Climatology of the CO vertical distribution on Mars based on ACS TGO measurements

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Abstract

Carbon monoxide is a non-condensable species of the Martian atmosphere produced by the photolysis of CO2. Its mixing ratio responds to the condensation and sublimation of CO2; from the polar caps, resulting in seasonal variations of the CO abundance. Since 2018, all three spectrometers of the Atmospheric Chemistry Suite (ACS) onboard the Trace Gas Orbiter have measured CO in infrared bands by solar occultation. Here we provide the first long-term monitoring of the CO vertical distribution at the altitude range from 0 to 80 km for 1.5 Martian years from Ls=163; of MY34 to the end of MY35. We obtained a mean CO volume mixing ratio of ~960 ppm at latitudes from 45S to 45N, mostly consistent with previous observations. We found a strong enrichment of CO near the surface at Ls=100-200; in high southern latitudes with a layer of 3000-4000 ppmv, corresponding to local depletion of CO2. At equinoxes we found an increase of mixing ratio above 50 km to 3000–4000 ppmv explained by the downwelling flux of the Hadley circulation on Mars, which drags the CO enriched air. The general circulation chemical model tends to overestimate the intensity of this process, bringing too much CO. The observed minimum of CO in the high and mid-latitudes southern summer atmosphere amounts to 700-750 ppmv, agreeing with nadir measurements. During the global dust storm of MY34, when the H2O abundance peaks, we see less CO than during the calm MY35, suggesting an impact of HOx chemistry on the CO abundance.
Supporting Information for
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Introduction
Supporting information file contains the validation of CO mixing ratio measurements between ACS experiments and additional figure with water vapor difference between MY34 and MY35 at Ls=180-240 for Section 3.6):

S.1 Validation of CO measurements between the ACS channels
From the beginning of Exomars TGO science program in 2018 the simultaneous observations of the same gases by TGO spectrometers allowed us to validate measurements and methods. It was done firstly for comparison of temperature and CO2 density profiles retrieved by ACS NIR and MIR in different CO bands (Alday et al., 2019; 2021; Fedorova et al., 2020).

S.1.1 Validation of NIR by TIRVIM
There are two CO bands within the TIRVIM spectral range: 2.3 µm (transition 2-0) and 4.7 µm (transition 1-0). The signal-to-noise ratio of TIRVIM is 90–100 for pure Sun in the 4.7-µm range to ˜150 at 2.3 µm. An example of TIRVIM spectra recorded during one occultation are shown at Figure S1. Despite the 4.7 µm spectral range being characterized by lower SNR compared to 2.3 µm, the fundamental 1-0 band is much stronger than 2-0 overtone (Fig. S1). We therefore used it to retrieve the CO vertical profiles based on the TIRVIM data.
Figure S1. Example of transmittance spectra recorded by TIRVIM in solar occultation at orbit 2520 at different altitude in comparison with direct modeling at target altitude of 20 km for three main gases CO$_2$, H$_2$O and CO. Shaded areas show the range of CO 1-0 and 2-0 bands at 4.7 and 2.3 μm used for retrieval in this work.

TIRVIM stopped working in December 2019 (Ls=115° MY35) having recorded ~1000 solar occultations. We found about 550 co-located observations where the retrieval was done with NIR temperature profiles (Fig. S2). Overall, the profiles are well consistent in different locations and seasons (Fig. S3). However, the large FOV of TIRVIM (~2° equal to ~60 km at the limb) makes the contribution of scattered light around the Sun close to the solar signal in the low atmosphere where the aerosol opacity reduces the signal. To make the valid retrieval of gaseous absorption in dusty condition the full radiative transfer with multiple scattering is needed, a difficult problem, given the poorly constrained FOV. We therefore limited the TIRVIM retrievals to transmittance of 0.6 (the aerosol slant optical depth of ~0.5).

Figure S2. Collocated TIR-NIR observations for MY34-35 (2018-2019). The background is the distribution of dust optical depth for MY34 from Montabone et al., 2020.
S.1.2 Validation of NIR with MIR

Nearly all measurements of ACS MIR were made simultaneously with ACS NIR. Figure S5 shows the difference of vmr values for simultaneous observations. It demonstrates good agreement between the two datasets, within 20% below 50 km.
Figure S5. CO mixing ratio distribution of latitude and altitude for different Ls bins for simultaneous NIR and MIR orbits.

Figure S6. Correlation between CO vmrs retrieved from NIR and TIRVIM spectra for 600 co-located orbits, and the corresponding altitude distribution. Blue-to-red color indicates the increasing density of points.

S.2 Water variations during the Ls=180-240 in MY34 and MY35
Figure S7. The latitudinal trend of the H₂O mixing ratio vertical profiles in ppmv into 10° Ls bins from Ls=180° to 240° for MY34 (left) and MY35 (middle) and relative difference in percent. On the top the seasonal distribution of ACS NIR solar occultation observation for MY 34 and 35 at Ls=180-240°. The colored background is the dust optical depth distribution in 9 μm for MY 34 from Montabone et al. (2020) with red color corresponding to maximal optical depth and blue color corresponding to minimal.
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Key points:

- The first climatology of CO vertical profiles is collected for the period Ls=163° of MY 34 to the end of MY 35.
- The mean CO VMR is ~960 ppmv at 0–35 km and 45°S–45°N.
• Strong enrichment of CO, >3000 ppmv, is detected at 10-20 km at Ls=100-200 in high southern latitudes and above 50 km at equinoxes near Poles.

Abstract

Carbon monoxide is a non-condensable species of the Martian atmosphere produced by the photolysis of CO2. Its mixing ratio responds to the condensation and sublimation of CO2 from the polar caps, resulting in seasonal variations of the CO abundance. Since 2018, all three spectrometers of the Atmospheric Chemistry Suite (ACS) onboard the Trace Gas Orbiter have measured CO in infrared bands by solar occultation. Here we provide the first long-term monitoring of the CO vertical distribution at the altitude range from 0 to 80 km for 1.5 Martian years from Ls=163° of MY34 to the end of MY35. We obtained a mean CO volume mixing ratio of ~960 ppm at latitudes from 45°S to 45°N, mostly consistent with previous observations. We found a strong enrichment of CO near the surface at Ls=100-200° in high southern latitudes with a layer of 3000-4000 ppmv, corresponding to local depletion of CO2. At equinoxes we found an increase of mixing ratio above 50 km to 3000–4000 ppmv explained by the downwelling flux of the Hadley circulation on Mars, which drags the CO enriched air. The general circulation chemical model tends to overestimate the intensity of this process, bringing too much CO. The observed minimum of CO in the high and mid-latitudes southern summer atmosphere amounts to 700-750 ppmv, agreeing with nadir measurements. During the global dust storm of MY34, when the H2O abundance peaks, we see less CO than during the calm MY35, suggesting an impact of HOx chemistry on the CO abundance.

Plain language summary

Carbon monoxide (CO) is a product of the photolysis of the main component of the Martian atmosphere, CO2 (96%). During the polar night on Mars, the temperature drops so low that ~30% of the global atmospheric carbon dioxide freezes out, condensed into snowflakes. They settle to the ground to form a seasonal polar cap, which sublimates in spring after. Unlike CO2, CO is not a condensable species, so its relative abundance increases when CO2 and the atmospheric pressure
drops, forming a prominent seasonal cycle. This behaviour of CO was well documented by nadir spacecraft observations, while its vertical distribution remained a white spot until recently. Still, it helps to separate the impact of photolysis and the atmospheric dynamics, addressing the problem of the Martian atmosphere's stability. We present the first climatology of the CO vertical distribution lasting more than one Martian year based on solar occultation by the Trace Gas Orbiter. We report a previously unobserved CO layer near the surface in high southern latitudes in late winter and spring and document the difference between MY34 and MY35 caused by the global dust storm. These observations give new challenges to the Martian GCMs for understanding the modern atmosphere of Mars.

1. Introduction

Carbon monoxide (CO) is produced by the photolysis of CO$_2$ and plays a crucial role in the photochemical cycle that stabilizes the atmosphere’s composition. CO was discovered by Kaplan et al. (1969). Its observed abundance is by two orders of magnitude lower than the expected abundance of $\sim$8% in the context of a dry atmosphere (Nair et al., 1994). This inconsistency posed a problem of the stability of CO$_2$ in the Martian atmosphere, later resolved by introducing catalytic reactions with the H$_2$O photolysis products (like OH) (McElroy and Donahue (1972); Parkinson and Hunten (1972)). Still, a problem persists in quantitative understanding of the HOx chemistry because current models mostly underestimate the amount of CO on Mars several times (Lefèvre & Krasnopolsky, 2017).

The CO abundance on Mars has been measured by high-resolution ground-based spectroscopy from infrared lines located in the 3-0 (1.57 $\mu$m, Krasnopolsky, 2003; Krasnopolsky, 2007), 2-0 (2.3 $\mu$m, Krasnopolsky, 2015; Billebaud et al., 1998) and 1-0 (4.7 $\mu$m, Billebaud et al., 1992) bands of CO and rotational microwave spectrum (Clancy et al., 1990; Lellouch et al., 1991). The column-averaged CO mixing ratios inferred from these observations represented mostly the abundance in the lower atmosphere. It varied from 600±150 ppmv (parts per million
by volume) to 800±200 ppmv. Krasnopolsky et al. (2003) first reported the north-south asymmetry of the CO distribution at Ls=112° with CO volume mixing ratios (VMRs) varying from 830 ppmv in the northern middle latitudes to 1250 ppmv at 50°S. The first map of CO abundance based on several latitudinal tracks (Krasnopolsky 2007) showed an increase of CO abundance up to 1600 ppmv at Ls=112-173°.

The first CO seasonal distribution has been obtained from the nadir observations made by OMEGA (Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité) and PFS (Planetary Fourier Spectrometer) onboard the Mars Express mission (Encrenaz et al., 2006; Billebaud et al., 2009; Sindoni et al., 2011; Bouche et al., 2019; 2021), CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) on board the Mars Reconnaissance Orbiter (Smith et al., 2009, 2018) and recently NOMAD (Nadir and Occultation for Mars Discovery) onboard the Trace Gas Orbiter (TGO) (Smith et al., 2021) using the 2.3 μm (2-0) and 4.7 μm (1-0) absorption bands. These observations have shown strong seasonal variations of CO, especially in high latitudes. The minimal values (down to 200 ppmv based on CRISM) have been found in the southern summer high latitudes. At low-to-mid latitudes, the CO$_2$ condensation-sublimation cycle leads to a broad peak at about Ls = 180° (evident in the models and CRISM, less so in NOMAD). The maximum column-integrated mixing ratio (~1300 ppmv) was observed in low-to-mid latitudes around the northern autumnal equinox about Ls=180° as a result of the transport of the CO enriched air from the winter polar region. CO behaves as other non-condensable gases like N$_2$, Ar, O$_2$, expected to vary in response to the condensation-sublimation cycle of CO$_2$ into and from the seasonal polar caps. Seasonal variations of argon were measured by Mars Odyssey gamma-ray spectrometer (Sprague et al., 2004; 2012); similarly, variations of Ar, N$_2$, O$_2$ and CO were found at the surface by Sample Analysis at Mars (SAM) onboard the Curiosity rover (Trainer et al., 2019). This phenomenon is well reproduced by general circulation model (GCM) simulations (Forget et al., 2008; Smith et al., 2018; Holmes et al., 2019).
The annual mean value of CO remains a topic of debate. Nadir measurements from PFS, CRISM and NOMAD support a global average of \( \sim 800 \) ppmv (Bouche et al., 2021, Smith et al., 2018, 2021). Earth-based observations yielded a lower value of \( \sim 700 \) ppmv (Krasnopolsky 2015). In situ measurements by SAM/Curiosity resulted in an even lower value of 580 ppmv (Trainer et al., 2019). After several Martian years of observations, such small mixing ratios were never confirmed from orbit at the MSL location (Smith et al., 2018, 2021).

While the global seasonal trends of the CO column are relatively well understood, its vertical distribution was poorly documented before the arrival of TGO at Mars. Using PFS, Bouche et al. (2019; 2021) retrieved CO abundances by exploiting the vertical sensitivity of the 4.7 μm band. These measurements carry information mainly on the CO column below 15 km with enhanced sensitivity near the surface. However, their inferred vertical gradients at 0–20 km cannot be reproduced by 3D climate models, which rely on our current understanding of Martian photochemistry (Forget et al., 2008). It made the authors attribute the observed vertical gradient to the method artefact.

In 2018, the ExoMars TGO began its science phase by observing Mars’ atmosphere from its orbit. Two scientific instruments onboard TGO, the Atmospheric Chemistry Suite (ACS) (Korablev et al., 2018) and NOMAD (Vandaele et al., 2018), can sound the vertical structure of the atmosphere in solar occultation mode. ACS includes three high-resolution infrared spectrometers: NIR (near-infrared), MIR (middle infrared) and TIRVIM (thermal infrared) (Korablev et al., 2018). All three channels measure the vertical distribution of CO in three spectroscopic bands used previously in ground-based and spacecraft observations: 1.57 μm (NIR), 2.3 μm (MIR and TIRVIM) and 4.7 μm (TIRVIM). The first CO vertical profiles were inferred from ACS MIR at altitudes 20–120 km and Ls=164–220° before and during the global dust storm (GDS) of Mars year (MY) 34. They showed a prominent depletion in the CO mixing ratio up to 100 km, pointing to the importance of CO oxidation during wetter GDS conditions (Olsen et al., 2021).
Here, we report the first long-term observations of the CO vertical distribution on Mars. They are based primarily on the ACS NIR dataset and compared to ACS MIR and TIRVIM solar occultation. We study the seasonal and latitudinal variations of the CO profiles for MY 34 and 35, focusing on the interannual variability, and compare our data with the LMD Global Climate Model results, including photochemistry (Lefèvre et al., 2004).

2. Measurements and the CO retrievals

2.1 Dataset

ACS is a dedicated solar occultation experiment, with all three channels operating in this mode. In solar occultation, the transmittance at different altitudes in the atmosphere is derived by rationing spectra with the reference solar spectrum obtained (before)after a (de)occultation when observing the Sun outside the atmosphere. The method provides high sensitivity since the airmass factor at the limb is ten times greater than in nadir, and the Sun is the brightest source of the Solar system. The polar and circular orbit of the spacecraft (78° of inclination, 2 hours period and 400 km above the surface of the planet) was optimized to provide vertical profiling at unprecedented spatial and temporal resolution (up to 24 occultations per day). The misalignment between ACS MIR and NOMAD lines-of-sight (LOS) does not allow simultaneous measurements of all occultation experiments onboard TGO. Thus, the number of occultations had to be divided between NOMAD and ACS. However, the field-of-view (FOV) of NIR and TIRVIM allow measurements with NOMAD pointing that result in different coverage and fullness of datasets for three ACS spectrometers.

The densest dataset, which constitutes the basis of this study, was produced by ACS NIR, which provides CO measurements in the 1.57 μm band at 0-60 km for each occultation. From the beginning of the TGO science phase in April 2018 (Ls=163° of MY34) to January 2021 (Ls=360° of MY35), ACS NIR collected about 6050 profiles (Figure 1). ACS NIR can use both kinds of pointing (ACS-driven and NOMAD-driven), and we analysed occultation profiles obtained with ACS and NOMAD pointing (the latter constituting ~40% of profiles).
ACS MIR gives access to a much stronger band of CO located at 2.35 μm, resulting in the capability to measure CO up to 90–110 km. The MIR dataset includes 620 occultations performed using secondary grating position 6 (see section 2.3). The validity of the NIR and MIR profiles was established by comparing the two sets of profiles.

ACS TIRVIM measures both the 2.35 μm band and the strongest fundamental 4.7 μm band. The interferogram can be obtained at high or low resolution observation mode defined by the maximum optical path difference (MOPD). The MOPD of the TIRVIM interferometer can be as large as 5 cm⁻¹. In the high-resolution mode (MOPD = 4.3 cm), the spectral sampling Δν and the spectral resolution (full width at half maximum of the instrumental function, FWHM, with Hamming apodization) are equal to 0.11 and 0.21 cm⁻¹, respectively. In the low resolution mode MOPD = 0.97 cm, Δν = 0.51 cm⁻¹ and FWHM = 0.94 cm⁻¹. The largest part of occultations was done in the low resolution mode and only 20 orbits with high resolution but with worse signal-to-noise ratio (SNR). For the analysis, we used the low resolution mode TIRVIM observations of the 4.7 μm band to validate NIR and MIR results at 0–40 km. TIRVIM ceased operations in December 2019 (Ls=115° MY 35) after having recorded ~1000 solar occultations since the beginning of the mission.

The following sections describe the datasets and the processing of ACS MIR, TIRVIM and NIR, and introduce the validation of the retrieved CO profiles. An in-depth comparison of CO VMRs retrieved from different channels can be found in Supplementary Material.
Figure 1. Observational coverage of ACS solar occultations. The color circles, where colours indicate the local time of the occultation, show NIR observations. Black squares show MIR observations of CO, and black crosses show TIRVIM observations.

2.2 NIR

ACS NIR combines an acousto-optical tunable filter (AOTF), used as a monochromator that can be commanded to isolate a specific wavelength bandpass whose width corresponds to the free spectral range of the echelle grating that operates at high diffraction orders. It covers the 0.7–1.7 μm spectral range using diffraction orders 101 through 49 (Trokhimovskiy et al., 2015a; Korabev et al., 2018). During an occultation, ACS NIR measures ten pre-selected diffraction orders every 2 s, including the absorption bands of H₂O and CO₂.

The instantaneous FOV in the direction perpendicular to the limb is small (~0.02°) and limited by the slit width. The FOV corresponds to an instantaneous vertical resolution of 500–600 m at the tangent altitude of the line of sight. The time to measure one diffraction order is 0.2 s. The effective vertical resolution depends on the β-angle (the angle between the orbit plane and the direction to the Sun). It is generally better than 1 km for each diffraction order. Horizontal resolution (along the slit) is 1.5–5 km and is determined by the number of stacked detector lines. The number of detector lines measured in a single occultation and its position on the detector
depends on the pointing direction (NOMAD and ACS MIR-driven) and the available downlink volume. It varies from 6 to 30 lines; the solar image size on the detector limits the upper boundary. Averaging 30 detector lines does not worsen vertical resolution since that dimension of FOV is oriented along the limb. The SNR for an individual pixel and pure solar signal in the AOTF maximum equals about ~600 for the MIR pointing and ~300 for the NOMAD pointing. We averaged 6–25 lines with the maximal signal, excluding the solar image edges, resulting in an SNR of 800–3000, depending on the occultation.

Diffraction order 49 (6318–6387 cm\(^{-1}\)) was initially used to retrieve the temperature and CO\(_2\) density using the 1.57 μm CO\(_2\) band. This order also contains a weaker overlapping CO band. Even if hardly noticeable within the strong CO\(_2\) band, the retrieval algorithm detects the CO lines well thanks to their periodic structure. It permits measuring the CO mixing ratio from 0 to 60-70 km. Figure 2 shows examples of spectra fitting in order 49 with and without CO. The 1.57 μm band was already used for measuring CO abundance in the Martian atmosphere using high-resolution ground-based observations (Krasnopolsky, 2003).
Figure 2. Example of ACS NIR spectrum measured in order 49 at 23 km altitude showing the benefit of fitting with a model including both CO$_2$ and CO. A): a synthetic model of CO$_2$ (blue) and CO (red, 1000 ppmv) absorption bands. B): spectrum observed (in black) at orbit 1917, Ls=167°, the latitude of 82°, east longitude of −92.3° and local time 21:15 with its best fit (in blue) without CO and fit residual; (C) the same observed spectrum with its best fit (in blue) with CO and fit residual.

The retrieval algorithm is based on a Levenberg–Marquardt iterative scheme and Tikhonov regularization to smooth the profile and minimize the uncertainties. A forward transmission model...
is computed using a look-up table of absorption cross-sections (as a function of pressure and temperature) for a corresponding number of atmospheric layers (40 to 130 depending on orbit). The spectral line parameters for the CO$_2$ and CO are taken from the HITRAN 2016 database (Gordon et al., 2017) with CO$_2$-broadening coefficients for CO (Li et al., 2015) and self-broadening for CO$_2$. The inverse problem is divided into two steps. The first step includes fitting for temperature, pressure and CO mixing ratio based on the shape of the spectra only. In the second step, we assume hydrostatic equilibrium to constrain the retrieval of temperature and pressure simultaneously. We define a pressure $P_0$ at an altitude level $z_0$ where the uncertainties are minimal (the highest data quality), and then compute the pressure profile from the hydrostatic equilibrium, integrating the retrieved $T$ profile above and below the $P_0$ level:

$$P(h) = P_0 \exp\left(-\int_{z_0}^{h} \frac{g(z)M(z)}{T(z)k} \, dz\right),$$

where $g(z)$ is the acceleration due to gravity, $M(z)$ is the molecular weight (taken from the Mars Climate Database (MCD) v5.3, Forget et al., 1999, Millour et al., 2018), $k$ is the Boltzmann constant, $z$ is the altitude, $h$ is the altitude level of pressure $P$. Once the pressure is calculated, we repeat the temperature retrieval with only two free parameters, temperature and CO vmr, and perform several iterations until the pressure and temperature profiles converge.

The retrieval products from order 49 are the CO$_2$ density, atmospheric temperature and CO mixing ratio, as shown in figure 5. The detailed retrieval algorithm is described in (Fedorova et al., 2020).

### 2.3 MIR

The ACS MIR (mid-infrared) channel is a crossed-dispersion echelle spectrometer dedicated to solar occultation measurements in the 2.3–4.5 μm range with spectral resolving power of ~30,000. The channel can only sample a fraction (~160 cm$^{-1}$) of the full range on a single observation. To access a particular interval, a secondary dispersion grating is rotated to one of 11
During an occultation, MIR is operated in one pre-chosen secondary grating position. Spectra are recorded on a two-dimensional detector, with the x-axis corresponding to wavenumber and the y-axis to diffraction orders. MIR measures up to 20 adjacent diffraction orders for each acquired frame, covering an instantaneous spectral range of 0.15–0.3 μm. Each diffraction order appears as a stripe over the detector, covering around 20 rows. The stripe results from the vertical FOV, and each row is a unique solar occultation spectrum separated by 100-200 m from its adjacent rows.

We use the strong 2.3 μm band for the CO retrieval, which can be measured in positions 6 or 7. Position 7 covers the strongest lines of the 2-0 transitions, located in orders 248–256, and allows measuring CO abundances up to 110 km. Thirty-two ACS MIR occultations have been used to assess the CO vertical distribution during the Global Dust Storm of MY 34 (Olsen et al., 2021). In position 6, the three CO isotopes (main C$^{12}$O$^{16}$, C$^{13}$O$^{16}$, C$^{12}$O$^{18}$) are measured in orders 246-249 (Figure 3). Position 6 also contains CO$_2$ and H$_2$O absorption features, used as a reference in the calibration pipeline, and CO monitoring was changed from position 7 to position 6 in November 2018. The line strengths are a little smaller than in Position 7, constraining the measurements of CO up to 90 km. The strongest lines are found in order 249, used for the retrieval. The instrument line shape is impacted by a doubling (or multiplying) of the image at the detector, originating from an optical anomaly somewhere along the incidence optical path. As a result, many diffraction orders display a doubling of absorption lines. The orders in the bottom part of the detector are mostly free from this effect, and the lines in order 249 located in the lowest part of the detector were preferable. Nevertheless, slight doubling was observed in order 249, and the instrumental function was parameterized using a double gaussian with the fitting of its halfwidth and the relative intensity of two maxima. These parameters are sought for each occultation. A similar approach was described in Alday et al. (2019), Olsen et al. (2021) and Belyaev et al. (2021). The FOV of MIR is small; its vertical resolution is mainly defined by the integration time and amounts to 2.5
We averaged ten detector lines near the stripe center for the retrieval, effectively increasing the vertical resolution to 3 km.

The retrieval algorithm of CO from MIR data is similar to that described for the NIR channel. Only two free parameter vectors are retrieved (the H$_2$O and CO VMRs). The CO$_2$ absorption band in order 249 is weak and contributes only in the lower atmosphere and at low temperatures. We fixed the CO$_2$ mixing ratio to 0.96 for the modeling. The HDO/H$_2$O ratio was assumed constant and equal to 5 (Alday et al., 2021). The pressure and temperature profiles used for constraining spectroscopic parameters are taken from the simultaneous NIR retrievals obtained for the same occultation. The MIR CO vertical profiles for two orbits of MY 34 concurrent with NIR observations are shown in Figure 5C, F.

Figure 3. An example ACS MIR spectrum measured in position 6 at 20 km altitude and the best fit including CO, CO$_2$ and H$_2$O contributions. A) the direct model of CO, H$_2$O, CO$_2$ and HDO absorption bands in orders 245-249 of position 6. B) spectrum observed at orbit 1853, Ls=164°,
81.7°N, 20.5°E and local time of 02:20 (black curve) and the best fit of the data (blue curve); C) residual for the spectrum.

2.4 TIRVIM

The thermal infrared (TIRVIM) channel is a Fourier transform spectrometer with solar occultation capability (Korablev et al., 2018; Shakun et al., 2018). TIRVIM operates mainly in the “climatology” mode in solar occultation geometry, covering the entire spectral range from 1.7 to 17 μm every 0.4 s, with a spectral resolution of 0.94 cm⁻¹. At 2.8°, the diameter of TIRVIM’s circular FOV is larger than the solar disk. The vertical resolution, determined by the angular diameter of the Sun, is close to one atmospheric scale height, varying with Sun-Mars distance from 8.8 to 10.6 km.

To retrieve CO from TIRVIM spectra, we used the strongest 4.7 μm band. The low SNR (≤100 only) allows for vertical profile retrievals of CO below 50 km. To increase the SNR, four consecutive spectra were averaged. The retrieval algorithm of CO from TIRVIM data is similar to that described for the NIR and MIR channels. The temperature profiles are prescribed, retrieved from coinciding NIR observations available for about half of TIRVIM occultations. For the remaining observations, we used temperature profiles from the LMD GCM (Forget et al., 1999; Montabone et al., 2020). The CO₂ density was retrieved from the nearby 4.9 μm CO₂ band. CO VMRs were obtained as the ratio of CO and CO₂ densities. Examples of TIRVIM spectra and fitting are presented in Figure 4, while CO VMR vertical profiles for two orbits in MY 34 are shown in Figure 5C, F.
Figure 4. An example of measured ACS TIRVIM spectrum and its best fit showing the benefit of fitting with a model including both CO$_2$ and CO. A) the direct model of CO, H$_2$O, CO$_2$ absorption bands in the spectral range 2000-2300 cm$^{-1}$. B) spectra observed at different altitudes at orbit 2520, Ls=194.8°, 60.2°N, 167°E and local time of 17:25; C, D) spectrum observed at 17 km at the same orbit 2520 (black curve) in the range of CO$_2$ and CO bands, respectively, and the best fit of the data (blue curve); F, E) residual for the spectrum of CO$_2$ and CO bands, respectively.
Figure 5. Example profiles retrieved from ACS NIR-MIR-TIRVIM occultations.

A) and D) pressure, derived from the CO$_2$ number density; B) and E) atmospheric temperature; C) and F) CO profiles from NIR (black), MIR (blue) and TIRVIM (red). The orbits 2266 (Ls=182.8°, 87°N, 37.4°E and local time of 7:55) and 2566 (Ls=197.1°, 50.9°N, –44.16°E and local time of 17:24) were completed before the global dust storm and during the storm, respectively. The retrieved covariance matrix gives the error bars (one-sigma).

3. Results

3.1 Seasonal trend of CO vertical distribution

According to photochemical models, carbon monoxide is expected to be well-mixed from the surface up to ~50 km in mid-and low latitudes (Lefèvre and Krasnopolsky, 2017; Daerden et al., 2019). To verify these theoretical predictions, we considered the evolution of CO measured at two characteristic altitudes, 20 km and 40 km for two Martian years, 34 and 35, as a function of
season and latitude (Figure 6). Below 20 km, profiles are strongly attenuated by aerosol extinction. Above 40 km, CO absorption is getting fainter, increasing uncertainty with altitude. However, aerosols frequently prevent accessing altitudes below 30 km (Figure 6A). Thus the measurements at 20 km are only available in mid-to high-latitudes (30°–80°) of both hemispheres. The observations at two altitudes show an apparent difference in VMR and latitudinal variations. The most considerable difference is observed toward the Poles, where downwelling from Hadley cell circulation strongly impacts the shape of the CO VMR vertical profiles, as shown in Olsen et al. (2021).

To follow the evolution of profiles with season and latitude in more detail, we grouped the NIR and MIR data in 30° bins of Ls and presented it as a function of latitude and altitude for both Martian years (Figure 7). Near the solstice in both hemispheres (Ls=60°–120° and 240°–300°), the latitude coverage is limited to ±60°. In the equinox period (Ls=330°–30° and 150°–210°), polar latitudes are well covered. Whereas NIR can only measure CO below 50 km, the MIR channel can probe CO up to 90 km in the most favorable cases, a higher altitude range than is accessible for NIR.

Overall, the vertical profiles of the CO mixing ratio were found far from being uniform. The minimal values of CO were observed during the southern summer in middle-high southern latitudes. This is consistent with trends observed by CRISM, while the NIR minimal values were within 400–500 ppmv compared to 300–400 ppmv reported by CRISM (Smith et al., 2018). The most prominent feature of the observed profiles is the pronounced maxima of CO VMR at high latitudes. They are present in the lower atmosphere during southern winter and spring and above 40 km. These polar and mid-latitude enrichments are discussed further in subsections 3.3 and 3.5.

We have also calculated the seasonal distribution of CO with the LMD GCM and its coupled photochemical module in the latest configuration described in Lefèvre et al. (2021). In this dedicated simulation, the GCM is initialized at Ls = 180° of Martian year 33. At this date, CO is set to a uniform (both in altitude and horizontal) initial mixing ratio of 1000 ppmv as previously
measured at low latitudes by CRISM (Smith et al., 2018) and MIR (Olsen et al., 2021). After a half Martian year of spin-up time, the model runs continuously until the end of Martian year 35 while being constrained by the observed dust climatology (Montabone et al., 2020). The CO vertical distribution calculated by the LMD GCM (Figure 7c) is in good general agreement with NIR and MIR at low-to-mid latitudes. A seasonal minimum is evident in the perihelion season of both years considered here. However, the model largely overestimates the downwelling of thermospheric CO measured during the equinoctial periods at high latitudes. In contrast, near the surface, the strong enrichment of CO measured at high southern latitudes in late winter is absent in the GCM after Ls = 150°.

Figure 6. Carbon monoxide mixing ratios (ppmv) from ACS NIR occultations at two altitudes. A) The minimal sounded altitude in km, corresponding to aerosol attenuation of 0.07–0.08; B) CO VMR at 20 km; C) CO VMR at 40 km.
3.2 The average CO mixing ratio

The global average CO mixing ratio was the focus of many previous observations and 1D modeling studies. To estimate the column-averaged mixing ratio of CO from the ACS profiles, we integrated them from the bottom to below 35 km, where all three spectrometers have good accuracy. We excluded the polar region and high latitudes where the CO$_2$ condensation-sublimation cycle and the Hadley circulation make CO vertical distribution non-uniform (e.g., Figure 7). Thus, we limited ACS measurements to the middle-low latitudes (45°S–45°N). Figure 8 shows the seasonal evolution of column average CO values for NIR, MIR and TIRVIM measurements, including the earlier results obtained from MIR (Olsen et al., 2021). The column average values for MIR from Olsen et al. (2021) were integrated below 40 km. The CO mean value shows a repeatable seasonal cycle from MY34 to MY35 with two maxima, the first and most prominent at Ls~180° and the second shortly after the spring equinox (Ls=0°) in the Northern hemisphere.

By averaging the Figure 8 data along Ls, we obtain estimates of the annual mean mixing ratio of CO: 971±126 ppmv from NIR, 976±142 ppmv from MIR. In case of TIRVIM the annual average equals 812±111 ppmv. The TIRVIM dataset resulted in the lowest average CO VMR, possibly explained by its limited Ls coverage (Ls=240° MY 34 to Ls=115° MY 35). TIRVIM did not probe the two equinox maxima near Ls=180°, resulting in underestimating the annual mean VMR by at least 10%. Therefore, the three channels of ACS appear to produce altogether a fairly reliable annual mean for CO of about 960 ppmv.

Figure 8 also shows the averages of CO measured in nadir by PFS/Mars Express in the 4.7 μm band (Bouche et al., 2021). A selection of PFS data for the same ±45° latitude belt was
averaged within 1° bins of Ls for all available martian years (MY26–33). The seasonal trend agrees well with ACS data.

Bouche et al. (2021) calculated a global mean for CO of 820 ppmv. Restricted to the mid-to-low latitudes, the PFS dataset results in a global mean of 844 ppmv, in agreement with TIRVIM results and 15% lower than NIR and MIR values. Our averaged values are also lower than the CRISM and NOMAD global means, both being of about 800 ppmv (Smith et al., 2018; Smith et al., 2021). From ground-based high-resolution observations Krasnopolsky (2015, 2017) obtained an annual mean of 681±13 ppmv, agreeing with the in situ measurements by Curiosity yielding 580±80 ppmv (Franz et al., 2015, Trainer et al., 2019).

The mean CO mixing ratio calculated by the LMD GCM in Figure 8 shows a very good quantitative agreement with the observations and qualitatively for what concerns the seasonal variation. For both Martian years, the calculated mixing ratio is maximum around Ls = 180°. This is in line with the seasonal evolution of CO at low-to-mid latitudes as measured by nadir-viewing satellites (e.g., Smith et al., 2021) and is, more generally, typical of the seasonal evolution of all long-lived non-condensible species (e.g., Trainer et al., 2019). This similarity suggests that the CO2 condensation-sublimation cycle at polar latitudes is the main driver of the seasonal signal in CO visible in Figure 8. Photochemistry should also play a role in this signal, especially in the CO decrease observed in the perihelion season, when larger amounts of H2O at all altitudes lead to much increased OH production. The relative contributions of the CO2 cycle and of photochemistry will be studied in a dedicated paper. Also, beyond the scope of the present study is the long-standing problem of the underestimation of CO by models (Lefèvre and Krasnopolsky, 2017), which requires overly lengthy simulations in order to reach the long-term equilibrium value of CO in the GCM. Therefore, this historical problem should not be considered as ‘solved’ from the sole good agreement found in Figure 8.

Addressing the difference between our observed global mean of 970 ppmv and the nadir results from CRISM and NOMAD, ~800 ppmv, we can consider two possibilities: 1) their annual
average is a real global average, i.e., including the polar regions in summer where CO is low. The Figure 11 of Smith et al. (2018) shows the annual mean at low latitudes significantly larger than 800 ppmv. Still, NOMAD CO in Smith et al. (2021) looks low. 2) The MIR/NIR vmr average is not exactly a column-average vmr because we don’t see near surface mixing ratio in lower latitudes. If CO increases with altitude below 35 km, the vmr average will be larger than the column-average vmr. This effect should be verified, but we note that except for the polar latitudes in summer (the CO₂ sublimation) the CO vmr in the GCM never decreases close to the surface.

Figure 8. The averaged values of CO from ACS profiles measured within ±45° latitude range and below 35 km. Blue points, purple and green triangles are individual NIR, MIR and TIRVIM occultations, respectively. Purple stars are the results of Olsen et al., 2021 from MIR position 7 (integrated below 40 km). Blue diamonds with error bars are averages of NIR data binned within 5° of Ls. Black squares are GCM model results corresponding to the NIR averages. Grey crosses are averages of PFS data (see text). All error bars are standard deviations.
3.3 Southern winter-spring CO enhancement

In the lower atmosphere, the maximal values of CO have been observed during the Southern winter/beginning of spring in southern polar latitudes from Ls=120° to 200°. In MY 34 the observations began only at Ls=163° and the increase in mixing ratio below 20 km was detected at Ls=187°–195° when the occultations reached high southern latitudes (see Figure 7). In MY35 the coverage was better. The near-surface layer with enhanced CO has been observed from Ls=120° to 195° by both NIR and MIR instruments (Figures 6, 7). Figure 9 shows individual CO profiles obtained in southern high latitudes at Ls=161°–174° and 185°–195°. During the first occultation campaigns in spring of 2018, a layer of CO at ~10 km reached values up to 3000–4000 ppmv. Twenty-five sols later (Ls=185°) the layer moved to ~15 km with a maximum of 2500–3000 ppmv and then disappeared at Ls≥198°. Above this layer, the CO mixing ratio gradually decreases to 2000 ppmv and then grows again at higher altitudes up to 3000 ppmv. The observed CO maximum correlates with the temperature minimum observed below 30 km at high southern latitudes. At Ls=167°–174° the minimum is observed at 18–20 km with values as low as 125-135 K 10 km above the CO layer. At Ls=185°–195° the minimum moved higher to 20-22 km with warmer values about 140-150K.

Enhancement of non-condensable species was previously observed in atmospheric argon from measurements of the gamma ray spectrometer (GRS) operated on the Mars-Odyssey orbiter (Sprague et al., 2004, 2007). The strong (a factor of 6) enhancement of Ar was measured over south polar latitudes (75°S to 90°S) for two consecutive Mars years near the onset of southern winter close to Ls=90°. In winter over the northern polar regions there was no similar strong enhancement of Ar and the seasonal peak was less obvious than in the south.

The nadir measurements of CO showed the strongest CO values at Ls=140°-180° in the southern hemisphere between 45° and 20°S with mixing ratio about 1100 ppmv (Smith et al., 2018; Smith et al., 2021; Bouche et al., 2021). In nadir, the signal is dominated by absorption from the denser layers and thus by the first scale heights below 20-30 km. Polar night regions are not
available due to limitation of data retrieval to solar zenith angles (SZA) <80°. This could explain why nadir experiments like CRISM and NOMAD do not show these maximal values at the poles (Smith et al., 2021).

Unlike nadir, solar occultations can access higher latitudes during the equinox and polar night seasons (>60°S). At Ls=60°–150° of MY35 ACS sounded at the edge of the southern polar night approaching to 65-70°S. During the same period, CRISM was limited to 45°S. CO mixing ratio apparently increased below 20 km at 60°S from 900 to 1500 ppmv during the Ls=90°–120° interval. Closer to equinox, occultations moved to higher latitudes where the low-atmospheric layer enriched progressively to 3000 ppmv at Ls=120°–150° (see Figures 7, 8 and the SM) and then 4000 ppmv at Ls=170°–175° (Figures 8, 9 and the SM).

In the middle of the southern winter, the column-averaged CO mixing ratio calculated by the LMD GCM reaches more than 4000 ppmv south of 75°S (not shown). However, the region most enriched in CO in the model is located far in the polar night, and only the northernmost tip of the CO-enriched layer near the surface is visible between Ls = 120–150° in Figure 7 (see also the SM). In that layer, the modeled enrichment in CO appears to be underpredicted compared to ACS, both in terms of absolute value and vertical extent. Later on, around the equinox, the GCM no longer predicts an enriched layer of CO at high southern latitudes, in strong disagreement with ACS which shows the persistence of an enriched layer in the Ls = 180–210° period. This indicates that the breakup of the polar vortex enriched in CO (and in other non-condensable species) and the subsequent mixing with midlatitude air occur too early with the settings of the LMD GCM used here.
3.4. Southern summer CO depletion

CRISM observations, followed later by PFS and NOMAD nadir measurements, observed a minimum of CO abundance during the southern summer. This depletion was related to the sublimation of the southern CO$_2$ polar cap and resulted in the strong decrease of the CO column mixing ratio to the 300-500 ppmv from Ls=210° to Ls=330° in the high and middle southern latitudes (Smith et al., 2018, 2021).

In Figure 6b at 20 km, the CO depletion is seen in both MY 34 and 35 between Ls 250° and 330° in the southern hemisphere. During this period, Mars’ GCM predicts a non-uniform
vertical distribution with strong vertical gradient and depletion near the surface (Holmes et al., 2019). So we decided to investigate the CO vertical distribution for the both observed southern summer seasons in more detail.

Figure 10. The evolution of the CO mixing ratio profiles for a sequence of occultations in the latitude range 45°S–90°S and Ls from 245° to 330° for MY 34 and 35; (top) the latitude coverage; (middle) ACS NIR individual profiles for Ls bins; (bottom) the averaged profile for each Ls bin for ACS NIR and GCM LMD. The shaded area is the standard deviation.

Figure 10 presents the evolution of the CO profiles in the latitude range from 45°S to 90°S and in the period from Ls=245 to 330° for both Martian years (34 and 35). In this dusty season, solar occultation can not sound deep in the atmosphere and the lowest altitude sounded is typically 20 km above the surface except for Ls=310°–325° of MY34 and Ls=291°–306° in MY35 where we could probe down to 10 km. For both years we do not see a prominent gradient below 40 km except at Ls=309–325° of MY 34 where nearly-constant mixing ratios were observed below 35 km, with an increase above. The average CO mixing ratio below 40 km was found to be 700–750 ppmv which is higher than those obtained by CRISM between 50°S and 70°S (400 ppmv at Ls=260° and 700 ppmv at Ls=330°) and by PFS in the same period (~600 ppmv).
The CO profiles calculated in summer by the LMD GCM are in broad agreement with ACS, but tend to anticipate the downwelling of enhanced CO mixing ratios by the Hadley circulation at the approach of the equinox (Ls = 318–330° in Figure 10).

3.5 High altitude equinox and solstice enhancement

The enhancement of CO at 50 km was first observed by Krasnopolsky (2014) based on CO (2-1) dayglow observations at 4.7 μm in the middle of northern summer (Ls=110°) using the CSHELL spectrograph at NASA IRTF. This dayglow is formed by CO molecules at 50 km. The mixing ratio was found to increase from 1100 ppm at 40°S to 1600 ppm at 70°N. This behavior was different from the trend observed at low altitudes, and was therefore attributed to the Hadley circulation characterized by the equator-to-pole Hadley cells in equinox and pole-to-pole cell in solstices. This circulation transports CO to the polar region where a downward flux of CO-rich air occurs.

The NIR and MIR observations in the same period also support the increase of the CO mixing ratio in the polar region above 50 km but the mixing ratio is much smaller than in the model (Figure 7). The most sensitive for the study is the MIR spectrometer that can measure CO up to 80 km and has better accuracy compared to NIR at altitudes between 50 and 60 km (see section 2 and SM). Figure 11 presents the observed and modelled mixing ratio profiles of CO in both hemispheres at latitudes from 70° to 90° over a time period that encompasses equinoxes. The equinoctial circulation is characterized by two symmetric Hadley cells facing each other about the equator and carrying airmasses from the equator to the poles. The equinox periods covered concern Ls=150° to 210° (MY35) for the northern spring and Ls=330°–30° (MY 34/35) for the southern spring. Before and after these ranges, the maxima are also observed, but the circulation is already being rearranged.

At both equinoxes, the model is in rather good agreement with ACS at latitudes about 70°, but overestimates CO when moving to the poles. In the northern spring of MY34 and 35 the
observed profiles have shown a weak gradient from 1000 ppm at 10 km to 2000–3000 ppm at 60 km depending on latitude with smaller values at lower latitudes. Above 60 km and at latitudes higher than 80°N the sharp increase of CO is visible at high latitudes to 5000 ppm at 80 km. The GCM profiles begin to grow from 30 km and overestimate the observations at least in 2 times since this altitude with 8000–10000 ppmv at 70–80 km. The same situation is observed in the southern spring except near the surface CO layer discussed in Section 3.3. In the southern and northern autumn of MY34 and 35, respectively, the CO mixing ratio changes from 1000 ppmv at 10 km to 4000 ppmv at 70 km but with a sharper gradient compared to the spring. The model begins to overestimate the data in some cases from 20 km. This suggests that the intensity of the Hadley cells at the equinox is too strong in the GCM, bringing too much CO from its region of production in the high atmosphere.

Figure 11. The evolution of the CO mixing ratio profiles for sequence of occultations for equinox season (Ls=150°–210° and 330°–30°) for MY 34 and 35 in high southern and northern latitudes (−70° to −90° and 70° to 90°, respectively). Colors indicate the latitude variations. Solid curves are the ACS MIR data, dashed curves represent the LMD GCM simulation.

3.6 Interannual variability due to the GDS of MY 34
In the lower atmosphere, provided there is water vapor, the loss of CO by reaction with OH exceeds its production. It should then end up making CO sensitive to changes in water content. Nevertheless, the lifetime of about five terrestrial years does not authorize prominent chemical variations of CO at the seasonal timescales.

MY 34 was characterized by the GDS that began at approximately Ls=185° (Guzewith et al., 2019; Smith, 2019) in the Northern hemisphere. The first phase of the storm from Ls=185° to 192° is better defined as a regional dust storm which then turned into a massive global event at Ls=197° after the secondary massive dust injection over Tharsis (Montabone et al., 2020). The decay phase of the storm started at Ls=210° and lasted until Ls=240°. It is now known that GDSs profoundly impact water vertical distribution in the atmosphere by transferring H2O to high altitudes (Fedorova et al., 2018; 2020, 2021; Heavens et al., 2018; Aoki et al., 2019). Dust heats the atmosphere and amplifies the Hadley cell circulation which in turn increases the altitude of the hygropause. The water vertical distribution during the GDS of MY 34 was studied with ACS and NOMAD on TGO (Fedorova et al., 2020; Aoki et al., 2019; Belyaev et al., 2021) and SPICAM (SPectroscopy for the Investigation of the Characteristics of the Atmosphere of Mars) on Mars Express using the solar occultation technique (Fedorova et al., 2021). Water was observed up to 120 km with mixing ratios of 20–50 ppmv. More water in the middle atmosphere provides more OH (hydroxyl) radicals once H2O is photolyzed. This has the effect of boosting the rate of reactions between CO and OH, and hence the reformation of CO2. So, the sensitivity of CO to water activity can provide an insight into the stability of the Martian atmosphere.

The first ever profiles of CO were produced by ACS MIR and reported for the period from Ls=163° (pre-storm) to Ls=220° (decay phase), which showed how CO was affected by this event (Olsen et al., 2021). After the onset of the dust storm, the mean CO mixing ratio was observed to decrease from 1260 to 1070 ppmv below 40 km which was explained as the enhanced presence of H2O and thus OH that subsequently accelerated CO loss. The same occurred at high altitudes where the rise of hygropause also resulted in the decrease of CO.
With two Martian years of observations, we can compare the CO vertical profiles during the GDS period of MY 34 with the more regular MY 35 using ACS NIR data. The panels of Figure 7 at Ls=180°–210° clearly show more CO in the high southern latitudes during MY 35 than during MY 34. On the other hand, CO in high northern latitudes at altitudes above 40 km is more abundant in MY 34. Over Ls=210°–240°, the observed CO mixing ratios between 30 and 60 km in low latitudes (30°S–30°N) is higher in MY 35 compared to MY 34. As shown in Figure 1, solar occultations in different years can have different latitudinal distribution and the observations can relate to different Ls. To exclude these uncertainties, we have selected smaller latitude bins than in Figure 7 (10° of Ls versus 30° of Ls) to compare nearly close in Ls and latitude observations for two years (Figure 12). We average the ACS dataset inside 10° of Ls, 10° of latitude and 10 km of altitude. In Figure 12 the CO values for the selected bins are shown as altitude-latitude maps for MY34 and MY35 together with their relative difference, where the Ls-latitude coverage permits.
Figure 12. The latitudinal trend of the CO mixing ratio vertical profiles in ppmv into 10° Ls bins from Ls=180° to 240° for MY34 (left) and MY35 (middle) and their relative difference in percent (right). On the top panel is the seasonal distribution of ACS NIR solar occultation observations for MY 34 and 35 at Ls=180–240°. The colored background is the dust optical depth distribution in 9 μm for MY 34 from Montabone et al. (2020) with red color corresponding to maximal optical depth and blue color corresponding to minimal.

For the first Ls bin (180°–190°) the data from the two years overlap only in high southern latitudes just before the beginning of GDS and the difference near 60°S does not exceed 10%. From Ls=190° to 230°, during the maximal dust loading, the CO mixing ratio in MY35 is larger than in MY34 at 30–40% both in the northern and southern hemispheres. On the decay of GDS, at Ls=230°–240°, the observations overlap in middle northern latitudes, and the difference between two years was within 10% again. The decrease of the CO mixing ratio in MY34 during the GDS is anti-correlated with increase of water vapor abundance in the atmosphere in both hemispheres for the same period (see Figure 8 of the SM). The notable CO depletion during the GDS of MY34 can indicate the response of CO₂ production rate to the strong increase in water vapor during this period (see., e.g. Fedorova et al., 2020).

Conclusions

We analyzed a large dataset of CO vertical profiles made using solar occultation observations of the three ACS spectrometers onboard the ExoMars Trace Gas Orbiter. The data has been collected from April 2018 (Ls=163° of MY 34) to March 2021 (Ls=360° of MY 35) and covers 1.5 Martian years. The most dense dataset is coming from the ACS NIR spectrometer collected for this period more than 6200 occultations. Based on this dataset we made the simultaneous retrieval of the CO₂ density and temperature profiles and CO mixing ratio in the spectral range of 1.65-1.67 μm (order 49 of the spectrometer) including of the 1.65 μm CO₂ band.
and the CO (3-0) overtone at 1.67 μm in range of altitude from 0 to 60 km for CO. The ACS TIRVIM provides the second dense dataset about 1000 occultations but the observations stopped in December 2019. The CO mixing ratio was retrieved based on the strong 4.7 μm CO absorption band and the CO$_2$ density from 4.9 μm band. The low SNR and spectral resolution limit the sounding altitude to 50 km. ACS MIR, the most sensitive channel of ACS has performed 620 occultations up to the end of MY35 and provided the measurements of CO VMR vertical profiles in 2.3 μm absorption band based on CO$_2$ density and temperature retrieved from simultaneous measurements of ACS NIR in the range of altitude from 0 to 80 km.

With this dataset we presented the first detailed analysis of CO vertical distribution on the long timescale and studied seasonal and latitudinal variation during the martian year:

1) We found a mean CO VMR of ~ 960 ppmv in the range of 10-35 km and in the low and middle latitudes (from 45°S to 45°N). Our averaged values are lower than the CRISM, NOMAD and PFS/MEX global means from nadir measurements, both being of about 800 ppmv (Smith et al., 2018; Smith et al., 2021; Bouche et al., 2021). The CO mean value shows a repeatable seasonal cycle from MY34 to MY35 with two maxima, the first and largest of the two at Ls~180° and the second shortly after spring equinox (Ls=0°) in the Northern hemisphere.

2) We found a strong enrichment of CO near the surface during the southern winter and spring (Ls=100–200°) in middle and high southern latitudes with a layer of 3000-4000 ppm at 10-20 km corresponding to local depletion of CO$_2$. In the Northern polar winter atmosphere, such a layer of CO was not observed. The GCM does not predict the enrichment in CO in this period, both in terms of absolute value and vertical extent. This indicates that the breakup of the polar vortex enriched in CO (and in other non-condensable species) and the subsequent mixing with midlatitude air occur too early with the settings of the LMD GCM used here.
3) In the equinox seasons both in the northern and southern spring, we found an increase of CO mixing ratio above 50 km to 3000–4000 ppmv which is related to the downwelling flux of the equinox Hadley circulation on Mars above the Poles enriched of CO molecules. The comparison with the general circulation chemical model has shown that it tends to overestimate the intensity of this process, bringing too much CO from its region of production in the high atmosphere.

4) The minimum of CO observed in the southern summer in the high and middle southern latitudes has average VMRs of 700–750 ppmv in the low atmosphere and agrees well with nadir measurements by CRISM/MRO and PFS/MEX even they have lower values of 400-700 ppmv and ~600 ppmv, respectively, in the same period. The CO profiles calculated in southern summer by the LMD GCM are in broad agreement with ACS.

5) The observations during the two Martian years allow us to study the interannual variability for the year with the global dust storm (MY34) and year without GDS (MY35). We observed the depletion of the CO mixing ratio at 30-40% both in the northern and southern hemispheres during the global dust storm of MY34 compared with the calm MY35. The decrease of the CO mixing ratio in MY34 can indicate the response of CO₂ production rate to the increase of water vapor abundance in the atmosphere for the same period that suggests an impact of HOx chemistry on the CO abundance.

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**Data availability.**

ACS data are available from ESA Planetary Science Archive (PSA) Level 2

https://archives.esac.esa.int/psa/#!Table%20View/ACS=instrument. The CO vertical profiles generated from ACS measurements and analyzed in this study are available on ftp://193.232.13.174/ACS_NIR_Results/CO_climatology/ for review purposes. Data will be stored in Mendeley repository at Fedorova, Anna (2022), “Carbon monoxide (CO) on Mars from ACS occultations (MY34-35)”, Mendeley Data, V1, doi: 10.17632/w2b89yr6x5.1.
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