



## Global phosgene observations from the Atmospheric Chemistry Experiment (ACE) mission

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[1] The first study of the global distribution of atmospheric phosgene ( $\text{COCl}_2$ ) has been performed using solar occultation measurements from the Atmospheric Chemistry Experiment (ACE) satellite mission. A total of 5614 measured profiles spanning the period February 2004 through May 2006 were used in the study. The phosgene concentrations display a zonally symmetric pattern with the maximum concentration located approximately over the equator at about 25 km in altitude and the concentration decreases towards the poles. A layer of enhanced concentration of phosgene spans the lower stratosphere over all latitudes, with volume mixing ratios of 20–60 pptv. The ACE observations show lower phosgene concentrations in the stratosphere than were obtained from previous observations in the 1980s and 1990s. This has been attributed to a significant decrease in its source species, particularly two major sources  $\text{CH}_3\text{CCl}_3$  and  $\text{CCl}_4$ , since the introduction of restrictions required by the Montreal Protocol and its amendments. **Citation:** Fu, D., C. D. Boone, P. F. Bernath, K. A. Walker, R. Nassar, G. L. Manney, and S. D. McLeod (2007), Global phosgene observations from the Atmospheric Chemistry Experiment (ACE) mission, *Geophys. Res. Lett.*, 34, L17815, doi:10.1029/2007GL029942.

### 1. Introduction

[2] Phosgene, also known as carbonyl chloride ( $\text{COCl}_2$ ), was synthesized by the chemist John Davy in 1812 using sunlight and a mixture of carbon monoxide and chlorine [Leonard, 1945]. Phosgene is a highly toxic colorless gas. It gained infamy through its use as a chemical weapon during World War I and was stockpiled as part of US military arsenals until well after World War II in the form of aerial bombs and mortar rounds. Phosgene plays a major role in the chemical industry, particularly in the preparation of pharmaceuticals, herbicides, insecticides, synthetic foams, resins, and polymers. Considering the health hazards associated with phosgene, the chemical industry is trying to find substitutes to eliminate its use [Aresta and Quaranta, 1997].

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[3] Phosgene is produced from the decomposition of chlorocarbon compounds. In the troposphere, phosgene is mainly formed by the OH-initiated oxidation of chlorinated hydrocarbons such as  $\text{CH}_3\text{CCl}_3$  and  $\text{C}_2\text{Cl}_4$  and is removed by water droplets in clouds or by deposition onto the ocean and other water surfaces [Singh, 1976; Helas and Wilson, 1992]. In the stratosphere, phosgene is produced from the photochemical decay of  $\text{CCl}_4$  together with oxidation of its tropospheric source gases [Crutzen *et al.*, 1978; Wilson *et al.*, 1988]. Phosgene can be slowly oxidized through ultraviolet photolysis to form  $\text{ClO}_x$ , which plays an important role in stratospheric ozone depletion [Wilson *et al.*, 1988]. However, this process is slower than the vertical transport of phosgene since it is a weak absorber in the near ultraviolet and does not react with OH [Kindler *et al.*, 1995].

[4] The first measurement of atmospheric phosgene was performed in situ by Singh [1976]. He obtained surface concentrations at six stations in California. Wilson *et al.* [1988] then measured phosgene during the flight of a Lear Jet aircraft between Germany and Spitzbergen. Toon *et al.* [2001] reported twelve volume mixing ratio (VMR) profiles of phosgene using the solar occultation technique from data recorded during nine MkIV spectrometer balloon flights near 34°N and 68°N between 1992 and 2000. To our knowledge, there have been no previous reports of the global distribution of phosgene.

### 2. Observations and Retrievals

[5] The Atmospheric Chemistry Experiment (ACE) satellite, also known as SCISAT-1, is a Canadian satellite for remote sensing of the Earth's atmosphere from a low Earth circular orbit (altitude 650 km, inclination 74°). The primary instrument on SCISAT-1, ACE-FTS, is a Fourier transform spectrometer (FTS) covering the spectral region 750 to 4400  $\text{cm}^{-1}$  with a resolution of 0.02  $\text{cm}^{-1}$  ( $\pm 25$   $\text{cm}^{-1}$  maximum optical path difference) [Bernath *et al.*, 2005]. ACE-FTS records spectra by solar occultation in which the sun is used as a light source and spectra are recorded in the limb geometry during sunrise and sunset. The measured spectra are inverted to obtain the VMR profiles of trace gases in the Earth's atmosphere, along with pressure and temperature profiles [Boone *et al.*, 2005]. The ACE-FTS version 2.2 data contains temperature and pressure profiles, and VMR profiles with 3–4 km vertical resolution of 27 atmospheric constituents with multiple isotopologues of some of these species.

[6]  $\text{COCl}_2$  VMR retrievals were performed using the spectral region 831 to 864  $\text{cm}^{-1}$  with spectroscopic line parameters taken from Brown *et al.* [1996] and Toon *et al.* [2001]. The spectroscopic parameters include data for both

**Table 1.** Sensitivity Study for the COCl<sub>2</sub> Retrieval, Evaluated From a Representative Set of Occultations in the Latitude Range 15–20°N<sup>a</sup>

Altitude, km	Mean VMR	Measurement Noise	Spectroscopic Data <sup>b</sup>	Pointing <sup>c</sup>	T <sup>d</sup>	CO <sub>2</sub> <sup>e</sup>	OCS <sup>f</sup>	C <sub>2</sub> H <sub>6</sub> <sup>g</sup>	Total Error, %
8.5	21.6	13.5	6.5	3.0	0.5	0.01	0.02	0.14	71
11.5	19.0	13.1	5.7	2.0	0.7	0.002	0.01	0.04	76
14.5	15.3	10.8	4.6	1.0	0.9	0.002	0.003	0.03	77
17.5	18.2	13.1	5.5	2.0	0.5	0.001	0.003	0.02	79
20.5	23.3	21.0	6.2	1.5	0.5	0.001	0.005	0.005	94
23.5	36.8	32.9	11.0	2.0	1.0	0.002	0.004	0.005	94
26.5	32.6	41.6	9.8	3.0	0.5	0.003	0.003	0.01	131
29.5	3.7	44.9	1.1	2.0	0.3	0.005	0.004	0.015	1215

<sup>a</sup>COCl<sub>2</sub> VMR values and uncertainties in the VMR are expressed in parts per trillion by volume (pptv). The total error is expressed as a percentage of the mean VMR.

<sup>b</sup>Based on spectroscopic uncertainty of 30% for COCl<sub>2</sub> (see text).

<sup>c</sup>Based on a tangent height uncertainty of 150 m.

<sup>d</sup>Based on a temperature uncertainty of 2 K.

<sup>e</sup>Based on an uncertainty of 1%.

<sup>f</sup>Based on an uncertainty of 5%.

<sup>g</sup>Based on an uncertainty of 10%.

the main isotopologue (CO<sup>35</sup>Cl<sub>2</sub>) and the most abundant minor isotopologue (CO<sup>35</sup>Cl<sup>37</sup>Cl). The altitude range of the retrievals extends from 8 to 30 km. Pressure and temperature for the retrievals were taken from ACE-FTS version 2.2 results. Molecules with interferences in the retrieval window are CCl<sub>3</sub>F (CFC-11), HNO<sub>3</sub>, O<sub>3</sub>, CO<sub>2</sub>, OCS, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub><sup>16</sup>O, and H<sub>2</sub><sup>18</sup>O. For molecules other than COCl<sub>2</sub>, spectroscopic line parameters and cross sections (CFC-11) were taken from the HITRAN 2004 database [Rothman *et al.*, 2005].

[7] During COCl<sub>2</sub> retrievals, VMR profiles are retrieved simultaneously for the interferers CFC-11, HNO<sub>3</sub>, O<sub>3</sub>, and H<sub>2</sub>O. The VMR for CO<sub>2</sub> is fixed to its assumed profile [Boone *et al.*, 2005], while the VMR profiles for OCS and C<sub>2</sub>H<sub>6</sub> are fixed to ACE-FTS version 2.2 results. The isotopologue H<sub>2</sub><sup>18</sup>O is a minor interference, only significant below ~9 km for tropical occultations and negligible for polar occultations. Contributions to the spectrum from CFC-11 are calculated from 55 cross section files in the HITRAN 2004 database that cover the pressure and temperature range of 0.01–1 atm and 190–296 K.

[8] Following the procedure outlined by Dufour *et al.* [2006], Table 1 presents an estimate of uncertainties associated with the retrievals for a representative set of occultations: tropical occultations with latitudes 15 to 20°N. The column labeled “Measurement Noise” is the statistical fitting error in the least squares analysis. Contributions from errors in temperatures, pointing, and interferences fixed during the retrieval (CO<sub>2</sub>, OCS, and C<sub>2</sub>H<sub>6</sub>) are also considered. The uncertainty of 30% on the COCl<sub>2</sub> spectroscopic parameters was deduced from information provided in the article by Toon *et al.* [2001], where average quantities were calculated from two sources that differed by up to 60% (much higher than the quoted precisions of 2 and 10%). Interferences analyzed simultaneously (CFC-11, HNO<sub>3</sub>, O<sub>3</sub>, and H<sub>2</sub>O) are not considered separately. The random errors from deficiencies in the retrievals of these molecules are reflected in the measurement noise column, and systematic contributions to the error are neglected. Of particular concern for COCl<sub>2</sub> retrievals is the broad, overlapping CFC-11 absorption feature. However, a systematic scaling of the CFC-11 cross sections in HITRAN 2004 would only affect the retrieved CFC-11 VMR profile. Systematic errors

in the COCl<sub>2</sub> retrievals from errors in CFC-11 spectroscopy would only arise if the shape of the calculated CFC-11 absorption feature was wrong, and there is no indication of such problems in the fitting residuals.

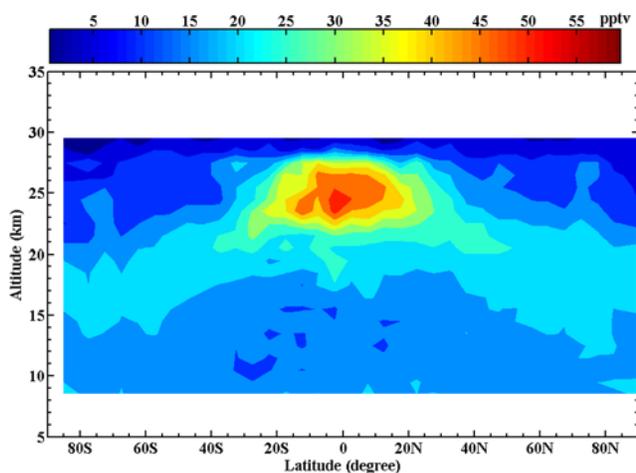
[9] It is worth noting that the numbers in Table 1 represent the uncertainties on the retrieval of a single VMR profile, including both random and systematic contributions. Uncertainties are a large percentage of the retrieved VMR values, and they exceed 100 percent at the highest retrieval altitudes, where the magnitude of the COCl<sub>2</sub> spectral signature approaches the noise level. Random contributions to the uncertainty (such as measurement noise) are greatly reduced (generally to less than 5 pptv) through averaging results for many occultations, as was done for the plots presented in this article.

[10] During polar winter/spring, the air mass contained within the polar vortex experiences a significant subsidence. As a consequence, VMR profiles of COCl<sub>2</sub> measured inside or at the edge of the polar vortex are smaller than those observed outside the vortex at a particular altitude [Toon *et al.*, 2001]. In order to avoid this temporary dynamical effect, occultations within the polar vortex or on the vortex edge were excluded from analysis. Using the potential vorticity derived from the Met Office meteorological analyses [Davies *et al.*, 2005], a two-step approach similar to that described by Nassar *et al.* [2005] was used to classify each of the 6758 occultations collected during the period February 2004 to May 2006 as being inside, outside, or on the edge of the vortex. Filtering out occultations inside or on the edge of the vortex yielded 5614 extravortex occultations, which were then used in the evaluation of the COCl<sub>2</sub> global distribution. The geographic locations of these 5614 occultations are shown in auxiliary Figure S1<sup>1</sup>.

### 3. Results and Discussion

[11] Within 5 degree latitudinal zones, the observed VMR profiles of COCl<sub>2</sub> show very similar characteristics in terms of peak altitude and VMR values at the peak. For this initial

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2007GL029942.



**Figure 1.** Latitudinal distribution of averaged  $\text{COCl}_2$  volume mixing ratio profiles (in pptv) spanning 8 to 30 km from ACE-FTS observations during the period February 2004 to May 2006 are displayed.

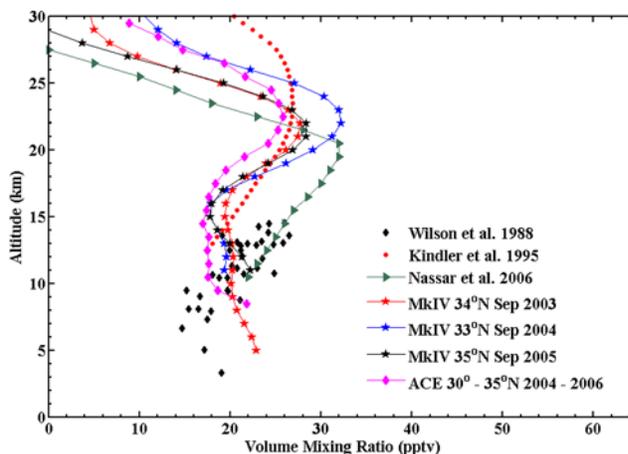
paper, the predicted small seasonal cycle [Kindler *et al.*, 1995] and the expected annual decrease due to the decline in atmospheric chlorine loading were not considered. The entire data set was therefore separated into 5 degree latitude bins, and all of the profiles within a given bin were averaged to generate a single profile with reduced noise. Although there are 36 bins between  $90^\circ\text{N}$  and  $90^\circ\text{S}$ , only 35 of the bins were used because there were no profiles in the region  $85$  to  $90^\circ\text{S}$ .

[12] The 35 averaged  $\text{COCl}_2$  VMR profiles shown in auxiliary Figure S2 were used to generate the contour plot shown in Figure 1. In the troposphere, phosgene has a generally even distribution, with VMR values of roughly 15 to 20 pptv. In the lower stratosphere,  $\text{COCl}_2$  exhibits a layer of higher concentration (25 to 60 pptv) with a thickness of 5 to 10 km. Within this layer,  $\text{COCl}_2$  concentrations are highest near the equator and decline poleward. There is a core of strongly enhanced  $\text{COCl}_2$  (VMRs 40 to 60 pptv) between 22 and 27 km in the region  $20^\circ\text{N}$  to  $20^\circ\text{S}$ . For all latitudes, the retrieved VMR drops rapidly to zero for altitudes above the  $\text{COCl}_2$  enhancement layer.

[13] The phosgene distribution pattern is determined by the chemical production and lifetime.  $\text{COCl}_2$  is believed to have five main precursor molecules. In the troposphere,  $\text{COCl}_2$  is produced primarily from the OH-initiated oxidation of  $\text{CH}_3\text{CCl}_3$ ,  $\text{CHCl}_3$ ,  $\text{C}_2\text{Cl}_4$ , and  $\text{C}_2\text{HCl}_3$  [Helas and Wilson, 1992]. In addition to these sources, the largest source of  $\text{COCl}_2$  is attributed to the photolysis of  $\text{CCl}_4$  contributing about 68% of the total  $\text{COCl}_2$  budget in the stratosphere according to model simulation results [Kindler *et al.*, 1995]. Tropospheric  $\text{COCl}_2$  has a lifetime of about 70 days due to fast wet removal [Singh, 1976; Singh *et al.*, 1977; Kindler *et al.*, 1995]. Stratospheric  $\text{COCl}_2$ , on the other hand, is expected to have a lifetime of several years since phosgene decomposes slowly through UV photolysis and has no reaction with OH. Interestingly Kindler *et al.* [1995] predict that a substantial amount of phosgene is returned to the troposphere from the stratosphere, where it is removed primarily by wet deposition.

[14] Based on the distribution in Figure 1, the bulk of the  $\text{COCl}_2$  appears over the tropics, likely because the tropics receive more insolation than higher latitudes, due to a smaller solar zenith angle. Because of its long lifetime, stratospheric  $\text{COCl}_2$  in the tropics can then be transported poleward by the Brewer-Dobson circulation. Hence, the high concentration of phosgene appears in the tropics, decreases poleward and shows a zonally symmetric pattern centered on the equator.

[15] Auxiliary Figure S3 shows  $\text{COCl}_2$  profiles corresponding to five different latitudinal zones ( $90$ – $60^\circ\text{N}$ ,  $60$ – $30^\circ\text{N}$ ,  $30^\circ\text{S}$ – $30^\circ\text{N}$ ,  $30$ – $60^\circ\text{S}$  and  $60$ – $85^\circ\text{S}$ ) averaged from the observed profiles spanning February 2004 through May 2006. In the stratosphere, the peak values of  $\text{COCl}_2$  VMR decrease significantly from the tropics to the poles. In a recent global inventory of stratospheric chlorine [Nassar *et al.*, 2006], mean  $\text{COCl}_2$  profiles were estimated from the MkIV measurements spanning September 1992 to March 2000 [Toon *et al.*, 2001], but with limited latitudinal coverage in those measurements, the presently observed latitudinal distribution of stratospheric  $\text{COCl}_2$  was not discerned. In the troposphere,  $\text{COCl}_2$  VMR increases slightly from the tropics to the poles. This may result from the fact that the troposphere at higher latitudes contains less liquid water than the tropical atmosphere, providing less opportunity for wet removal. In addition, larger tropospheric phosgene mixing ratios at higher latitudes may be a result of recirculation from the stratosphere by the Brewer-Dobson circulation. The averaged VMR profiles for northern ( $0$ – $90^\circ\text{N}$ ) and southern ( $0$ – $85^\circ\text{S}$ ) hemispheres in auxiliary Figure S3 are very similar, suggesting



**Figure 2.** Averaged  $\text{COCl}_2$  volume mixing ratio profiles (solid magenta diamond line) for  $30$ – $35^\circ\text{N}$ , latitudinal zone observed by ACE mission during the period February 2004 to May 2006 are presented along with in situ aircraft measurements of Wilson *et al.* [1988] between Germany and Spitzbergen ( $50$ – $78^\circ\text{N}$ ) at altitudes of 5–12 km (solid black diamonds), plus the results presented in Figure 11 in the model prediction of Kindler *et al.* [1995] (dotted red line), the Nassar *et al.* [2006] (solid green triangle line) estimates for 2004 based on a best-fit line to the Toon *et al.* [2001] MkIV points in the 10–30 km range measured near  $34^\circ\text{N}$  and  $68^\circ\text{N}$  between September 1992 and March 2000, and phosgene profiles measured in 2003, 2004, and 2005 using MkIV spectrometer by G. C. Toon *et al.* (private communication, 2007).

that both hemispheres have similar amounts of  $\text{COCl}_2$ . This observation is at variance with the model results of *Kindler et al.* [1995], which predict a significant hemispheric asymmetry with an enhancement in the troposphere of the Northern Hemisphere though the hemispheric differences of source gases are smaller than they were in the 1980s and 1990s.

[16] Above the peak in all of the averaged ACE-FTS  $\text{COCl}_2$  profiles, around 22 to 25 km depending on the latitude range,  $\text{COCl}_2$  VMR decreases rapidly with increasing altitude and becomes essentially zero above 28 km. This is consistent with the results from MkIV spectrometer [*Toon et al.*, 2001] measured near  $34^\circ\text{N}$  and  $68^\circ\text{N}$  between September 1992 and March 2000. Both ACE-FTS and MkIV results are inconsistent with the model results [*Kindler et al.*, 1995], which are plotted with the red dotted line in Figure 2. Results from aircraft observations collected by *Wilson et al.* [1988] between Germany and Spitzbergen ( $50^\circ$ – $78^\circ\text{N}$ ) at altitudes of 5–12 km are also included in Figure 2.  $\text{COCl}_2$  VMRs in the stratosphere from ACE-FTS are smaller than the observations from both of them.

[17] The differences in ACE-FTS  $\text{COCl}_2$  VMR in the stratosphere compared to previous studies likely arise from changes in the concentrations of sources species. Ground based studies indicate sharp declines over the past 10 to 15 years as a result of emission restrictions on its two major sources  $\text{CH}_3\text{CCl}_3$  and  $\text{CCl}_4$  required by the Montreal Protocol and its amendments. For example, the Atmospheric Lifetime Experiment, the Global Atmospheric Gases Experiment and the Advanced Global Atmospheric Gases Experiment (ALE/GAGE/AGAGE) [*Prinn et al.*, 2000, 2005; *Simmonds et al.*, 2006; *World Meteorological Organization (WMO)*, 2006], the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) [*Montzka et al.*, 1996, 1999; *Thompson et al.*, 2004; *WMO*, 2006], and the University of California at Irvine (UCI) [*Blake et al.*, 1996, 2001; *WMO*, 2006] measure the concentrations of the five main phosgene precursor molecules.

[18] From these in situ data sets,  $\text{CCl}_4$  concentrations dropped 10% between 1988 and 2005 [*Montzka et al.*, 1996, 1999; *Blake et al.*, 1996, 2001; *Thompson et al.*, 2004; *Prinn et al.*, 2000, 2005; *WMO*, 2006]. Levels of tropospheric  $\text{CH}_3\text{CCl}_3$  declined rapidly between 1991 and 2004. During this period, the  $\text{CH}_3\text{CCl}_3$  mixing ratio declined 85% [*Prinn et al.*, 2000, 2005; *WMO*, 2006]. Between 1989 and 2002, annual mean  $\text{C}_2\text{Cl}_4$  mixing ratios for the extratropical northern hemisphere dropped from 13.9 pptv to less than half this value (6.5 pptv), and global averages declined from 6.3 pptv to 3.5 pptv [*Simpson et al.*, 2004; *WMO*, 2006]. Recent ambient atmospheric data suggest that the amounts of  $\text{CHCl}_3$  and  $\text{C}_2\text{HCl}_3$  are also declining. *Prinn et al.* [2000] reported data for  $\text{CHCl}_3$  from 1983–1998 with a trend ranging from  $-0.1$  to  $-0.4$  ppt/year. The decreasing rate of  $\text{C}_2\text{HCl}_3$  was reported as 0.01 ppt/year during the period July 1999 to December 2004 [*Simmonds et al.*, 2006]. Given these significant changes in atmospheric chlorine content, differences on the order of 25% for  $\text{COCl}_2$  in the stratosphere as compared to older data sets are quite reasonable. Abundances in the troposphere are not substantially lower than observed by measurements made 10–15 years earlier, in contrast to what

one might expect from reduced abundances of chemicals thought to be the main precursors of phosgene in the troposphere. The reason for this inconsistency is not known.

#### 4. Summary and Conclusion

[19] The first study of the global distribution of atmospheric phosgene ( $\text{COCl}_2$ ) has been performed using data from the ACE satellite mission. A total of 5614 profiles from the period February 2004 to May 2006 were used, after filtering out occultations that were inside or near the polar vortex. No seasonal variation was observed in the data, but there was a significant variation as a function of latitude.

[20] A major source region for atmospheric phosgene appears in the stratosphere over the tropics (around 25 km), where the highest VMRs (40–60 pptv) are observed. There are also likely enhanced abundances of the  $\text{COCl}_2$  parent species in this region, but an in-depth study of the parent species is beyond the scope of this paper. The Brewer-Dobson circulation transports the  $\text{COCl}_2$  toward the poles. A long lifetime in the lower stratosphere leads to an enhanced layer in this region. For altitudes above the enhancement layer, VMR values are small because the molecule undergoes UV photolysis. In the troposphere,  $\text{COCl}_2$  VMR values are relatively low (17–20 pptv) as a result of the 70-day lifetime which is governed by fast wet removal.

[21] Comparisons of  $\text{COCl}_2$  VMRs between ACE-FTS observations and measurements from previous work [*Wilson et al.*, 1988; *Toon et al.*, 2001] show reasonable agreement. ACE-FTS results indicate a decline in  $\text{COCl}_2$  concentrations in the stratosphere since those studies, as one would expect from the decline in parent species [*Blake et al.*, 1996; *Montzka et al.*, 1996, 1999; *Blake et al.*, 2001; *Simpson et al.*, 2004; *Thompson et al.*, 2004; *Prinn et al.*, 2000, 2005; *Simmonds et al.*, 2006; *WMO*, 2006].

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