Spatial and temporal changes of the ozone sensitivity in China based on satellite and ground-based observations

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Received: 20 October 2020 – Discussion started: 14 December 2020
Revised: 21 March 2021 – Accepted: 23 March 2021 – Published: 12 May 2021

Abstract. Ground-level ozone (O₃) pollution has been steadily getting worse in most parts of eastern China during the past 5 years. The non-linearity of O₃ formation with its precursors like nitrogen oxides (NOₓ = NO + NO₂) and volatile organic compounds (VOCs) are complicating effective O₃ abatement plans. The diagnosis from space-based observations, i.e. the ratio of formaldehyde (HCHO) columns to tropospheric NO₂ columns (HCHO/NO₂), has previously been proved to be highly consistent with our current understanding of surface O₃ chemistry. HCHO/NO₂ ratio thresholds distinguishing O₃ formation sensitivity depend on regions and O₃ chemistry interactions with aerosol. To shed more light on the current O₃ formation sensitivity over China, we have derived HCHO/NO₂ ratio thresholds by directly connecting satellite-based HCHO/NO₂ observations and ground-based O₃ measurements over the major Chinese cities in this study. We find that a VOC-limited regime occurs for HCHO/NO₂ < 2.3, and a NOₓ-limited regime occurs for HCHO/NO₂ > 4.2. The HCHO/NO₂ between 2.3 and 4.2 reflects the transition between the two regimes. Our method shows that the O₃ formation sensitivity tends to be VOC-limited over urban areas and NOₓ-limited over rural and remote areas in China. We find that there is a shift in some cities from the VOC-limited regime to the transitional regime that is associated with a rapid drop in anthropogenic NOₓ emissions and VOC emissions controls is essential for O₃ abatement plans.

1 Introduction

Ground-level ozone (O₃) is one of the major air pollutants that has negative impacts on human health and can result in eye and nose irritation, respiratory disease, and lung function impairment (Jerrett et al., 2009; Khaniabadi et al., 2017; Huang et al., 2018). Y. Tian et al. (2020) observed increased admissions for pneumonia associated with O₃ exposure, especially for elderly people. In addition, it also has important impacts on climate as a greenhouse gas by absorbing thermal radiation (Fishman et al., 1979; IPCC, 2014). Photochemical tropospheric O₃ is formed in a non-linear manner from O₃ precursors such as volatile organic compounds (VOCs) and nitrogen oxides (NOₓ = NO + NO₂) in the presence of sunlight (Crutzen, 1974; Jacob, 2000).

In 2008, China was found to be the largest contributor to Asian emissions of carbon monoxide (CO), NOₓ, non-methane volatile organic carbon (NMVOC), and methane (CH₄) (Kurokawa et al., 2013). Because of these large emissions of anthropogenic air pollutants, the Chinese State Council released the “Air Pollution Prevention and Action Plan” (APPAP) on September 2013, which has as a key task to prevent and control air pollution in China (Cai et al., 2017). Since then, critical emission control strategies have been carried out that are designed to reduce the concentrations of six environmental pollutants: sulfur dioxide (SO₂), nitrogen dioxide (NO₂), CO, O₃, and particulate mat-
ter (PM$_{2.5}$ and PM$_{10}$) (Zhang et al., 2016; Feng and Liao, 2016). During the past decade, the concentrations of many pollutants including SO$_2$, NO$_2$, CO, PM$_{2.5}$, and PM$_{10}$ have declined in most cities; however, O$_3$ concentrations showed an increasing trend (W. N. Wang et al., 2017; Z. Wang et al., 2019; Zeng et al., 2019). Therefore, reducing O$_3$ concentrations has become the focus of China’s next air quality control strategy (Cheng et al., 2018).

In terms of O$_3$ concentrations, the effectiveness of emissions control strategy depends on whether the photochemical regime of O$_3$ formation is a VOC-limited or NO$_x$-limited regime (Jin et al., 2020). In the VOC-limited (or NO$_x$-saturated) regime, VOC emission reductions reduce the chemical production of organic radicals (RO$_2$), which in turn lead to decreased cycling with NO$_x$ and consequently lower concentration of O$_3$ (Milford et al., 1989). In the NO$_x$-limited (or VOC-saturated) regime, NO$_x$ emission reductions reduce NO$_2$ photolysis, which is the primary source of free oxygen atoms. Therefore, in a NO$_x$-limited regime, NO$_x$ reductions reduce ambient O$_3$. In contrast, in a VOC-limited regime, NO$_x$ acts to reduce O$_3$, so a NO$_x$ decrease in emissions promotes O$_3$ production (Kleinman, 1994).

The observed photochemical indicators and observation-based models (OBMs) are the most commonly used tools to diagnose the O$_3$ formation sensitivity. O$_3$ production efficiency (OPE = $\Delta$O$_3$ / ANO$_x$) and the H$_2$O$_2$/NO$_2$ (or H$_2$O$_2$/$\text{HNO}_3$) ratio are two widely used indicators to infer the O$_3$ formation regimes (Chou et al., 2011; Ding et al., 2013). T. Wang et al. (2017) concluded that lower OPE values (e.g. <4) indicate a VOC-limited regime. In contrast, higher OPE values (e.g. >7) indicate a NO$_x$-limited regime. OPE values in the medium range (e.g. 4 < OPE < 7) mark the transition between the two regimes. Another indicator of the O$_3$ formation sensitivity regime is the H$_2$O$_2$/NO$_2$ ratio. Hammer et al. (2002) defined that, in the VOC-limited regime, lower H$_2$O$_2$/NO$_2$ ratios would be expected and higher H$_2$O$_2$/NO$_2$ ratios indicate the NO$_x$-limited regime. In the past decade, the observed photochemical indicators have been applied to identify the O$_3$ formation sensitivity in different periods and regions of China.

The OBM combines in situ field observations and chemical box modelling. It is built on widely used chemistry mechanisms (e.g. Master Chemical Mechanism (MCM), Carbon Bond, Regional Atmospheric Chemical Mechanism (RACM), Statewide Air Pollution Research Center mechanism (SAPRC)) and applied to the observed atmospheric conditions to simulate various atmospheric chemical processes, including the in situ O$_3$ production rate. However, ground-based measurements are often limited in time period and spatial extent. The OBM analysis requires measuring nitric oxide (NO) at sub-ppb levels and more than 50 different types of VOCs with high accuracy, which is difficult to achieve (T. Wang et al., 2017).

Satellite remote sensing provides an alternative way to investigate long time periods of O$_3$ formation sensitivity on large spatial scales. For over 2 decades, satellite-based spectrometers have provided continuous global observations on a daily basis for two species indicative of O$_3$ precursors, i.e. NO$_2$ for NO$_x$ (Martin et al., 2004; Lamsal et al., 2014) and formaldehyde (HCHO) for VOCs (Palmer et al., 2003; Fu et al., 2007). NO$_x$ can be approximated from satellite observation of NO$_2$ column because of the short lifetime of NO$_2$ and high ratio of NO$_2$/NO$_x$ in the boundary layer (Duncan et al., 2010; Jin and Holloway, 2015). HCHO is an intermediate of the oxidation reaction of various VOCs in the atmosphere. The production of HCHO is approximately proportional to the summed rate of reactions of VOC with OH radicals (Sillman, 1995). Therefore, HCHO can be used as a tracer for VOCs in the absence of other VOC observations (Martin et al., 2004; Duncan et al., 2010). The O$_3$ formation sensitivity is defined by the ratio of HCHO to NO$_2$ (referred to as FNR) (Martin et al., 2004). Duncan et al. (2010) combined models and Ozone Monitoring Instrument (OMI) HCHO and NO$_2$ data to show certain ranges of FNR that can be useful for classifying a region into VOC-limited or NO$_x$-limited regime. An FNR smaller than 1 indicates the VOC-limited conditions, and an FNR higher than 2 indicates the NO$_x$-limited conditions. An FNR in the range of 1–2 should generally be considered indicative of the transitional regime. These FNR thresholds defined by Duncan et al. (2010) have been widely used for various regions (Choi and Souri, 2015; Jin and Holloway, 2015; Souri et al., 2017; Jeon et al., 2018) and with different satellite instruments (Choi et al., 2012).

However, these prior studies linked FNR with surface O$_3$ sensitivity in models (Martin et al., 2004; Duncan et al., 2010). Modelled and observed HCHO columns, NO$_2$ columns, and surface O$_3$ often disagree. Jin et al. (2017) found that the spatial and temporal correlations between the modelled and satellite-derived FNR vary over the used satellite instruments. Brown-Steiner et al. (2015) found persistent O$_3$ biases under all configurations of a global climate-chemistry model (GCCC) with detailed tropospheric chemistry. Although FNR thresholds defined by Duncan et al. (2010) have been used previously to investigate O$_3$-NO$_x$-VOC sensitivity in China (Witte et al., 2011; Tang et al., 2012; Jin and Holloway, 2015), their conclusions were based on the atmospheric situations in the United States and may not be suitable for the more complicated air pollution in China, concerning the different emission factors, sources, pollution levels, and climatology. For example, compared with the United States, most cities in China have higher aerosol levels (van Donkelaar et al., 2010; X. Li et al., 2019). Secondary aerosol production may become a large sink of radicals, which could shift O$_3$ production toward a VOC-limited regime under these FNR thresholds suited to the United States (Liu et al., 2012; K. Li et al., 2019). It is therefore useful to describe surface O$_3$ sensitivity using FNR thresholds derived entirely from satellite-observed FNR and ground-based measurements of O$_3$. In addition, Schroeder et al. (2017) using airborne measurements suggested that the
range and span of FNR marking the transitional regime varies regionally.

In this study, we assess whether space-based HCHO / NO₂ ratios capture the non-linearity of O₃ chemistry by matching satellite observations with ground-based O₃ measurements over major Chinese cities. Thresholds suited for China between space-based HCHO / NO₂ and the ground-based O₃ response patterns are derived from observations instead of model results. We focus on the spatial and temporal variability of O₃ formation sensitivity using our FNR thresholds on a nationwide scale and in typical cities from 2016 to 2019.

More recently, a new unique situation has occurred with the outbreak of the COVID-19 pandemic, which provided a unique opportunity to demonstrate our predicted effects on O₃ pollution in China. Efforts to halt the spread of COVID-19 have drastically reduced human activities worldwide (Siciliano et al., 2020; H. Tian et al., 2020). As a result of these restrictions, a significant reduction in primary air pollutant emissions, especially in the concentration of NO₂, has been noticed in China and several European and American countries (Tobias et al., 2020; Wang and Su, 2020; Bauwens et al., 2020; Ding et al., 2020). By contrast, increasing O₃ concentrations during the same period were observed in densely populated metropolitan areas throughout the world (Siciliano et al., 2020; Zoran et al., 2020; Huang et al., 2020).

Section 2 describes the data and methods used in this study. Section 3 presents our derived FNR thresholds method and variations of O₃ formation sensitivity in China. In addition, impacts of the COVID-19 outbreak on O₃ levels are discussed. Finally, Sect. 4 gives a brief summary.

2 Data

2.1 Satellite data

We use the NO₂ and HCHO observations from the Ozone Monitoring Instrument (OMI) aboard the National Aeronautics and Space Administration (NASA) satellite Aura, which was launched in July 2004 (Levent et al., 2006). In an ascending sun-synchronous polar orbit, OMI passes the Equator at about 13:40 LT (local time), providing global measurements of aerosol parameters, cloud, and various trace gases (NO₂ and HCHO among them) (Levent et al., 2006). The high spatial resolution (13 km × 24 km at nadir) allows for observing fine details of atmospheric parameters (Jin and Holloway, 2015). OMI data are considered to be reliable and of good quality for the full mission thus far (Zara et al., 2018). In addition, the OMI overpass time is well suited to detect the O₃ formation sensitivity during the afternoon, when O₃ photochemical production peaks and when the boundary layer is high and the solar zenith angle is small, maximizing instrument sensitivity to HCHO and NO₂ in the lower troposphere (Jin et al., 2017).

We use the OMI tropospheric NO₂ and HCHO data products from the European Quality Assurance for Essential Climate Variables project (QA4ECV, http://www.qa4ecv.eu/, last access: 6 May 2021). NO₂ data are compiled by the Royal Netherlands Meteorological Institute (KNMI). The tropospheric NO₂ column density is defined as the vertically integrated number of NO₂ molecules between the Earth’s surface and the tropopause per unit area. We select QA4ECV NO₂ daily observations following the recommendations given in the product specification document (Boersma et al., 2011) for this data product: (1) no processing error, (2) less than 10 % snow or ice coverage, (3) solar zenith angle less than 80°, and (4) cloud radiance fraction less than 50 %. The QA4ECV NO₂ monthly datasets are processed with a spatial resolution of 0.125° × 0.125°. Boersma et al. (2018) reported the single-pixel uncertainties for the QA4ECV NO₂ columns are 35 %–45 % in the polluted regions; the monthly mean NO₂ columns are estimated to have an uncertainty of ±10 %.

The OMI tropospheric HCHO data are retrieved by the Belgian Institute for Space Aeronomy (BIRA-IASB) (Smedt et al., 2017a). We select processing_quality_flags = 0 or > 255, providing a selection of observations that is considered optimal. Zara et al. (2018) found that the QA4ECV HCHO slant column densities (SCDs) have uncertainties of 8–12 × 10¹² molecule/cm² and a remarkably stable trend (increase < 1 %/yr). The QA4ECV HCHO monthly datasets are available with a spatial resolution of 0.05° × 0.05°. Temporal averaging has been shown to reduce the HCHO measurements uncertainty and noise (Millet et al., 2008). We regrid the monthly OMI HCHO data (0.05° × 0.05°) to the same grid as for the monthly OMI NO₂ data (0.125° × 0.125°).  

2.2 NOₓ emission

Emission inventories of air pollutants are important sources of information for policy makers and form essential input for air quality models. Bottom-up inventories are usually compiled from statistics on emitting activities and their typical emission factors but are sporadically updated (Li et al., 2017). Satellite-derived emission inventories have important advantages over bottom-up emission inventories: they are spatially consistent, have high temporal resolution, and provide up-to-date emission information (Mijling and van der A, 2012). In this study, we use monthly mean NOₓ surface emission estimates derived from OMI observations of tropospheric NO₂ columns (the QA4ECV product discussed in Sect. 2) by the Daily Emission estimation Constrained by Satellite Observations (DECSO) algorithm. Mijling and van der A (2012) for the first time developed DECSO (version 1) by calculating the sensitivity of concentration to emission based on a chemical transport model and using trajectory analysis to account for transport away from the source. Ding et al. (2015) improved DECSO (version 3) and demonstrated that it is able to detect the monthly change of NOₓ emis-
2.3 Ground-based observations

Since 2012, the Chinese government at various levels began to establish a national air quality monitoring network, which released real-time ground-level O$_3$ monitoring data to the public. By 2016, the establishment of more than 1000 sites was completed, covering more than 300 cities across the country. At each monitoring site, the concentration of O$_3$ is measured using the ultraviolet absorption spectrometry method and differential optical absorption spectroscopy; NO$_2$ is measured using the chemiluminescence method by a set of commercial instruments. The instrumental operation, maintenance, data assurance, and quality control were conducted based on the most recent revisions of China environmental protection standards (CMEE, 2013). We use hourly O$_3$ and NO$_2$ concentrations (in standard conditions: 273 K, 101.325 kPa) from the network of ~1000 sites operated by the China Ministry of Ecology and Environment (CMEE) since 2016. CMEE revised the monitoring of pollutants to a new reference conditions (298 K, 101.325 kPa) since 1 September 2018 (CMEE, 2018). Daily ground-based O$_3$ and NO$_2$ observations are calculated from hourly observations at OMI overpass time (average of 13:00 and 14:00LT). In this study, we convert the gas concentrations before 1 September 2018 from the standard conditions to the reference conditions. The temperature dependence is according to Charles’s law (Eq. 1),

\[
\frac{V_{\text{std}}}{V_{\text{ref}}} = \frac{T_{\text{ref}}}{T_{\text{std}}},
\]

where $V_{\text{std}}$ is the volume of a gas under standard conditions, $V_{\text{ref}}$ is the volume of a gas under reference conditions, $T_{\text{std}}$ (unit: K) is the thermodynamic temperature of standard conditions, and $T_{\text{ref}}$ (unit: K) is the thermodynamic temperature of reference conditions. The gas concentration conversion follows

\[
\frac{C_{\text{std}}}{C_{\text{ref}}} = \frac{M/V_{\text{std}}}{M/V_{\text{ref}}} = \frac{V_{\text{ref}}}{V_{\text{std}}},
\]

where $C_{\text{std}}$ is the gas concentration under standard conditions, and $C_{\text{ref}}$ is the gas concentration under reference conditions.

Because the Chinese national air quality monitoring network stations are mostly located in the centre of cities or densely populated areas, which are usually the most polluted regions, we select the Naha station, located on the small island of Okinawa in Japan, as a location with a clean atmosphere. The hourly O$_3$ and NO$_2$ observations of Naha station are provided by the Japanese Atmospheric Environmental Regional Observation System (AEROS; http://soramame.taiki.go.jp/index.php, last access: 6 May 2021).

2.4 CLASS model

We simulate the non-linear relationship among O$_3$, NO$_2$, and HCHO using the Chemistry Land-surface Atmosphere Soil Slab model (CLASS). We performed a series of numerical experiments with the same dynamic and chemistry conditions listed in Table 1, but we modified only the concentrations of NO$_2$ and HCHO. The initial mixing ratios of chemical species are shown in Table S1 in the Supplement. The initial mixing ratio data are from van Stratum et al. (2012). All other species (except for molecular oxygen and nitrogen) are initialized at zero, and we modified only the concentrations of NO$_2$ and HCHO.

The CLASS model solves the diurnal evolution of dynamical variables (temperature, specific humidity, and wind) and chemical species over time in a well-mixed convective atmospheric boundary layer (ABL) in which entrainment and boundary layer growth are considered (Vilà-Guerau de Arellano et al., 2015; van Heerwaarden et al., 2010). All these variables are assumed to be constant with height due to intense turbulent mixing driven by convection (van Heerwaarden et al., 2010). The surface is assumed to be homogeneous in this box model. Chemistry is represented by a chemical scheme based on 27 reactions that control O$_3$ formation described by van Stratum et al. (2012), with O$_3$, NO$_2$, and isoprene as the most important species. This simplified chemical scheme is able to represent the evolution of chemical species in semirural areas (Janssen et al., 2012; van Stratum et al., 2012). This chemical scheme is able to represent the evolution of the O$_3$–NO$_2$–VOC–HO$_x$ cycle in semirural areas (Vilà-Guerau de Arellano et al., 2011; Janssen et al., 2012; van Stratum et al., 2012). The model has been validated under various dynamical conditions (Barbaro et al., 2014; Janssen et al., 2012; van Heerwaarden et al., 2010).

3 Results

3.1 O$_3$ formation sensitivity regime classification

In Fig. 1a, the CLASS model is applied to generate O$_3$ isopleths, which illustrate O$_3$ as a function of NO$_2$ and HCHO values. The isopleths show that O$_3$ formation is a highly non-linear process in relation to NO$_2$ and HCHO. When NO$_2$ is low, the O$_3$ increases with increasing NO$_2$. As NO$_2$ increases, the O$_3$ eventually reaches a local maximum. At
higher NO$_2$ concentrations, the O$_3$ would decrease with increasing NO$_2$.

We first evaluate if satellite-based HCHO and NO$_2$ columns can capture the non-linear O$_3$–NO$_2$–HCHO chemistry shown by the CLASS model. In order to obtain a representative observation sample, we create monthly mean ground-based O$_3$ and NO$_2$ observations of 360 cities across China from the Chinese national air quality monitoring network from 2016 to 2019 and the background station observations from Naha, Japan, for comparison. Temperature is also a major factor in O$_3$ chemistry. O$_3$ pollution is rare when the ambient temperature is below 20°C (Sillman, 2003). The seasonality of ground-level O$_3$ concentrations also exhibited monthly variability peaking in summer and reaching the lowest levels in winter over China (W. N. Wang et al., 2017). In addition, long NO$_3$ lifetime and low concentrations of OH and RO$_2$ radicals would lead most regions of China to a VOC-limited regime in winter (Shah et al., 2020). Therefore, we focus in this study on May–October as the summer period when meteorology is favourable for O$_3$ formation (Jin et al., 2017).

By directly connecting HCHO columns from OMI observations with ground-based measurements of NO$_2$ and O$_3$ from 360 cities across China during May–October from 2016 to 2019 in Fig. 1b, we find that the satellite-based HCHO columns and ground-based NO$_2$ concentrations can capture non-linear O$_3$ chemistry consistent with the CLASS model results. It indicates that tropospheric HCHO columns from OMI can represent the near-surface HCHO environment as revealed by previous studies (Martin et al., 2004; Duncan et al., 2010; Jin et al., 2017). The overall O$_3$–NO$_2$–HCHO chemistry is also captured by satellite-based HCHO and NO$_2$ columns in Fig. 1c, where we construct the O$_3$ isopleth using only observations.

Having established this relationship between satellite-based HCHO / NO$_2$ columns and surface O$_3$ concentrations, we subsequently derive the FNR thresholds marking the O$_3$ transitional regime. The local O$_3$ maximum can be thought of as a dividing line separating two different photochemical regimes (Sillman, 1999). According to the Chinese national ambient air quality standards released in 2012, 1 h average O$_3$ concentration should below 160 µg/m$^3$ in rural regions and below 200 µg/m$^3$ in urban regions (Li et al., 2018). We assume that the monthly O$_3$ concentration (daily O$_3$ data are averaged at 13:00 and 14:00:LT) exceeding 160 µg/m$^3$ has a large component that is due to local photochemical production not meteorology or regional transport. We calculated for each city the monthly mean surface O$_3$ as a function of the monthly column densities of NO$_2$ and HCHO for all months during May–October from 2016 to 2019. The results are shown in Fig. 1c. We only consider observations of monthly HCHO columns higher than 2 × 10$^{15}$ molecule/cm$^2$ (detection limitation), NO$_2$ columns more than 1.5 × 10$^{15}$ molecule/cm$^2$ (which are defined as polluted regions), and O$_3$ columns above 160 µg/m$^3$ (minimizing the effect of background ozone). We then plot in Fig. 1d the surface O$_3$ concentrations as a function of the FNR to determine the range of FNRs, which includes the O$_3$ maximum for most (> 60 %) cities. We define this range as the transition between the NO$_x$-limited and VOC-limited regimes.

It should be noted that the actual split between NO$_x$-limited and VOC-limited regimes includes a broad transitional region rather than a sharp dividing line (Sillman, 1999). Although we reduce the noise by gridding, there is a blurry transition between NO$_2$-limited and VOC-limited regimes. The lack of sharp and clear transitions between two O$_3$ sensitivity regimes is likely influenced by factors such as meteorology, chemical and depositional loss of O$_3$, and noisy satellite data. We find a relationship between FNR and the O$_3$ response patterns that is qualitatively similar but quantitatively distinct across cities. Taking into account the range of transitional regime, the FNR thresholds [2.3, 4.2], marking the transitional regime, are defined as the ±30 % range of the median (3.28), covering the O$_3$ maximum in most (60 %) studied cities.

To minimize the effect of background O$_3$ by transport or meteorological variability, we use monthly mean O$_3$ concentrations above 160 µg/m$^3$ in summertime when the O$_3$ chemistry is strongest. We assume that the results are applicable for the whole of China. To check this assumption, we investigate the FNR thresholds in different latitude zones (18–28° N, 28–38° N, and 38–53° N) in Fig. S1 in the Supplement. Generally, we conclude that the derived FNR thresholds range of [2.3, 4.2] for the whole domain is a good representation for all latitude zones in China.

Figure S2a in the Supplement shows monthly O$_3$ concentration in winter (December–January–February), which rarely exceed 160 µg/m$^3$, including the FNR thresholds derived using summertime data. Based on Fig. S2b, we assume that our FNR thresholds [2.3, 4.2] derived using summertime data will be valid for all seasons. Three regimes can be roughly identified from the FNR thresholds we adopted: a VOC-limited regime should occur when the FNR < 2.3, and a NO$_x$-limited regime should occur when the FNR > 4.2.

### Table 1. Configuration and settings of the CLASS modelling system.

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<td>Time step</td>
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<td>Initial temperature jump at height</td>
<td>1 K</td>
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<tr>
<td>Wind</td>
<td>Off</td>
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<tr>
<td>Surface scheme (sea or land)</td>
<td>Off</td>
</tr>
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<td>Chemistry</td>
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</tbody>
</table>

https://doi.org/10.5194/acp-21-7253-2021
Figure 1. (a) The simulated O₃ isopleths versus NO₂ and HCHO using the CLASS model. (b) The 360 cities’ monthly mean in situ O₃ concentrations versus in situ NO₂ concentrations and HCHO columns from OMI observations in the summer during 2016–2019. Note that daily ground-based O₃ and NO₂ observations are calculated from hourly observations at OMI overpass time (averaged at 13:00 and 14:00 LT). The O₃ numeric value of the grid cells is average of all points falling in each bin. (c) Same as (b) but with NO₂ columns from OMI observations. (d) The top 10 % monthly O₃ values and corresponding FNRs of each city. FNR thresholds are defined as the ±30 % range from the median of monthly O₃ exceeding 160 µg/m³ in the top 10 % dataset.

The FNR between 2.3 and 4.2 reflects the transition between the two regimes.

3.2 Variations in O₃ formation sensitivity in China

Figure 2a and b show the photochemical regime classification over China in summer of 2016 and 2019 using our FNR thresholds. Combined with the China provincial administrative division in Fig. S3 in the Supplement, we see the VOC-limited regimes mainly appear in the North China Plain (NCP), the Yangtze River Delta (YRD), and the Pearl River Delta (PRD), and the NOₓ-limited regimes dominate the remaining areas, which are consistent with results from N. Wang et al. (2019) and Jin and Holloway (2015). In the NCP, the VOC-limited regimes are found in Beijing and some big cities in Hebei province, central regions in Shandong province, and Henan province. Transitional regimes control the remaining regions of Shandong province and Henan province and most regions of Hefei province. In the YRD, the VOC-limited regimes are found in Shanghai and southern Jiangsu province. In the PRD, the VOC-limited regimes are found in Guangzhou. Outside the NCP, YRD and PRD, the VOC-limited regimes concentrate in city centres of Shenyang, Chengdu, Chongqing, Xi’an, and Wuhan, which are surrounded by transitional regimes in the suburban areas. It has been acknowledged that the urban O₃ formations are generally VOC-limited due to the large amount of NOₓ emissions from diverse sectors, like transportation, industry, residential sector, and power plants (Shao et al., 2009; Wang et al., 2009; Sun et al., 2011). The NOₓ-limited or transitional regimes dominated O₃ formation in the suburban and rural areas of eastern China (Xing et al., 2011; Jin et al., 2017).

Comparison of O₃ sensitivities between 2016 and 2019 shows noticeable changes from VOC-limited regime to transitional regime in the NCP, YRD, and PRD. In the NCP, the continuous area of VOC-limited regimes that occurred in 2016 change to transitional regimes in 2019. The VOC-limited regimes remain in central Beijing, Tianjin, Shijiazhuang, Jinan, and Zhengzhou. In the YRD, Shanghai and Nanjing remain in the VOC-limited regime, and other cities mostly change to the transitional regime. In the PRD, the VOC-limited regime still controls Guangzhou, while the transitional regimes control its surrounding cities.
Figure 2. (a) Photochemical regime classification over China in the summer of 2016. (b) Same as (a) but for 2019. Note that no data grids in (a) and (b) corresponds to monthly HCHO columns below the detection limit ($2 \times 10^{15}$ molecule/cm$^2$) or NO$_2$ columns lower than $1.5 \times 10^{15}$ molecule/cm$^2$.

(c) Mean HCHO columns from OMI over China in the summer of 2016. (d) Same as (c) but for 2019. (e) Mean NO$_2$ columns from OMI over China in the summer of 2016. (f) Same as (e) but for 2019.

Figure 2c and d show mean HCHO columns over China in the summer of 2016 and 2019. The columns exceed $15 \times 10^{15}$ molecule/cm$^2$ in megacity clusters, such as in the NCP, YRD, and PRD, as well as the Sichuan Basin. Shen et al. (2019) found large increases of HCHO columns during May–September over 2005–2016 in the NCP and the YRD, consistent with the trend of anthropogenic VOC emissions. Our results show that the satellite HCHO columns increase in the NCP and the YRD and decrease in the PRD and in the Sichuan Basin during May–October of the 2016–2019 period. Figure 2e shows mean NO$_2$ columns over China in the summer of 2016. The NCP, YRD, PRD, Sichuan Basin, and Urumqi have high levels ($80 \times 10^{15}$ molecule/cm$^2$) of NO$_2$ columns. Figure 2f shows the satellite NO$_2$ columns have a strong decline in the NCP, the PRD, Hunan, Hubei, and Jiangxi provinces in summer from 2016 to 2019. However, the YRD shows increasing NO$_2$ columns in 2019.
We select typical cities (Beijing, Shanghai, Guangzhou, Neijiang, Lhasa, and Naha) to analyse in more detail the O$_3$ formation sensitivity in the summers of 2016 to 2019 in Fig. 3. These cities are selected based on their different chemical regimes in 2016. The locations of the six cities are shown in Fig. S4 in the Supplement. Economically developed megacities or provincial capital cities such as Beijing, Shanghai, and Guangzhou, with high levels of tropospheric NO$_2$ and HCHO, remain in the VOC-limited regime over 2016–2019. The reduction of tropospheric NO$_2$ results in a shift in the O$_3$ formation sensitivity in cities such as Neijiang over 2016–2019. Lhasa as a city with low NO$_2$ and the background station in Naha with even lower HCHO and NO$_2$ columns remain in the NO$_x$-limited regime over 2016–2019.

As we know, O$_3$ increases with increasing NO$_x$ in the NO$_x$-limited regime and decreases with increasing NO$_x$ in the VOC-limited regime. The contrast between NO$_x$-limited and VOC-limited regimes illustrates the difficulties involved in developing policies to reduce O$_3$ in NO$_x$ polluted regions. Reductions in VOCs will only be effective in reducing O$_3$ if VOC-limited chemistry predominates. Reductions in NO$_x$ will be effective only if NO$_x$-limited chemistry predominates and may actually increase O$_3$ in VOC-sensitive regions. If cities belonging to the VOC-limited regime like Beijing only focus on the reduction of NO$_x$ while ignore the control of VOC emissions, they will experience a process of rising O$_3$ concentrations, the more NO$_x$ decrease, the greater the increase in O$_3$ will be.

3.3 Observed response of ground-level O$_3$ to chemical formation sensitivity

To validate the regimes derived from satellite observations, we also analyse the surface NO$_2$ observations from ground-based measurements. Figure 4a and b show the mean ground-based NO$_2$ concentrations in summer of 2016 and 2019. According to the NO$_x$ surface emission estimates derived with DECSO from OMI observations, the NO$_x$ emissions in eastern China (18° N, 104° E, 41.5° N, 124° E) decrease from 5.93 Tg/yr in 2016 to 4.21 Tg/yr in 2019. Such a strong decline in NO$_x$ emissions led to decreasing ambient NO$_2$ concentrations at NCP (Beijing, Shijiazhuang, Zhengzhou, Jinan) and YRD (Hefei and other cities in Anhui province). In Fig. 4c, the national average NO$_2$ concentration decrease by 14.4% in summer from 2016 to 2019.

Figure 4d and e show the mean ground-based O$_3$ concentration of about 360 cities across China in summer of 2016 and 2019. Generally, the O$_3$ levels in western China are lower than in eastern China. In 2016, few cities have an average O$_3$ concentration above 140 µg/m$^3$. In 2019, cities with a mean O$_3$ concentration exceeding 140 µg/m$^3$ occurred at the NCP (Tianjin, Shijiazhuang, some cities in Shandong and Henan province), the YRD (Nanjing), and the PRD (Guangzhou). In Fig. 4f, we see the number of cities with average O$_3$ values above 140 µg/m$^3$ increases rapidly from 2.20% in 2016 to 31.37% in 2019. The cities with an average O$_3$ value below 80 µg/m$^3$ decrease from 11.02% in 2016 to 2.24% in 2019. In addition, the nationwide O$_3$ average in summer increases year by year from year from 2016 (104.86 µg/m$^3$) to 2019 (125.14 µg/m$^3$). K. Li et al. (2019) reported the increasing O$_3$ trends in summer in megacity clusters of eastern China and the highest O$_3$ concentrations are in the NCP, which are consistent with our results.

A complex coupling of primary emissions, chemical transformation, and dynamic transport at different scales determine the O$_3$ pollution (Jacob, 1999). NO$_x$ and VOCs play important roles in O$_3$ formation. Emissions of NO$_x$ and VOCs to the environment are the starting point of O$_3$ pollution problems. During the past decade in China, ambitious steps have been taken to control NO$_x$ emissions. In 2013, the Chinese State Council issued the APPAP. Stringent control measures were carried out since then, including phasing out highly emitting industries, closing outdated factories, tightening industrial emission standard, improving fuel quality (N. Wang et al., 2019). However, to the other important O$_3$ precursors, VOCs, less attention has been given in emission control strategy. M. Li et al. (2019) concluded that anthropogenic NMVOC emissions in China during 1990–2017 have been increasing continuously due to the dramatic growth in activity rates and absence of effective control measures. Following China’s past control strategy on VOCs, we can regard VOC emissions as rising or in steady state.

The reduction of the NO$_x$ emissions for cities in the VOC-limited regime is one of the main reason for the increasing of O$_3$. Figure 5a shows the difference of total NO$_x$ emissions derived from OMI observations in summer in east China between 2019 and 2016. A decline in NO$_x$ emissions centres at the NCP, YRD and PRD, where most areas belong to the VOC-limited regime. In order to provide further insight into the impact of NO$_x$ emission variations on O$_3$ concentrations, five selected typical cities (Beijing, Shanghai, Guangzhou,
Neijiang and Naha) are shown in more detail (see Fig. 5b and c). For cities under the control of VOC-limited chemistry (Beijing, Shanghai and Guangzhou), accompanied with decreasing NOx emissions, O3 concentrations generally show an opposite behaviour to NOx emissions. The O3 formation sensitivity in Neijiang shows a shift from the transitional to the NOx-limited regime over 2016–2019. The reduction of NOx emissions in the transitional regime is accompanied by decreasing O3 in Neijiang. Although the O3 data in Naha for 2016–2018 are unavailable, we see that O3 concentrations in Naha are low in 2019, and NOx emissions are stable during 2016–2019. Note that we find a qualitative relationship between NOx emission and the O3 response patterns, confirming the non-linear O3–NO2–VOC chemistry but not in a quantitative sense. For example, the changes of NOx emissions in Beijing (-2.17 Gg N/cell), Shanghai (-1.18 Gg N/cell), Guangzhou (-0.28 Gg N/cell), and Neijiang (-0.15 Gg N/cell) during 2016–2019 lead to different levels of O3 changes in Beijing (10.43 µg/m^3), Shanghai (7.81 µg/m^3), Guangzhou (25.54 µg/m^3), and Neijiang (-22.66 µg/m^3). Because of the VOC-limited chemistry conditions, O3 increases with decreasing NOx emissions in Bei-
Figure 5. (a) Differences in total NO\textsubscript{x} emissions derived from OMI observations in summer in east China between 2019 and 2016. (b) Variations in total NO\textsubscript{x} emissions in five cities (Beijing, Shanghai, Guangzhou, Neijiang, and Naha) in summer from 2016 to 2019. (c) Variations in mean ground-based O\textsubscript{3} concentrations in five cities in summer from 2016 to 2019.

jing, Shanghai, and Guangzhou. The NO\textsubscript{x}-limited conditions lead to decreasing O\textsubscript{3} with decreasing NO\textsubscript{x} emissions in Neijiang. Compared with Beijing, NO\textsubscript{x} emissions in Guangzhou remained basically constant in 2016 and 2019. But O\textsubscript{3} concentrations in Guangzhou increased more than in Beijing. The local O\textsubscript{3} formation sensitivity is helpful to present the way that O\textsubscript{3} responds to NO\textsubscript{x} emission, but VOC emission are needed when discussing their relationship in a quantitative way.

3.4 Enhanced O\textsubscript{3} levels during the COVID-19 lockdown in China

The measures in response to the outbreak of the COVID-19 lead to sudden changes of NO\textsubscript{x} emissions and anthropogenic HCHO emissions in China in the beginning of 2020 (Wang et al., 2020; Hui et al., 2020). We analyse the change of O\textsubscript{3} concentrations during the lockdown period to validate our method. To look into COVID-19 lockdown impacts on short-term O\textsubscript{3} level, we choose two time periods covering 357 cities across China: period I (3–23 January 2020) and period II (9–29 February 2020), to avoid the coincidence of Chinese New Year holidays (24 January to 8 February 2020).

Figure 6a shows enhanced O\textsubscript{3} levels in most cities of eastern China during the COVID-19 lockdown, except for some cities in PRD and Fujian province. The cities with O\textsubscript{3} concentration increases of more than 40 µg/m\textsuperscript{3} are located in the NCP and the YRD, i.e. the populous regions of China, indicating a potential negative health effect from O\textsubscript{3} exposure in these regions. Figure 6b shows strong reductions in NO\textsubscript{x} emissions in eastern China, especially in Henan, Hubei, and Jiangsu provinces, where as a consequence of the lockdown, transportation, construction, and light industry activities have been dramatically decreased.

Assuming that our observation-based FNR thresholds derived using summertime data also apply during winter, we see that most regions of eastern China belong to the VOC-limited regime during periods I and II in Fig. 6c and d. Previous studies also reported that the O\textsubscript{3} chemistry in the urban areas in China in wintertime is in a VOC-limited regime due to the relative lack of HO\textsubscript{x} radicals (Seinfeld and Pandis, 2016). During winter (VOC-limited conditions), when the concentration of NO\textsubscript{x} is high and the level of UV radiation is low, the O\textsubscript{3} production varies inversely with the NO\textsubscript{x} concentration (Sillman et al., 1990). During the lockdown period, both the anthropogenic emissions of NO\textsubscript{x} and VOCs were reduced. The NO\textsubscript{x} reduction during the lockdown is higher than the VOC reduction according to Sicard et al. (2020). The reductions of VOC emissions are generally effective in reducing O\textsubscript{3} concentrations. However, such air quality improvements are largely offset by reductions in NO\textsubscript{x} emissions leading to increases in O\textsubscript{3} concentrations due to the strongly VOC-limited conditions in the NCP in winter (Xing et al., 2020). The NO\textsubscript{x} reduction during the lockdown is higher than the VOC reduction (Sicard et al., 2020). Thus,
Figure 6. (a) Differences in mean ground-based $O_3$ concentrations in east China between period I and period II. (b) Differences in mean $NO_x$ emissions in east China between period I and period II. (c) $O_3$ formation sensitivity in east China during period I. (d) Same as (c), but for period II. Note that period I (3–23 January 2020) is before the lockdown, and period II (9–29 February 2020) is during the lockdown.

A reduction in $NO_x$ leads to an increase in the $O_3$ concentrations in most regions of eastern China during period II. Besides, reduction of freshly emitted NO in particular from road traffic alleviates $O_3$ titration locally (Seinfeld and Pandis, 2016; Levy et al., 2014). The $O_3$ titration occurs particularly in winter (less photolysis reactions of $NO_2$) under high $NO_x$ levels (Sillman, 1999). However, the lockdown measures result primarily in a lower titration of $O_3$ by NO due to the reduction in local $NO_x$ emissions by road transport, which also enhances $O_3$ levels in urban areas. On the other hand, some cities, mainly located in southeastern China, showed decreasing $O_3$ levels. Zhao et al. (2020) concluded that the cause of $O_3$ decline in these cities is the emission changes of $NO_x$ and VOC. In Fig. 6c we see that some cities in Fujian and Guangdong provinces belong to the transitional regime. Theoretically, the transitional regime should correspond to the conditions at which $O_3$ formation is most efficient, indicating that reductions or increases in $NO_x$ and VOCs will reduce the $O_3$ concentration.

4 Conclusion

Satellite-based HCHO / $NO_2$ ratios and ground-based $O_3$ measurements were directly connected to capture the non-
linearity of surface O₃ chemistry over major Chinese cities in this study. Evaluating the FNR thresholds marking the O₃ transitional regime in which O₃ formation is less sensitive to the precursors, we found a broad transitional region, which reflects differences in factors among 360 cities, such as emissions, meteorology, and regional transport. The national FNR thresholds are defined as follows: a VOC-limited regime should occur for FNR < 2.3 and a NOₓ-limited regime should occur for FNR > 4.2. The FNR between 2.3 and 4.2 reflects the transition between the two regimes. Our FNR thresholds derived from satellite and ground-based observations are higher than previously reported model-based values. The non-linear chemistry of O₃ depends on its precursors NO₂ and VOCs with contributions from both local and regional sources (Xue et al., 2014). Modelling studies are good at simulating the response of surface O₃ to an overall reduction in NOₓ or VOC emissions. The FNR thresholds derived with in situ O₃ observations will be more indicative of the local O₃ chemistry than the model, including the effect of NOₓ titration over urban areas (Jin et al., 2020).

We analysed the spatial and temporal variability of O₃ formation sensitivity using our FNR thresholds over China from 2016 to 2019. Our results showed that O₃ formation sensitivity tends to be VOC-limited over urban areas and NOₓ-limited over rural and remote areas in China. In 2016, the VOC-limited regimes mainly appear in the NCP, the YRD, and the PRD. In 2019, there was a shift in most NCP regions from the VOC-limited to the transitional regime. The area with a VOC-limited regime in the YRD and PRD also shrank. We found that O₃ formation sensitivity changes in these regions were associated with a strong decline in tropospheric NO₂ columns in the NCP and the PRD. For megacities such as Beijing and Guangzhou, although they remained in the VOC-limited regime over 2016–2019, there was still a decrease in NO₂ columns. Consistent with decreasing tropospheric NO₂ columns, the national average surface NO₂ concentration decreased by 14.4 % in summer from 2016 to 2019 and the NOₓ emissions in eastern China decreased from 5.93 Tg/yr in 2016 to 4.21 Tg/yr in 2019. This detected spatial expansion of the transitional regime and NOₓ emission reduction in the VOC-limited regime has contributed to rising surface O₃ concentrations. The nationwide averaged O₃ concentration in summer increased year by year from 2016 (104.86 µg/m³) to 2019 (125.14 µg/m³). The cities with average O₃ values above 140 µg/m³ increased rapidly from 2.20 % in 2016 to 31.37 % in 2019.

Satellite instruments measure the vertically integrated column density, which we use as a proxy of the actual surface concentrations. To reduce the effect of short-term variability in vertical distributions caused by meteorological changes, we use monthly mean averages. Therefore, our satellite-based HCHO/NO₂ method is limited to identification of long-term evolution in O₃ sensitivity, focusing on understanding the average air quality.

We presented the level of O₃ formed from photo-oxidation of total measured HCHO only not differentiating the contributions from different sources (directly emitted or photochemically formed). Due to the higher temperature and stronger solar radiation in summer, the higher concentration level of HCHO mainly results from the intense photo-oxidation of VOCs. Emission sources of HCHO, as a tracer of VOCs, can be anthropogenic and biogenic. Shen et al. (2019) found that the OMI HCHO distribution follows their anthropogenic inventory in megacity clusters over China, while it does not follow the biogenic emissions inventory. Despite the fact that local sources of anthropogenic VOCs are difficult to identify, our FNR thresholds derived from satellite-based information have the potential to provide important information to air quality planners. Compared with stringent control measures for NOₓ emissions, VOC emissions got less attention as the other O₃ precursor in China. The case study of O₃ level changes during the COVID-19 lockdown in China demonstrated that the strong reductions in anthropogenic NOₓ emissions resulted in significant O₃ enhancement due to the VOC-limited regime in winter. It indicates that a protocol with strict measures to control NOₓ emissions, without simultaneous VOC emissions controls for power plants and heavy industry, such as petrochemical facilities, achieves only limited effects on O₃ pollution.

Data availability. Satellite data used in this research can be obtained from public sources. The OMI tropospheric NO₂ product from the QA4ECV project can be obtained from https://doi.org/10.21944/qa4ecv-no2-omi-v1.1 (Boersma et al., 2017), and the HCHO product can be obtained from https://doi.org/10.18758/71021031 (De Smedt et al., 2017b).

The hourly O₃ and NO₂ observations of Chinese ground stations can be accessed from third parties (http://www.temis.nl/emissions/region_asia/databasen.php (Ding et al., 2018)). The hourly O₃ and NO₂ observations of Chinese ground stations can be accessed from third parties (http://www.temis.nl/emissions/region_asia/databasen.php (Ding et al., 2018)). The hourly O₃ and NO₂ observations of Chinese ground stations can be accessed from third parties (http://www.temis.nl/emissions/region_asia/databasen.php (Ding et al., 2018)).

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/acp-21-7253-2021-supplement.

Author contributions. WW and RvdA provided satellite data, tools and analysis. RvdA, JD, MvW and TC undertook the conceptualization and investigation. WW prepared the original draft. RvdA and JD carried out the review and editing. All authors discussed the results and commented on the paper.
Competing interests. The authors declare that they have no conflict of interest.

Special issue statement. This article is part of the special issue “Regional assessment of air pollution and climate change over East and Southeast Asia: results from MICS-Asia Phase III”. It is not associated with a conference.

Acknowledgements. The support provided by China Scholarship Council (CSC) during a visit by Wannan Wang to Royal Netherlands Meteorological Institute (KNMI) is acknowledged.

Review statement. This paper was edited by Tim Butler and reviewed by two anonymous referees.

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https://doi.org/10.5194/acp-21-7253-2021 Atmos. Chem. Phys., 21, 7253–7269, 2021


