

RESEARCH LETTER

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Key Points:

- A 13-year global time series of phosgene in the upper troposphere/lower stratosphere is presented from ACE-FTS data
- The observations provide evidence for an increase in phosgene in the upper troposphere and an overall decrease in the stratosphere
- The increase in the upper troposphere is consistent with the increase in chlorine product gas injection predicted by a 3-D model

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Phosgene in the Upper Troposphere and Lower Stratosphere: A Marker for Product Gas Injection Due to Chlorine-Containing Very Short Lived Substances

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Abstract Phosgene in the atmosphere is produced via the degradation of carbon tetrachloride, methyl chloroform, and a number of chlorine-containing very short lived substances (VSLS). These VSLS are not regulated by the Montreal Protocol even though they contribute to stratospheric ozone depletion. While observations of VSLS can quantify direct stratospheric source gas injection, observations of phosgene in the upper troposphere/lower stratosphere can be used as a marker of product gas injection of chlorine-containing VSLS. In this work we report upper troposphere/lower stratosphere measurements of phosgene made by the ACE-FTS (Atmospheric Chemistry Experiment Fourier Transform Spectrometer) instrument and compare with results from the TOMCAT/SLIMCAT three-dimensional chemical transport model to constrain phosgene trends over the 2004–2016 period. The 13-year ACE-FTS time series provides the first observational evidence for an increase in chlorine product gas injection. In 2016, VSLS accounted for 27% of modeled stratospheric phosgene, up from 20% in the mid-2000s.

Plain Language Summary Atmospheric phosgene, a chlorine-containing molecule, is produced via the degradation of the reasonably long lived species carbon tetrachloride and methyl chloroform, and a number of very short lived substances (VSLS), including dichloromethane, chloroform, and tetrachloroethene. Whereas the former are regulated by the Montreal Protocol because they contribute to stratospheric ozone depletion, these latter species are not. It is therefore important that we continue to monitor VSLS and the degradation products to determine how much additional chlorine, which catalyzes the destruction of ozone, is reaching the stratosphere. VSLS can either reach the stratosphere directly, via so-called source gas injection, or degrade in the troposphere into products such as phosgene, which are then delivered into the stratosphere via so-called product gas injection (PGI). Monitoring phosgene in the upper troposphere/lower stratosphere is therefore a marker for PGI due to chlorine-containing VSLS. In this work we report measurements of phosgene in the upper troposphere/lower stratosphere made by the ACE-FTS (Atmospheric Chemistry Experiment Fourier Transform Spectrometer) instrument. The 13-year ACE-FTS time series provides the first observational evidence for an increase in chlorine PGI, which has been predicted by atmospheric models.

1. Introduction

The majority of chlorine (Cl) in the atmosphere has arisen from anthropogenic emissions of *organic* species such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). Due to their long lifetimes, many of these species reach the stratosphere where they break down, liberating chlorine which catalyzes the destruction of ozone (e.g., Carpenter et al., 2014). The principal *inorganic* degradation products of Cl-containing organic species are carbonyl chloride (phosgene, COCl₂), carbonyl chloride fluoride (COClF), hydrogen chloride (HCl), and, since many of the source gases also contain fluorine, carbonyl fluoride (COF₂) and hydrogen fluoride (HF). Of these, phosgene is probably the most notorious, having been used as a chemical weapon during World War I. In the lower stratosphere, where the phosgene mixing ratios

peak, the principal sources are the photolysis of carbon tetrachloride (CCl_4) and, to a lesser extent, the reaction of the hydroxyl radical (OH) with methyl chloroform (CH_3CCl_3).

Smaller contributions to the phosgene budget are known to arise from the atmospheric degradation of very short lived substances (VSLs), species with tropospheric lifetimes under 6 months, such as dichloromethane (CH_2Cl_2), chloroform (CHCl_3), and tetrachloroethene (C_2Cl_4). These VSLs can degrade in the troposphere to produce phosgene, some of which is directly transported into the stratosphere via so-called product gas injection (PGI). They can also directly reach the stratosphere (e.g., Laube et al., 2008), via so-called source gas injection (SGI), where small amounts will convert to phosgene. Either way, this transport of chlorine into the stratosphere could potentially pose an additional challenge to the recovery of stratospheric ozone (Hossaini et al., 2017). VSLs, with significant anthropogenic sources, are not regulated by the Montreal Protocol and are, in the case of CH_2Cl_2 , increasing in the atmosphere (e.g., Hossaini et al., 2015; Leedham Elvidge et al., 2015).

Whereas the concentrations of the VSL source gases near the tropopause can be measured straightforwardly and to high precision, for example, by the National Aeronautics and Space Administration (NASA) Airborne Tropical Tropopause Experiment (ATTREX; e.g., Navarro et al., 2015), the product gas phosgene is only measured (to a lower precision) by spectroscopic remote-sensing instruments, for example, located on satellite platforms. This makes the PGI of phosgene somewhat harder to quantify than SGI and has led to its relative neglect in studies of VSL-derived chlorine entering the stratosphere. Additionally, phosgene is important as a marker for the stratospheric removal of carbon tetrachloride, CCl_4 , which has attracted particular interest recently on account of the inconsistency between observations of its abundance and estimated sources and sinks (e.g., Liang et al., 2014). Therefore, the role of phosgene as a marker for PGI requires a holistic approach, which combines observations of phosgene in the upper troposphere/lower stratosphere (UTLS) with a detailed understanding of its stratospheric sources and sinks.

Over the past two decades there have been a number of investigations of phosgene in the UTLS by infrared remote-sensing instruments. The first of these by Toon et al. (2001) yielded 12 vertical profiles from nine MkIV spectrometer balloon flights: seven profiles at northern midlatitudes ($33\text{--}36^\circ\text{N}$) between 1992 and 1996 and five profiles at northern high latitudes ($64\text{--}68^\circ\text{N}$) between 1997 and 2000. The first global distribution of phosgene was derived from measurements by the Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS)—in total 5,614 vertical profiles between February 2004 and May 2006 were used (Fu et al., 2007). More recently Valeri et al. (2016) used Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) measurements, in particular 28,000 vertical profiles from the 18th and 20th of each month of 2008, to investigate the seasonality and latitudinal distribution of phosgene in the UTLS region.

This work presents an important and novel long-term record of COCl_2 observations made by the ACE-FTS instrument between 2004 and 2016. These data are compared with new modeling results from the stratospheric configuration of the TOMCAT/SLIMCAT three-dimensional chemical transport model (CTM). Observations and model are used to constrain COCl_2 trends over the 2004–2016 period. To date, there have been no detailed studies comparing global phosgene measurements with atmospheric models. In fact, the only modeling study to look at both tropospheric and stratospheric phosgene is that of Kindler et al. (1995), but this used a simple two-dimensional model to simulate the tropospheric cycle, and a simple one-dimensional model for its production in the stratosphere. Hossaini et al. (2015) presented a detailed VSL tropospheric Cl scheme incorporated into TOMCAT/SLIMCAT; however, this did not include any stratospheric Cl chemistry and therefore did not extend into the region of the atmosphere where phosgene volume mixing ratios (VMRs) peak. For the present work, detailed stratospheric phosgene chemistry is included in the TOMCAT/SLIMCAT scheme for the first time.

2. Satellite Observations of Phosgene

The ACE-FTS instrument (Bernath, 2017), which has been recording atmospheric limb transmittance spectra during sunrise and sunset (*solar occultation*) since 2004, is currently the only satellite instrument capable of measuring phosgene vertical profiles on account of its high signal-to-noise ratio (by using the Sun as a light source) and long atmospheric limb paths ($\sim 300\text{-km}$ effective length). With a spectral resolution of 0.02 cm^{-1} over the range $750\text{ to }4,400\text{ cm}^{-1}$, ACE has an excellent vertical resolution of about $\sim 3\text{ km}$

Table 1
Upper Tropospheric Mixing Ratios (ppt) of VLSL Species Included in Simulation ACT2

	CH ₂ Cl ₂	CHCl ₃	C ₂ Cl ₄	COCl ₂
2000	14.01	5.08	0.83	2.58
2001	14.61	4.92	0.89	2.40
2002	14.24	4.81	0.81	2.32
2003	14.94	4.84	0.76	2.42
2004	14.98	4.69	0.70	2.33
2005	15.60	4.69	0.67	2.35
2006	16.42	4.67	0.66	2.35
2007	18.38	4.82	0.62	2.44
2008	19.27	4.79	0.62	2.54
2009	20.03	4.65	0.62	2.46
2010	23.12	4.80	0.65	2.50
2011	23.13	4.88	0.53	2.54
2012	24.49	5.18	0.51	2.55
2013	29.27	5.37	0.55	2.83
2014	32.15	5.90	0.57	3.08
2015	31.84	5.66	0.56	2.96
2016	31.98	5.79	0.52	3.08

(Clerbaux et al., 2005) but no horizontal discrimination. It measures during a maximum of 30 occultation events per day, each sampling the atmosphere from 150 km down to the cloud tops (or 5 km in the absence of clouds). Over the course of a year, ACE records over a large portion of the globe, although due to its orbit the majority of measurements are at high latitudes.

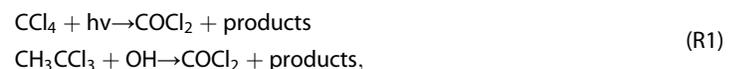
Version 3.5/3.6 of the ACE-FTS retrieval software (Boone et al., 2013) was used for the phosgene VMR retrievals. In short, vertical VMR profiles of trace gases (along with temperature and pressure) are derived from the ACE transmittance spectra via a nonlinear least squares global fit to the selected spectral region(s) for all measurements within the altitude range of interest. Retrievals were performed using a microwindow from 830 to 858 cm⁻¹. Interferers retrieved simultaneously with COCl₂ were CCl₃F (CFC-11), CO₂, HNO₃, O₃, OCS, C₂H₆, H₂O, and H₂¹⁸O. The lower altitude limit for the retrievals varied with latitude, 10 km near the equator and 8 km near the poles, with an upper limit of 23.5–28.5 km. Spectroscopic line parameters and absorption cross sections for all molecules except COCl₂ were taken from the HITRAN 2004 database (Rothman et al., 2005); spectroscopic line parameters for phosgene were taken from Brown et al. (1996) and Toon et al. (2001).

3. Model Simulations of Phosgene

TOMCAT/SLIMCAT (hereafter simply TOMCAT) is a state-of-the-art off-line global three-dimensional CTM (Chipperfield, 2006). Its outputs have been widely evaluated against observations of tropospheric and stratospheric composition; for example, it reproduces well the tropospheric abundance of chlorine-containing VLSL (Hossaini et al., 2015) and the stratospheric abundance of hydrogen fluoride (Harrison et al., 2016). The model is forced with meteorological fields, including winds and temperatures, from European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-Interim reanalyses.

Due to the large demands placed on processing resources, TOMCAT exists in two configurations, one focusing on the troposphere and the other on the stratosphere. This work makes use of the stratospheric model configuration, which contains a comprehensive stratospheric chemistry scheme, including the major species in the O_x, NO_y, HO_x, F_y, Cl_y, and Br_y chemical families. Time-dependent surface boundary conditions for the source gases, for example, CFCs, are specified using data sets prepared for the World Meteorological Organization/United Nations Environment Programme (2011) ozone assessment.

Two model simulations were run over 2000–2016 at a horizontal resolution of 2.8° × 2.8° with 32 levels from the surface to ~60 km; the levels are not evenly spaced in altitude, but the resolution in the stratosphere is ~1.5–2.0 km. For the first of these, ACT1, phosgene is assumed to be produced only from carbon tetrachloride and methyl chloroform in the two reactions,



with assumed yields of 100%. Loss of phosgene occurs via photodissociation and reaction with O(¹D),



For the second simulation, ACT2, the production of stratospheric phosgene from the SGI of VLSL is directly considered, as is the stratospheric PGI of phosgene from the troposphere. Upper tropospheric mixing ratios for the injected phosgene parent molecules, CH₂Cl₂, CHCl₃, C₂Cl₄, and COCl₂, are given in Table 1. Trends are imposed by supplying time-dependent mixing ratios from 2000 to 2016; these are the upper tropospheric outputs from the full tropospheric configuration of TOMCAT, an update of

Table 2
VLSL Sources of Stratospheric Phosgene

Source	COCl ₂ yield	References and notes
CHCl ₃ + OH	1	Kindler et al. (1995)
CHCl ₃ + Cl	1	Assumed as for CHCl ₃ + OH
CH ₂ Cl ₂ + OH	ξ	Hossaini et al. (2018)
CH ₂ Cl ₂ + Cl	ξ	Assumed as for CH ₂ Cl ₂ + OH
C ₂ Cl ₄ + OH	0.47	Tuazon et al. (1988), as discussed by Kindler et al. (1995)
C ₂ Cl ₄ + Cl	0.47	Assumed as for C ₂ Cl ₄ + OH
C ₂ Cl ₄ + hv	1	Model assumes the same J rate as for CHCl ₃ + hv

Hossaini et al. (2015), as used by Chipperfield et al. (2018). Yields for the different VLSL reaction pathways producing stratospheric phosgene are listed in Table 2. Phosgene production from CH₂Cl₂ was parameterized using an expression adapted from the full degradation mechanism (Hossaini et al., 2018):

$$\xi = \frac{0.7k_3[\text{HO}_2] + 0.4k_4[\text{CH}_3\text{O}_2]}{k_1[\text{NO}] + k_2[\text{NO}_3] + k_3[\text{HO}_2] + k_4[\text{CH}_3\text{O}_2]}, \quad (1)$$

where k_1 , k_2 , k_3 , and k_4 are rate constants for the reactions of CHCl₂O₂ with NO, NO₃, HO₂, and CH₃O₂, respectively; ξ is typically less than 0.05 at the tropopause for all latitudes.

4. Results and Discussion

The overall stratospheric distribution of COCl₂ is determined by a complex combination of its production, lifetime, and transport. The most notable feature from the zonal mean plots in Figure 1, which show all 12 months of ACE-FTS data and TOMCAT simulation ACT2 in 2005, is the peak in VMRs observed at ~22–27 km over the tropics. Young, carbon-tetrachloride-rich air in the lower tropical stratosphere combined with the high solar insolation due to the small solar zenith angle results in increased phosgene yields via the carbon-tetrachloride-photodissociation pathway, the main production route. COCl₂ has a stratospheric lifetime of 1.65 years (calculated from the ACT2 outputs: the total modeled stratospheric burden divided by the total stratospheric loss rate), so it is long-lived enough to be transported poleward by the Brewer-Dobson circulation. Higher in the stratosphere, above the COCl₂ VMR maxima, there is net loss of phosgene at all latitudes, primarily via photolysis (98.4%) and secondarily through reaction with O¹D;

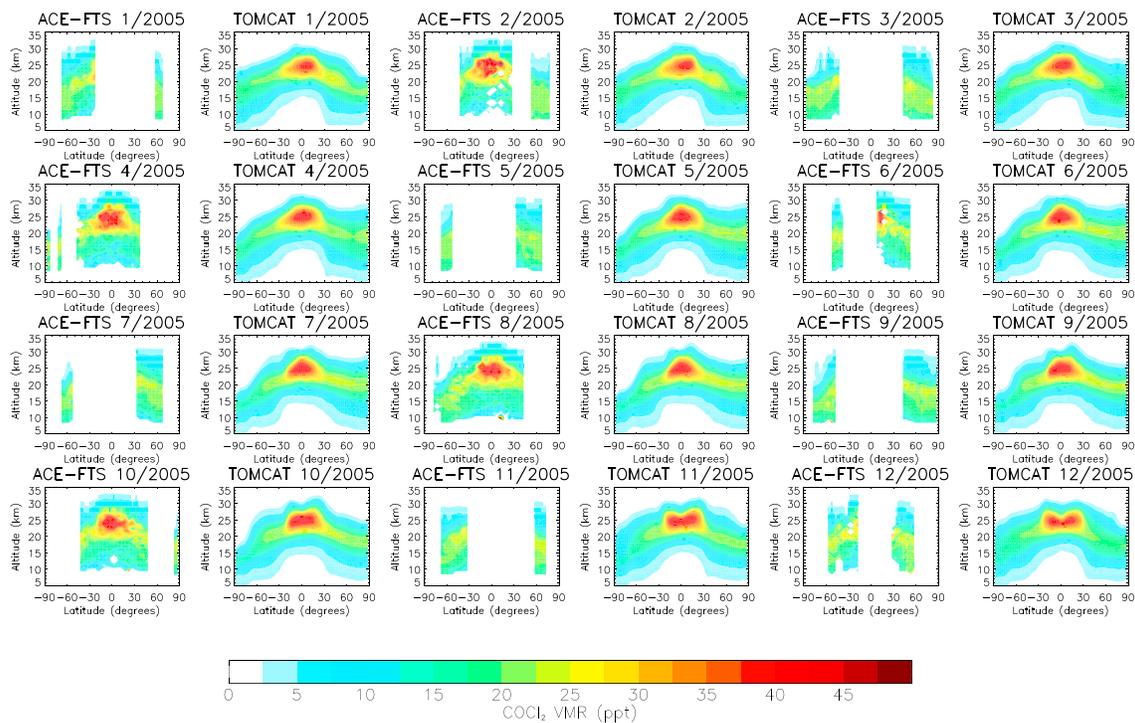


Figure 1. A comparison between Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) and TOMCAT simulation ACT2 (with very short lived substances) COCl₂ zonal means for 2005. The plotted volume mixing ratios (VMRs) are the averages for each month of all filtered data at each altitude within 5° latitude bins. TOMCAT does have a slightly higher vertical resolution in the stratosphere (~1.5–2.0 km) compared with the ACE-FTS (~3 km); since the differences are not too large, these are not explicitly accounted for in the comparisons.

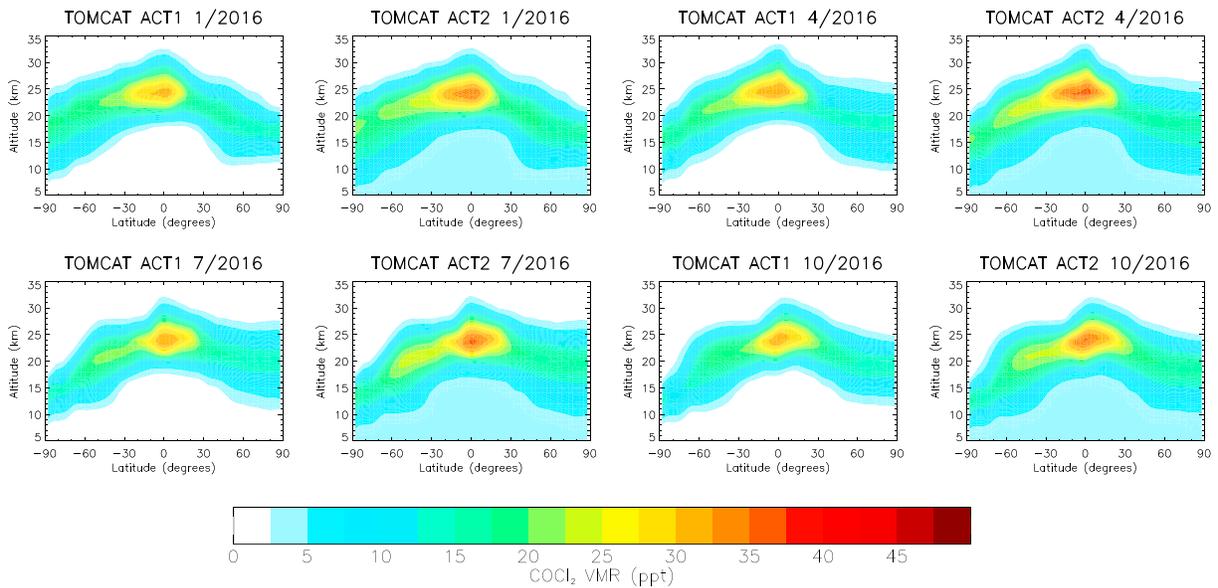


Figure 2. A comparison between the TOMCAT simulations ACT1 (without very short lived substances) and ACT2 (with very short lived substances) COCl_2 zonal means for January, April, July, and October 2016.

1.6%). The impact of the inclusion of VLS in simulation ACT2 can be visualized in Figure 2, which features COCl_2 zonal mean plots of the TOMCAT simulations ACT1 and ACT2 for 4 months of 2016. VLS make a small contribution to the phosgene vertical profiles, increasing the VMRs at most by $\sim 3\text{--}4$ ppt from the troposphere up to the stratospheric VMR peak in each latitude band, above which this contribution drops off.

The zonal mean plots of Figure 1 show good agreement between ACE-FTS and TOMCAT calculations in terms of the location of the peak VMRs; however, there are still some differences. First, the ACE-FTS measurements for a given month are relatively noisy, a consequence of there being a maximum of only 30 ACE-FTS measured profiles per day. Due to the nature of the orbit, the widest range of latitude coverage of the atmosphere only occurs over four calendar months—February, April, August, and October. The majority of measurements throughout the year are taken at high latitudes. Second, in the upper troposphere the modeled phosgene is 10–20 ppt lower than ACE-FTS. This bias was also observed in a comparison of an averaged tropical ACE-FTS profile with outputs of TOMCAT in its tropospheric Cl-chemistry configuration. This remains unexplained but could arise from an underestimate of the in-mixing of phosgene-containing air from the lower stratosphere (Hossaini et al., 2015), a missing phosgene source in the model, or an underestimate of the yield from an existing source. Very recent work by Hossaini et al. (2018) for phosgene in the tropics notes that a substantial reduction in the bias is achieved if the parameter ξ is set to unity, although this comes at the expense of the agreement at higher altitudes. This does not necessarily indicate that ξ should be unity but that the mechanism and yield of COCl_2 production requires more investigation.

It is also possible that ACE-FTS phosgene retrievals are simply biased high in the troposphere. However, this would likely require a missing spectroscopic contribution from a species absorbing in the same spectral region as phosgene, with a concentration that drops off at the tropopause; there is no evidence for this. It was noted in the original ACE-FTS study (Fu et al., 2007) that the phosgene retrieval uncertainty is dominated by spectroscopic errors, assumed to be $\sim 30\%$, resulting from uncertainties in line intensities and the lack of hot bands in the linelist. A recent MIPAS phosgene data set (Valeri et al., 2016) used a new and improved spectroscopic linelist for phosgene. The upper tropospheric values are comparable to those of the ACE-FTS, although it needs to be recognized that this was an optimal-estimation scheme making use of ACE-FTS profiles as the a priori. This new phosgene linelist (Gordon et al., 2017) and a new set of trichlorofluoromethane absorption cross sections (Harrison, 2018) will be used for the next processing version of ACE-FTS data.

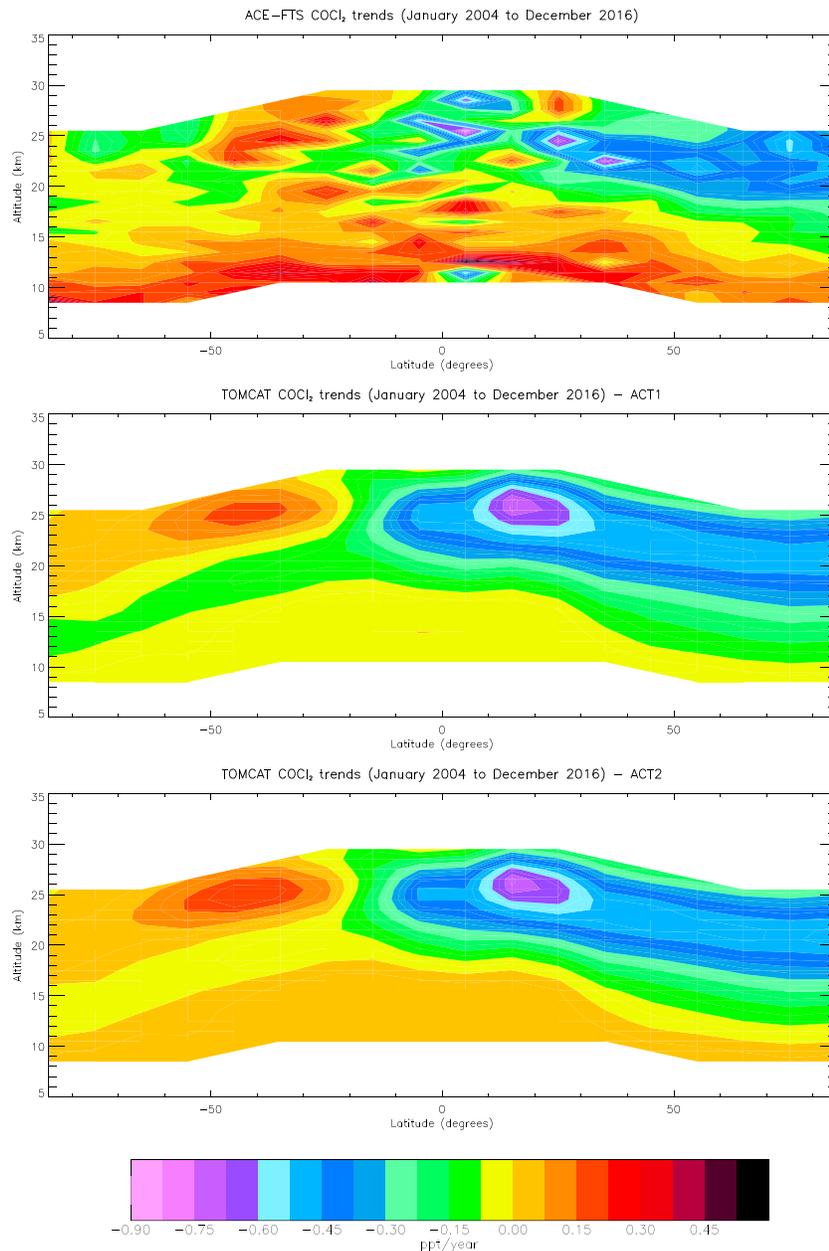


Figure 3. Trends in the growth of COCl_2 (ppt/year; January 2004 to December 2016) as a function of latitude and altitude for (a) Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS), (b) TOMCAT simulation ACT1 (without very short lived substances), and (c) TOMCAT simulation ACT2 (with very short lived substances).

ACE-FTS and TOMCAT trends have been calculated for the 13-year time period January 2004 to December 2016, as a function of altitude (on a 1-km grid) and latitude (in 10° bins) from linear regression fits to monthly anomalies in COCl_2 zonal mean VMRs; the approach used is similar to that presented in Harrison et al. (2016). Uncertainties in the ACE-FTS anomalies for each regression are the standard deviations, with those for TOMCAT anomalies arbitrarily set to 0; final trend uncertainties are the $1-\sigma$ uncertainty estimates for each linear regression. Figure 3 contains trend plots for ACE-FTS and both TOMCAT simulations ACT1 and ACT2. The TOMCAT plots share a number of similarities with the ACE plot, namely, the region from the tropics to the North Pole at the highest retrieved altitudes (20–25 km) where the trends are predominantly large and negative, and the region in the southern midlatitudes at the highest altitudes where the trends are positive. These trends, associated with lower stratospheric phosgene, are influenced by changing stratospheric dynamics

over the period of the observations and reveal differences between southern and northern hemispheres. The off-line formulation of TOMCAT, which uses specified ECMWF meteorology, does not allow for any rigorous explanation of the changing stratospheric dynamics that are responsible for the observed trends; however, these are in line with previous observations of stratospheric species (e.g., Harrison et al., 2016; Mahieu et al., 2014).

With the steady decline in the atmospheric concentration of carbon tetrachloride, the main phosgene source gas, the expectation is that phosgene is declining in the atmosphere as a whole. Certainly, calculating a VMR-weighted trend over the entire altitude range of the ACE-FTS observations reveals that this is the case: -0.057 ± 0.030 ppt/year; all reported uncertainties are the standard errors of the weighted trends. One of the principal points of interest in the plots in Figure 3 concerns the upper tropospheric phosgene trends. Whereas those for the ACT2 run, which includes VSLS, are slightly positive, in line with the positive trend in the upper tropospheric phosgene values provided in Table 2, those for the ACT1 run, without VSLS, are negative. The positive observed ACE-FTS upper tropospheric trends therefore provide evidence for an increase in chlorine PGI from VSLS, as predicted by models but not previously observed. The overall VMR-weighted upper tropospheric trend for ACE-FTS, calculated for the upper tropospheric region where the ACT2 trends are positive, is 0.119 ± 0.030 ppt/year; this is slightly higher than for the ACT2 trend of 0.042 ± 0.001 ppt/year. The overall VMR-weighted trends for the two model runs are -0.273 ± 0.005 ppt/year for ACT1 (no VSLS) and -0.209 ± 0.005 ppt/year for ACT2 (with VSLS). The inclusion of VSLS in ACT2 introduces a gradually increasing phosgene source, which slightly offsets the declining phosgene produced from carbon tetrachloride. Note, however, that the values from both model simulations are still more negative than the ACE-FTS value of -0.057 ppt/year, which contains a larger weighting from the upper troposphere, where VMRs are higher than the model and the trend is positive.

From the stratospheric phosgene burdens calculated for runs ACT1 and ACT2, and using a climatological tropopause pressure (Lawrence et al., 2001) defined as

$$p = 300 - 215 \cos^2(\phi), \quad (2)$$

where p is the pressure in hPa and ϕ is the latitude, we have calculated the fractional contribution that phosgene derived from VSLS makes to the overall stratospheric phosgene budget. This contribution is approximately constant at $\sim 20\%$ from 2004 until 2008 when it gradually increases to 27% by 2016. This is relatively large and reflects the fact that VSLS contribute to phosgene mixing ratios in the lower stratosphere where air density is larger than at higher altitudes. An increase in this contribution is to be expected as the amount of carbon tetrachloride in the stratosphere gradually drops, and the VSLS, in particular dichloromethane and chloroform, slowly increase in the troposphere.

5. Conclusions

In this work, 13 years of ACE-FTS phosgene data, from 2004 to 2016, are analyzed and compared with the output of the stratospheric configuration of the TOMCAT/SLIMCAT CTM; this work represents the most detailed stratospheric modeling study of phosgene to date. In addition to the traditionally recognized and decreasing sources of long-lived carbon tetrachloride and methyl chloroform, contributions from VSLS are also included via direct source-gas and product-gas injection into the stratosphere. A decrease in stratospheric phosgene, due to the long-lived sources, is confirmed by both ACE-FTS observations and model. The comparison in the upper troposphere, however, reveals differences; namely, the model calculates phosgene VMRs ~ 10 – 20 ppt lower. Despite this bias, the upper tropospheric positive trend in the ACE-FTS observations, the reverse of that in the stratosphere, is consistent with an increase in phosgene prescribed by the TOMCAT outputs when VSLS are included. These observations thus provide the first observational evidence for an increase in chlorine PGI.

Phosgene in the upper troposphere, far from the region where carbon tetrachloride photolyzes, is therefore a marker for Cl-containing VSLS entering the stratosphere. However, before more quantitative conclusions can be drawn, the nature of the upper-tropospheric bias between observation and model needs to be understood. Future modeling work should investigate the mechanism and yield of phosgene production from dichloromethane. Future work on the observation side will include reprocessing the ACE-FTS data with the new and more accurate COCl_2 and CFC-11 spectroscopic data and compare these with MIPAS data

processed using the same reference spectroscopy. With MIPAS measurements being uniform in space and time, these comparisons can potentially provide information on biases caused by the sparse sampling of the ACE-FTS instrument. With a set of observations using the most accurate reference spectroscopy and the latest v4.0 ACE-FTS processing algorithm, weaknesses in the model can be more robustly diagnosed.

Acknowledgments

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