Ozone seasonal evolution and photochemical production regime in polluted troposphere in eastern China derived from high resolution FTS observations

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Abstract:

The seasonal evolution of O₃ and its photochemical production regime in a polluted region of eastern China between 2014 and 2017 has been investigated using observations. We used tropospheric ozone (O₃), carbon monoxide (CO) and formaldehyde (HCHO, a marker of VOCs (volatile organic compounds)) partial columns derived from high resolution Fourier transform spectrometry (FTS), tropospheric nitrogen dioxide (NO₂, a marker of NOx (nitrogen oxides)) partial column deduced from Ozone Monitoring Instrument (OMI), surface meteorological data, and a back trajectory cluster analysis technique. A broad O₃ maximum during
both spring and summer (MAM/JJA) is observed; the day-to-day variations in
MAM/JJA are generally larger than those in autumn and winter (SON/DJF).
Tropospheric O₃ columns in June are 1.55×10¹⁸ molecules*cm⁻² (56 DU (Dobson
Units)) and in December are 1.05×10¹⁸ molecules*cm⁻² (39 DU). Tropospheric O₃
columns in June were ~ 50% higher than those in December. Compared with
SON/DJF season, the observed tropospheric O₃ levels in MAM/JJA are more
influenced by transport of air masses from densely populated and industrialized areas,
and the high O₃ level and variability in MAM/JJA is determined by the photochemical
O₃ production. The tropospheric column HCHO/NO₂ ratio is used as a proxy to
investigate the photochemical O₃ production rate (PO₃). The results show that the PO₃
is mainly nitrogen oxides (NOₓ) limited in MAM/JJA, while it is mainly VOC or mix
VOC-NOₓ limited in SON/DJF. Statistics show that NOₓ limited, mix VOC-NOₓ
limited, and VOC limited PO₃ accounts for 60.1%, 28.7%, and 11% of days,
respectively. Considering most of PO₃ are NOₓ limited or mix VOC-NOₓ limited,
reductions in NOₓ would reduce O₃ pollution in eastern China.

1 Introduction

Human health, terrestrial ecosystems, and materials degradation are impacted by
poor air quality resulting from high photochemical ozone (O₃) levels (Wennberg and
Dabdub, 2008; Edwards et al., 2013; Schroeder et al., 2017). In polluted areas,
tropospheric O₃ generates from a series of complex reactions in the presence of
sunlight involving carbon monoxide (CO), nitrogen oxides (NOₓ = NO (nitric oxide)
+ NO₂ (nitrogen dioxide)), and volatile organic compounds (VOCs) (Oltmans et al.,
2006; Schroeder et al., 2017). Briefly, VOCs first react with the hydroxyl radical (OH)
to form a peroxy radical (HO₂ + RO₂) which increases the rate of catalytic cycling of
NO to NO₂. O₃ is then produced by photolysis of NO₂. Subsequent reactions between
HO₂ or RO₂ and NO lead to radical propagation (via subsequent reformation of OH).
Radical termination proceeds via reaction of OH with NOₓ to form nitric acid (HNO₃)
(reaction (1), referred to as LNOₓ) or by radical-radical reactions resulting in stable
peroxide formation (reactions (2) – (4), referred to as LROₓ, where ROₓ = RO₂ +
Typically, the relationship between these two competing radical termination processes (referred to as the ratio $L_{RO}/L_{NO}$) can be used to evaluate the photochemical regime. In high-radical, low-NO$_x$ environments, reactions (2) – (4) remove radicals at a faster rate than reaction (1) (i.e., $L_{RO} \gg L_{NO}$), and the photochemical regime is regarded as “NO$_x$ limited”. In low-radical, high-NO$_x$ environments the opposite is true (i.e., $L_{RO} \ll L_{NO}$) and the regime is regarded as “VOC limited”. When the rates of the two loss processes are comparable ($L_{NO} \approx L_{RO}$), the regime is said to be at the photochemical transition/ambiguous point, i.e., mix VOC-NO$_x$ limited (Kleinman et al., 2005; Sillman et al., 1995a; Schroeder et al., 2017).

Understanding the photochemical regime at local scales is a crucial piece of information for enacting effective policies to mitigate O$_3$ pollution (Jin et al., 2017; Schroeder et al., 2017). In order to determine the regime, the total reactivity with OH of the myriad of VOCs in the polluted area has to be estimated (Sillman, 1995a; Xing et al., 2017). In the absence of such information, the formaldehyde (HCHO) concentration can be used as a proxy for VOC reactivity because it is a short-lived oxidation product of many VOCs and is positively correlated with peroxy radicals (Schroeder et al., 2017). Sillman (1995a) and Tonnesen and Dennis (2000) found that in situ measurements of the ratio of HCHO (a marker of VOCs) to NO$_2$ (a marker of NO$_x$) could be used to diagnose local photochemical regimes. Over polluted areas, both HCHO and tropospheric NO$_2$ have vertical distributions that are heavily weighted toward the lower troposphere, indicating that tropospheric column measurements of these gases are fairly representative of near surface conditions. Many studies have taken advantage of these favorable vertical distributions to investigate surface emissions of NO$_x$ and VOCs from space (Boersma et al., 2009; Martin et al., 2004a; Millet et al., 2008; Streets et al., 2013). Martin et al. (2004a) and
Duncan et al. (2010) used satellite measurements of column HCHO/NO\textsubscript{2} ratio to explore tropospheric O\textsubscript{3} sensitivities from space and disclosed that this diagnosis of O\textsubscript{3} production rate (PO\textsubscript{3}) is consistent with previous finding of surface photochemistry. Witte et al. (2011) used the similar technique to estimate changes in PO\textsubscript{3} to the strict emission control measures (ECMs) during Beijing Summer Olympic Games period in 2008. Recent papers have applied the findings of Duncan et al. (2010) to observe O\textsubscript{3} sensitivity in other parts of the world (Choi et al., 2012; Witte et al., 2011; Jin and Holloway, 2015; Mahajan et al., 2015; Jin et al., 2017).

With in situ measurements, Tonniesen and Dennis (2000) observed a radical-limited environment with HCHO/NO\textsubscript{2} ratios < 0.8, a NOx-limited environment with HCHO/NO\textsubscript{2} ratios >1.8, and a transition environment with HCHO/NO\textsubscript{2} ratios between 0.8 and 1.8. With 3-d chemical model simulations, Sillman (1995a) and Martin et al. (2004b) estimated that the transition between the VOC- and NO\textsubscript{x}-limited regimes occurs when the HCHO/NO\textsubscript{2} ratio is ~ 1.0. With a combination of regional chemical model simulations and the Ozone Monitoring Instrument (OMI) measurements, Duncan et al. (2010) concluded that O\textsubscript{3} production decreases with reductions in VOCs at column HCHO/NO\textsubscript{2} ratio < 1.0 and NO\textsubscript{x} at column HCHO/NO\textsubscript{2} ratio > 2.0; both NO\textsubscript{x} and VOCs reductions decrease O\textsubscript{3} production when column HCHO/NO\textsubscript{2} ratio lies in between 1.0 and 2.0. With a 0-D photochemical box model and airborne measurements, Schroeder et al. (2017) presented a thorough analysis of the utility of column HCHO/NO\textsubscript{2} ratios to indicate surface O\textsubscript{3} sensitivity and found that the transition/ambiguous range estimated via column data is much larger than that indicated by in situ data alone. Furthermore, Schroeder et al. (2017) concluded that many additional sources of uncertainty (regional variability, seasonal variability, variable free tropospheric contributions, retrieval uncertainty, air pollution levels and meteorological conditions) may cause transition threshold vary both geographically and temporally, and thus the results from one region are not likely to be applicable globally.

With the rapid increase in fossil fuel consumption in China over the past three decades, the emission of chemical precursors of O\textsubscript{3} (NO\textsubscript{x} and VOCs) has increased
dramatically, surpassing that of North America and Europe and raising concerns about worsening O₃ pollution in China (Tang et al., 2011; Wang et al., 2017; Xing et al., 2017). Tropospheric O₃ was already included in the new air quality standard as a routine monitoring component (http://www.mep.gov.cn, last access on 23 May 2018), where the limit for the maximum daily 8 h average (MDA8) O₃ in urban and industrial areas is 160µg/m³ (~ 75 ppbv at 273 K, 101.3 kPa). According to air quality data released by the Chinese Ministry of Environmental Protection, tropospheric O₃ has replaced PM2.5 as the primary pollutant in many cities during summer (http://www.mep.gov.cn/, last access on 23 May 2018). A precise knowledge of O₃ evolution and photochemical production regime in polluted troposphere in China has important policy implications for O₃ pollution controls (Tang et al., 2011; Xing et al., 2017; Wang et al., 2017).

In this study, we investigate O₃ seasonal evolution and photochemical production regime in the polluted troposphere in eastern China with tropospheric O₃, CO and HCHO derived from ground-based high resolution Fourier transform spectrometry (FTS) in Hefei, China, tropospheric NO₂ deduced from the OMI satellite (https://aura.gsfc.nasa.gov/omi.html, last access on 23 May 2018), surface meteorological data, and a back trajectory cluster analysis technique. Considering the fact that most NDACC (Network for Detection of Atmospheric Composition Change) FTS sites are located in Europe and Northern America, whereas the number of sites in Asia, Africa, and South America is very sparse, and there is still no official NDACC FTS station that covers China (http://www.ndacc.org/, last access on 23 May 2018), this study can not only improve our understanding of regional photochemical O₃ production regime, but also contributes to the evaluation of O₃ pollution controls.

This study concentrates on measurements recorded during midday, when the mixing layer has largely been dissolved. All FTS retrievals are selected within ± 30 min of OMI overpass time (13:30 local time (LT)). While the FTS instrument can measure throughout the whole day, if not cloudy, OMI measures only during midday. For Hefei, this coincidence criterion is a balance between the accuracy and the number of data points.
2 Site description and instrumentation

The FTS observation site (117°10′E, 31°54′N, 30 m a.s.l. (above sea level)) is located in the western suburbs of Hefei city (the capital of Anhui Province, 8 million population) in central-eastern China (Figure S1). Detailed description of this site and its typical observation scenario can be found in Tian et al. (2018). Similar to other Chinese megacities, serious air pollution is common in Hefei throughout the whole year (http://mep.gov.cn/, last access on 23 May 2018).

Our observation system consists of a high resolution FTS spectrometer (IFS125HR, Bruker GmbH, Germany), a solar tracker (Tracker-A Solar 547, Bruker GmbH, Germany), and a weather station (ZENO-3200, Coastal Environmental Systems, Inc., USA). The near infrared (NIR) and middle infrared (MIR) solar spectra were alternately acquired in routine observations (Wang et al., 2017). The MIR spectra used in this study are recorded over a wide spectral range (about 600 – 4500 cm$^{-1}$) with a spectral resolution of 0.005 cm$^{-1}$. The instrument is equipped with a KBr beam splitter & MCT detector for O$_3$ measurements and a KBr beam splitter & InSb detector for other gases. The weather station includes sensors for air pressure (± 0.1hpa), air temperature (± 0.3° C), relative humidity (± 3%), solar radiation (± 5%), wind speed (± 0.2 m/s), wind direction (± 5°), and the presence of rain.

3 FTS retrievals of O$_3$, CO and HCHO

3.1 Retrieval strategy

The SFIT4 (version 0.9.4.4) algorithm is used in the profile retrieval (Supplement section A; https://www2.acom.ucar.edu/irwg/links, last access on 23 May 2018). The retrieval settings for O$_3$, CO, and HCHO are listed in Table 1. All spectroscopic line parameters are adopted from HITRAN 2008 (Rothman et al., 2009). A priori profiles of all gases except H$_2$O are from a dedicated WACCM (Whole Atmosphere Community Climate Model) run. A priori profiles of pressure, temperature and H$_2$O are interpolated from the National Centers for Environmental Protection and National Center for Atmospheric Research (NCEP/NCAR) reanalysis (Kalnay et al., 1996). For O$_3$ and CO, we follow the NDACC standard convention with respect to micro windows (MW) selection and the interfering gases consideration (https://www2.acom.
ucar.edu/irwg/links, last access on 23 May 2018). HCHO is not yet an official
NDACC species but has been retrieved at a few stations with different retrieval
settings (Albrecht et al., 2002; Vigouroux et al., 2009; Jones et al., 2009; Viatte et al.,
2014; Franco et al., 2015). The four MWs used in the current study are chosen from a
harmonization project taking place in view of future satellite validation (Vigouroux et
al., 2018). They are centered at around 2770 cm\(^{-1}\) and the interfering gases are CH\(_4\),
O\(_3\), N\(_2\)O, and HDO.

We assume measurement noise covariance matrices \(S_\varepsilon\) to be diagonal, and set its
diagonal elements to the inverse square of the signal to noise ratio (SNR) of the fitted
spectra and its non-diagonal elements to zero. For all gases, the diagonal elements of
a priori profile covariance matrices \(S_a\) are set to standard deviation of a dedicated
WACCM run from 1980 to 2020, and its non-diagonal elements are set to zero.

We regularly used a low-pressure HBr cell to monitor the instrument line shape
(ILS) of the instrument and included the measured ILS in the retrieval (Hase et al.,
2012; Sun et al., 2018).

### 3.2 Profile information in the FTS retrievals

The sensitive range for CO and HCHO is mainly tropospheric, and for O\(_3\) is both
tropospheric and stratospheric (Figure S2). The typical degrees of freedom (DOFS)
over the total atmosphere obtained at Hefei for each gas are included in Table 2: they
are about 4.8, 3.5, and 1.2 for O\(_3\), CO, and HCHO, respectively. In order to separate
independent partial column amounts in the retrieved profiles, we have chosen the
altitude limit for each independent layer such that the DOFS in each associated partial
column is not less than 1.0. The retrieved profiles of O\(_3\), CO, and HCHO can be
divided into four, three, and one independent layers, respectively (Figure S3). The
troposphere is well resolved by O\(_3\), CO, and HCHO, where CO exhibits the best
vertical resolution with more than two independent layers in the troposphere.

In this study, we have chosen the same upper limit (12 km) for the tropospheric
columns for all gases (Table 2), which is about 3 km lower than the mean value of the
tropopause (~15.1 km). In this way we ensured the accuracies for the tropospheric O\(_3\),
CO, and HCHO retrievals, and minimized the influence of transport from stratosphere,
i.e., the so called STE process (stratosphere-troposphere exchange).

### 3.3 Error analysis
The results of the error analysis presented here based on the average of all measurements that fulfill the screening scheme, which is used to minimize the impacts of significant weather events or instrument problems (Supplement section B). In the troposphere, the dominant systematic error for \( \text{O}_3 \) and CO is the smoothing error, and for HCHO is the line intensity error (Figure S4). The dominant random error for \( \text{O}_3 \) and HCHO is the measurement error, and for CO is the zero baseline level error (Figure S5). Taken all error items into account, the summarized errors in \( \text{O}_3 \), CO, and HCHO for 0–12 km tropospheric partial column and for the total column are listed in Table 3. The total errors in the tropospheric partial columns for \( \text{O}_3 \), CO, and HCHO, have been evaluated to be 8.7%, 6.8%, and 10.2%, respectively.

4 Tropospheric \( \text{O}_3 \) seasonal evolution

4.1 Tropospheric \( \text{O}_3 \) seasonal variability

Figure 1(a) shows the tropospheric \( \text{O}_3 \) column time series recorded by the FTS from 2014 to 2017, where we followed Gardiner’s method and used a second-order Fourier series plus a linear component to determine the annual variability (Gardiner et al., 2008). The analysis did not indicate a significant secular trend of tropospheric \( \text{O}_3 \) column probably because the time series is much shorter than those in Gardiner et al. (2008), the observed seasonal cycle of tropospheric \( \text{O}_3 \) variations is well captured by the bootstrap resampling method (Gardiner et al., 2008). As commonly observed, high levels of tropospheric \( \text{O}_3 \) occur in spring and summer (hereafter MAM/JJA). Low levels of tropospheric \( \text{O}_3 \) occur in autumn and winter (hereafter SON/DJF). Day-to-day variations in MAM/JJA are generally larger than those in SON/DJF (Figure 1(b)). At the same time, the tropospheric \( \text{O}_3 \) column roughly increases over time at the first half of the year and reaches the maximum in June, and then decreases during the second half of the year. Tropospheric \( \text{O}_3 \) columns in June are \( 1.55 \times 10^{18} \) molecules\( \text{cm}^{-2} \) (56 DU (Dobson Units)) and in December are \( 1.05 \times 10^{18} \) molecules\( \text{cm}^{-2} \) (39 DU). Tropospheric \( \text{O}_3 \) columns in June were ~50% higher than those in December.

Vigouroux et al. (2015) studied the \( \text{O}_3 \) trends and variabilities at eight NDACC FTS stations that have a long-term time series of \( \text{O}_3 \) measurements, namely,
Ny-Ålesund (79° N), Thule (77° N), Kiruna (68° N), Harestua (60° N), Jungfraujoch (47° N), Izaña (28° N), Wollongong (34° S) and Lauder (45° S). All these stations were located in non-polluted or relatively clean areas. The tropospheric columns at these stations are of the order of \(0.7 \times 10^{18}\) molecules\(\cdot\)cm\(^{-2}\) to \(1.1 \times 10^{18}\) molecules\(\cdot\)cm\(^{-2}\). The results showed a maximum tropospheric O\(_3\) column in spring at all these stations except at the high altitude stations Jungfraujoch and Izaña where it extended into early summer. This is because the STE process is most effective during late winter and spring (Vigouroux et al. 2015). In contrast, we observed a broader maximum at Hefei which extends over MAM/JJA season, and the values are \(\sim 35\%\) higher than those studied in Vigouroux et al. (2015). This is because the observed tropospheric O\(_3\) levels in MAM/JJA are more influenced by air masses originated from densely populated and industrialized areas (see section 4.2), and the MAM/JJA meteorological conditions are more favorable to photochemical O\(_3\) production (see section 5.1). The selection of tropospheric limits 3 km below the tropopause minimized but cannot avoid the influence of transport from stratosphere, the STE process may also contribute to high level of tropospheric O\(_3\) column in spring.

### 4.2 Regional contribution to tropospheric O\(_3\) levels

In order to determine where the air masses came from and thus contributed to the observed tropospheric O\(_3\) levels, we have used the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model to calculate the three-dimensional kinematic back trajectories that coincide with the FTS measurements from 2014 - 2017 (Draxler et al., 2009). In the calculation, the GDAS (University of Alaska Fairbanks GDAS Archive) meteorological fields were used with a spatial resolution of 0.25°\(\times\)0.25°, a time resolution of 6 h and 22 vertical levels from the surface to 250 mbar. All daily back trajectories at 12:00 UTC, with a 24 h pathway arriving at Hefei site at 1500 m a.s.l., have been grouped into clusters, and divided into MAM/JJA and SON/DJF seasons (Stunder, 1996). The results showed that air masses in Jiangsu and Anhui Province in eastern China, Hebei and Shandong Province in northern China, Shaanxi, Henan and Shanxi Province in northwestern China, Hunan and Hubei Province in
central China contributed to the observed tropospheric $O_3$ levels.

In MAM/JJA season (Figure 2(a)), 28.8% of air masses are east origin and arrived at Hefei through the southeast of Jiangsu Province and east of Anhui Province; 41.0% are southwest origin and arrived at Hefei through the northeast of Hunan and Hubei Province, and southwest of Anhui Province; 10.1% are northwest origin and arrived at Hefei through the southeast of Shanxi and Henan Province, and northwest of Anhui Province; 10.1% are north origin and arrived at Hefei through the south of Shandong Province and north of Anhui Province; 10.1% are north origin generated in south of Anhui Province. As a result, air pollution from megacities such as Shanghai, Nanjing, Hangzhou and Hefei in eastern China, Changsha and Wuhan in central-southern China, Zhengzhou and Taiyuan in northwest China, and Jinan in north China could contribute to the observed tropospheric $O_3$ levels.

In SON/DJF season, trajectories are generally longer and originated in the northwest of the MAM/JJA ones (Figure 2(b)). The direction of air masses originating in the eastern sector shifts from the southeast to northeast of Jiangsu Province, and that of local air masses shifts from the south to the northwest of Anhui province. Trajectories of east origin, west origin, and north origin air masses in SON/DJF are 6.5%, 13.1%, and 0.7% less frequent than the MAM/JJA ones, respectively. As a result, the air masses outside Anhui province have 20.2% smaller contribution to the observed tropospheric $O_3$ levels in SON/DJF than in MAM/JJA. In contrast, trajectories of local origin air masses in SON/DJF are 20.2% more frequent than the MAM/JJA ones, indicating a more significant contribution of air masses inside Anhui province in SON/DJF.

The majority of the Chinese population lives in the eastern part of China, especially in the three most developed regions, the Jing-Jin-Ji (Beijing-Tianjin-Hebei), the Yangtze River Delta (YRD; including Shanghai-Jiangsu-Zhejiang-Anhui), and the Pearl River Delta (PRD; including Guangzhou, Shenzhen, and Hong Kong). These regions consistently have the highest emissions of anthropogenic precursors (Figure S6), which have led to severe region-wide air pollution. Particularly, the Hefei site located in the central-western corner of the YRD, where the population in the
southeastern area is typically denser than the northwestern area. Specifically, the southeast of Jiangsu province and the south of Anhui province are two of the most developed areas in YRD, and human activities therein are very intense. Therefore, when the air masses originated from these two areas, O$_3$ level is usually very high. Overall, compared with SON/DJF season, the more southeastern air masses transportation in MAM/JJA indicated that the observed tropospheric O$_3$ levels could be more influenced by the densely populated and industrialized areas, broadly accounting for higher O$_3$ level and variability in MAM/JJA.

5 Tropospheric O$_3$ production regime

5.1 Meteorological dependency

Photochemistry in polluted atmospheres, particularly the formation of O$_3$, depends not only on pollutant emissions, but also on meteorological conditions (Lei et al., 2008; Wang et al., 2016; Coates et al., 2016). In order to investigate meteorological dependency of O$_3$ production regime in the observed area, we analyzed the correlation of the tropospheric O$_3$ with the coincident surface meteorological data. Figure 3 shows time series of temperature, pressure, humidity, and solar radiation recorded by the surface weather station. The seasonal dependencies of all these coincident meteorological elements show no clear dependencies except for the temperature and pressure which show clear reverse seasonal cycles. Generally, the temperatures are higher and the pressures are lower in MAM/JJA than those in SON/DJF. The correlation plots between FTS tropospheric O$_3$ column and each meteorological element are shown in Figure 4. The tropospheric O$_3$ column shows positive correlations with solar radiation, temperature, and humidity, and negative correlations with pressure.

High temperature and strong sunlight primarily affects O$_3$ production in Hefei in two ways: speeding up the rates of many chemical reactions and increasing emissions of VOCs from biogenic sources (BVOCs) (Sillman and Samson, 1995b). While emissions of anthropogenic VOCs (AVOCs) are generally not dependent on temperature, evaporative emissions of some AVOCs do increase with temperature.
(Rubin et al., 2006; Coates et al., 2016). Elevated O$_3$ concentration generally occurs on days with wet condition and low pressure in Hefei probably because these conditions favor the accumulation of O$_3$ and its precursors. Overall, MAM/JJA meteorological conditions are more favorable to O$_3$ production (higher sun intensity, higher temperature, wetter condition, and lower pressure) than SON/DJF, which consolidates the fact that tropospheric O$_3$ in MAM/JJA are larger than those in SON/DJF.

**5.2 PO$_3$ relative to CO, HCHO, and NO$_2$ changes**

In order to determine the relationship between tropospheric O$_3$ production and its precursors, the chemical sensitivity of PO$_3$ relative to tropospheric CO, HCHO, and NO$_2$ changes was investigated. Figure 5 shows time series of tropospheric CO, HCHO, and NO$_2$ columns that are coincident with O$_3$ counterparts. The tropospheric NO$_2$ was deduced from OMI product selected within the $\pm 0.7^\circ$ latitude/longitude rectangular area around Hefei site. The retrieval uncertainty for tropospheric column of is less than 30% (https://disc.gsfc.nasa.gov/datasets/OMNO2_V003/). Tropospheric HCHO and NO$_2$ show clear reverse seasonal cycles. Generally, tropospheric HCHO are higher and tropospheric NO$_2$ are lower in MAM/JJA than those in SON/DJF. Pronounced tropospheric CO was observed but the seasonal cycle is not evident probably because CO emission is not constant over season or season dependent.

Figure 6 shows the correlation plot between the FTS tropospheric O$_3$ column and the coincident tropospheric CO, HCHO, and NO$_2$ columns. The tropospheric O$_3$ column shows positive correlations with tropospheric CO, HCHO, and NO$_2$ columns. Generally, the higher the tropospheric CO concentration, the higher the tropospheric O$_3$, and both VOCs and NO$_x$ reductions decrease O$_3$ production. As an indicator of regional air pollution, the good correlation between O$_3$ and CO (Figure 6(a)) indicates that the enhancement of tropospheric O$_3$ is highly associated with the photochemical reactions which occurred in polluted conditions rather than due to the STE process. The relative weaker overall correlations of O$_3$ with HCHO (Figure 6 (b)) and NO$_2$ (Figure 6 (c)) are partly explained by different lifetimes of these gases, i.e., several
hours to 1 day in summer for NO\textsubscript{2} and HCHO, several days to weeks for O\textsubscript{3}. So older O\textsubscript{3} enhanced air masses easily lose trace of NO\textsubscript{2} or HCHO. Since the sensitivity of PO\textsubscript{3} to VOCs and NO\textsubscript{x} is different under different limitation regimes, the relative flat overall slopes indicates that the O\textsubscript{3} pollution in Hefei can neither be fully attributed to NO\textsubscript{x} pollution nor VOCs pollution.

5.3 O\textsubscript{3}-NO\textsubscript{x}-VOCs sensitivities

5.3.1 Transition/ambiguous range estimation

Referring to previous studies, the chemical sensitivity of PO\textsubscript{3} in Hefei was investigated using the column HCHO/NO\textsubscript{2} ratio (Martin et al., 2004; Duncan et al., 2010; Witte et al., 2011; Choi et al., 2012; Jin and Holloway, 2015; Mahajan et al., 2015; Schroeder et al., 2017; Jin et al., 2017). The methods have been adapted to the particular conditions in Hefei. In particular the findings of Schroeder et.al (2017) have been taken into account.

Since the measurement tools for O\textsubscript{3} and HCHO, the pollution characteristic and the meteorological condition in this study were not the same as those of previous studies, the transition thresholds estimated in either previous studies were not straightforwardly applied here (Martin et al., 2004a; Duncan et al., 2010; Witte et al., 2011; Choi et al., 2012; Jin and Holloway, 2015; Mahajan et al., 2015; Schroeder et al., 2017; Jin et al., 2017). In order to determine transition thresholds applicable in Hefei, China, we iteratively altered the column HCHO/NO\textsubscript{2} ratio threshold and judged whether the sensitivities of tropospheric O\textsubscript{3} to HCHO or NO\textsubscript{2} changed abruptly. For example, in order to estimate the VOC-limited threshold, we first fitted tropospheric O\textsubscript{3} to HCHO that lies within column HCHO/NO\textsubscript{2} ratios < 2 (an empirical start point) to obtain the corresponding slope, and then we decreased the threshold by 0.1 (an empirical step size) and repeated the fit, i.e., only fitted the data pairs with column HCHO/NO\textsubscript{2} ratios < 1.9. This has been done iteratively. Finally, we sorted out the transition ratio which shows an abrupt change in slope, and regarded this as the VOC-limited threshold. Similarly, the NO\textsubscript{x}-limited threshold was determined by iteratively increasing the column HCHO/NO\textsubscript{2} ratio threshold till the sensitivity of
tropospheric O$_3$ to NO$_2$ changed abruptly.

The transition threshold estimation with this scheme exploits the fact that O$_3$ production is more sensitive to VOCs if it is VOCs-limited and is more sensitive to NO$_x$ if it is NO$_x$ limited, and it exists a transition point near the threshold (Martin et al., 2004). Su et al. (2017) used this scheme to investigate the O$_3$-NO$_x$-VOCs sensitivities during the 2016 G20 conference in Hangzhou, China, and argued that this diagnosis of PO$_3$ could reflect the overall O$_3$ production conditions.

### 5.3.2 PO$_3$ limitations in Hefei

Through the above empirical iterative calculation, we observed a VOC-limited regime with column HCHO/NO$_2$ ratios < 1.3, a NO$_x$-limited regime with column HCHO/NO$_2$ ratios > 2.8, and a mix VOC-NO$_x$-limited regime with column HCHO/NO$_2$ ratios between 1.3 and 2.8. Column measurements sample a larger portion of the atmosphere, and thus their spatial coverage are larger than in situ measurements. So the photochemical scene disclosed by column measurement is larger than the in-situ measurement. Specifically, this study reflects the mean photochemical condition of the troposphere.

Schroeder et. al. (2017) argued, the column measurements from space have to be used with care because of the high uncertainty and the inhomogeneity of the satellite measurements. This has been mitigated in this study by the following:

- The FTIR measurements have a much smaller footprint than the satellite measurements. Also we concentrate on measurements recorded during midday, when the mixing layer has largely been dissolved.

- The measurements are more sensitive to the lower parts of the troposphere, which can be inferred from the normalized AVK’s. This reason is simply, that the AVK’s show the sensitivity to the column, but the column per altitude decreases with altitude.

- Figure 7 shows time series of column HCHO/NO$_2$ ratios which varied over a wide range from 1.0 to 9.0. The column HCHO/NO$_2$ ratios in summer are typically larger than those in winter, indicating that the PO$_3$ is mainly NO$_x$ limited in summer and mainly VOC limited or mix VOC-NO$_x$ limited in winter. Based on the calculated
transition criteria, 106 days of observations that have coincident O$_3$, HCHO, and NO$_2$ counterparts in the reported period are classified, where 57 days (53.8%) are in MAM/JJA season and 49 days (46.2%) are in SON/DJF season. Table 4 listed the statistics for the 106 days of observations, which shows that NO$_x$ limited, mix VOC-NO$_x$ limited, and VOC limited PO$_3$ accounts for 60.3% (64 days), 28.3% (30 days), and 11.4% (12 days), respectively. The majority of NO$_x$ limited (70.3%) PO$_3$ lies in MAM/JJA season, while the majorities of mix VOC-NO$_x$ limited (70%) and VOC limited (75%) PO$_3$ lie in SON/DJF season. As a result, reductions in NO$_x$ and VOC could be more effective to mitigate O$_3$ pollution in MAM/JJA and SON/DJF season, respectively. Furthermore, considering most of PO$_3$ are NO$_x$ limited or mix VOC-NO$_x$ limited, reductions in NO$_x$ would reduce O$_3$ pollution in eastern China.

6 Conclusion

We investigated the seasonal evolution and photochemical production regime of tropospheric O$_3$ in eastern China from 2014 – 2017 by using tropospheric O$_3$, CO and HCHO columns derived from Fourier transform infrared spectrometry (FTS), tropospheric NO$_2$ column deduced from Ozone Monitoring Instrument (OMI), the surface meteorological data, and a back trajectory cluster analysis technique. A pronounced seasonal cycle for tropospheric O$_3$ is captured by the FTS, which roughly increases over time at the first half year and reaches the maximum in June, and then it decreases over time at the second half year. Tropospheric O$_3$ columns in June are 1.55×10$^{18}$ molecules*cm$^{-2}$ (56 DU (Dobson Units)) and in December are 1.05×10$^{18}$ molecules*cm$^{-2}$ (39 DU). Tropospheric O$_3$ columns in June were ~ 50% higher than those in December. A broad maximum within both spring and summer (MAM/JJA) is observed and the day-to-day variations in MAM/JJA are generally larger than those in autumn and winter (SON/DJF). This differs from tropospheric O$_3$ measurements in Vigouroux et al. (2015). However, Vigouroux et al. (2015) used measurements at relatively clean sites.

Back trajectories analysis showed that air pollution in Jiangsu and Anhui Province in eastern China, Hebei and Shandong Province in northern China, Shaanxi,
Henan and Shanxi Province in northwest China, Hunan and Hubei Province in central China contributed to the observed tropospheric $O_3$ levels. Compared with SON/DJF season, the observed tropospheric $O_3$ levels in MAM/JJA are more influenced by transport of air masses from densely populated and industrialized areas, and the high $O_3$ level and variability in MAM/JJA is determined by the photochemical $O_3$ production. The tropospheric column HCHO/NO$_2$ ratio is used as a proxy to investigate the chemical sensitivity of $O_3$ production rate ($PO_3$). The results show that the $PO_3$ is mainly nitrogen oxide (NO$_x$) limited in MAM/JJA, while it is mainly VOC or mix VOC-NO$_x$ limited in SON/DJF. Reductions in NO$_x$ and VOC could be more effective to mitigate $O_3$ pollution in MAM/JJA and SON/DJF season, respectively. Considering most of PO$_3$ are NO$_x$ limited or mix VOC-NO$_x$ limited, reductions in NO$_x$ would reduce $O_3$ pollution in eastern China.

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on the Internet. The authors would also like to thank Dr. Jason R. Schroeder and three anonymous referees for useful comments that improved the quality of this paper.

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Figure 1. (a): FTS measured and bootstrap resampled tropospheric O$_3$ columns at Hefei site. The linear trend and the residual are also shown. Detailed description of the bootstrap method can be found in Gardiner et al., 2008. (b): Tropospheric O$_3$ column monthly means derived from (a).
Figure 2. One-day HYSPLIT back trajectory clusters arriving at Hefei at 1500 m a.s.l that are coincident with the FTS measurements from 2014 - 2017. (a) Spring and summer (MAM/JJA), and (b) Autumn and winter (SON/DJF) season. The base map was generated using the TrajStat 1.2.2 software (http://www.meteothinker.com).
Figure 3. Minutely averaged time series of temperature, pressure, humidity, and solar radiation recorded by the surface weather station.

Figure 4. Correlation plot between the FTS tropospheric O$_3$ column and the coincident surface meteorological data. Black dots are data pairs within MAM/JJA season and green dots are data pairs within SON/DJF season.
Figure 5. Time series of tropospheric CO, HCHO, and NO$_2$. Tropospheric CO and HCHO were derived from FTS observations which is the same as tropospheric O$_3$ and tropospheric NO$_2$ is derived from OMI data.
Figure 6. Correlation plot between the FTS tropospheric O₃ column and coincident tropospheric CO (upper), HCHO (middle), and NO₂ (bottom) columns. The CO and HCHO data are retrieved from FTS observations and the NO₂ data were deduced from OMI product.
Figure 7. Time series of column HCHO/NO₂ ratios.

Tables

Table 1. Summary of the retrieval parameters used for O₃, CO, and HCHO. All micro windows (MW) are given in cm⁻¹.

<table>
<thead>
<tr>
<th>Gases</th>
<th>O₃</th>
<th>CO</th>
<th>HCHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retrieval code</td>
<td>SFXT4 v 0.9.4.4</td>
<td>SFXT4 v 0.9.4.4</td>
<td>SFXT4 v 0.9.4.4</td>
</tr>
<tr>
<td>Spectroscopy</td>
<td>HITRAN2008</td>
<td>HITRAN2008</td>
<td>HITRAN2008</td>
</tr>
<tr>
<td>P, T, H₂O profiles</td>
<td>NCEP</td>
<td>NCEP</td>
<td>NCEP</td>
</tr>
<tr>
<td>A priori profiles for target/interfering gases except H₂O</td>
<td>WACCM</td>
<td>WACCM</td>
<td>WACCM</td>
</tr>
<tr>
<td>MW for profile retrievals</td>
<td>1000-1004.5</td>
<td>2057.7-2058</td>
<td>2763.42-2764.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2069.56-2069.76</td>
<td>2765.65-2766.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2157.5-2159.15</td>
<td>2778.15-2779.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2780.65-2782.0</td>
</tr>
<tr>
<td>Retrieved interfering gases</td>
<td>H₂O, CO₂, C₂H₄, ⁶⁶⁸O₃, ⁶⁸⁸O₃</td>
<td>O₃, N₂O, CO₂, OCS, H₂O</td>
<td>CH₄, O₃, N₂O, HDO</td>
</tr>
<tr>
<td>SNR for de-weighting</td>
<td>None</td>
<td>500</td>
<td>600</td>
</tr>
<tr>
<td>Regulatization</td>
<td>Sₐ</td>
<td>Diagonal: 20%</td>
<td>Diagonal: 11% ~ 27%</td>
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<tr>
<td></td>
<td>No correlation</td>
<td>No correlation</td>
<td>No correlation</td>
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<tr>
<td>ILS</td>
<td>LINEFIT145</td>
<td>LINEFIT145</td>
<td>LINEFIT145</td>
</tr>
<tr>
<td>Error analysis</td>
<td>Systematic error:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-Smoothing error (smoothing)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-Errors from other parameters: Background curvature (curvature), Optical path difference (max_opd), Field of view (omega), Solar line strength (solstrnth), Background slope (slope), Solar line shift (solshft), Phase (phase), Solar zenith angle (sza), Line temperature broadening (linetair_gas), Line pressure broadening (linepair_gas), Line intensity (lineint_gas)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Random error:</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>-Interference errors:</td>
<td></td>
<td></td>
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<td>retrieval parameters (retrieval_parameters), interfering species (interfering_species)</td>
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<td></td>
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<tr>
<td></td>
<td>-Measurement error (measurement)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Errors from other parameters: Temperature (temperature), Zero level (zshift)</td>
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</tbody>
</table>
Table 2. Typical degrees of freedom for signal (DOFs) and sensitive range of the retrieved O₃, CO, and HCHO profiles at Hefei site.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Total column DOFs</th>
<th>Sensitive range (km)</th>
<th>Tropospheric partial column (km)</th>
<th>Tropospheric DOFs</th>
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</thead>
<tbody>
<tr>
<td>O₃</td>
<td>4.8</td>
<td>Ground - 44</td>
<td>Ground - 12</td>
<td>1.3</td>
</tr>
<tr>
<td>CO</td>
<td>3.5</td>
<td>Ground - 27</td>
<td>Ground - 12</td>
<td>2.7</td>
</tr>
<tr>
<td>HCHO</td>
<td>1.2</td>
<td>Ground - 18</td>
<td>Ground - 12</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 3. Errors in % of the column amount of O₃, CO, and HCHO for 0–12 km tropospheric partial column and for the total column.

<table>
<thead>
<tr>
<th>Gas</th>
<th>O₃</th>
<th>CO</th>
<th>HCHO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0–12</td>
<td>0–12</td>
<td>0–12</td>
</tr>
<tr>
<td>Total random</td>
<td>3.2</td>
<td>0.59</td>
<td>3.8</td>
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<tr>
<td>Total systematic</td>
<td>8.1</td>
<td>4.86</td>
<td>5.7</td>
</tr>
<tr>
<td>Total errors</td>
<td>8.7</td>
<td>5.0</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.95</td>
</tr>
<tr>
<td></td>
<td>10.2</td>
<td>5.7</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Table 4. Chemical sensitivities of PO₃ for the selected 106 days of observations that have coincident O₃, HCHO, and NO₂ counterparts.

<table>
<thead>
<tr>
<th>Items</th>
<th>Proportion</th>
<th>Autumn and winter</th>
<th>Spring and summer</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>days</td>
<td>percentage</td>
<td>days</td>
</tr>
<tr>
<td>NOx limited</td>
<td>64</td>
<td>60.3%</td>
<td>19</td>
</tr>
<tr>
<td>Mix VOC-NOx limited</td>
<td>30</td>
<td>28.3%</td>
<td>21</td>
</tr>
<tr>
<td>VOC limited</td>
<td>12</td>
<td>11.4%</td>
<td>9</td>
</tr>
<tr>
<td>Sum</td>
<td>106</td>
<td>100%</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>57</td>
</tr>
</tbody>
</table>