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Multi-decadal records of stratospheric composition and their relationship to stratospheric circulation change

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Abstract. Constituent evolution for 1990-2015 simulated using the Global Modeling Initiative chemistry and transport model driven by meteorological fields from the Modern-Era Retrospective analysis for Research and Applications version 2 (MERRA-2) is compared with three sources of observations: ground-based column measurements of HNO3 and HCl from two stations in the Network for the Detection of Atmospheric Composition Change (NDACC, ~1990ongoing), profiles of CH₄ from the Halogen Occultation Experiment (HALOE) on the Upper Atmosphere Research Satellite (UARS, 1992–2005), and profiles of N₂O from the Microwave Limb Sounder on the Earth Observing System satellite Aura (2005-ongoing). The differences between observed and simulated values are shown to be time dependent, with better agreement after ~ 2000 compared with the prior decade. Furthermore, the differences between observed and simulated HNO₃ and HCl columns are shown to be correlated with each other, suggesting that issues with the simulated transport and mixing cause the differences during the 1990s and that these issues are less important during the later years. Because the simulated fields are related to mean age in the lower stratosphere, we use these comparisons to evaluate the time dependence of mean age. The ongoing NDACC column observations provide critical information necessary to substantiate trends in mean age obtained using fields from MERRA-2 or any other reanalysis products.

1 Introduction

The composition of the stratosphere is changing in response to changes in ozone-depleting substances (ODSs), nitrous oxide (N₂O) and methane (CH₄) with consequences for the ozone layer, stratospheric circulation, stratosphere-troposphere exchange and climate. ODSs (primarily chlorine- and bromine-containing compounds) are decreasing due to cessation of their production as a result of the Montreal Protocol and its amendments. These man-made compounds are greenhouse gases (Ramanathan, 1975). N₂O and CH₄ are sources of nitrogen and hydrogen radicals, and are also greenhouse gases. The concentrations of N₂O and CH₄ are presently increasing, as discussed by Carpenter et al. (2014) for recent decades, and reflected in boundary conditions that are prescribed for the simulations (Sect. 3). The stratospheric climate is changing in response to composition change, as increased greenhouse gases both cool the stratosphere and accelerate the stratospheric circulation (Butchart and Scaife, 2001). Both decreases in ODSs and cooling due to the increase in greenhouse gases cause ozone to increase by reducing ozone loss. Acceleration of the circulation causes column ozone to decrease in the tropics and increase at middle and high latitudes (Li et al., 2009). The net ozone layer response is a combination of photochemical and dynamical changes, as well as feedbacks in ozone heating and photochemistry that link them.

Future evolution of the ozone layer is commonly investigated using three-dimensional chemistry–climate models (CCMs) that combine a general circulation model (GCM) with a representation of photochemical and radiative processes. A common feature of middle-atmosphere GCMs

(without interactive chemistry) and CCMs (with interactive chemistry) is the intensification of the Brewer–Dobson circulation (BDC) in the 21st century due to increases in greenhouse gases (Butchart et al., 2006). BDC strengthening could manifest itself in many ways that impact ozone. Some observations in the tropics support BDC acceleration during the past few decades, but overall attempts to verify this prediction of models with measurements has resulted in mixed conclusions, as exemplified in the following paragraphs.

Kawatani and Hamilton (2013) find that tropical radiosonde observations for 1953-2012 show weakening of the quasi-biennial oscillation (QBO) that is consistent with increased tropical upwelling. Thompson and Solomon (2009) argue that for 1979-2006, microwave sounding unit channel 4 temperature retrievals and the merged total ozone data set (McPeters et al., 2013; Frith et al., 2014) are consistent with BDC acceleration after accounting for the effects of volcanic eruptions. Integrated ozone profiles from the Stratospheric Aerosol and Gas Experiment (SAGE I and SAGE II) show ozone decreases of about 10 DU (Dobson units) between 1979 and 2005 (Randel and Wu, 2007), consistent with decreases in tropical lower-stratospheric ozone from a record for 1984-2009 obtained by combining SAGE II data with SHADOZ ozonesondes (Randel and Thompson, 2011), but inconsistent with the nearly constant time series of tropical total column ozone (Pawson and Steinbrecht, 2015). Tropical lower-stratospheric ozone increases measured by the Scanning Imaging Absorption Spectrometer for Atmospheric CHartographY (SCIAMACHY), an instrument on Envisat (2002-2012), are also not consistent with a predicted circulation increase (Gebhardt et al., 2014). Harris et al. (2015) report no statistically significant O₃ trend in the tropical lower stratosphere. Simulations reported by Shepherd et al. (2014) produce an increase in tropospheric ozone that compensates for the stratospheric decrease, potentially resolving the discrepancy between the total column ozone record and the records that combine SAGE II with SAGE I or SHADOZ. Polvani et al. (2017) find that the ODSs themselves are primary drivers of tropical upwelling, in which case the decrease in ODSs over the coming decades will counter or reverse the impact of other greenhouse gases on the circulation. The future evolution of tropical column ozone is complex and may be influenced by circulation change, changes in tropospheric pollution or both.

In the extratropics, intensification of the BDC will alter the distributions of source gases, including anthropogenic chlorofluorocarbons (Butchart and Scaife, 2001), increase the midlatitude stratosphere-to-troposphere ozone flux (Hegglin and Shepherd, 2009) and decrease the stratospheric mean age (Li and Waugh, 1999; Austin and Li, 2006). Although all CCMs predict increased tropical upwelling in the 21st century, both the rate of tropical increase and the response of the extratropical circulation differ substantially. Douglass et al. (2014) show that differences in the details of the intensification of the extratropical circulation make major contribu-

tions to the spread in the stratospheric ozone level projected for 2100 obtained from the CCMs that contributed to a comprehensive effort to evaluate these models (SPARC CCM-Val, 2010) and the Scientific Assessment of Ozone Depletion: 2010 (WMO, 2011).

There have been efforts to quantify BDC trends and variability as expressed in meteorological analyses. Diallo et al. (2012) report statistically significant negative age trends in the extratropics using meteorological fields from ERA-Interim for 1989-2010. Abalos et al. (2015) find common features that support negative age trends in the advective Brewer–Dobson circulation for 1979–2012 in ERA-Interim, the Modern-Era Retrospective analysis for Research and Applications (MERRA) and the Japanese 55-year Reanalysis for 1979-2012. Ploeger et al. (2015) use the Chemical Lagrangian Model of the Stratosphere (CLaMS), driven by ERA-Interim reanalysis, to show how changes in both mixing and the residual circulation contribute to trends in age of air. Any of these results would be affected by changes in the observing system, and Diallo et al. (2012) caution that such changes may lead to false trends in the age obtained from analyzed fields. They emphasize the need for comparisons with trends derived from tracer observations. Furthermore, deficiencies in the GCM component of a reanalysis system such as lack of a spontaneous QBO may lead to spurious tropical ascent and subtropical mixing, also contributing to false trends (Tan et al., 2004; Coy et al., 2016).

Long-lived constituents (e.g., CFCl₃, CF₂Cl₂, N₂O), reservoir species that are products of their destruction (e.g., HNO₃ and HCl), and age tracers like SF₆ and CO₂ all carry information about changes in the circulation and mixing (Hall, 2000). Engel et al. (2009) find no statistically significant trend in the northern midlatitude mean age derived from sparse balloon profiles of SF₆ and CO₂ between 1985 and 2005. Ray et al. (2010) used the same observations and trends in the tropical vertical velocity obtained from reanalysis data sets to show how trends in both horizontal mixing and upwelling affect the midlatitude age trends, and they find that the age changes indicated by the measurements differ from those produced by the CCMVal models. Garcia et al. (2011) show the importance of accounting for nonlinear growth rates of the age tracers when comparing simulated ages with those derived from balloon observations. Ray et al. (2014) identify seasonal, quasi-biennial and decadal scales of variability in the middle latitude mean age by extending their previous analysis, accounting for variable growth rates in SF₆ and CO₂ and adjusting the measurementbased mean ages to a common equivalent latitude that is representative of the Northern Hemisphere (NH).

Prior use of source gases to infer variability in mean age is limited. Schoeberl et al. (2005) explored the relationship between mean age and trace gas distributions in a chemistry transport model (CTM) driven by winds from a GCM, interpreting their results using observations of CH_4 , N₂O, and chlorofluorocarbons CF_2Cl_2 and $CFCl_3$ from the cryogenic limb array etalon spectrometer (CLAES) on NASA's Upper Atmosphere Research Satellite (Roche et al., 1996) and from the Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS) on the Canadian SCISAT (Bernath et al., 2005). They associate young mean ages with high values of tracers seen by CLAES at the northern lower middle latitudes in 1993 and older mean ages with lower values for ACE-FTS tracers in 2005, speculating that the different relationships during these two periods are evidence of quasibiennial variability in the mean age. Strahan et al. (2015) showed the signature of the QBO in the variability of the southern midlatitude middle stratosphere N₂O and mean age using 9 years of observations from the Microwave Limb Sounder (MLS) on NASA's Earth Observing System (EOS) Aura.

A recent analysis of HCl column measurements from stations in the Network for the Detection of Atmospheric Composition Change (NDACC) highlights the relationship between mean age, low-frequency variability and the HCl column amounts. Both satellite and ground-based observations show an increase in NH column and lower-stratospheric HCl between 2007 and 2011 (Mahieu et al., 2014). CTM simulations using meteorological fields from ERA-Interim reproduce the lower-stratospheric pattern of NH HCl increase and Southern Hemisphere (SH) decrease, consistent with an increase in the mean age and a slowdown in the NH midlatitude lower-stratospheric circulation. The HCl increase indicates air with older mean age that has spent more time at higher altitudes (Hall, 2000), where it experiences rapid chlorofluorocarbon destruction leading to higher levels of HCl. The magnitude and duration of the HCl column increase attests to the importance of quantifying the natural variability that produced it. Large natural multi-annual variations make it more difficult to quantify trends in the circulation, to identify a decrease in inorganic chlorine caused by the decrease in ODSs or to attribute an ozone increase to ODS decrease.

The goal of this work is to use multi-decadal observations of source and reservoir trace gases from satellite and groundbased instruments, along with a hindcast simulation from the Global Modeling Initiative chemistry transport model (GMI CTM), driven by meteorological fields from MERRA version 2 (MERRA-2), to explore extratropical variability and trends in lower-stratospheric transport and mean age between 1990 and 2015. This work establishes a framework for the use of ground-based and satellite observations of constituents other than ozone to identify and quantify long-term changes in the residual circulation. We argue that the simulation must reproduce the interannual and longer-timescale variability seen in the observed data records to confirm the realism of trends in the simulated mean age. We consider two overarching questions:

1. Do comparisons of modeled and observed trace gases support the trends in circulation and mean age inferred from reanalyses? 2. Are the ongoing sparse data sets available from the early 1990s sufficient to characterize multiyear variability and thereby provide more robust trend estimates?

Observations used in this work include columns of reservoir gases at several NDACC stations (~ 1990–ongoing), profiles from the Halogen Occultation Experiment (HALOE) on the Upper Atmosphere Research Satellite (UARS) (1991–2005) and near-global profile data sets from the MLS on EOS Aura (mid-2004–ongoing); these are described in Sect 2. Models are discussed in Sect. 3. Comparisons of simulations with observations and their relationship to simulated mean age are found in Sect. 4. Discussion and conclusions follow in Sect. 5.

2 Observations

2.1 Network for the detection of atmospheric composition change

Here we use total column measurements of HCl described by Mahieu et al. (2014) and version 7 HNO₃ (Ronsmans et al., 2016) from Fourier transform infrared (FTIR) instruments at two stations (Jungfraujoch, Switzerland, 46.6° N, 7.98° E, and Lauder, New Zealand, 45.0° S, 169.7° E). Both of these stations belong to the NDACC (http://www. ndacc.org). The data, courtesy of Emmanual Mahieu (PI for the NDACC Jungfraujoch station) and Dan Smale (PI for the NDACC Lauder station), are publicly available through an anonymous FTP at ftp://ftp.cpc.ncep.noaa. gov/ndacc/station/jungfrau/ and ftp://ftp.cpc.ncep.noaa.gov/ ndacc/station/lauder/. This analysis is limited to midlatitudes, and these stations are chosen for comparison with the simulation because of the length of their records (~ 1987 ongoing at Jungfraujoch and \sim 1990–ongoing at Lauder). The comparison of the simulation with data from other northern midlatitude stations is similar to that reported here but is not discussed here because the length of record is important to this analysis.

2.2 UARS Halogen Occultation Experiment (HALOE)

HALOE on UARS (Russell III et al., 1993) measured profiles of ozone and other gases including methane (CH₄) using solar occultation from September 1991 until the end of the mission in late 2005. HALOE nominally obtained 15 sunrise and sunset profiles daily, providing near-global coverage in about a month. HALOE obtained profiles between 270 and 320 days yr⁻¹ between 1992 and 1995, but operational issues limited measurements to about 180 days per year for 1996 until the end of the mission in November 2005. These issues precluded observations during some seasons at specific latitude bands later in the mission. We take this into account by restricting comparisons with the simulation to winter between 35 and 55° latitude, where the number of observations per year is nearly constant in both hemispheres. Profiles used here are retrieved using algorithm version 19 and interpolated to 13 UARS standard pressure levels starting at 100 hPa (i.e., $p_i = 100 \cdot \exp(i/6)$, where *i* is an integer). The combined systematic and random uncertainty of single CH₄ profiles in the lower stratosphere is 11–19% (Grooß and Russell III, 2005).

2.3 Aura Microwave Limb Sounder (MLS)

Livesey et al. (2017) describe the version 4.2 (v4) MLS data products, their precision, accuracy and screening procedures to identify and eliminate profiles that are not recommended for scientific use. Here we use MLS observations for 2005–2015 for the source gas nitrous oxide (N_2O). The v4 data set retrieved from the band 12 640 GHz (N₂O-640) is scientifically useful from 100 to 0.46 hPa. This data set begins shortly after launch but ends in mid-2013 due to band failure. The second v4 data set, retrieved from band 3190 GHz (N₂O-190), begins shortly after launch and is ongoing. Aura MLS provides \sim 3495 profiles daily between 81° S and 81° N; data are averaged in 2° latitude bins (30– 60 profiles per bin after screening), reducing precision uncertainty. Monthly, seasonal and annual averages are compared with simulations that are described below. The highest pressure level for useful measurements is 68 hPa for N2O-190 compared with 100 hPa for N₂O-640. In addition, percentage differences (N₂O-190 - N₂O-640)/N₂O - 640 · 100 vary both seasonally and temporally at middle latitudes. For example, NH monthly zonal mean differences at 68 hPa are between 4 and 8 % in 2005 and decrease to 0-5 % by 2012, with greater temporal dependence during winter months. We limit comparisons with simulated N₂O to 46.4 hPa and lower pressures where the bias and its temporal dependence are smaller.

3 Models

3.1 GMI CTM

A GMI CTM hindcast simulation was integrated in 1 January 1980–2015 using MERRA-2 meteorological fields (Gelaro et al., 2017). MERRA-2 ingests recent satellite observations and uses an improved GCM (Molod et al., 2015) compared with MERRA (Rienecker et al., 2011). This GMI CTM simulation has 2° latitude $\times 2.5^{\circ}$ longitude horizontal resolution and 72 vertical levels with ~ 1 km resolution between 300 and 10 hPa. Details of a similar GMI CTM simulation using the earlier MERRA fields at 1° latitude $\times 1.25^{\circ}$ longitude resolution are found in Strahan et al. (2013) and references therein. Reaction rates and cross sections are from the JPL evaluation 18 (Burkholder et al., 2015). Surface mixing ratio boundary conditions for all organic halogen and long-lived source gases follow the WMO A1 2010 and RCP 8.5 scenarios, respectively, and include 5 ppt of additional CH₃Br to account for bromine from short-lived source gases. Time-dependent stratospheric aerosols come from International Global Atmospheric Chemistry (IGAC) as prescribed for the SPARC Chemistry-Climate Model Initiative (CCMI) simulations. The simulation was initialized with December 1979 MERRA-2 meteorological fields using source gas and reservoir constituent fields from a prior simulation. The same MERRA-2 meteorological fields were used to integrate a clock tracer. The clock tracer is a linearly increasing conservative transport tracer forced at the two lowest model levels and has no atmospheric losses. It is always reset to the current date at the surface.

3.2 GEOSCCM

The Goddard Earth Observing System chemistry–climate model (GEOSCCM) couples the GEOS version 5 GCM (Rienecker et al., 2008; Molod et al., 2012) to the GMI stratosphere–troposphere chemical mechanism (Duncan et al., 2007; Strahan et al., 2007; Oman et al., 2013). The simulation used is run on the cubed sphere at c48 resolution, equivalent to a 2° horizontal resolution, with the same vertical layers as GMI CTM. The surface mixing ratio boundary conditions are the same, except GEOSCCM uses the WMO A1 2014 halogen scenario instead of the A1 2010 used in the GMI CTM (these are very similar). Reaction rates and cross sections are the same as described for the GMI CTM. Observed sea surface temperatures and sea ice concentrations are also used to force this free-running simulation (Rayner et al., 2003).

4 Results

The global daily observations of the long-lived tracer N_2O obtained from MLS are ideal for determining whether circulation trends inferred from analyses and/or from simulated age of air trends are consistent with observations. The MLS data set began in mid-2004 and is ongoing, but the projected changes in the BDC are multi-decadal. We therefore consider whether the sparse data sets available from the early 1990s are sufficient to characterize multi-annual variations, piecing together space-based observations from UARS HALOE and the multi-decadal ground-based column measurements of HNO₃ and HCl. For 2005 onward we test whether information from the ground-based column measurements is consistent with that obtained from MLS.

The first step towards meeting these goals is to examine the relationships between tracer and reservoir species and the mean age as produced by simulations using the GMI CTM and the GEOSCCM (Sect. 4.1). Our focus in Sect. 4.2 is to test whether the simulated changes track the observations of CH₄ (UARS HALOE), N₂O (Aura MLS), and of reservoir gases HCl and HNO₃ from 1987 to present (NDACC groundbased column measurements).

A. R. Douglass et al.: Multi-decadal records of stratospheric composition

4.1 Relationships among simulated age, N₂O, CH₄ and reservoir gases

4.1.1 Source gases N₂O and CH₄

Strahan et al. (2011) show that N₂O observations from ACE-FTS are anticorrelated with mean age observations for N₂O values less than 150 ppbv and mean age less than 4.5 years. Here we focus on the relationship between annual mean values to emphasize interannual and longer-timescale variability in circulation, noting that peak-to-peak seasonal variations in N₂O and CH₄ (\sim 10 % of their respective means) and age (\sim 20 % of the mean) are also anticorrelated (not shown). Examples of the evolution of annual mean age, N₂O and CH₄ in the GMI CTM, driven by MERRA-2 winds, show that mean age is anticorrelated with both N₂O and CH₄ (Fig. 1a and b).

The GMI CTM results show a large N₂O increase between \sim 1987 and \sim 1995 in the northern midlatitudes, followed by a decrease from 2002 to 2004 through 2010 and another increase from 2010 to 2013. These are indicators of multiyear variability in MERRA-2 transport. The evolution of CH₄ parallels that of N₂O after about 1997. The relationship between these tracers and age is similar in the SH, with shorter periods of smaller increases or decreases in both tracers compared with the NH. Annual mean N₂O changes are generally reflected in the time series of annual mean age; the correlation coefficients between N₂O and mean age for this example are -0.77 (NH) and -0.66 (SH).

Comparison of the evolution of mean age, N₂O and CH₄ in the GMI CTM (Fig. 1a and b) with that in the GEOSCCM (Fig. 1c and d) illuminates dynamical differences between the models as the simulations use the same boundary conditions for these gases. GEOSCCM changes in N₂O and CH₄ are reflected in the time series of mean age (correlation coefficients between annually averaged N_2O and age are -0.91in the NH and -0.96 in the SH), but the multivear variability is smaller. The percentage change per decade is calculated for successive 10-year periods beginning in 1980 for both hemispheres (Fig. 1e and f). In GEOSCCM, the rate of N₂O increase in the extratropics is always close to the tropical rate of increase of ~ 2.6 % decade⁻¹, with a small signature of the effect of the Pinatubo aerosols on the circulation. In contrast, the decadal rate of change in the GMI CTM extratropics may be 2-3 times greater or of the opposite sign compared with the rate of increase at the tropical tropopause (the same in both simulations as it is controlled by the boundary condition).



Figure 1. The GMI CTM differences from the 1980–2015 mean for mean age (black), N_2O (blue) and CH₄ (blue dashed) at 72 hPa for (**a**) 46° N and (**b**) 46° S. The GEOSCCM differences from the 1980–2015 mean for mean age (black), N_2O (red) and CH₄ (red dashed) at 72 hPa for (**c**) 46° N and (**d**) 46° S. Trends calculated for successive 10-year periods at 72 hPa are shown for N_2O (blue, GMI CTM; red, GEOSCCM) and CH₄ (blue dashed, GMI CTM; red dashed, GEOSCCM) at (**e**) 46° N and (**f**) 46° S. Tropical trends at 100 hPa (black, N_2O ; black dashed, CH₄) are shown in (**e**). They are the same for both simulations and reflect the boundary conditions.

4.1.2 Mean age and fractional release

The age spectrum for a stratospheric air parcel is the distribution of transit times between entry to the stratosphere and the parcel location for each of the elements that comprise the parcel. The mean age is the average of this distribution, and comparisons of simulated mean age with that obtained from measurements such as SF_6 (a long-lived trace gas that is increasing in the troposphere) provide information about the realism of the advective and mixing processes that control the parcel paths. Hall et al. (1999) used mean age comparisons to show lack of realism in the transport produced by various models that participated in Model and Measurements Intercomparison II (Park et al., 1999). Hall (2000) and Schoeberl et al. (2000) used trajectory calculations to show

that, on average, the oldest elements have risen to highest altitudes; thus, evidence of loss of a long-lived gas in a parcel found in the lower stratosphere indicates that the age spectrum includes parcel elements that have experienced high altitude where source gas destruction occurs. These older elements of the age spectrum contribute to the mean age and determine the amount of destruction of long-lived gases. This relationship between the oldest elements of the age spectrum and the probability of destruction leads to compact, inverse relationships between mean age and gases with tropospheric sources. Indeed, aircraft observations show that the destruction of long-lived gases including chlorofluorocarbons, N₂O and CH₄ is related to the mean age obtained from SF₆. Schauffler et al. (2003) use aircraft observations to compute the fractional release f_r :

$$f_{\rm r} = \left(1 - \frac{X(x)}{X_i}\right),\tag{1}$$

where X(x) is the mixing ratio of a source gas in a parcel at location x (latitude, altitude, pressure, time) and X_i is the mixing ratio at entry to the stratosphere, finding a near-linear relationship between f_r and the SF₆ mean age. Waugh and Hall (2002, and references therein) discuss the relationship between tracer distributions and transport timescales in the stratosphere, noting the connection between the BDC and the wave-driven quasi-horizontal mixing that controls distributions of stratospheric trace gases. Because the fractional release depends on destruction of the source gas and therefore on the portion of the age spectrum that reaches high altitude where destruction is possible, the relationship between fractional release and mean age is a stronger test of the realism of simulated transport than the simple comparisons of mean age distributions. The older elements of the age spectrum that contribute to the mean age make the largest contribution to the fractional release. Mean age is negatively correlated with source gases and positively correlated with the products of their destruction (e.g., HCl and HNO₃).

In GEOSCCM the BDC is fully consistent with the planetary wave breaking that results in horizontal mixing and plays a role in driving the BDC. This consistency is not guaranteed in the MERRA-2 fields. Comparison of fractional release and its relationship to mean age with values obtained from observations tests the balance between horizontal mixing and vertical transport. Waugh et al. (2007) apply these concepts to the simulated amounts of inorganic chlorine (Cl_y) released from source gases in a CTM using different grid resolution and meteorological fields, finding large differences in Cl_y for the same mean age. Within the same CTM, different meteorological fields or different implementation of meteorological fields may produce the same mean age but different values for the fractional release because the mean transport pathways differ.

In GMI CTM the fractional release of N_2O for fixed mean age varies substantially between 1990 and 2000 in both hemispheres (Fig. 2a and b). In contrast, in GEOSCCM the frac-



Figure 2. Contours of the evolution of N₂O fractional release simulated by GMI CTM for 1990–2015 as a function of mean age at (a) 46° N and (b) 46° S. Same for the GEOSCCM at (c) 46° N and (d) 46° S. The ratio of the standard deviation of the N₂O fractional release to the mean value from GMI CTM (black) and from GEOSCCM (blue) averaged from 1990 to 2000 (solid) and from 2005 to 2015 at (e) 46° N and (f) 46° S.

tional release at the fixed mean age varies slowly (Fig. 2c and d). The changing relationship between fractional release and mean age in the GMI simulation reveals decadal variations in the relationship between horizontal and vertical transport processes in MERRA-2. After about 2000, the small variations in f_r for fixed mean age in GMI CTM are comparable to the variations obtained throughout the period for GEOSCCM. We illustrate this by comparing the ratio of the f_r standard deviation to its mean for 1990– 2000 and 2005-2015 for each simulation for both hemispheres (Fig. 2e and f). In GEOSCCM the ratio is about 2 % for both time periods and for both hemispheres. For GMI CTM the ratio for 1990-2000 is between 6 and 8 % for the age range 2-3.5 years in both hemispheres. For 2005-2015 the GMI CTM ratio is comparable to that obtained from GEOSCCM, although still larger than GEOSCCM in the SH. The smaller values of f_r at the fixed mean age found during the early 1990s suggest that the balance between horizontal and vertical transport processes up until about 2000 is substantially different in both hemispheres in the first half of the 1990s than in subsequent years. This changing relationship contributes to the lower correlations of mean age with long-lived tracers in GMI CTM compared with GEOSCCM noted in Sect. 4.1.1 and also affects the relationship of mean age with reservoir gases discussed below.

4.1.3 Reservoir gases HCl and HNO₃

Hydrochloric acid is the most abundant of the chlorine product species throughout the stratosphere, and more than 80 % of the HCl column resides below 20 hPa. The sources of HCl increased by ~5% yr⁻¹ up until about 1992 but leveled off during the late 1990s. The long-lived gases CFCl₃ and CF₂Cl₂ have been decreasing slowly since ~2000 (<1% yr⁻¹) due to cessation of ODS production as a result of the Montreal Protocol and its amendments. Methyl chloroform (CH₃CCl₃) is shorter lived and contributed about ~15% of total inorganic chlorine in the lower stratosphere in 1995, decreasing rapidly thereafter. Prior to ~2000, growth of the HCl column and the HCl lower-stratospheric mixing ratio was controlled by the rapid growth of the source gases.

After ~ 2000, the simulated evolution of lowerstratospheric HCl and its column broadly matches mean age in both hemispheres (Fig. 3), although neither is a perfect surrogate for mean age variability at a particular level. Multiyear changes in the midlatitude HCl columns that are larger or opposite in sign to the source gas decrease reflect changes in the residual circulation (Mahieu et al., 2014). This is seen in the SH, where simulated column decreases are more rapid than can be accounted for by the decrease in source gases between 2005 and 2011. During this period the SH mean age decreases throughout the lower stratosphere (maximum rate of decrease 1 % yr⁻¹ at 100 hPa), contributing to the decrease in simulated HCl column.

Nitric acid is similar to HCl in that both are produced from radicals released by destruction of tropospheric source gases in the upper stratosphere. It is the dominant component of total odd nitrogen (NO_{y}) between the tropopause and ~ 50 hPa, poleward of about 40° in both hemispheres. Lower-stratospheric N₂O is anticorrelated with NO_{ν} and also with HNO₃ during winter when HNO₃ is $\sim 90\%$ of NO_y. The stratosphere below 50 hPa contains $\sim 80 \%$ of the total winter column HNO₃. Except when the lower-stratospheric aerosol layer is enhanced by a Pinatubo-type volcanic eruption, a "trend" in the residual circulation may be identified by an increase in middle-latitude HNO₃ columns that is faster or slower than the trend in N₂O increase ($\sim 0.3 \% \text{ yr}^{-1}$) for several consecutive years. The HNO3 column, lowerstratospheric HNO₃ mixing ratio and the mean age simulated using GMI CTM track one another at middle latitudes in both hemispheres starting in 1993, about 18 months after the eruption of Mt. Pinatubo (Fig. 4).



Figure 3. The evolution of the GMI CTM HCl mixing ratio (green) and mean age (black) at 72 hPa and the HCl column (blue) at (a) 46° N and (b) 46° S. The HCl column is $N \times 10^{15}$ molecules per cm², where N is the right blue axis. The time interval begins in 2000 when the chlorine-containing source gases have stopped increasing or begun to decline.

Although neither the total column HNO₃ or HNO₃ mixing ratio at a particular level correlates perfectly with the mean age, Fig. 4 shows decadal-scale upward trends in both hemispheres in the HNO₃ column, HNO₃ mixing ratio and mean age for \sim 1998 to 2010. The simulated winter HNO₃ mixing ratio and mean ages are correlated with levels above and below and with each other between 25 and 85 hPa. The column, mean age and lower-stratospheric mixing ratio are positively correlated throughout the middle latitudes of both hemispheres.

4.2 Observations, GMI CTM simulation and mean age

The relationships of constituents and mean age apparent in the GMI CTM simulation driven by MERRA-2 fields suggest that quantitative information about residual circulation change at middle latitudes can be obtained from existing and ongoing measurements. The following discussion considers the NH and SH separately. In each we compare the simulation with ground-based FTIR column measurements of reservoir gases HCl and HNO₃, available from the early 1990s at some stations, with HALOE measurements of the source gas CH₄ (1992–2005) and with Aura MLS measurements of N₂O (2005–present).



Figure 4. The evolution of the GMI CTM HNO₃ mixing ratio (green) and mean age (black) at 72 hPa and the HNO₃ column (blue) at (a) 46° N and (b) 46° S. The HNO₃ column is $N \times 10^{15}$ molecules cm⁻², where N is the right blue axis. The time interval begins in 1993, about 18 months after the eruption of Mt. Pinatubo.

4.2.1 Northern Hemisphere

NDACC - Jungfraujoch, Switzerland (46.6° N, 7.98° E)

When sampled for the time and location of the observations, the NH NDACC column observations of HNO₃ and HCl are highly correlated with the GMI columns (Fig. 5). These scatter plots include daily and seasonal variability as well as any trend in HCl and HNO₃ due to trends in their source gases during the 26 years of measurements (1989–2014). The mean of the GMI HCl columns is within 3 % of the mean of observations. The mean of the GMI HNO₃ columns is 21 % lower than the mean of the observations.

The time series of differences between observed and simulated HCl columns reveals a bias that changes over the course of the integration (Fig. 6a). The simulation is biased low before 2000 (positive differences) but has greatly reduced bias after ~ 2004 . The time series of differences between observed and simulated HNO₃ columns is similar to that of the HCl columns. The changing bias is demonstrated by comparing histograms of the percentage difference between observations and simulation for 1989–2004 and 2005–2015 (Fig. 6b and c). The bin size for each gas is equal to one-third of the standard deviation of all measurements. In both cases the distribution of differences for 1989–2004 is shifted



Figure 5. Simulated and observed columns 1989-2014 for (**a**) HCl and (**b**) HNO₃. Both simulated species are highly correlated with the observations when the simulation is sampled for the location and days of the measurements.



Figure 6. (a) Time series of the differences between observed and simulated HCl columns at Jungfraujoch. Histogram of the percentage differences for 1989–2004 (green) and 2005–2015 (blue) (b) for HCl and (c) HNO₃.

towards the right compared with the distribution for 2005-2015. There are fewer observation days per year prior to 1996 (average 37, standard deviation – SD 24) than 1997 onward (average 95, SD 27), but subsampling later years to match the observation frequency and seasonality of early years does not change this result. The shift towards better agreement is not sensitive to the exact time interval (i.e., similar results are obtained comparing the distribution for 1989–2000



Figure 7. The differences between simulated and observed columns at Jungfraujoch for HCl are correlated with the differences for HNO₃, whether considering daily average (black), monthly average (blue) or yearly average (orange) values.

with 2000–2015). We chose to emphasize 2005–2015 because Aura MLS obtained global data sets during this period.

Figure 7 shows that on days when both HCl and HNO₃ are measured, the differences between measured and simulated HNO₃ are strongly correlated with the differences between measured and simulated HCl. This correlation is found whether daily, monthly or annual averaged timescales are considered. On the annual timescale, the correlation is found whether averaging all measurements for each gas each year or when averaging only measurements on days both gases were reported. We conclude that the similar time dependencies of the differences (Δ HCl and Δ HNO₃) are caused by substantial differences in the transport characteristics of MERRA-2 fields during the 1990s compared with the period 2004 and onward. The correlation between differences cannot be explained by photochemistry because unrelated processes control partitioning of the chlorine- and nitrogencontaining reservoir species in the lower stratosphere. Furthermore, this correlation holds even though anthropogenic chlorine source gases increased until ~ 2000 and declined thereafter, while the source gas N₂O increased steadily for the entire period. Our conclusion is consistent with the change in the relationship between the fractional release and mean age found in the NH lower stratosphere (Fig. 2a and e). The lower values of fractional release during the 1990s are consistent with the shift in the distribution of HCl column differences from a low bias in the 1990s to a much smaller low bias after 2004. This also explains the shift in the distributions of HNO₃, but does not explain the low bias in simulated HNO₃ that remains after 2004 (20%), when the difference between simulated and observed HCl is within experimental error.



Figure 8. The 46° N annual zonal mean N₂O in the GMI CTM (black), the MLS N₂O-640 (green), the MLS N₂O-190 (blue) and the mean age (orange dashed) at (a) 46.4 hPa and (b) 31.6 hPa. The simulated N₂O tracks the observed values and is anticorrelated with the mean age at both levels (-0.86 and -0.83 at 46.4 and 31.6 hPa, respectively).

Aura MLS Northern Hemisphere

As discussed in detail by Strahan et al. (2011), the mean age is a near-linear function of N₂O for N₂O values greater than about \sim 150 ppbv (about half the value at the tropical tropopause). Here we focus on midlatitude annual averages at two MLS levels (46.4 and 31.8 hPa), noting that the difference between the simulated and zonal mean MLS N₂O (640 GHz receiver) is less than 10 % for MLS annual means greater than 150 ppby. To emphasize multiyear variations, we compare simulated annual averages with observed values from both MLS N2O bands at 46° N at 46.4 and 32 hPa (Fig. 8). There is a 6% bias between the annual means for N₂O-190 compared with N₂O-640 at 46.4 hPa. Simulated N₂O agrees well with observations throughout the period and is strongly anticorrelated with the simulated mean age. The observed and simulated 2006-2011 decreases are accompanied by simulated increases in mean age, consistent with column increases in both HCl and HNO₃ (Mahieu et al., 2014).

UARS HALOE Northern Hemisphere

Because HALOE sampling is not uniform, the simulation output is subsampled at the location and time of the HALOE measurements. We focus on January–February–March for



Figure 9. Histograms of percentage differences between HALOE and simulated CH_4 at 46.4 hPa (blue), 31.6 hPa (black) and 21.4 hPa (red) for all HALOE profiles between 35 and 55°. The distributions at all levels shift towards better agreement with observations for 1999–2005 compared with 1992–1998.

35–55° N because the number of profiles obtained at midlatitudes during each winter is similar over the life of the mission (see Sect. 2.2).

Factors other than nonuniform sampling complicate the relationship of HALOE CH₄ with circulation and mean age. First, because aerosols from the eruption of Mt. Pinatubo interfere with HALOE measurements below 46 hPa in 1992 and 1993, we focus on comparisons at 46.4, 31.6 and 21.5 hPa. Second, the rate of CH₄ increase at the tropical tropopause (specified by the boundary condition) is variable and may be substantially larger, about the same or smaller than the rate of increase in N_2O (Fig. 1). The rate of CH_4 increase in the tropics at 100 hPa is greater than $1 \% \text{ yr}^{-1}$ in 1979, falls to less than $0.1 \% \text{ yr}^{-1}$ between 2000 and 2005, and increases to $1 \% \text{ yr}^{-1}$ by the end of the integration. Assuming that the observationally derived boundary condition is correct, comparisons of observed and simulated CH₄ test the fidelity of the transport. Finally, we note that normalized vertical and horizontal CH₄ gradients are smaller than the N₂O gradients, making CH₄ less sensitive to circulation changes.

The differences between HALOE and simulated CH₄ for 1992–1998 are compared with differences for 1999–2005 by examining histograms of the percentage differences for each time period at 46.4, 31.6 and 21.5 hPa (Fig. 9). At all three levels, the distributions shift towards a smaller difference in the later time period. The observed and simulated values are positively correlated for 1992–1998 (between 0.7 and 0.8), but correlations are larger during the later period (slightly larger than 0.8). The larger differences during the earlier period are consistent with greater horizontal mixing



Figure 10. Percentage differences between 1994–1999 and 2000–2005 winter mean CH₄ profiles at 35–55° N for HALOE (blue) and GMI CTM (black). The difference between the 35–55° N winter mean age profiles for the same periods is shown in red.

and with the unexpected time dependence in the relationship of fractional release and simulated mean age.

We look at observed and simulated CH₄ changes over the period of the HALOE observations by computing the difference between 1994–1999 and 2000–2005 mean profiles (Fig. 10). The HALOE mean CH₄ decreases between 68 and 10 hPa, whereas the GMI CH₄ increases (Fig. 10a). The very small differences between HALOE and GMI at the two lowest levels suggest that the time dependence of the mixing ratio at stratospheric entry is realistic. The simulated mean ages for 2000–2005 are younger for 68–10 hPa compared with 1994–1999, consistent with the increase in GMI CH₄. However, the HALOE data do not support this decrease in mean age as produced by the MERRA-2 meteorological fields.

To summarize the NH comparisons, the simulated columns of HNO₃ and HCl follow NDACC observations at the Jungfraujoch station after ~ 2000 with higher fidelity than prior years. The simulated columns of both constituents are lower than the observed columns during the middle 1990s; this is consistent with lower values for fractional release for a given mean age in the 1990s compared with the 2000s (Fig. 2). The comparison of simulated CH₄ with HALOE observations similarly shows that the age change produced by the GMI CTM using MERRA-2 meteorology between 68 and \sim 20 hPa during the 1990s is not realistic. The mean fractional release for fixed mean ages is larger after 2000 (Fig. 2a), indicating that after 2000 MERRA-2 transport pathways take more air parcels to higher altitudes than during the 1990s (Hall, 2000). The simulated long-lived species HCl, HNO₃, CH₄ and N₂O are all closer to the observations after 2000, indicating that transport characteristics



Figure 11. The GMI CTM and observed columns at Lauder station in 1990–2014 for (a) HCl and (b) HNO_3 . Histogram of the percentage difference between simulated and observed columns in 1990–2004 (blue) and 2005–2014 (green) for (c) HCl and (d) HNO_3 .

of the GMI CTM using MERRA-2 are more realistic in this period.

Together, the observations do not support the MERRA-2 mean age evolution before 2000, but do support the realism of the increase in northern midlatitude lower-stratospheric mean age between 2005 and 2011 following the quiescent period 2000–2004. The strong relationship between variability in simulated lower-stratospheric mean age, MLS N₂O and the NDACC HNO₃ columns demonstrates the value of these observations for evaluating the residual circulation and mixing in meteorological analyses. Furthermore, the duration of periods of positive or negative changes in the circulation shows that multi-decadal records are required to identify a geophysically significant trend in the stratospheric circulation.

4.2.2 Southern Hemisphere

NDACC Lauder, New Zealand (45.0° S, 169.7° E)

As for the NH Jungfraujoch station, the simulation is sampled for the time and location of the HCl and HNO_3 column observations at the Lauder station. The simulated columns for both species are correlated with observations (Fig. 11a



Figure 12. The differences between observed and simulated Lauder HCl columns are correlated with the differences between observed and simulated HNO₃ columns, whether considering daily values (black), monthly averages (blue) or yearly averages (orange).

and b), although there is more scatter in the relationship between observed and simulated HCl columns evidenced by the lower SH correlation (0.73) compared with the NH (0.90). The mean bias between observations and simulation is less than 4 % for HCl and about 18 % for HNO₃, comparable to the NH. The distributions of differences shift slightly towards better agreement for 2004–2014 compared with 1990–2004. The shifts are smaller than found for the NH.

Like the NH, the differences between observed and simulated HNO₃ columns are correlated with the differences between observed and simulated HCl columns (Fig. 12) for daily values (r = 0.62), monthly averages (r = 0.61) or annual averages (r = 0.71).

Aura MLS Southern Hemisphere

As expected, at middle latitudes the annual means of GMI N_2O and mean age (shown at 46° S) are correlated at 46.4 and 31.6 hPa (Fig. 13). The GMI N_2O tracks the observed N_2O -640 at both levels and N_2O -190 only at 31.6 hPa. At 31 hPa the two retrievals maintain a near-constant bias as a function of time, whereas bias is year dependent at 46.4 hPa. At 46.4 hPa the simulated N_2O reflects some of the observed year-to-year differences and agrees better with N_2O -640, while at 31.6 hPa it agrees very closely with N_2O -190. At 31.6 hPa, both retrievals are consistent with the mean age changes between 2004 and 2015.

4.2.3 UARS HALOE Southern Hemisphere

We focus on SH winter months July–August–September for $35-55^{\circ}$ S because the number of profiles obtained at midlatitudes during each winter is similar over the life of the mission (see Sect. 2.2). As in the NH, we compare the differences between HALOE and simulated CH₄ for 1992–1998 with 1999–2005 by examining histograms of the percentage differences for each time period at 46.4, 31.6 and 21.5 hPa



Figure 13. (a) The 46° S annual zonal mean N_2O in the GMI CTM (black) follows MLS N_2O -640 (green) but not N_2O -190 (blue) at 46.4 hPa. The simulated N_2O is anticorrelated with the mean age and with MLS N_2O -640. (b) The GMI CTM N_2O follows both MLS products at 31.6 hPa and is anticorrelated with mean age.

(Fig. 14). Again, the distributions shift towards smaller differences during the later time period. The observed and simulated values are positively correlated for 1992–1998 (0.63– 0.78 on the three levels); correlations are nearly unchanged in the later period. As in the NH, the comparison improves as the integration proceeds, consistent with the evolving relationship between mean age and fractional release discussed above.

As in Fig. 10, we look at mean age and observed and simulated CH₄ changes over the period of the HALOE observations (Fig. 15). The age increase below 50 hPa has little impact on the simulated profile change because the gradients are weak. The mean age for 2000–2005 is younger compared with 1994–1999 for 50–10 hPa. Both the observed and simulated profile changes are positive, consistent with the age decrease, but the simulated change is substantially larger than that observed for most of the profile, casting doubt on the realism of the simulated age decrease (Fig. 1b).

To summarize, comparison of constituent evolution from four data sets (NDACC HNO₃ and HCl columns, HALOE CH₄, Aura MLS N₂O) with the GMI CTM simulation leads us to similar conclusions in both hemispheres regarding MERRA-2 transport. Horizontal transport and mixing during the 1990s generally led to somewhat older mean age, but agreement with observations improves as the relation-



Figure 14. Histograms of percentage differences between HALOE and simulated CH₄ at 46.4 hPa (blue), 31.6 hPa (black) and 21.4 hPa (red) for all HALOE profiles between 35 and 55° S for 1992–1998 (solid) and 1999–2005 (dashed).



Figure 15. Percentage differences between 1994–1999 and 2000–2005 winter mean CH_4 profiles at 35–55° S for HALOE (blue) and GMI CTM (black). The difference between the 35–55° S winter mean age profiles for the same periods is shown in red.

ship between mean age and fractional release evolves in the 2000s. This indicates that transport in the GMI CTM using MERRA-2 becomes more realistic as the simulation progresses. Lower fractional release for a given mean age leads to underestimates of the reservoir species during the 1990s. Overall, the differences between observed and simulated columns of HCl are correlated with the differences between observed and simulated HNO₃, strongly indicating transport as their cause and casting doubt on MERRA-2-driven GMI CTM lower-stratospheric mean ages in the 1990s. In contrast, the agreement with MLS N₂O during the Aura period, along with better agreement with observed HCl and HNO_3 columns, indicates the realism of age variations obtained from 2005 onward.

5 Discussion and conclusions

Reanalysis data sets such as MERRA-2 depend on the data assimilation system, its general circulation model and the data sets that are ingested by the system. Global data sets are of limited duration, and even though the same system is used to produce a multi-decadal reanalysis, differences in the quality and type of data sets that make up the observing system are unavoidable (Gelaro et al., 2017). Such differences may lead to nonphysical trends in analysis products and in constituents simulated using reanalysis meteorological fields in frameworks such as the GMI CTM. Although the relationship between the fractional release and mean age is expected to change in the midlatitude lower stratosphere if the BDC strengthens due to climate change (Douglass et al., 2008), the observations are not consistent with the large changes in fractional release for fixed mean age obtained during the 1990s using GMI CTM compared with the changes in GEOSCCM.

Global observations of tracers such as N_2O , obtained by Aura MLS since mid-2004, are ideal for evaluating the transport circulation in reanalysis data sets. The comparisons of simulated and observed fields demonstrated here for the annual average midlatitudes in both hemispheres and in a previous work using MERRA during the Arctic winter (e.g., Strahan et al., 2016) attest to the realism of MERRA and MERRA-2 meteorological fields from 2004 to present. Apparent trends in constituents in both hemispheres, seen in MLS N₂O and ground-based column measurements of HNO₃ and HCl, are consistent with the changes in the lowerstratospheric residual circulation that caused an increase in mean age between 2007 and 2011 in the NH accompanied by smaller and opposing transport and mean age changes in the SH (Mahieu et al., 2014).

For the 1990s, in contrast, comparison of the simulated values with HALOE CH₄ and ground based columns reveals multiple issues in both hemispheres. The MERRA-2 circulation produces multiyear constituent trends that are not observed. The comparisons are markedly better after 2000, strongly suggesting that differences in the observing system affect the MERRA-2 fields. The differences between observed and simulated HCl and HNO₃ are correlated with each other whether considering daily, monthly or yearly averages, strongly suggesting that issues with transport produced by GMI CTM using MERRA-2 fields cause the differences during the 1990s. The change in the simulated relationship between the fractional release and the mean age between the 1990s compared with later years suggests a difference in the mean parcel paths such that the highest altitude reached by the older air in the 1990s is lower than in the 2000s. The underestimate of simulated HNO3 and HCl in the 1990s seen in Fig. 6 is consistent with fewer elements in the age spectrum experiencing altitudes high enough for rapid destruction of source gases.

Understanding and accounting for these time-varying residual circulation trends is necessary for many applications: (1) to identify the expected decrease in stratospheric inorganic chlorine as the chlorine source gases decrease due to the Montreal Protocol and its amendments; (2) to identify and quantify the expected increase in stratospheric ozone due to the chlorine decrease, separate from multiyear variability in dynamics and transport; (3) to characterize and quantify the change in the Brewer-Dobson circulation due to increasing greenhouse gases; and (4) to characterize and quantify the expected midlatitude increase in stratospheric ozone caused by the aforesaid change in Brewer-Dobson circulation. Because the comparisons of observed and simulated HCl and HNO₃ columns are consistent with comparisons of observed and simulated fields of source gases (HALOE CH₄, 1992–2005; MLS N₂O, 2005–ongoing), continuation of these column data sets provides a robust means to evaluate the transport and mean age produced by reanalysis products in offline models such as the GMI CTM, including their effects on stratospheric ozone. Finally, periods of positive or negative constituent trends due to transport variability may be 5 years or longer in both hemispheres; this observation supports the requirement for multi-decadal records in order to identify a geophysically significant trend in the stratospheric circulation.

Data availability. The NDACC data are publicly available through an anonymous FTP at ftp://ftp.cpc.ncep.noaa.gov/ndacc/station/ jungfrau/ and ftp://ftp.cpc.ncep.noaa.gov/ndacc/station/lauder/ (accessed 10 March 2017). The HALOE data (Russell III, 1999) and MLS data (Lambert et al., 2015) are obtained from the Goddard Earth Sciences Data and Information Services Center (GES DISC). The GMI CTM simulation is publicly available through an anonymous FTP https://gmi.gsfc.nasa.gov (accessed 10 March 2017).

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