HCl product gas $(-0.31\pm0.03\%/\text{year})$. In contrast, many fluorine-containing molecules that do not destroy stratospheric ozone, but typically have large global warming potentials, HFC-134a, CHF₃, CF₄, SF₆, as well as the product gases COF₂ $(0.33\pm0.12\%)$ and HF $(0.86\pm0.05\%)$ year), are all increasing. The main greenhouse gases, CO₂, CH₄, N₂O, are increasing as expected, and stratospheric H_2O vapour is also increasing $(0.23\pm0.03\%/\text{year})$ which provides a net heating at the surface. For organic gases that impact air quality, ethane has had a substantial increase in the Northern Hemisphere (1.2 \pm 0.3%/year) as has acetone $(2.5 \pm 0.5\%/\text{year})$, but acetylene has declined $(-1.7 \pm 0.4\%/\text{year})$. Tropospheric carbon monoxide, which is a product of incomplete combustion, has declined $(-0.51\pm0.14\%/\text{year})$; the combustion-related HCN and CH₃CN molecules show no significant trend. Tropospheric PAN, a reservoir for NO₂, has been decreasing substantially since 2012 at $-12\pm2\%/\text{year}$. The members of the NO_y family in the stratosphere have not changed except for HNO₃, which has increased $(0.60\pm0.17\%/\text{year})$ and ClONO₂, which has decreased $(-0.54\pm0.09\%/\text{year})$. Of the sulfur-containing molecules, background levels (i.e., excluding volcanic eruptions) of SO₂ have not changed, but OCS showed an increase of $0.48\pm0.04\%/\text{year}$ until 2016 and is now declining at $-1.54\pm0.08\%/\text{year}$. Stratospheric ozone shows a small, marginally significant, increase of $0.14\pm0.07\%/\text{year}$.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

P.F. Bernath: Methodology, Supervision, Writing - original draft. **J. Steffen:** Formal analysis, Visualization. **J. Crouse:** Formal analysis, Visualization. **C.D. Boone:** Writing - review & editing.

Acknowledgements

The remarkable ACE-FTS was built in Quebec City by ABB Space and Defense Systems by a team headed by M.-A. Soucy; we are grateful for its excellent design and fabrication. The satellite bus was built in Winnipeg by Magellan Aerospace. We thank the Mission Operations Centre at the Canadian Space Agency for downlinking ACE data and sending it to the Science Operations Centre at the University of Waterloo, where all ACE-FTS data products (available at https://databace.scisat.ca/level2/ace_v4.0) are produced. We are grateful for the global CO₂ data in Fig. 4, obtained from the web site https://www.esrl.noaa.gov/gmd/ccgg/ trends/global.html. The published NOAA CFC-11 data is available at ftp://ftp.cmdl.noaa.gov/hats/cfcs/cfc11/flasks/GCMS/publication/. The ACE satellite mission is funded by the Canadian Space Agency.

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