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Ozone profile retrievals from TROPOMI: Implication for the variation of tropospheric ozone during the outbreak of COVID-19 in China

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HIGHLIGHTS
• First ozone profiles are retrieved from TROPOMI based on the optimization estimation.  
• The mean biases of the retrieved profile are within 15% with soft calibration.  
• The TOC over east China increase by 10% from pre-lockdown to post-lockdown.  
• The decrease of NOx emission causes an increase of ozone in eastern China.

GRAPHICAL ABSTRACT

ABSTRACT
During the outbreak of the coronavirus disease 2019 (COVID-19) in China in January and February 2020, production and living activities were drastically reduced to impede the spread of the virus, which also caused a strong reduction of the emission of primary pollutants. However, as a major species of secondary air pollutant, tropospheric ozone did not reduce synchronously, but instead rose in some region. Furthermore, higher concentrations of ozone may potentially promote the rates of COVID-19 infections, causing extra risk to human health. Thus, the variation of ozone should be evaluated widely. This paper presents ozone profiles and tropospheric ozone columns from ultraviolet radiances detected by TROPOspheric Monitoring Instrument (TROPOMI) onboard Sentinel-5 Precursor (S-5P) satellite based on the principle of optimal estimation method. We compare our TROPOMI retrievals with global ozonesonde observations, Fourier Transform Spectrometry (FTS) observation at Hefei (117.17°E, 31.7°N) and Global Positioning System (GPS) ozonesonde sensor (GPSO3) ozonesonde profiles at Beijing (116.46°E, 39.80°N). The integrated Tropospheric Ozone Column (TOC) and Stratospheric Ozone Column (SOC) show excellent agreement with validation data. We use the retrieved TOC combining with tropospheric vertical column density (TVCD) of NO2 and HCHO from TROPOMI to assess the changes of tropospheric ozone.

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during the outbreak of COVID-19 in China. Although NO\textsubscript{2} TVCD decreased by 63%, the retrieved TOC over east China increase by 10% from the 20-day average before the lockdown on January 23, 2020 to 20-day averaged after it. Because the production of ozone in winter is controlled by volatile organic compounds (VOCs) indicated by monitored HCHO, which did not present evident change during the lockdown, the production of ozone did not decrease significantly. Besides, the decrease of NO\textsubscript{2} emission weakened the titration of ozone, causing an increase of ozone.

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1. Introduction

In early 2020, a novel coronavirus SARS-CoV-2 (COVID-19) emerged in the city of Wuhan, China, and has spread all over the world by March 2020 (World Health Organization, 2020). To curb the transmission of COVID-19 in China, many policy interventions, such as the travel restrictions, the shutdown of factories and halting mass transportation, have been implemented by the Chinese government, which was marked by the lockdown of Wuhan on January 23, 2020. These measures have also caused a great impact on the environment (Wang and Su, 2020; Xu et al., 2020; Zambrano-Monserrate et al., 2020). Many previous researches indicate that the concentrations of primary air pollutants, such as like NO\textsubscript{2}, SO\textsubscript{2}, have sharply reduced due to large decrease of emissions (Liu et al., 2020). However, the changes of secondary pollutants like secondary aerosol and ozone were various, and their concentrations in some cities even increased due to the change of chemical reactions (Chinazi et al., 2020; Le et al., 2020; Shi and Brasseur, 2020).

Ozone has different effects at different altitudes in the atmosphere. Most of the ozone distributed in the stratosphere can absorb strong ultraviolet radiation that can cause health problems in humans (Bell et al., 2004; Norval et al., 2007; Su et al., 2017; Nuvolone et al., 2018; Zhang et al., 2020). A small amount of ozone in the troposphere, which is mainly produced from the photochemical reaction between volatile organic compounds (VOCs) and nitrogen dioxides (NO\textsubscript{x}) (Littman and Magill, 1953; Sillman, 1995), shows harmful effects to humans. Therefore, the vertical distribution of ozone is very important for us to understand the photochemical process of ozone. Especially, Zoran et al. (2020) found that ambient ozone may increase the COVID-19 infections, in addition to direct harm to human health. However, previous studies were all confined in the scale of city. Spatial distribution of ozone on regional and national scales should be obtained due to complex ozone chemistry in different regions.

Satellite-based remote sensing can monitor several species of trace constituents in the atmosphere on the global scale, which is an ideal means to analyse the spatio-temporal distribution of air pollutants. Total ozone column has been measured using backscattered UV radiation since 1970 with instruments like Backscatter UltraViolet (BUV) and Solar Backscatter Ultra Violet (SBUV) instruments (Bhartia et al., 1996), as well as since 1995 by the Global Ozone Monitoring Experiment (GOME) (Hoogen et al., 1999). The SBUV make ~10 monochromatic measurements at the spectral resolution of ~1.0 nm. Therefore, the profile information is limited to the stratosphere with SBUV and the tropospheric column ozone is estimated using residual-based methods with a lot of approximations. The GOME first measures the full UV/VIS spectrum with a moderate spectral resolution of 0.2–0.4 nm and ozone profile retrievals down to the troposphere have been implemented (van der A et al., 2002; Liu et al., 2005). Ozone Monitoring Instrument (OMI) on aboard the EOS Aura spacecraft, GOME-2 aboard the Metop and Ozone Mapping and Profiler Suite (OMPS) aboard the Suomi National Polar-Orbiting Partnership (SNPP) continued observation of atmospheric ozone as successors of GOME (Dirksen et al., 2006; Seftor et al., 2014).

Ozone profiles retrieved from OMI has been extensively validated using ground-based data (Huang et al., 2017a; Xing et al., 2017; Zhang et al., 2019) and satellite data (Liu et al., 2010a; Huang et al., 2017b; Su et al., 2017). The OMI instrument provides a favorable opportunity to contribute to the understanding of chemical and physical functions especially in the troposphere due to its high spatial resolution (13 km along the track × 24 km across the track at nadir). However, since the occurrence of OMI row anomaly in 2007 and worsened in 2009, a portion of cross-track positions have been affected and the data from these positions can no longer be used for scientific research (Huang et al., 2017a). The OMPS is designed to measure total column and stratospheric ozone profile with spatial resolution of 50 × 50 km\textsuperscript{2}, but Bak et al. (2017) retrieves the tropospheric column ozone with careful measurement calibration in spite of insufficient spectral information.

TROPOMI, which is the only payload of Sentinel-5 precursor mission, was launched on 13 October 2017. The TROPOMI works on a 817 km sun-synchronous polar orbit with a mean Local Solar Time of 13:30 at Ascending Node (Veefkind et al., 2012). TROPOMI has a similar instrument concept to OMI but has higher spatial resolutions and extend spectral range than those of OMI. Details on TROPOMI instrument parameters are discussed in later sections.

The purpose of this paper is to describe the inversion algorithm of TROPOMI ozone profile and validate the results using various in-situ measurements as well as satellite data, which is further used to evaluate the variation of tropospheric ozone in different regions in China. To the best of our knowledge, TROPOMI ozone profiles have not been published in the literature. For this purpose, we adopt an optimal estimation based the algorithm which has been implemented for GOME, GOME-2, OMI and OMPS instruments (Liu et al., 2010b; Cai et al., 2012; Bak et al., 2017). Accurate forward model simulation, absolute wavelength/radiometric calibration and good knowledge of a priori are essential for ozone profile retrievals. The adopted algorithm needs to be modified for TROPOMI, mainly with respect to the fitting windows, instrument slit function, wavelength/radiometric correction. Therefore, to improve the fitting accuracy, we thoroughly characterize the radiometric calibration spectrum from the comparison between simulated and measured radiances. We present a validation of the retrievals including ozone profile, SOC and TOC.

This paper proceeds as follows: Section 2 introduces the retrieval algorithm and TROPOMI L1b data, description of the forward model, retrieval scheme and examination of different slit function impacts on the reduction of fitting residuals and radiometric calibration and evaluate the effect of soft calibration by comparison of spectral fitting residuals with and without correction at all latitudes. In Section 3, we talk about retrieval characterization. The validation results of retrievals are discussed in Section 4, the impact of COVID-19 on tropospheric ozone are discussed in Section 5 and conclusions are described in Section 6.

2. Data and method

2.1. TROPOMI data

The S—5P is a polar orbiting satellite, which was launched on 13 October 2017. The S—5P will fill the gap between the end of OMI and the Sentinel-5 mission. The TROPOMI is the only payload of the S—5P (Veefkind et al., 2012). There are four different spectrometers, each with its own optics and detector: medium-wave UV, longwave UV combined with visible (UVIS), NIR, and SWIR (Kleipool et al., 2018). TROPOMI is a double channel push-broom imaging spectrometer measuring radiance and irradiance in the ultraviolet (band-1:
267–300 nm, band-2: 300–332 nm), visible (band-3: 305–400 nm, band-4: 400–499 nm), near-infrared (band-5: 661–725 nm, band-6: 725–786 nm), and the shortwave infrared (band-7: 2300–2343 nm, band-8: 2343–2389 nm) that provide daily global trace gases concentration information. The spectral resolution varies from 0.5 nm in UV, UVIS, and NIR bands, to 0.23 nm in SWIR band. Ozone profile information is contained in band 1–3 measurements. But we found that band-1 radiances have opposite systematic biases between tropics and mid/high latitudes and band-2 noise is larger than band-3 (Fig. 2). Therefore, we retrieve ozone profile using optimal estimation technique from the band-3 (314–340 nm) where typical resolution is 0.54 nm.

TROPOMI has a wide field-of-view (108°) across the track and a small field-of-view along the track and the instantaneous swath width is 2600 km at the earth’s surface. There are 450 cross-track positions used for spatial coverage and hence a smaller pixel size of 7 km (along the track, now reduced to 5.5 km) × 3.5 km (across the track) is acquired compared to its precursors OMI and OMPS.

TROPOMI is commanded to perform a solar irradiance measurement every 15 orbits. If no solar measurements are available in the data granule being processed, no irradiance product will be generated. The solar irradiance measurement follows the same binning scheme as the Earth radiance measurements. The impact of the reflectance degradation on retrieved ozone profiles is shown to be large (Cai et al., 2012). The comprehensive long-term analysis of the reflectance degradation for TROPOMI shows that the irradiance degrades 5% around 314 nm and by 2% around 340 nm from April 2018 through April 2019. However, we found that the reflectance changes less over time by comparing with soft calibration spectrum (more details in Section 3) of different months in 2018. Therefore, the radiances show similar attenuation and long-term changes as the irradiance and we use the daily solar irradiance to normalize the earthshine radiances.

2.2. Other data

The OMPS-LP ozone product measures the vertical distribution of ozone in the stratosphere and lower mesosphere. The algorithm derives ozone profile values along with errors in the UV from 29.5 km and 52.5 km, and in the visible from 12.5 km to 37.5 km (Deland, 2017).

The FTS observation station, located in Hefei city in central-eastern China, has continuously measured ozone profile since April 2014. Thus it is significant to validate the retrieved profile in this region. The precision of the tropospheric ozone column (0–12 km) is approximately ~3% and the accuracy is estimated to be ~8%. A detailed description of the FTS station can be see in Sun et al. (2018) and Tian et al. (2018). A total of 129 days of data from 1 March 2018 to 1 May 2019 are available.

The GROMPS instrument was designed and manufactured by the Institute of Atmospheric Physics of the Chinese Academy of Sciences (CAS) and validated by (Wang et al., 2012). The accuracy of measured ozone profile was ±2% for pressure ≥ 150 nb and ±15% for pressure < 10 nb (Zhang et al., 2014). The ozonesonde profiles used here were measured once a week over Beijing (116.46°E, 39.80°N) from January 2018 to February 2019.

Ozone sonde data during 2018–2019 are obtained from the World Ozone and Ultraviolet Data Center (WOUDC, http://www.woudc.org) and the Southern Hemisphere ADditional Ozonesondes (SHADOZ, https://tropo.gsfc.nasa.gov/shadoz/) (Thompson et al., 2017; Witte et al., 2017; Sterling et al., 2018; Witte et al., 2018), Ozonesonde data with vertical resolution ~100–150 m and typically 5–10% accuracy and 3–5% precision have been widely used and validated (Huang et al., 2017a; Xing et al., 2017; Sterling et al., 2018).

2.3. Simulated radiance calculation

The “soft-calibration” spectra can be derived by comparing measured radiance and simulated radiance with “true” atmosphere as an input. Following the method proposed by Liu et al. (2010b), the Vector Linearized Discrete Ordinate Radiative Transfer (VLIDORT) is used to simulate radiances and weighting functions (Liu et al., 2005, 2010b; Cai et al., 2012). The Ring spectrum is directly characterized by a single scattering RRS model has been used in previous ozone profile retrievals (Sioris and Evans, 2000; Liu et al., 2010b; Cai et al., 2012). The radiances is simulated for a Rayleigh atmosphere which excludes the effects of water vapor and aerosols. The surface and clouds are assumed to be Lambertian equivalent reflections. We treated clouds as a Lambertian surfaces at cloud-top with a fixed reflectivity of 80%. We use the independent Pixel Approximation (IPA) to assume that partial clouds are a mixture of clear and cloudy scene. In the IPA, the cloud-top pressure we are used are derived from the TROPOMI FRESCO algorithm (Coldewey-Egbers et al., 2018). We acquired an initial cloud fraction at 347 nm based on surface albedo derived from the OMI surface climatology. High-resolution ozone absorption cross section is determined from Brion et al. (1993) according to the recommendation made in Liu et al. (2007) and Liu et al. (2013). Daily temperature profiles and surface pressures derived from National Centers for Environmental Protection (NCEP) final (FNL) operational global reanalysis data (1° × 1°) (https://rda.ucar.edu/) are used in our retrievals.

Table 1 summarizes the VLIDORT inputs used in simulation.

| Parameters                      | Data source                                                  |
|---------------------------------|--------------------------------------------------------------|
| Cloud top pressure              | FRESCO                                                       |
| Cloud fraction                  | Derived at 347 nm                                           |
| Surface albedo                  | OMI surface climatology (Kleipool et al., 2008)             |
| ozone cross sections            | (Brion et al., 1993)                                        |
| A priori ozone profile          | (Bak et al., 2013)                                          |
| Surface temperature,            | Daily National Centers for Environmental Protection         |
| temperature profile,            | Prediction (NCEP) final (FNL) operational global analysis    |
| surface/tropopause pressure     | data                                                       |

2.4. Slit function

The Instrument Spectral Response Function (ISRF) has a crucial influence on the high fitting precision. We compare the fitting residuals (not shown here) using the pre-flight ISRF measurements (TROPOMI ISRFs v3.0.0) and on-orbit ISRF derived from solar irradiance measurements assuming the analytic function forms of standard Gaussian and supper Gaussian.

According to comparisons of retrievals using three different slit functions, we found the fitting residuals show similar changes as a function of cross-track positions and using the TROPOMI ISRFs v3.0.0 function shows smaller residuals for all cross-track positions. Therefore, TROPOMI ISRFs v3.0.0 slit functions are used in this study (more details please refer to Xia. et al., manuscript in preparation).

2.5. TROPOMI ozone profile retrievals

The retrieval algorithm, that has been applied to GOME (Liu et al., 2005), GOME-2 (Cai et al., 2012), OMI (Liu et al., 2010b), and OMPs (Bak et al., 2017), is based on principle of optimal estimation method (Rodgers, 2000). The algorithm simultaneously minimize the difference between calculated and measured radiances, and between a priori (Xa) and retrieved (X) state vectors during iteration. The state vectors are constrained by a priori error covariance matrix and measurement error covariance matrix. The cost function and a posteriori solution can be given as:

$$
\chi^2 = \left[ S_y^{-1} (X_{i+1} - X_i) - (Y - R(X)) \right]^T \left[ S_y^{-1} + S_{y1}^{-1} (X_{i+1} - X_2)^T \right]^{-1} \left[ S_y^{-1} (X_{i+1} - X_2) \right]
$$

$$
X_{i+1} = X_i + \left( K_l^T S_y^{-1} K_i + S_{y1}^{-1} \right)^{-1} \left[ K_l^T S_y^{-1} (Y - R(X)) - S_{y1}^{-1} (X_i - X_2) \right]
$$
where $X_i$ and $X_{i+1}$ are the previous and current state vectors contains the ozone profile and other parameters, respectively. $Y$ is the measured radiance normalized to the daily solar irradiance; $R$ is the radiation transfer model; $R(X_i)$ is the computed radiances using the radiation transfer model $R$ and normalized with $X_i$; $S_i$ is the diagonal covariance matrix calculated from the measurement error. $K_i$ is defined as the weighting function matrix, $K_i = S/R^T/S$; Partial ozone column densities in 24 layers are divided by 25 pressure levels. The state vector consists of 33 parameters, including 24 partial ozone columns, one cloud parameter and three reflectivity parameters. It also includes two wavelength shift parameters, one Ring effect scaling parameter, BrO and HCHO vertical column densities (VCDs). Table 2 summarizes the fitting variables, a priori and corresponding a priori errors.

The measurement errors are derived from TROPOMI level 1b random-noise errors. The a priori ozone profile and a priori error covariance matrix is derived from the ozone climatology calculated based on tropopause that has been used in retrievals by (Bak et al., 2013). It can improve the precision of retrieved ozone profile, especially in the upper troposphere and lower stratosphere (UTLS). In the OMI retrievals, invariable floor noise errors are used as preliminary measurement constraint (Liu et al., 2010b). For TROPOMI, we directly use the TROPOMI radiance random-noise errors constrain our retrievals.

### 2.6. Soft calibration

The high quality of reflectance is required to extract the independent information on the ozone profile, especially for the tropospheric ozone. The reflectance however is strongly affected by instrument performance and pre-launch calibration. Similar to OMI, 2-dimensional CCD array is used to measure TROPOMI radiance and irradiance and the CCD detector array is susceptible to systematic wavelength registration errors and cross-track dependent biases, which are likely to cause striping in ozone and other trace gas retrievals. To evaluate and eliminate such systematic biases, the “soft calibration,” implemented in OMI (Liu et al., 2010b), OMPS (Bak et al., 2017) and GOME-2 (Cai et al., 2012) ozone profile retrievals, is also applied to TROPOMI radiances in this paper. This soft calibration is in general based on the comparison of measured radiances with expected values. The keys to soft calibration are the choice of regions, the a priori profile and the use of daily means. The a priori ozone profile from TOA (top of atmosphere) to 215 hPa are derived from the latest version 4 Aura Microwave Limb Sounder (MLS) instrument (Waters et al., 2006). This version and earlier versions have been extensively validated (Liu et al., 2010a; Huang et al., 2017b) and been used as a priori profile by Liu et al. (2010b) and Cai et al. (2012). We obtain a priori profiles by merging ozone climatology from McPeters et al. (2007) for pressure greater than 215 hPa with zonal mean MLS ozone profiles below 215 hPa. The tropical measurements were typically characterized where ozone change is relatively small (Bak et al., 2017), and cloud-contaminated pixels and extreme viewing-geometries are screened out to reduce the errors in radiative transfer calculation, with the criteria: latitude <10°N/S, cloud fraction <0.2, and solar zenith angle <40°.

The correction spectrum is the ratio of measured radiances and simulated radiances. The correction $C_{\lambda i}$ can be written as follows:

$$C_{\lambda i} = \frac{S_{\lambda i}}{M_{\lambda i}}$$

where $M_{\lambda i}$ is the measured radiance at wavelength $\lambda_i$ and $S_{\lambda i}$ is the corresponding simulated radiances. In this paper, one day of TROPOMI measurements on 3 April 2018 is used to characterize ratios of measured to calculated radiances in the spectral range 305–360 nm (band-3) for all cross-track positions (Fig. 1).

At wavelengths longer than 314 nm, the mean differences steadily decrease from ~10% with fluctuations at 314 nm to a few percent at ~350 nm, and increase sharply at wavelengths below 314 nm to 40–50%. The standard deviations vary from 0.01–0.5% at wavelengths longer than 346.7 nm to 0.5–9.5% between 305 and 346 nm. These spectral variations do not change much with cross-track position. Therefore, we do not use wavelengths below 314 nm for ozone profile fitting.

The cross-track dependent correction spectra shown in Fig. 1(a) are applied to TROPOMI radiances before the fitting starts. Fig. 2(c) and (d) shows comparisons of fitting residuals both with and without correction at all latitudes for band-3. Before applying the correction spectrum to TROPOMI radiances, the mean fitting residuals are within 1%, 0.8% and 0.4% for high-latitude, mid-latitude and tropics regions, respectively. The soft calibration remarkably reduces the fitting residuals for all latitudes, especially for tropics and mid-latitudes. Fitting residuals are improved to 0.1–0.2% in the tropics and 0.2–0.4% in the mid-latitudes. However, there are large systematic measurement biases in high latitudes with the fact that the derived soft calibration does not

![Fig. 1.](image-url) (a) Soft correction spectrum derived from ratio between TROPOMI measured radiances and simulated radiances at initial iteration, as a function of ranging from 305 nm to 360 nm. The vertical solid line indicates 305 nm. (b) Standard deviations of fitting residuals. The 450 cross-track positions are shown in different colors.
account for the dependence of systematic fitting residuals on the solar zenith angle. Therefore, our retrievals are still susceptible to these errors that vary latitudinally and seasonally. To determine the temporal variation of the soft calibration spectra, we derived the correction spectrum every month between April 2018 and December 2018. The mean differences can vary by up to ~2% at center cross-track position and ~1% at the edge cross-track position from month to month, respectively, but the overall structure is similar and there is no noticeable time-dependent degradation. Therefore, we do not account for the time dependence in the soft calibration. We also calculate correction spectrum

![Fig. 2. Comparison of fitting residuals of band1–2 on 22 June 2018 with (a) and without (b) soft calibration for 3 cases: high-latitudes (green), mid-latitudes (blue), and tropics (red) for cloud fraction <0.3. (c), (d) similar to (a) and (b) but for band-3.](image)

![Fig. 3. Maps of (a) total ozone column, (b) stratospheric ozone column, (c) tropospheric ozone column and (d) cloud fraction on 1 June 2018. The data are gridded on 0.1° latitude × 0.1° longitude.](image)
from 300 to 330 nm of band-2 and 270–330 nm of combination of band-1 and band-2 (Fig. 2(a), (b)). However, we found that there are large systematic biases in radiance at wavelength shorter 290 nm and the retrieval residuals in the 314–330 range of band-2 are larger than those of band-3 (Fig. 2(c), (d)). We also compare the retrievals, using spectral in the wavelength range 302.5–330 nm of band-2, with ozonesonde profiles and ground total ozone taken from WOUDC. The difference of retrieved and ground Total column Ozone (TO) using band-2 spectral are larger than that using band-3. The retrieved profiles in the spectral range 302.5–330 nm show larger positive biases at higher altitudes than those using band-3 (not shown here).

2.7. Verification of the soft calibration

Fig. S1 shows the effect of soft calibration on TROPOMI TOC retrievals through the comparison with FTS data. The details of FTS data and coincidence criteria are described in Section 4.1. Compared to FTS TOC, the preliminary retrievals are considerably biased with 12 ± 10.77 DU when the soft calibration is not applied. Applying soft calibration significantly improves both the mean biases and standard deviations to −1.2 ± 5.09 DU.

We also compare TROPOMI ozone profiles retrievals with coincident OMPS Limb Profiler (OMPS-LP) profiles at OMPS layers (0.6–186 hPa) for 1 June 2018 globally. The coincidence criteria are within 100 km and 6 h time and we obtained a total of 2005 coincident pairs. The effect of soft calibration on the TROPOMI ozone profile retrievals is shown in Fig. S2.

To eliminate the effects of different vertical resolution and grid of OMPS-LP and TROPOMI ozone profiles caused by the observation mode, OMPS-LP ozone profiles in volume mixing ratios are first integrated down to partial columns, and then the converted OMPS-LP profiles are interpolated to TROPOMI vertical grids and convolved with TROPOMI averaging kernels. For profile comparison, both convolved OMPS-LP and TROPOMI profiles are interpolated to the OMPS-LP grids.

Before applying soft calibration, there are biases of <10% at higher altitudes (0.6–50 hPa) and the biases increase to 50% with the increasing pressure. The standard deviations of mean biases are within 15% from 0.6 to 10 hPa, increasing to 15–20% between 10 hPa and 70 hPa and to −40% at bottom layers. The retrieved profiles after soft calibration show better consistency with OMPS-LP profiles above 2 hPa. The mean biases with soft calibration are within 10% at all layers above 100 hPa except 26% at the bottom layer. The standard deviations vary from
-5% at top pressure to ~38% around 186 hPa. The soft calibration improves the ozone profile retrievals by reducing cross-track-dependent bias and improving the systematic bias in the radiances by a factor of 1.1 between 314 and 340 nm.

3. Characterization of retrievals

Fig. 3 shows the global distribution of retrieved results on 1 June 2018. Large value of TO and SOC occur at northern mid and high latitudes and southern mid latitudes. Zonal bands of high TOC are found in north hemispheres (10°N-90°N). Large values of TOC at northern latitudes occur at north of India, east of China, southwest of the United States, north of Africa and west of Alaska. The enhanced ozone over the east coast of Asia is probably caused by high cloudiness (Fig. 4). Low values (<24 DU) of TOC occur over the Pacific Ocean and southern mid and high latitudes (~35°S-65°S). High cloud fraction occurs in southern mid-latitudes, east of Asia, east of Europe, northwest of the United States, west of Canada and northwest of Atlantic Ocean.

Fig. 4 shows an example of TROPOMI ozone vertical distribution for the center cross-track position of orbit 3274 on 1 June 2018. This orbit starts in the South Pacific, passes through Beijing, and finally extends to the Arctic Ocean. The peaks of the retrieved ozone profile appear at ~25 km in the tropics and ~20 km at high latitudes, respectively and vary with the change of tropopause height. The top height of retrieval profiles increase from the southern hemisphere to the northern hemisphere. The fitted surface albedo is typically within 5–10% except for greater than 60% near 60°S and 58°N, respectively, partly due to inadequate cloud modeling, as well as at 71°N-83°N probably due to snow and ice. The region with surface albedo >0.2 are located around 60°S, 55°-60°S and 30°-80°N. High values at the bottom of the profile around 30°N may be due to heavy ozone pollution in eastern China and at northern Russia may be due to transmission from stratosphere, respectively. Fig. 5 shows the TO, SOC and TOC, degree of freedom for signal (DFS) and random noise errors and solutions errors corresponding to the retrievals in Fig. 4. Total DFS and stratospheric DFS are much smaller than those of OMI retrievals due to lack of information below 314 nm but the tropospheric DFS is only slightly reduced.

4. Validation

4.1. Comparison with ground-based ozone profiles in China

To screen out TROPOMI data for comparisons, we only use TROPOMI data under the following conditions: cloud fraction <30%, solar zenith angle <75°. The collocation criteria is similar to that used by Huang et al. (2017a). We first selected TROPOMI data with cloud fraction <0.3, a time difference within 6 h and within ±1° latitude, ±1° longitude from the ground site and then obtain the nearest TROPOMI pixel for comparison. The ozonesonde profiles are interpolated to the TROPOMI grid and then TROPOMI averaging kernels are convolved with the interpolated profile to remove smoothing errors. After filtering TROPOMI data that does not meet the above conditions, approximately 120 coincidence pairs are used in the comparison. Fig. 5 shows the comparisons of the retrieved, a priori and FTS TOC with and without Fig. 5. (a) Scatter plots of FTS TOC with (red) and without (blue) retrieval averaging kernels vs retrieved TOC and a priori (black). The dashed line denotes the linear regression and 1:1 relationship. Mean biases and standard deviations, the linear regression and correlation coefficients, and the number of coincident pairs are also shown in legends. (b) Time series of TROPOMI (green), a priori (black), and FTS (red) TOC at Hefei, China.

Fig. 6. Similar to Fig. 5, but for ozonesonde observations in Beijing, China.
TROPOMI AK. The integrated TOC shows good agreement with FTS measurements. The a priori TOC is much lower than the FTS TOC with the mean bias of $-16.9$ DU and standard deviation of 12.01 DU. The correlation coefficient between FTS and a priori TOC is 0.74. The retrieved TOC values with TROPOMI AK are substantially improved over the climatological profiles. The mean bias reduce to $-1.2$ DU, standard deviation decrease to 5.09 DU and correlation coefficient improve to 0.95. We can also see that the slope increases from 0.216 to 0.934 and the offset decreases from 23.855 to 2.171 DU.

The retrieved, a priori and GPSO3 TOC are shown in Fig. 6 and the total number of TROPOMI-GPSO3 pairs is 48. The mean bias between a priori and ozonesonde TOC is $-16.0$ DU and the standard deviation...
is 15.10 DU. The biases between retrieved and ozonesonde TOC are mostly within 20 DU. The mean biases and standard deviation are $-4.3 \pm 9.69$ DU and the correlation is 0.86 with applying TROPOMI AK. The larger mean bias after applying TROPOMI AK is partly due to the overestimation of tropospheric ozone by GPSO3.

4.2. Comparison with ozonesonde globally

We validate TROPOMI ozone profile, TOC and SOC retrievals with global ozonesonde data except for in the northern high latitudes from 2018 to 2019. There are no sufficient ozonesonde data for statistical analysis in the northern high latitudes. We only used ozonesonde profiles with correction factors between 0.8 and 1.15. The tropopause pressure derived from TROPOMI and ozonesonde burst pressure are used to calculate TOC and SOC. The column concentration integrated from the surface to the tropopause is defined as TOC and the SOC is defined as the integral of ozone profile from the tropopause pressure to the burst pressure.

We selected 5 stations to compare ozone profiles between ozonesondes and the retrieved (Fig. 7). The a priori profiles show a large negative bias, with a maximum negative bias of $-80\%$, below 30 hPa at most stations. TROPOMI agrees with ozonesonde to within $\pm 5\%$ from 0.8–30 hPa and within $\pm 15\%$ below 30 hPa. TROPOMI retrievals show significant reduction in mean biases over the climatological profiles below 30 hPa. The retrieved ozone profiles above 20 hPa show worse agreement with ozonesonde than the a priori profile mainly due to not using information below 314 nm.

Fig. 54 shows the scatter plots of SOC between TROPOMI and ozonesonde for each of the four latitude bands from March 2018 to December 2019. The TROPOMI SOC shows good agreement with ozonesonde profiles in all regions. After applying TROPOMI AK to ozonesonde data, the mean biases are most within 4.2 DU except for a positive bias of 7.4 DU at southern mid-latitudes and standard deviations are within 13.15 DU. The correlation coefficients are greater than 0.94 and the slopes are close to 1. The comparison of TROPOMI and ozonesonde TOC for each of the four latitude bands from March 2018 to December 2019 is shown in Fig. S5. A priori TOC show negative biases of 0.3–4.6 DU compared to ozonesonde TOC at mid and high latitudes but the retrieved TOC have positive biases compared to ozonesonde TOC at all latitudes. The mean biases between the retrieved and ozonesonde TOC before applying TROPOMI AK are within 1.7 DU and the corresponding standard deviations are within 9.22 DU. The correlation coefficients vary from 0.394 in the tropics to 0.762 at southern high latitudes. After eliminating the ozonesonde profile smoothing error with TROPOMI AK, the correlation coefficients increase to greater than 0.922 except for 0.703 in the tropics and mean biases vary from 0.9 DU in the tropics, 1.6–2.1 DU at mid latitudes to 2.4 DU. The slopes range from 0.92 to 1.257 and the standard deviations are within 3.64 DU except for 5.99 DU in the tropics. The large standard deviation, and the small slope in the tropics are partly due to a “drop off” existed in SHADOZ data (Sterling et al., 2018).

5. Ozone variation in eastern China during the COVID-19

20-day average of TROPOMI NO2 (Copernicus Sentinel-5P (processed by ESA), 2018a), HCHO (Copernicus Sentinel-5P (processed by ESA), 2018b) TVCD and the retrieved TOC before and during the lockdown of Wuhan on January 23, 2020 (hereafter referred to as the “pre-lockdown” and “post-lockdown” periods) are shown in Fig. 8. NO2 TVCD over east of China fell by as much as 63% and HCHO TVCD slightly reduced by 6% from pre-lockdown period to lockdown period, respectively. However, the TROPOMI TOC over east of China increase by 10% due to the temperature rise and the uncoordinated reduction of NO2 and HCHO TVCD. Tropospheric ozone is mainly formed through photochemical reactions of nitrogen oxidation (NOx = NO+NO2) indicated by NO2 and volatile organic compounds (VOCs) indicted by HCHO (Sillman, 1995). However, the interrelations among ozone, NOx and VOCs are nonlinear. The chemical formation of ozone is controlled by NOx or VOCs, namely NOx-limited or VOC-limited regimes, depending upon which substance is inadequate in the reactions (Chameides et al., 1992). Because ozone production in the winter in China is usually controlled by VOCs, slight decrease of VOCs in eastern China may not cause an obvious declining of ozone formation from photochemical reaction (Lu et al., 2019). Besides, the decrease of NOx emission would reduce the concentration of NO, which can titrate ozone in the ambient (Li et al., 2016; Zou et al., 2019), causing more accumulation of ozone. Especially, in the BTH region, the NO2 TVCD sharply reduce by 77% much higher than the average decreasing amplitude in the eastern China; however, HCHO TVCD even increased by 18%. This variation tendency of NOx and VOCs caused TOC in BTH region greatly increased by 17%. The Yangtze River Delta (YRD) and Pearl River Delta (PRD) regions show similar ozone pollution characteristics to eastern China.

6. Conclusions

The variation of tropospheric ozone in eastern China during the outbreak of COVID-19 was evaluated using satellite-based observation. We have adapted and modified the OMI ozone profile algorithm to retrieve TROPOMI ozone profiles. Compared to the derived on-orbit ISRFs assuming standard Gaussian and super Gaussian, the pre-flight ISRF measurements (TROPOMI ISRFs v3.0.0) is demonstrated as a best representative in term of the spectral fitting accuracy.

To eliminate the effect of systematic measurement errors in the TROPOMI radiances that depend on wavelength and cross-track positions, we apply “soft calibration” to TROPOMI radiances before the fitting starts. After applying the correction spectrum to TROPOMI, the fitting residuals have been significantly improved for five latitude bands, especially in the tropics and mid latitudes. The fitting residuals reduce by $-71\%$ and 46% in the low and middle latitudes, respectively.

We have validated our retrievals against FTS data and GPSO3 ozonesonde data observations in China between March 2018 and December 2019. The integrated TOC shows excellent agreement with FTS and GPSO3 TOC after the application of TROPOMI AKs, respectively. The comparisons of the retrieved and ozonesondes profiles show that the retrievals have better consistency with the ozonesonde profile than a priori at most of selected stations, especially in the troposphere. However, the mean biases and standard deviations between TROPOMI and ozonesondes profiles above 20 hPa are larger than those between a priori and ozonesondes profiles partly due to missing information below 314 nm. The retrieved SOC show good agreement with ozonesonde data. The validation of integrated TOC with applying TROPOMI AKs against ozonesonde shows that TROPOMI is in very good agreement with ozonesonde within 2.4 DU at all latitudes. The correlations are greater than 0.922 except for 0.703 in the tropics partly due to a “drop off” in SHADOZ data after –2014.

Based on the retrieved TOC as well as TCVD of NO2 and HCHO from TROPOMI, we evaluated the change of ozone in the lockdown period during which special measures were conducted to prevent the spread of COVID-19 and also caused large decrease of primary pollutant emission. The retrieved TOC over east of China increased by 10% compared with that during the pre-lockdown period, due to the uncoordinated reduction of NO2 and HCHO TVCD. In the BTH region, the NO2 TVCD sharply reduced by 77% but HCHO TVCD increased by 18%. This variation tendency of NOx and VOCs caused TOC in BTH region greatly increased by 17%. It indicated that in the VOC-limited region, sharp reduction of NOx emission took no role on the mitigation of ozone pollution, but even caused the increase of ozone concentration.

CRediT authorship contribution statement

Fei Zhao: Software, Writing - original draft. Cheng Liu: Conceptualization, Funding acquisition. Zhaonan Cai: Methodology. Xiong Liu: Science of the Total Environment 764 (2021) 142886
Writing - review & editing. Juseon Bak: Writing - review & editing. Jae Kim: Writing - review & editing. Qihou Hu: Writing - review & editing.

Conflicts of interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data
Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.142886.
