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Historical trend of ozone-depleting substances and hydrofluorocarbon concentrations during 2004–2020 derived from satellite observations and estimates for global emissions^{\star}

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ABSTRACT

Global concentrations (or mole fractions) and emissions of ozone-depleting substances (ODSs) and their hydrofluorocarbon (HFCs) substitutes that are controlled by the Montreal Protocol and its Amendments and adjustments (MP) are of great interest to both the scientific community and public. Previous studies on global concentrations and emissions have mostly relied on ground-based observations. Here, we assess the global concentrations and emissions of eight MP controlled substances and methyl chloride from ACE-FTS (Atmospheric Chemistry Experiment high—resolution infrared Fourier transform spectrometer) satellite observations: CFC-11 (CFCl₃), CFC-12 (CF₂Cl₂), CCl₄, HCFC-22 (CHClF₂), HCFC-141b (C₂H₃Cl₂F), HCFC-142b (C₂H₃ClF₂), HFC-23 (CHF₃), HFC-134a (C₂H₂F₄), and CH₃Cl. Results show that the ACE-FTS satellite observations can be used to derive the concentrations and emissions of these ODSs, HFCs, and CH₃Cl, as they are consistent with those derived from the ground-based observations. Our findings imply that the changes in the concentrations and emissions of the regulatory status of the MP, and satellite observations can be used to monitor the past and future progress of the MP.

1. Introduction

The Montreal Protocol on Substances that Deplete the Ozone Layer and its Amendments (MP) was signed in 1987 and has been amended several times since then (UNEP, 2020). The objective of the MP is to phase out the production and consumption of ozone-depleting substances (ODSs), such as chlorofluorocarbons (CFCs), carbon tetrachloride (CCl₄), halons, methyl bromide (CH₃Br), and interim-substitute hydrochlorofluorocarbons (HCFCs). Hydrofluorocarbons (HFCs), which do not deplete the ozone layer (Ravishankara et al., 1994; Ellis et al., 2001), are widely used as substitutes for the ODSs. Although the HFCs do not destroy the ozone layer, they are powerful greenhouse gases (GHGs) and have recently been added to the MP to avoid erosion of the GHG emission reductions achieved by it (Velders et al., 2009; Zickfeld et al., 2017). Methyl chloride (CH₃Cl) is not controlled by the MP, however, it is a ODS and contributes to the tropospheric chloride load by \sim 17% (WMO, 2014).

Many ground-based observations, including the National Oceanic and Atmospheric Administration and Advanced Global Atmospheric Gases Experiment (AGAGE), measure atmospheric concentrations (or mole fractions) of the ODSs and HFCs (Prinn et al., 2018). Based on these observations, studies have evaluated the changes in global concentrations and emissions of the ODSs and HFCs, such as CFCs (Montzka et al., 2018; Park et al., 2021), CCl₄ (Dunse et al., 2005; Fraser et al., 2014), HCFCs (O'Doherty et al., 2004; Saikawa et al., 2012), CH₃Cl (Cox et al., 2003; Simmonds et al., 2004), and HFCs (Fang et al., 2015; Stanley et al.,

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2020). The ground-based Fourier transform infrared (FTIR) solar absorption measurements also makes it possible to measure the total column concentration of CFC-11 (CFCl₃), CFC-12 (CF₂Cl₂), and HCFC-22 (CHClF₂) (e.g., Zander et al., 2008; Zhou et al., 2016; Polyakov et al., 2021; Pardo Cantos et al., 2022). However, the ground-based observations have limitations. For example, they do not fully cover all latitudinal zones because of their non-uniform distribution and may not cover some periods due to instrument failure or extreme weather events, such as typhoons (WMO, 2018; Chu, 2021). Satellite-based observations can be used to supplement ground-based observations for assessing the global concentrations and emissions of the ODSs and HFCs. The Atmospheric Chemistry Experiment high-resolution infrared Fourier transform spectrometer (ACE-FTS) is a pioneer in the ODSs satellite observations for measuring the concentrations of several ODSs and HFCs (Dufour et al., 2005; Harrison et al., 2012; Dodangodage et al., 2021). It has been measuring vertical profiles of the ODSs and HFCs since August 2003 (Nassar et al., 2003). Many studies have validated the ACE-FTS satellite data (De Maziere et al., 2008; Hegglin et al., 2008; Kerzenmacher et al., 2008; Mahieu et al., 2008; Sica et al., 2008; Strong et al., 2008; Wolff et al., 2008; Dupuy et al., 2009) and analyzed the atmospheric concentration trends of some ODSs and HFCs (Brown et al., 2011; Steffen et al., 2019). However, the global emissions of the ODSs and HFCs have not been further analyzed and compared with ground-observation-based emission estimates.

This study aims to assess the temporal concentrations of nine substances from the ACE-FTS instrument, namely CFC-11 (CFCl₃), CFC-12



Fig. 1. Altitude-concentration distributions of ODSs and HFCs during 2004–2020 derived from satellite ACE-FTS observations. Data with an altitude of <5 km are seldomly available from the ACE-FTS measurements. For CH₃Cl, data with an altitude of <9 km are unavailable from the ACE-FTS measurements. Each point represents the average concentration at 1 km (point at height 5.5 km represents 5.0–6.0 km range).

(CF₂Cl₂), CCl₄, HCFC-22 (CHClF₂), HCFC-141b (C₂H₃Cl₂F), HCFC-142b (C₂H₃ClF₂), HFC-23 (CHF₃), HFC-134a (C₂H₂F₄), and CH₃Cl, and compared them with the ground-based observations. Based on the ACE-FTS concentration data, this study estimates the global emissions of these ODSs and HFCs using a one-box model. This study explores the consistency and inconsistency between the ACE-FTS- and ground-observation-based emission estimates and indicated the usefulness of satellite observations of these compounds. Finally, this study analyzes the impact of the MP on the concentrations and emissions of these ODSs and HFCs.

2. Methods

2.1. Calculations of global concentrations

The data used in this study were downloaded from Level 2 ACE dataset version 4.1 (https://databace.scisat.ca/level2/; last accessed Oct 4, 2022) (Bernath et al., 2020; Bernath et al., 2021). First, we excluded concentration outliers that were higher than average plus 10 times standard deviation or lower than average minus 10 times standard deviation (0.02% of data rejected). Table S1 exhibits that the changes in concentrations and emissions, respectively, are 0.002% and 0.048% when choosing five times (0.16% of data rejected), and 0.014% and 0.498% when choosing three (0.64% of data rejected), rather than 10 times the standard deviation as the screening indicator. Each data point from the ACE-FTS corresponded to the measured time, longitude, latitude, altitude, and concentration (parts per trillion or ppt). Second, we excluded the measured time, longitude, and latitude for the height-concentration distribution. For each substance, we averaged all concentration data at the same height. Fig. 1 shows the concentrations of nine substances within an altitude of 5-10 km, which represents the height of the free troposphere (data with an altitude of <5 km is unavailable from the ACE-FTS measurements). Finally, we derived the global annual mean concentrations of each substance, which were then compared with the AGAGE ground-based observations (http://agage. mit.edu/data; last accessed Oct 4, 2022).

The AGAGE ground-based observations are the monthly global means of baseline data (background conditions) derived from the AGAGE measurements, which are available at https://agage2.eas.gate ch.edu/data archive/global mean/(last accessed Oct 4, 2022). The atmospheric concentrations of the ODSs and HFCs were measured using gas chromatography coupled with mass spectrometry in "Medusa" with "multidetector," namely, electron-capture, flame-ionization, and mercuric oxide reduction detection (Prinn et al., 2018). The global monthly mean concentrations were obtained from five primary stations: Cape Grim (Australia, 41° S, 145° E, 1978-present), Cape Matatula (Samoa, 14° S, 171° W, 1978-present), Ragged Point (Barbados, 13° N, 59° W, 1978-present), Trinidad Head (USA, 41° N, 124° W, 1995-present), and Mace Head (Ireland, 53° N, 10° W, 1987-present) (Prinn et al., 2018). It's worth pointing out that the mean latitude (58°) sampled from ACE-FTS measurements is larger than that (32°) of the ground-based AGAGE measurements, which may influence the ability to detect future emissions from lower latitudes.

2.2. Calculations of global emissions

We calculated the global emissions to assess (1) the emissions calculated using ACE-FTS satellite observations were consistent with those using AGAGE ground-based observations, and (2) whether the calculated emissions were consistent with the phase-out process of the MP. We used the global annual mean concentrations, calculated using the ACE-FTS data and AGAGE ground-based observations, with the one-box model to calculate the global emissions of the ODSs and HFCs from 2005–2020. The calculation formula for the one-box model (Fang et al., 2018) is described below. The annual emissions of specific substance *i* in year *j* were calculated from the concentrations of specific substance,

molecular weight, lifetime of this substance, number of global atmospheric molecules, and other input data (equations (1)-(3)).

$$\frac{\mathrm{d}C_{ij}}{\mathrm{d}t} = F_i \times E_{ij} - \frac{C_{ij}}{\tau_i} \tag{1}$$

Equation (1) equals

$$E_{ij} = \frac{\frac{dC_{ij}}{dt} + \frac{C_{ij}}{\tau_i}}{F_i}$$
(2)

Here C_{ij} is the concentration of specific substance *i* in year *j* (ppt), E_{ij} is the annual emission of the substance (kg/yr; kilogram per year), τ_i is the lifetime of the substance (yr), and F_i (ppt/kg) is a factor that relates the mass emitted to global concentrations.

$$F_i = \left(\frac{N_A}{N_a}\right) \frac{F_{surf}}{M_i} = 5.68 \times 10^{-9} \frac{F_{surf}}{M_i}$$
(3)

Here M_i is the molecular weight of substance *i* (kg/mol), N_a is the number of global atmospheric molecules, N_A is the Avogadro number, and F_{surf} is a factor that relates the global mean surface concentrations to global mean atmospheric concentrations, which is 1.07 in this study for all ODSs (Velders and Daniel, 2014; WMO, 2018). Because our concentration data came from satellite-based observations rather than global mean surface concentrations, we took the difference in emissions caused by considering F_{surf} equal to 1 instead of 1.07 as the magnitude of our calculation uncertainty. The molar mass of the troposphere is ~0.82 times the molar mass of the entire atmosphere. When ~88% of the ODS molar mass is in the troposphere, the F_{surf} is 1.07 (Velders and Daniel, 2014). The use of constants 1.07 for F_{surf} ignores changes in values that may be caused by changes in the circulation, changes in surface emissions, and changes in the vertical distribution of the atmosphere (Velders and Daniel, 2014).

3. Results and discussions

3.1. Concentrations and emissions of CFCs and CCl4

Fig. 2 shows the global annual mean concentrations of CFC-11, CFC-12, and CCl₄ derived from the ACE-FTS satellite observations compared with those of the AGAGE observations. Results reveal that CFC-11, CFC-12, and CCl₄ concentrations, derived from the ACE-FTS and AGAGE observations, were on average 240 ppt and 237 ppt, 531 ppt and 525 ppt, and 80 ppt and 84 ppt, respectively, during 2004–2020. The reasons for these differences may be because the ACE-FTS satellite observations are for high-altitude concentrations, while the AGAGE ground-based observations are for near-surface concentrations, and that the concentration measurement instruments and methods differ between the ACE-FTS instrument and AGAGE observations.

Although there were some discrepancies in concentrations between the ACE-FTS and AGAGE observations, the changes in trends of CFC-11, CFC-12, and CCl₄ ACE-FTS concentrations were well consistent with the AGAGE observations because 95% confidence intervals of the slopes of their trends (e.g., -1.6 ± 0.1 ppt/yr and -1.7 ± 0.1 ppt/yr for CFC-11) overlapped with each other. We calculated the slopes and 95% confidence intervals using the least-squares method. The rates of change of CFC-11, CFC-12, and CCl₄ concentrations in the ACE-FTS observations during 2004–2020 were -1.6 \pm 0.1 ppt/yr (–0.66% \pm 0.03%) (95% confidence interval, same below), -2.4 ± 0.3 ppt/yr ($-0.4\% \pm 0.1\%$), and -0.9 ± 0.1 ppt/yr ($-1.2\%\pm0.1\%$), respectively, while the annual rates of change of CFC-11, CFC-12, and CCl₄ concentrations in the ground-based AGAGE observations during 2004–2020 were -1.7 ± 0.1 ppt/yr (–0.72% \pm 0.04%), –2.7 \pm 0.2 ppt/yr (–0.52% \pm 0.03%), and -1.05 ± 0.02 ppt/yr ($-1.24\% \pm 0.02\%$), respectively (Fig. 2). In addition, the Pearson correlation coefficients of the global annual mean concentrations, derived from the ACE-FTS observations and AGAGE



Fig. 2. Concentrations of ODSs and HFCs during 2004–2020 derived from satellite ACE-FTS observations (red line) compared with AGAGE ground observations (black line). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

observations, were 0.996, 0.990, and 0.994 for CFC-11, CFC-12, and CCl₄, respectively (Table S2).

Fig. 3 demonstrates CFC-11, CFC-12, and CCl₄ emissions during 2005–2020, derived using the ACE-FTS and AGAGE concentration data and one-box model. CFC-11, CFC-12, and CCl₄ emissions were on average 71 Gg/yr (gigagrams per year) using the ACE-FTS data and one-box model and 63 Gg/yr, 61 Gg/yr and 49 Gg/yr, and 39 Gg/yr and 40 Gg/yr using the AGAGE data and one-box model, respectively. The annual change rates of CFC-11, CFC-12, and CCl₄ emissions during 2005–2020, estimated using the satellite ACE-FTS observations and one-box model, were -1.3 ± 2.4 Gg/yr, -6.1 ± 3.2 Gg/yr, and -0.1 ± 2.0 Gg/yr, respectively. The corresponding annual change rates of CFC-11,

CFC-12, and CCl₄ emissions, estimated using the AGAGE observations and one-box model, were 0.5 \pm 0.9 Gg/yr, $-3.7 \pm$ 0.9 Gg/yr, and $-0.7 \pm$ 0.4 Gg/yr, respectively. The precision of the AGAGE observations for all substances was less than 1% (Prinn et al., 2018), while the precision of the ACE-FTS observations was on average 9% (Table S3). It can be assumed that larger variation in satellite-observed concentrations contributes to the inter-annual variation in emissions derived from ACE-FTS having a larger vibration than AGAGE. The annual change rates of CFC-11, CFC-12, and CCl₄ emissions during 2005–2016, estimated using the AGAGE observations and 12-box model (WMO, 2018), were 0.8 \pm 0.8 Gg/yr, -4.5 ± 1.5 Gg/yr, and -1.1 ± 0.6 Gg/yr, respectively. The 12-box model is used to infer global emissions from global



Fig. 3. Global annual emissions of ODSs and HFCs during 2005-2020 estimated using concentration data from ACE-FTS and AGAGE observations.

concentrations, which is a two-dimensional model of trace gas chemistry and transport, dividing the atmosphere into four equal-mass latitudinal sections (divided at 30°N, 0°N, and 30°S) and three vertical layers (divided at 500 hPa and 200 hPa) (Cunnold et al., 1983; Rigby et al., 2013). Emission trends estimated by these three approaches are consistent with each other due to overlaps of 95% confidence intervals of the slopes of their trends (e.g., -1.3 ± 2.4 Gg/yr, 0.5 ± 0.9 Gg/yr, and 0.8 ± 0.8 Gg/yr for CFC-11, respectively, Table S2). The derived trends for CFC-11 are not statistically significant in either data set (p > 0.05).

Non-Article 5 (primarily developed countries) and Article 5 parties (primarily developing countries) of the MP were obliged to phase out the production and consumption of CFC-11 and CFC-12 by 1996 and of CCl₄ by 2010 (with possible critical use exemptions). An unexpected increase during 2012–2018 (Montzka et al., 2018) and a decline during 2018–2019 in the global emissions of CFC-11 (Park et al., 2021) were observed, which were also observed in our estimates using the ACE-FTS observations and one-box model (Fig. 3). This indicates that satellite observations of CFC-11 can be used to effectively monitor unexpected emissions. CFC-12 emissions estimated from either the ACE-FTS or

AGAGE observations decreased during 2005–2020 (Fig. 3), which is consistent with the fact that the production and consumption of CFC-12 has been phased out in non-Article 5 countries since 1996 and in Article 5 countries since 2010. During 2005–2020, CCl₄ concentrations derived from the ACE-FTS observations decreased rapidly, while the emissions were stable at ~40 Gg/yr, consistent with those derived from the AGAGE observations. Although the dispersive use of CCl₄ was phased out in non-Article 5 countries by 1995 and in Article 5 countries by 2010, continued emissions of CCl₄ were found in many regions, such as the USA (Hu et al., 2016), China (Lunt et al., 2018), and Europe (Graziosi et al., 2016), and the discrepancy between the bottom-up and top-down estimates of CCl₄ emissions has not been fully resolved (SPARC et al., 2016; Sherry et al., 2018).

3.2. Concentrations and emissions of HCFCs

Fig. 2 also exhibits the global mean concentrations of HCFCs from the ACE-FTS observations compared with those of the ground-based AGAGE observations. HCFC-22 concentrations continuously increased during 2004–2020, with 5.8 ± 0.5 ppt/yr and 5.5 ± 0.5 ppt/yr derived from the

ACE-FTS and AGAGE observations, respectively. Gaps were observed in HCFC-141b concentrations derived from the ACE-FTS and AGAGE observations at 33 ppt and 22 ppt on average, respectively, during 2004-2020. Nevertheless, the trends of HCFC-141b concentrations derived from the ACE-FTS and AGAGE observations were consistent, with an increase rate of \sim 0.8 ppt/yr during 2004–2015 and a decrease rate of ~0.2 ppt/yr during 2015-2020. Gaps were also observed in HCFC-142b concentrations derived from the ACE-FTS and AGAGE observations, with 16 ppt and 20 ppt on average, respectively, during 2004–2020. Nevertheless, the trends of concentrations derived from the ACE-FTS and AGAGE observations were consistent, with an increase rate of ~0.70 ppt/yr and ~0.04 ppt/yr during 2004–2015 and 2015–2020, respectively, as shown by the observation data of both ACE-FTS and AGAGE. The Pearson correlation coefficients of the global annual mean concentrations, derived from the ACE-FTS and AGAGE observations, were 0.999, 0.964, and 0.987 for HCFC-22, HCFC-141b, and HCFC-142b, respectively (Table S2).

HCFC-22, HCFC-141b, and HCFC-142b emissions were estimated based on the ACE-FTS and AGAGE observations and box models (Fig. 3). HCFC-22 emission were relatively stable at 344 \pm 20 Gg/yr during 2005–2020, which was consistent between the two approaches (340 \pm 21 Gg/yr from the ACE-FTS + one-box model and 334 \pm 18 Gg/yr from the AGAGE + one-box model). The AGAGE data demonstrated an increase in HCFC-141b emissions during 2005–2012 and a subsequent decrease, while the ACE-FTS data exhibited that HCFC-141b emissions reversed in 2014. Both ACE-FTS and AGAGE data revealed that HCFC-142b emissions increased before 2008 and then decreased subsequently. Thus, the annual emissions and trends of estimated HCFCs based on the ACE-FTS and AGAGE observations were consistent.

Non-Article 5 and Article 5 parties of the MP were obliged to freeze the production and consumption of HCFCs by 1996 and 2013, with ultimate phase out by 2020 and 2030, respectively (with possible essential use exemptions). Thus, the increase in emissions of HCFC-22, HCFC-141b, and HCFC-142b, derived from the ACE-FTS and AGAGE observations, was not surprising during the 2000s and early 2010s, as shown in Fig. 3. Since the production and consumption of HCFCs started phasing out in 1996 and 2013 in non-Article 5 parties and Article 5 parties, respectively, HCFC-141b and HCFC-142b emissions decreased after 2013 and 2008, respectively, as exhibited by the emission estimates from the ACE-FTS and AGAGE observations (Fig. 3). HCFC-141b emission sources primarily include foam blowing and solvent sectors, while HCFC-142b emission sources primarily include foam blowing, aerosol propellant, and refrigerant sectors (Simmonds et al., 2017), leading to different peak emission years.

3.3. Concentrations and emissions of HFCs

The global annual mean concentration of HFC-23 derived from the ACE-FTS satellite, a by-product of HCFC-22 production, was 10 ppt during 2004–2020, which was 19% lower than 13 ppt derived from the ground-based AGAGE observations, whereas HFC-134a concentrations only differed by 8% between the ACE-FTS and AGAGE observations. The Pearson correlation coefficients of the global annual mean concentrations, derived from the ACE-FTS and AGAGE observations, were higher than 0.999 for both HFC-23 and HFC-134a (Table S2). The global annual mean growth (0.77 \pm 0.03 ppt/yr (3.5% \pm 0.1%)) of HFC-23 derived from the satellite ACE-FTS is close to that (0.94 \pm 0.04 ppt/yr (3.7% \pm 0.2%)) derived from AGAGE observations during 2004–2020. The global annual mean growth of HFC-134a derived from the ACE-FTS and AGAGE observations were 5.1 \pm 0.2 ppt/yr (7.3% \pm 0.3%) and 5.2 \pm 0.2 ppt/yr (7.5% \pm 0.2%), respectively (Fig. 2).

Fig. 3 exhibited that HFC-23 emissions increased on average by 0.2 \pm 0.2 Gg/yr (ACE-FTS + one-box model), which were consistent with 0.3 \pm 0.2 Gg/yr derived from the AGAGE + one-box model during 2005–2020. After 2006, a large proportion of HFC-23 was incinerated following the Clean Development Mechanism (CDM) project of the

United Nations Framework Convention on Climate Change (Fang et al., 2014), which is consistent with the downward trend of emissions estimated from the ACE-FTS (-1.4 ± 1.3 Gg/yr) AGAGE observations (-1.2 ± 0.4 Gg/yr). After around 2010, the CDM project started to terminate and HFC-23 emissions were expected to increase, which is consistent with an increase in the emissions estimated from the ACE-FTS (1.7 ± 1.5 Gg/yr) and AGAGE (1.3 ± 0.5 Gg/yr) data during 2010–2014. The increase in global HFC-23 emissions after 2016 was attributed to the substantial unreported production of HCFC-22 in China because it is a by-product of HCFC-22 (Stanley et al., 2020).

HFC-134a emissions increased on average by 8.9 ± 1.0 Gg/yr (ACE-FTS + one-box model) during 2005–2020, which was consistent with 8.2 ± 0.7 Gg/yr derived from AGAGE + one-box model (Fig. 3). Non-Article 5 parties of the MP started reducing the production and consumption of HFC-134a in 2019, whereas most Article 5 parties will start freezing its production and consumption in 2024. Thus, as an important alternative to CFC-12, HFC-134a emissions are expected to increase due to the success of the MP's control over CFC-12 (Fortems-Cheiney et al., 2015), which is consistent with the increasing emissions estimated from the ACE-FTS observations (Fig. 3).

3.4. Concentrations and emissions of CH₃Cl

The global annual mean concentrations of CH_3Cl derived from the ACE-FTS and AGAGE observations were 578 ppt and 541 ppt, respectively, during 2004–2020.

The change rates of CH₃Cl derived from the ACE-FTS and AGAGE observations, were -0.01 ± 1.29 ppt/yr and 0.56 ± 0.50 ppt/yr, respectively, indicating approximately no change in its global concentration. The Pearson correlation coefficient of CH₃Cl, derived from the ACE-FTS and AGAGE observations, was 0.56. There were no significant trends in CH₃Cl global emissions (5334 Gg/yr and 5003 Gg/yr derived from the ACE-FTS + one-box model, AGAGE + one-box model, respectively, and 5210 Gg/yr derived from the AGAGE + 12-box model during 2005–2016), which was consistent among the three approaches because atmospheric CH₃Cl originates from natural sources (Yokouchi et al., 2000; Archibald et al., 2015).

3.5. Supplement to ground-based observations

Ground-based observations may fail to cover certain time periods. For example, the Gosan observatory in South Korea suffered from typhoon damage, which resulted in large data gaps in 2016, 2017, and 2018 (Chu, 2021; Park et al., 2021). In addition, the concentration data of Ragged Point and Cape Matatula AGAGE stations were not available for several months, such as, July—November 2014, June—August 2016, November 2018—February 2019, and May—October 2019 for Ragged Point and December 2017—April 2018 for Cape Matatula. (https:// agage2.eas.gatech.edu/data_archive/data_figures/monthly/pdf/HCFC-22_mm.pdf). In contrast, satellite data were available for all months (Fig. 4).

Ground-based observations fail to cover all latitudinal zones owing to the non-uniform distribution of these observatories. For example, the five AGAGE stations used in the global monthly concentration data cover only five latitudes (Section 2), whereas the ACE-FTS satellite covers the region between 85° S and 87° N (Fig. 5). Thus, it has a wider temporal and spatial coverage of observations than ground stations. Satellite data have higher spatial coverage, so errors are reduced by the extensive spatial averaging. It can be expected that with the further increase of the number of satellite data, the uncertainty of satellite data will be further reduced. Moreover, this study showed that the concentrations and emissions of seven ODSs and two HFCs from the satellite matched those from AGAGE ground observations. This study also found good agreements between the ACE-FTS satellite observations and the ground FTIR observations (Table S4). For example, the annual change rates for 2004–2010 derived from ACE-FTS satellite observations and



Fig. 4. Monthly number of observations and concentrations of CFC-11 per month derived from ACE-FTS during 2004–2020 between 5–10 km altitude (before data exclusion criteria). Add up the data for all months for a total of 99,371 data. The lower number of observations before 2010 is due to the lower number of occultations in 2004, 2006, 2007 and 2008 (Brown et al., 2011). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 5. Number of observations derived from ACE-FTS during 2004–2020 between 90°S and 90°N latitude and 5–10 km altitude (before data exclusion criteria). Add up the data for all latitudes for a total of 99,371 data.

the ground FTIR observations, respectively, are $-0.99\% \pm 0.10\%$ and $-0.90\% \pm 0.10\%$ for CFC-11, $-0.38\% \pm 0.07\%$ and $-0.40\% \pm 0.07\%$ for CFC-12, $3.52\% \pm 0.08\%$ and $3.70\% \pm 0.08\%$ for HCFC-22; the annual change rates for 2009–2019 derived from ACE-FTS satellite observations and the ground FTIR observations, respectively, are $-0.40\% \pm 0.07\%$ and $-0.64\% \pm 0.08\%$ for CFC-11, $-0.49\% \pm 0.05\%$ and $-0.57\% \pm 0.05\%$ for CFC-12, $2.12\% \pm 0.13\%$ and $2.15\% \pm 0.24\%$ for HCFC-22. Therefore, satellite-based observations of the ODSs and HFCs can supplement lacking ground-based observations.

However, satellite data is not perfect due to the difficulty to replicate the accuracy nor the high time resolution of ground-based observations. For example, the precision of the ACE-FTS observations was on average 9%, poorer than that (<1%) of the AGAGE observations (Table S3). Moreover, the ACE orbital inclination angle is 74° (Brown et al., 2011), which results in relatively few data from latitude between 45°N and 45°S (Fig. 5). Thus, the number of ACE-FTS observations for some specific regions, is very limited (e.g., annual ~200 for East Asia from ACE-FTS observations compared to ~2000 from Gosan ground observations in East Asia), it would be difficult to use the data to detect regional emissions.

3.6. Impact of the MP on ODSs and HFCs

This study suggests that the concentration and emission trends of the ODSs and HFCs closely match the regulatory status of the MP. The concentrations of substances whose production and consumption has been banned, such as CFCs and CCl₄ (phase-out by 1995 for non-Article 5 countries and by 2010 for Article 5 countries), have dropped rapidly (Fig. 2), and their emissions have not risen since 2004 (except for an unexpected increase in CFC-11 emissions) (Fig. 3). The concentrations and emissions of substances whose production and consumption are being phased out, such as HCFCs (phase-out by 2020 for non-Article 5 countries and 2030 by Article 5 countries), are reaching a turning point. However, the concentrations and emissions of HFCs and CH₃Cl did not decrease before 2019 because of the lack of control.

Fig. 6 exhibits the mass, CFC-11-equivalent (CFC-11-eq), and CO₂equivalent (CO₂-eq) emissions of eight substances controlled by the MP (CH₃Cl is not included), derived from the ACE-FTS observations. For total mass emissions, the proportions of CFCs and CCl₄ emissions decreased from 41% in 2005 to 21% in 2020, while the proportions of HCFCs and HFCs increased. The total CFC-11-eq emissions decreased from 297 Gg/yr in 2005 to 163 Gg/yr in 2020, indicating that the MP has led to reductions in CFC-11-eq ODSs emissions. For CO₂-eq emissions, the combined proportion of CFCs, CCl₄, and HCFCs to total emissions decreased from 92% in 2005 to 78% in 2020, whereas the HFCs proportion increased from 8% in 2005 to 22% in 2020, reflecting that HFCs are rapidly replacing the ODSs. Thus, concentration and emission estimates derived from the ACE-FTS observations can be used to assess the past and future progress of the MP.

4. Conclusions

In this study, we assessed the global concentrations and emissions of eight MP-controlled substances and methyl chloride from the ACE-FTS satellite observations. Results show that the ACE-FTS satellite observations can be used to derive the concentrations and emissions of the ODSs, HFCs, and CH₃Cl, as they are consistent with those derived from ground-based observations. Ground-based observations may fail to cover some periods or all latitudinal zones, whereas satellite-based observations can



Fig. 6. Global emissions of ODSs and HFCs during 2005–2020 using ACE-FTS observations and a one-box model. (a) Mass emissions, (b) CFC-11-equivalent emissions, and (c) CO₂-equivalent emissions.

supplement the lacking ground-based observations on these substances.

Additionally, this study suggested that the trends in the concentrations and emissions of the ODSs and HFCs closely match the regulatory status of the MP. The concentrations of substances whose production and consumption has been banned, such as CFCs and CCl4 (phase-out by 1995 for non-Article 5 and by 2010 for Article 5 countries), have dropped rapidly (-1.6 ± 0.1 ppt/yr ($-0.66\% \pm 0.03\%$) for CFC-11, -2.4 \pm 0.3 ppt/vr (-0.4% \pm 0.1%) for CFC-12, and -0.9 \pm 0.1 ppt/vr (-1.2%) \pm 0.1%) for CCl₄), and their emissions have not increased since 2004 (except for some unexpected increases in CFC-11 emissions). The concentrations and emissions of substances whose production and consumption are being phased out, such as HCFCs (phase-out by 2020 for non-Article 5 and by 2030 for Article 5 countries), are reaching a turning point (2015 and 2014 for concentrations and emissions of HCFC-141b, respectively). However, the concentrations and emissions of HFCs and CH₃Cl did not decrease before 2019 because of the lack of control. These results imply that satellite observations can be used to monitor the past and future progress of the MP.

Author statement

Ao Chen: Conceptualization, Methodology, Investigation, Writing – original draft. Di Chen: Writing – review & editing. Xiaoyi Hu: Writing – review & editing. Christina M. Harth: Resources, Writing – review & editing. Dickon Young: Resources, Writing – review & editing. Jens Mühle: Resources, Writing – review & editing. Paul B. Krummel: Resources, Writing – review & editing. Simon O'Doherty: Resources, Writing – review & editing. Ray F. Weiss: Resources, Writing – review & editing. Ronald G. Prinn: Resources, Writing – review & editing. Xuekun Fang: Conceptualization, Project administration, Supervision, Writing – review & editing.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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