Relationships of ozone formation sensitivity with precursors emissions, meteorology and land use types, in Guangdong-Hong Kong-Macao Greater Bay Area, China

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ABSTRACT

Due to the influences of precursors emissions, meteorology, geography and other factors, ozone formation sensitivity (OFS) is generally spatially and temporally heterogeneous. This study characterized detailed spatial and temporal variations of OFS in Guangdong-Hong Kong-Macao Greater Bay Area (GBA) from 2012 to 2016 based on OMI satellite data, and analyzed the relationships of OFS with precursors emissions, meteorology and land use types (LUTs). From 2012 to 2016, the OFS tended to be NOx-limited in GBA, with the value of FNR (HCHO/NO2) increasing from 2.04 to 2.22. According to the total annual emission statistics of precursors, NOx emissions decreased by 33.1% and VOCs emissions increased by 35.2% from 2012 to 2016, directly resulting in OFS tending to be NOx-limited. The Grey Relation Analysis results show that total column water (TCW), surface net solar radiation (SSR), air temperature at 2 m (T2) and surface pressure (SP) are the top four meteorological factors with the greatest influences on OFS. There are significant positive correlations between FNR and T2, SSR, TCW, and significant negative correlations between FNR and SP. In GBA, the OFS tends to be NOx-limited regime in wet season (higher T2, SSR, TCW and lower SP) and VOCs-limited regime in dry season (lower T2, SSR, TCW and higher SP). The FNR displays obvious gradient variations on different LUTs, with the highest in “Rural areas”, second in “Suburban areas” and lowest in “Urban areas”.

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Introduction

Stratospheric ozone (the ozone layer) can block excessive ultraviolet entering the troposphere and reaching the earth’s surface, but tropospheric ozone is harmful to human health and the environment (Anjea and Li, 1992; Weisel et al., 1995). Tropospheric ozone is a component of photochemical smog, which is detrimental to the eyes, respiratory system and lung function of human beings, and it can reduce crop production, especially at high concentrations (Reich and Amundson, 1985; Linn et al., 1994; White et al., 1994; Wang, 1999). Ozone is also a greenhouse gas (Xing et al., 2011).

The frequently reported air pollution episodes of fine particulate matter (PM$_{2.5}$) and ozone (O$_3$) are ascribed to rapid industrialization, urbanization, and growth of motor vehicles in China (Wang et al., 2006; Zhang et al., 2008a; Shao et al., 2009; Zhao et al., 2009; Jiang et al., 2010; Peng et al., 2011a). To improve air quality, the Chinese government has implemented stringent air pollution control measures for the reduction of sulfur dioxide (SO$_2$), nitrogen oxides (NO$_x$), particulate matter (PM) and volatile organic compounds (VOCs) from 2013 to 2017, which was embodied in the Action Plan for the Prevention and Control of Air Pollution.

According to 74 cities’ monitoring results in China, the percentage of ozone non-compliant cities had increased from 23% to 38% from 2013 to 2017. However, other pollutants achieved marked improvement (2013-2017 Report on the State of Environment in China, available at http://www.me.gov.cn, in Chinese). There was a same circumstance in Guangdong-Hong Kong-Macao Greater Bay Area (GBA), with annual average ozone concentrations increasing from 48 to 58 $\mu$g/m$^3$, whereas, other pollutants (SO$_2$, NO$_x$, and PM$_{10}$) decreased by 36 $\mu$g/m$^3$, 12 $\mu$g/m$^3$, and 25 $\mu$g/m$^3$, respectively, from 2006 to 2017 (Guangdong-Hong Kong-Macao-Pearl River Delta Regional Air Quality Monitoring Network: A Report of Monitoring Results in 2017, available at http://www.gdep.gov.cn, in Chinese). In conclusion, ozone pollution control is urgent in GBA, and it needs more scientific strategies by considering ozone chemical formation sensitivity.

Near-surface ozone forms via a complex series of photochemical reactions among NO$_x$ and VOCs in the presence of sunlight (Haagen-Smit, 1952). The correct strategies for controlling ozone formation depend on the applicable photochemical regime, namely, whether ozone production is NO$_x$-limited or VOCs-limited (Dodge, 1987). The major indicators of ozone formation sensitivity (OFS) to its precursors include VOCs/NO$_x$ ratio method, Smog Production Model, and Relative Incremental Reactivity (Li et al., 2017a). The VOCs/NO$_x$ ratio method is generally used in investigating the OFS based on satellite data. Formaldehyde (HCHO) is a short-lived oxidation product of VOCs, so it is usually regarded as a proxy for VOCs reactivity, especially in regions where biogenic activity is intense (Sillman, 1995; Witte et al., 2011). Sillman (1995) first used the concentrations ratio of HCHO to total reactive nitrogen (NO$_x$) to determine the chemical sensitivity of ozone production. Martin et al. (2004) extended Sillman’s method to space-based measurement from Global Ozone Monitoring Experiment (GOME) and proposed that the HCHO/NO$_x$ ratio (FNR) is a more reasonable OFS indicator. Based on this indicator, many scholars explored the OFS around the world using satellite data. Martin et al. (2004) found that the surface ozone was more sensitive to NO$_x$ emissions than VOCs emissions, over most continental regions of the Northern Hemisphere in summer. Duncan et al. (2010) found that surface ozone formation became more sensitive to NO$_x$ over most regions of the United States from 2005 to 2007, due to substantially reduction of NO$_x$ emission and increment of biogenic isoprene with rising temperature. Jin and Holloway (2015) implied that NO$_x$ controls would be more effective for O$_3$ reduction in Pearl River Delta (PRD), regardless of season. Among several commonly used satellite data, the OMI data is more applicable for revealing the spatial and temporal gradient variations of OFS because of its finer resolution (Witte et al., 2011; Jin and Holloway, 2015; Shan et al., 2016; Jin et al., 2017; Wu et al., 2018).

Influenced by ozone precursors emissions, meteorology, geography and other relative factors, OFS is usually spatially and temporally heterogeneous (Zhang et al., 2008a; Xing et al., 2011; Li et al., 2013). There are many researches investigating the effects of chemical precursors and meteorology on surface ozone but seldom on surface OFS (Tu et al., 2007; Lou et al., 2015; Yadav et al., 2016; Sharma et al., 2017; Wang et al., 2017; Li et al., 2019; Wang et al., 2019). The emitted precursors are directly involved in the production of ozone and determine the sensitivity of local ozone formation. In addition to local precursors emissions, meteorological conditions are critical in the formation and transmission of ozone. Air temperature, solar radiation, relative humidity, boundary layer height, wind speed and direction play an important role in the formation, dilution, diffusion and transport of ozone and its precursors.

Furthermore, the OFS characteristics are different between urban sites and rural sites (Duncan et al., 2010; Peng et al., 2011b; Carrillo-Torres et al., 2017), but few studies have investigated the OFS based on land use type classifications.

In this study, we presented the spatial and temporal characteristics of O$_3$-VOCs-NO$_x$ sensitivity over GBA from 2012 to 2016, based on OMI remote sensing data with finer resolution of 0.125°. Subsequently, the impacts of chemical precursors emissions and meteorological factors on OFS were analyzed. Furthermore, the relationships between OFS and different land use types (LUTs) were given. This study can be combined with meteorological forecast and sources emission simulation to comprehensively evaluate and predict the OFS on regions. What’s more, it will provide an important scientific basis for formulating more local and scientific ozone pollution prevention and control measures based on the refined spatial and temporal variation characteristics of OFS and the relationships between OFS and its associated factors.

1. Materials and methods

1.1. Study area

The GBA is located in southern China (Fig. 1). It consists of 11 cities, including Guangzhou (GZ), Shenzhen (SZ), Foshan (FS), Dongguan (DG), Zhuhai (ZH), Zhongshan (ZS), Zhaoqing (ZQ), Jiangmen (JM), Huizhou (HZ), Hong Kong (HK) Special Administrative Region (SAR) and Macao (MC) SAR. The GBA covers a total area of about 56,000 square kilometers, and the resident population was more than 70 million in 2018. In recent years, the total gross domestic product of GBA was increasing rapidly, around 1.34 trillion dollars in 2018 (available at http://www.cnbayarea.org.cn, in Chinese). It is expected to become the fourth international first-class bay area and world-class urban agglomeration in the near future. Therefore, special attention has been paid to the air quality in GBA.

1.2. Satellite-based observation

1.2.1. OMI observation

OMI is one of the four sensors carried on the National Aeronautics and Space Administration (NASA) earth observation satellite Aura, which was launched into a solar synchronous orbit in July 2004. Its daily transit time is about 13:45, local standard time. OMI contains two ultraviolet light channels and one visible light channel, with spectral resolution of 0.42–0.63 nm and spatial resolution of approxi-
mately 13 × 24 km². This gives OMI better spatial resolution than either GOME or Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) instrument. NO₂, HCHO, SO₂, bromine oxide (BrO), chlorine dioxide (ClO₂), aerosols and some other air quality components are measured by OMI. In this study, the tropospheric column products of NO₂ and HCHO were used.

The OMI monthly gridded data products of tropospheric column NO₂ (version 2) and tropospheric column HCHO (version 14), are acquired from the Tropospheric Emission Monitoring Instrument Service (TEMIS, http://www.temis.nl/index.php), which is supported by European Space Agency (ESA) and hosted by Royal Netherlands Meteorological Institute (KNMI) (Smedt et al., 2008; Boersma et al., 2011; Smedt et al., 2012; De Smedt et al., 2015). The retrieval of tropospheric trace gas species has uncertainties, related to clouds, surface albedo, trace gas profile, stratospheric column and aerosols (Boersma et al., 2004). The total uncertainty of TEMIS NO₂ data is approximately 15%, which is principally due to the cloud fractions (Celarier et al., 2008). The Royal Belgian Institute for Space Aeronomy (BIRA-IASB) has made progress in resolving issues associated with stripping effects and instrumental degradation in the version 14 of TEMIS HCHO data (Witte et al., 2011), the total uncertainty of which is about 25% (Baek et al., 2014). The spatial resolutions of TEMIS OMI NO₂ and TEMIS OMI HCHO are 0.125° and 0.25°, respectively. The OFS indicator FNR is derived from HCHO divided by NO₂, which requires a consistent spatial resolution of HCHO and NO₂. Consequently, the TEMIS OMI HCHO needs to be resampled to 0.125°. According to Duncan et al.’s (2010) findings regarding the FNR, the FNR < 1.0 indicates VOCs-limited regime; the FNR > 2.0 indicates NO₂-limited regime; the FNR between 1.0 and 2.0 indicates transitional regime.

1.2.2. MODIS land cover product
A LUT classification for the GBA, covering urban, suburban, and rural areas, was established based on the 2016 MODIS land cover type (LCT) product (MCD12Q1, version 6) (Zhuang et al., 2019). The whole world is divided into 18 × 36 stripes in MCD12Q1 product, in which the stripe h28v06 covers the GBA. MCD12Q1 was acquired by processing one-year Terra and Aqua observations, which is Level-3 data with a spatial resolution of 500 m. The primary land cover classification scheme in MCD12Q1 is defined by the International Geosphere Biosphere Programme, which identifies 17 types of land cover (Friedl et al., 2010). To establish a LUT classification for the GBA, the 17 types were merged into 4 major types (Ran et al., 2010), as shown in Table S1.

Grids with resolution of 0.125°×0.125° were created on the MCD12Q1 image to match with the OMI resolution in ArcGIS. Then, the definition (“Urban areas”, “Suburban areas”, “Rural areas” or “Ocean areas”) of each grid was determined according to the proportions of 4 major LCTs in one grid (Fig. 1). The LUT classification criteria were as follows: (1) when the proportion of “Urban and built-up” LCT was > 10%, the grid was assigned as “Urban areas”; (2) when the proportion of “Urban and built-up” LCT was between 1% and 10%, the grid was assigned as “Suburban areas”; (3) when the proportion of “Urban and built-up” LCT was < 1%, the grid was assigned as “Rural areas”; (4) when the proportion of “Water” LCT was > 80%, the grid was assigned as “Ocean areas”.

For validating the accuracy and applicability of the LUT classification results, 78 grids were selected from 406 grids in GBA, based on statistical principle of random sampling, with confidence level of 95% and confidence interval of 10%. We checked the landform and building density of the 78 selected grids on Google Earth (Fig. S1). The checking results are generally consistent with our LUT classification results (Table S2).

1.3. Ozone precursors emission data
For analyzing the spatial relationships of OFS with its precursors emissions, the Multi-resolution Emission Inventory for China (MEIC) in 2015 was used (Li et al., 2017b), which provides emission data of 10 major atmospheric chemical components, including SO₂, NOₓ, CO, NH₃, non-methane volatile organic compounds (NMVOC), PM₁₀, PM₂.₅, biogenic carbon (BC), organic carbon (OC) and CO₂. The MEIC inventory provides annual and monthly gridded emission data with the spatial resolution of 0.25°, including 10 emission sectors for NOₓ (power plant, industry combustion, other industry process, cement, steel, domestic fossil fuel, domestic bio-fuel, road transport, non-road transport and open burning) and 9 emission sectors for NMVOC (domestic solvent use, industry solvent use, industrial combustion, domestic combustion, open burning, industry process, on-road transport, off-road transport and other domestic use).

For analyzing the annual variations of ozone precursors emissions, the NOₓ and NMVOC emission data of FRD, HK and MC were collected, respectively, from 2012 to 2016. The annual NOₓ emission data of FRD were obtained from 2017.

1.4. Reanalysis meteorological data

For analyzing the relationships of OFS with meteorological factors, the ERA-Interim reanalysis meteorological data from the European Centre for Medium-range Weather Forecasting (ECMWF) were used, which is a global atmospheric reanalysis data set from 1979 to 2019. In this study, we used monthly surface ERA-Interim data covering GBA with resolution of 0.125° at 6:00 UTC (equal to 14:00 China standard time, close to the OMI transit time), including air temperature at 2 m (T2), surface pressure (SP), total column water (TCW), wind speed at 10 m (WS10), boundary layer height (BLH) and surface net solar radiation (SSR). The grey relation analysis (GRA) method was used to determine the relative impact degree of major meteorological factors on OFS in GBA. The GRA results are obtained by Eq. (1):

\[ \xi_i(k) = \frac{\min \min \Delta_i(k) + \rho \max \max \Delta_i(k)}{\Delta_i(k) + \rho \max \max \Delta_i(k)} \]

where, \( \Delta_i(k) = |y(k) - x_i(k)| \), and the value of \( \rho \) is generally 0.5 (Deng, 1989).

2. Results and discussion

2.1. OMI ozone formation sensitivity

2.1.1. Spatial and temporal characteristics

The spatial variations of NOx, HCHO column concentrations and FNR in GBA from 2012 to 2016 are shown in Fig. 2. The spatial distribution of NOx was characterized by higher concentrations in central cities (GZ, FS, DG, SZ, ZS, ZH, HK and MC) and lower concentrations in peripheral cities (ZQ, HZ and JM). The NO2 pollution is generally occurred in areas with larger populations, more industry and traffic, where human activities are comparably active (Boersma et al., 2008). The severe NO2 polluted areas are generally contiguous, which is attributed to the mutual influence among the cities (Liu et al., 2015). There is a significant decreasing trend of NOx in central cities, dropped by \( 1.82 \times 10^{15} \text{ mol/cm}^2 \) during the five

Fig. 2 – Spatial variations of annual averaged NOx, HCHO column concentrations and FNR in Guangdong-Hong Kong-Macao Greater Bay Area (GBA), from 2012 to 2016. The GBA is made of Guangzhou (GZ), Shenzhen (SZ), Foshan (FS), Dongguan (DG), Zhuhai (ZH), Zhongshan (ZS), Zhaoqing (ZQ), Jiangmen (JM), Huizhou (HZ), Hong Kong (HK) and Macao (MC).
years (Fig. 3a). The decreasing trend is not so significant in peripheral cities, dropped by $0.95 \times 10^{15} \text{ mol/cm}^2$. Spearman correlation coefficients could reflect the annual variation trend. Positive and negative Spearman correlation coefficients represent upward and downward trend, respectively. The average NO$_2$ column concentrations are highly significantly ($p < 0.01$) reduced in SZ, DG and JM, and are significantly ($p < 0.05$) reduced in GZ, FS, ZS and ZQ (Table 1). The seasonal variation extent of NO$_2$ column concentrations is larger in central cities than that in peripheral cities, and the NO$_2$ column concentrations are lower in summer and higher in winter (Fig. 3d).

The HCHO column concentrations show a downward trend as a whole, but slightly rebounded in central cities in 2015 (Fig. 2). It decreased by $1.77 \times 10^{15} \text{ mol/cm}^2$ in central cities and $0.64 \times 10^{15} \text{ mol/cm}^2$ in peripheral cities from 2012 to 2016 (Fig. 3b). The Spearman correlation coefficients of HCHO are negative in all cities in GBA, but HK is the only city with significantly decreasing trend (Table 1). The seasonal variation extent of HCHO column concentrations is larger in central cities than that in peripheral cities, and the HCHO column concentrations are higher in summer and lower in winter (Fig. 3e). In summer and autumn, the temperature is higher and the biogenic VOCs emission activity is stronger (Duncan et al., 2009). In GBA, the vegetation coverage is lower in central cities than that in peripheral cities (Fig. 2). However, in summer, the HCHO column concentrations are higher in central cities than that in peripheral cities, indicating that the anthropogenic emission of VOCs is dominant in summer in central cities, mainly due to more volatilization of solvents in the process of production, storage and transportation under higher temperature (Withe et al., 2011).

The VOCs-limited areas shrank year by year, reaching the smallest in 2015 (Fig. 2). The OFS is mainly VOCs-limited in central areas, and mainly transitional or NO$_2$-limited in peripheral areas. The FNR presents an upward trend, which is more significant in peripheral cities than that in central cities. The FNR increased from 1.17 to 1.18, from 2.47 to 2.74, from 2.04 to 2.22, respectively in central cities, peripheral cities and the whole GBA, from 2012 to 2016 (Fig. 3c). Among the 11 cities in GBA, the Spearman correlation coefficients of 8 cities are positive, implying that the OFS tends to be NO$_2$-limited in most cities of GBA, of which JM is highly significant ($p < 0.01$) and ZQ is significant ($p < 0.05$) (Table 1). The seasonal variation extent of FNR is smaller in central cities than that in peripheral cities, with a characteristic of higher values in summer and lower values in winter (Fig. 3f). The OFS tends to be NO$_2$-limited in peripheral cities in summer and VOCs-limited in central cities in winter. The stronger solar radiation and higher temperature in summer accelerate the photochemical reaction process of NO$_2$, so its lifetime is short and its ambient concentrations are lower (Beirle et al., 2003). However, the VOCs are easy to volatile under higher temperature, so their ambient concentrations are higher in summer. The situation

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**Table 1 – Spearman correlation coefficients of NO$_2$, HCHO and FNR in 11 cities of Guangdong-Hong Kong-Macao Greater Bay Area (GBA), during 2012-2016.**

<table>
<thead>
<tr>
<th>Cities in GBA</th>
<th>Spearman Correlation Coefficient of NO$_2$, HCHO and FNR</th>
<th>Spearman Correlation Coefficient of NO$_2$ and HCHO</th>
<th>Spearman Correlation Coefficient of NO$_2$ and FNR</th>
<th>Spearman Correlation Coefficient of HCHO and FNR</th>
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</thead>
<tbody>
<tr>
<td>Guangzhou</td>
<td>$-0.90^*$</td>
<td>$-0.70$</td>
<td>$0.50$</td>
<td></td>
</tr>
<tr>
<td>Shenzhen</td>
<td>$-1.00^*$</td>
<td>$-0.70$</td>
<td>$-0.10$</td>
<td></td>
</tr>
<tr>
<td>Foshan</td>
<td>$-0.90^*$</td>
<td>$-0.70$</td>
<td>$0.80$</td>
<td></td>
</tr>
<tr>
<td>Dongguan</td>
<td>$-1.00^*$</td>
<td>$-0.60$</td>
<td>$0.60$</td>
<td></td>
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<tr>
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<td>$-0.60$</td>
<td>$0.60$</td>
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<tr>
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<td>$-0.80$</td>
<td>$-0.90^*$</td>
<td>$-0.50$</td>
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<tr>
<td>GBA</td>
<td>$-1.00^*$</td>
<td>$-0.90^*$</td>
<td>$0.90^*$</td>
<td></td>
</tr>
</tbody>
</table>

* Correlation is significant at the $p < 0.05$ level (Two tailed).

$^*$ Correlation is highly significant at the $p < 0.01$ level (Two tailed).
is reversed in winter. Consequently, there are significant seasonal variation characteristics in OFS.

From Fig. 4, the proportion of VOCs-limited regime is obviously larger in central cities than that in peripheral cities, and the NO$_x$-limited regime is obviously larger in peripheral cities than that in central cities. The proportion of transitional regime is relatively high in central cities due to its frequent appearance in most months of the year and dominance in spring and autumn. The proportion of VOCs-limited regime decreased by 5.66%, 0.41% and 2.47%, respectively, in central cities, peripheral cities and the whole GBA, from 2012 to 2016. On the contrary, the proportion of NO$_x$-limited regime increased by 0.00%, 10.12% and 6.16%, respectively, in central cities, peripheral cities and the whole GBA, from 2012 to 2016. In conclusion, the OFS was tending to be NO$_x$-limited in GBA (Li et al., 2014).

2.1.2. Comparisons with previous studies

Previous studies have investigated OFS in several regions of GBA, and our findings were compared with those from previous studies in Table 2. It indicates that our results are mostly consistent with previous studies in identifying the OFS in GBA, even though the study periods and methods are not identical.

Based on ground air quality monitoring station (AQMS) data, Wang et al. (2016) used an Empirical Kinetics Modeling Approach (EKMA) and found that GZ and Wanqingsha (WQS) AQMS were under VOCs-limited and transitional regimes, respectively, in the autumn of 2013. Shawan (SW) and Shiqiao (SQ) AQMS were under VOCs-limited regime in the autumn and winter of 2013. In the summer of 2014, WQS AQMS and Guangzhou Institute of Geochemistry (GIG) AQMS were under NO$_x$-limited and VOCs-limited regime, respectively. A photo-chemical box model coupled with the Master Chemical Mechanism (PBM-MCM) was used by Ling et al. (2014) to simulate the photochemistry of O$_3$ formation. They found that the OFS in Tsuen Wan (TW) was VOCs-limited from September to November in 2010. Also based on EKMA, Li (2015) found that the Luhu (LH) AQMS, Liyuan (LY) AQMS, Huijingcheng (HJC) AQMS and Haogang (HG) AQMS were under transitional regime in August, and VOCs-limited regime in October, respectively, in 2010. The WQS AQMS was under VOCs-limited regime in August and October of 2010. The southwest of JM was under NO$_x$-limited regime in August and transitional regime in October. Ye et al. (2016) utilized the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem) and found that the OFS was VOCs-sensitive in the central FRD and downwind area, while that was NO$_x$-sensitive in the upwind areas (northern GZ and HZ), in November 2009. An observation-based model (OBM) was used by Cheng et al. (2010) to research the OFS in FRD, and they found that it was VOCs-limited in WQS and Tung Chung (TC) in the October and November of 2007.

Our findings are generally consistent with conclusions above, but it seems that the OFS was slightly overestimated by our research based on OMI satellite, compared with researches based on model. For example, Ye et al. (2016) found that the central FRD and its downwind areas were both characterized by VOCs-limited regime in November. However, we found that these two areas were under VOCs-limited and transitional regime, respectively. Such overestimation implies that FNR thresholds need to be localized for applying in different regions, which will be considered in our next research work.

2.2. Influence factors on ozone formation sensitivity

2.2.1. Effects of NO$_x$ and VOCs emissions on ozone formation sensitivity

NO$_x$ and VOCs both play important roles in the chemical mechanism of ozone formation process. The influences of ozone precursors (NO$_x$ and VOCs) emissions on surface ozone have been investigated by many scholars (Cheng et al., 2010; Chi et al., 2018; Wang et al., 2011; Zhang et al., 2008b), but few of them examined the effects of NO$_x$ and VOCs emission on OFS in GBA. The spatial distribution of total emissions of NO$_x$ and NMVOC from 2015 MEIC inventory are presented in Fig. 5a, b, respectively. The emissions of NO$_x$ and NMVOC both have apparent gradient distribution characteristics in GBA, with higher concentrations in central areas and lower concentrations in peripheral areas of GBA. Oppositely, the FNR has lower values in central areas and higher values at the edge of GBA (Fig. 5c).
The main components of NO\textsubscript{x} are NO and NO\textsubscript{2}, whose lifetime greatly depends on the temperature, surface solar radiation and the atmospheric oxidation. In clean air (peripheral cities), the NO\textsubscript{x} is primarily oxidized to HNO\textsubscript{3} due to the stronger atmospheric oxidation. However, in polluted air (central cities), the NO is mostly oxidized to NO\textsubscript{2} due to the weaker atmospheric oxidation. (Beire et al., 2003; Lin and Zhao, 2009). There are significant negative correlations between the monthly averaged NO\textsubscript{x} emissions and the monthly averaged OMI NO\textsubscript{2} in most regions of GBA, especially in peripheral cities, where the atmospheric oxidation is stronger so that the emitted NO\textsubscript{x} are generally oxidized to HNO\textsubscript{3} (Fig. 5d). HCHO is a short-lived oxidation product of many VOCs and it is positively correlated with peroxy radicals (Silliman, 1995). There are significant positive correlations between the monthly averaged NMVOC emissions and the monthly averaged OMI HCHO, especially in central cities, where NMVOC is easily oxidized to HCHO (Fig. 5e) (Duncan et al., 2009).

From 2012 to 2016, the annual averaged NO\textsubscript{x} emissions and the annual averaged OMI NO\textsubscript{2} column concentrations both display obvious downward trends in GBA, reflecting that a variety of emission reduction policies and measures for NO\textsubscript{x} have achieved good results (Liu et al., 2013) (Fig. 6). There is a highly significant positive correlation between the annual averaged NO\textsubscript{x} emissions and the annual averaged OMI NO\textsubscript{2} column concentrations ($R = 0.97, p < 0.01$). In recent years, with the rapid development of industries and vehicles, anthropogenic VOCs emissions have an upward trend, whereas, the OMI HCHO shows an opposite trend, which might result from higher contributions of biogenic VOCs and its decreasing trend in PRD (Jin and Holloway, 2015). The emission ratio of VOCs to NO\textsubscript{x} presents an apparent upward trend, and the FNR increased slightly. There is a positive correlation between them ($R = 0.67$).

### 2.2.2. Meteorological impacts on ozone formation sensitivity

It is investigated that meteorological factors have great relationships with ozone episodes (Yadav et al., 2016; Sharma et al., 2017; Wang et al., 2019). However, few researches have considered the relationships between meteorological factors and OFS. The ERA-Interim reanalysis meteorological data, covering GBA, from 2012 to 2016, were used to analyze the meteorological impacts on OFS.

There are positive correlations between individual meteorological factors (T2, SSR and TCW) and FNR in most areas of GBA, that is, the OFS is more sensitive to NO\textsubscript{x} (higher FNR) as the meteorological factors (T2, SSR and TCW) increase (Fig. 7). In central cities, the correlation coefficients between in-

<table>
<thead>
<tr>
<th>No.</th>
<th>Research period</th>
<th>Research area</th>
<th>Indicator</th>
<th>OFS (Our research)</th>
<th>Method and reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Autumn 2013</td>
<td>GZ AQMS (GZ)</td>
<td>VOCs/NO\textsubscript{x}</td>
<td>VOCs-limited regime</td>
<td>EKMA (Wang et al., 2016)</td>
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<td>WQS AQMS (GZ)</td>
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<td>SW and SQ AQMS (GZ)</td>
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<td>VOCs-limited regime</td>
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<td>Autumn and winter 2013</td>
<td>WQS AQMS (GZ)</td>
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<td>NO\textsubscript{x}-limited regime</td>
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<td>GIG AQMS (GZ)</td>
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<td>2</td>
<td>September 2010</td>
<td>TW (HK)</td>
<td>The total OH reactivity ($R_{OH_TOTAL}$)</td>
<td>VOCs-limited regime</td>
<td>PBM-MCM (Ling et al., 2014)</td>
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<td>October and November 2010</td>
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<td>(September 2012)</td>
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<td>Southwest of JM</td>
<td>NO\textsubscript{x}-limited regime</td>
<td>NO\textsubscript{x}-limited regime</td>
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<td>August and October 2010</td>
<td>LH AQMS (GZ) LY AQMS (SZ) HJC AQMS (DG)/HGC AQMS (FS)</td>
<td>VOCs/NO\textsubscript{x}</td>
<td>Transitional regime (August)</td>
<td>EKMA (Li, 2015)</td>
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<td>WQS AQMS (GZ)</td>
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<td>Transitional regime (November)</td>
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<td>NO\textsubscript{x}-limited regime</td>
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<td>November 2009</td>
<td>The central PRD and its downwind areas</td>
<td>H\textsubscript{2}O\textsubscript{2}/HNO\textsubscript{3}</td>
<td>VOCs-sensitive regime</td>
<td>WRF-Chem model (Ye et al., 2016)</td>
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<td>October and November 2007</td>
<td>The upwind areas [northern GZ and HZ]</td>
<td>H\textsubscript{2}O\textsubscript{2}/NO\textsubscript{2}</td>
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<td>WQS (GZ)</td>
<td>relative incremental reactivity (RIR)</td>
<td>VOCs-limited regime</td>
<td>Observation-based model (OBM) (Cheng et al., 2010)</td>
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* The results in parentheses after the “AQMS” represent the city where the AQMS located in. The relevant abbreviations are mentioned in the Sections 2.1 and 3.1.2.

* When the research periods of previous studies were earlier than ours, the OFS results of us in 2012 were used for comparison.

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**Table 2 - Ozone formation sensitivity (OFS) comparisons with previous studies.**
Fig. 5 – Spatial distribution of (a) NOx emissions (MEIC, 2015), (b) NMVOC emissions (MEIC, 2015), (c) FNR, (d) the correlation coefficients between the monthly averaged NOx emissions and the monthly averaged OMI NO2, and (e) the correlation coefficients between the monthly averaged NMVOC emissions and the monthly averaged OMI HCHO, in Guangdong-Hong Kong-Macao Greater Bay Area (GBA).

Fig. 6 – Annual variations of (a) NOx emissions, (b) VOCs emissions and (c) the emission ratio of VOCs to NOx, which are individually compared with the annual variations of OMI NO2, OMI HCHO and FNR in Guangdong-Hong Kong-Macao Greater Bay Area (GBA), respectively.

dividual meteorological factors (T2, SSR and TCW) and FNR are greater than 0.5, 0.4 and 0.5, respectively, except in part areas of SZ, HK and GZ. In peripheral cities, the correlation coefficients of JM are higher, while those in the northwest of ZQ and the eastern HZ are lower. There are negative correlations between SP and FNR in most areas of GBA, that is, the OFS is more sensitive to VOCs (lower FNR) as the SP increases. In central cities, the absolute values of correlation coefficients between SP and FNR are greater than 0.6, except for some areas of SZ, HK and GZ. In peripheral cities, the absolute values of correlation coefficients are greater than 0.6 in JM, while that in the northwest of ZQ and the eastern HZ are less than 0.5. There are no consistent correlations between WS10 and FNR in the whole GBA, but there are significant negative correlations between WS10 and FNR in coastal areas, where the OFS is more sensitive to VOCs (lower FNR) as the WS10 increases. When the wind speed is higher by the sea, the aerosols generated by the splashing waves are more, which accelerates the reactive uptake of HO2 by aerosol particles and thus the OFS is more VOCs-limited (Li et al., 2019). The correlations between BLH and FNR are slightly different in central areas and peripheral areas. The BLH is negatively correlated with the FNR in central cities (except in some areas of GZ, SZ and HK), while positively correlated with the FNR in peripheral cities (especially in ZQ and HZ). According to the research of Lin et al. (2008), the BLH has more great effects on
the diurnal cycle of surface ozone. This should be considered in the next step research about the influences of BLH to diurnal cycle of OFS.

The temporal variation characteristics of meteorological factors in central cities (Fig. S3) and peripheral cities (Fig. S4) were investigated. In central cities, the variation trends of T2, SSR and TCW are consistent with those of FNR, which are higher in summer and lower in winter. The variation trend of SP is opposite to that of FNR, which is lower in summer and higher in winter. The WS10 fluctuates frequently, but the overall trend is still opposite to that of FNR. The variation trend of BLH shows no significant correlation with FNR but reaches the maximum in October. The atmospheric dilution and diffusion capacity is better with the higher BLH (Yadav et al., 2016). However, the ozone episodes occurred frequently in October. This may be attributed to the still active photochemical reaction with higher ozone precursors concentrations, stronger T2 and SSR, less TCW and lower WS10 in October of GBA. In peripheral cities, the variation characteristics of meteorological factors and FNR are basically consistent with those in central cities.

In central cities, there are highly significant positive correlations between T2, SSR, TCW and FNR, with the correlation coefficients of 0.88, 0.71 and 0.87, respectively (Fig. 8a, b, c). There are highly significant negative correlations between SP, WS10 and FNR, with the correlation coefficients of -0.88 and -0.44, respectively (Fig. 8d, e). There is no significant correlation between BLH and FNR (Fig. 8f). The ozone formation tends to be limited by VOCs, when the values of T2 less than 296 K, SSR less than $1.0 \times 10^7$ J/m$^2$, TCW less than 37.4 kg/m$^2$, SP greater than 101,050 Pa, respectively. The ozone formation tends to be limited by NO$_x$ when the values of T2 greater than 302 K, SSR greater than $1.15 \times 10^7$ J/m$^2$, TCW greater than 55 kg/m$^2$, SP less than 100,250 Pa, respectively. In peripheral cities, there are highly significant positive correlations between T2, SSR, TCW and FNR, with the correlation coefficients of 0.84, 0.62 and 0.88, respectively (Fig. S5a, S5b, S5c). There is a highly significant negative correlation between SP and FNR ($R = -0.89$) (Fig. S5d). There are no significant correlations between WS10, BLH and FNR (Fig. S5e, S5f). The ozone formation tends to be transitional regime, when the values of T2 less than 293 K, SSR less than $8 \times 10^6$ J/m$^2$, TCW less than 30 kg/m$^2$, SP greater than 99,900 Pa, respectively. The ozone formation tends to be limited by NO$_x$, when the values of T2 greater than 293 K, SSR greater than $8 \times 10^6$ J/m$^2$, TCW greater than 30 kg/m$^2$, SP less than 99,900 Pa, respectively.

To figure out the influence extent of meteorological factor mentioned above on OFS, the GRA method was utilized. The GRA results show that the rank of the first four meteorological factors with greatest influence on OFS is TCW, SSR, T2 and SP, no matter in central cities, peripheral cities or the whole GBA (Table 3). WS10 and BLH are ranked in the last two. It seems that the GRA results of 6 meteorological factors in Table 3 show minor difference in values, especially that of SP, WS10 and BLH. However, it can be seen that SP has obvious monthly change cycle as T2, SSR and TCW and it has significant negative correlation with FNR (Fig. S3, S4). These are characteristics that WS10 and BLH do not have. Among the 11 cities in GBA, the ranks of the first four meteorological factors with greatest influence on OFS are the same, except in HZ (Table S3). In HZ, the rank of the first four meteorological factors with greatest influence on OFS is T2, SP, SSR and TCW. The T2 has a greater
influence on the process of natural source emissions of biogenic VOCs (Duncan et al. 2009) and there is high vegetation coverage in Huizhou (Fig. S2), which might lead to the specialty of Huizhou.

2.2.3. Relationships between LUT classification and ozone formation sensitivity

The terrain and landform of GBA are special, which is surrounded by mountains on three sides and facing the sea on one side. According to our research, the land cover types of GBA were nearly unchanged from 2012 to 2016. The “Urban and built-up Land” is principally distributed in central cities; the “Greenland” is principally distributed in peripheral cities and the north of GZ; the “Cropland” is distributed sporadically in each city, among which JM accounts more (Fig. S2). According to our LUT classification results, the proportion of “Urban areas” in central cities is higher than that in peripheral cities, and the proportions of “Suburban areas” and “Rural areas” in peripheral cities are higher than that in central cities (Fig. S6). The classification of LUTs is of great significance for the study of the relationships between LUTs and OFS in GBA.

The annual averaged NO$_2$ column concentrations present obvious gradient changes in different LUTs, and the order is as follows: “Urban areas” > “Suburban areas” > “Rural areas”. In the same season, the NO$_2$ column concentrations vary greatly among different LUTs (Fig. 9). The sequence of seasonal averaged NO$_2$ column concentrations in different LUTs is as follows: “Urban areas” > “Suburban areas” > “Rural areas”, no matter in which season. The seasonal difference of NO$_2$ is more obvious in “Urban areas” than in “Rural areas”. The sequence of annual averaged HCHO column concentrations in different LUTs is the same with NO$_2$ (Fig. 9). The vegetation coverage is lower in “Urban areas” than that in “Suburban areas” or “Rural areas” (Fig. S2). In summer and autumn, the biogenic VOCs emission activity is strong due to higher temperature, but the seasonal averaged HCHO column concentrations are still larger in “Urban areas” than that in “Suburban areas” and “Rural areas”, indicating that the ambient VOCs are greatly affected by anthropogenic emissions in warm seasons (Fig. 9). However, in spring and winter, the seasonal averaged HCHO column concentrations are smaller in “Urban areas” than that in “Suburban areas”, indicating that the ambient VOCs are weakly affected by anthropogenic emissions in cold seasons. The annual averaged FNR is largest in “Rural areas”, second in “Suburban areas” and smallest in “Urban areas”, displaying obvious gradient changes and slight increasing trends (Fig. 9). FNR is higher in summer and lower in winter in all three LUTs (Fig. 9). The sequence of seasonal averaged FNR in different LUTs is as follows: “Urban areas” < “Suburban areas” < “Rural areas”. In summer, the OFS tends to be NO$_2$-limited in “Suburban areas” and “Rural areas”, while in winter, it tends to be VOCs-limited in “Urban areas”.

As shown in Fig. 10, the proportion of VOCs-limited regime is much larger in “Urban areas” than that in “Suburban areas” and “Rural areas”, and the proportion of NO$_2$-limited

Fig. 8 – Correlations between FNR and (a) air temperature at 2 m (T2), (b) surface net solar radiation (SSR), (c) total column water (TCW), (d) surface pressure (SP), (e) wind speed at 10 m (WS10) and (f) boundary layer height (BLH), in central cities of Guangdong–Hong Kong–Macao Greater Bay Area (GBA) (* Correlation is significant at the $p < 0.05$ level (Two tailed), ** Correlation is highly significant at the $p < 0.01$ level (Two tailed)).

Table 3 – Grey relation analysis between FNR and meteorological factors (Air temperature at 2 m (T2), surface net solar radiation (SSR), total column water (TCW), surface pressure (SP), wind speed at 10 m (WS10) and boundary layer height (BLH)) in central cities and peripheral cities of Guangdong–Hong Kong–Macao Greater Bay Area (GBA).

<table>
<thead>
<tr>
<th>Meteorological factor</th>
<th>Central cities</th>
<th>Peripheral cities</th>
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<tr>
<td></td>
<td>GCD Sort number</td>
<td>GCD Sort number</td>
</tr>
<tr>
<td>T2</td>
<td>0.639 3</td>
<td>0.628 3</td>
</tr>
<tr>
<td>SSR</td>
<td>0.696 2</td>
<td>0.707 2</td>
</tr>
<tr>
<td>TCW</td>
<td>0.799 1</td>
<td>0.765 1</td>
</tr>
<tr>
<td>SP</td>
<td>0.626 4</td>
<td>0.610 4</td>
</tr>
<tr>
<td>WS10</td>
<td>0.589 6</td>
<td>0.596 6</td>
</tr>
<tr>
<td>BLH</td>
<td>0.596 5</td>
<td>0.601 5</td>
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</tbody>
</table>

GCD: gray correlation degree.
regime is on the contrary. In “Urban areas”, the proportion of VOCs-limited regime decreased from 44.44% to 36.75% (-7.69%), while the proportion of NOx-limited regime increased from 7.69% to 12.82% (+5.13%), from 2012 to 2016. In “Suburban areas” and “Rural areas”, the proportions of VOCs-limited regime both remained unchanged, while the proportions of NOx-limited regime both increased, from 42.45% to 50.94% (+8.48%) and from 84.51% to 90.14% (+5.63%), respectively. From the significant increasing of NOx-limited regime proportions and the decreasing or unchanged of VOCs-limited regime proportions, we concluded that the OFS was becoming more sensitive to NOx in GBA, no matter in which LUT.

3. Conclusions

During the research period, the NO2 column concentrations decreased by $1.82 \times 10^{15}$ mol/cm$^2$ in central cities and $0.95 \times 10^{15}$ mol/cm$^2$ in peripheral cities, while the HCHO column concentrations decreased by $1.77 \times 10^{15}$ mol/cm$^2$ in central cities and $0.64 \times 10^{15}$ mol/cm$^2$ in peripheral cities. As a result, the FNR increased in GBA, indicating that OFS was tending to be more sensitive to NOx during the five years. The OFS results are mostly consistent with those investigated by other scholars, though the research periods and methods are not identical. However, it seems that the OFS was slightly overes-
timated based on the FNR threshold referring to Duncan et al. (2010); hence the FNR threshold may need to be localized to apply in different regions in the world.

Based on the research of spatial and temporal variations of OFS, the relationships between OFS and its associated factors have been analyzed. The NOx and VOCs emissions present similar apparent spatial gradient distribution characteristics, with higher concentrations in central cities and lower concentrations in peripheral cities. From 2012 to 2016, the total annual NOx emissions decreased significantly, while the total annual VOCs emissions increased obviously, which directly resulted in the increasing of FNR (the OFS tending to be more NOx-limited). As for meteorological factors, there are significant positive correlations between FNR and T2, SSR, TCW, and significant negative correlations between FNR and SP. The OFS tends to be NOx-limited in wet season, when the values of T2 less than 296 K, SSR less than 1.0 × 10^7 J/m^2, TCW less than 37.4 kg/m^2, SP greater than 101,050 Pa, respectively. However, it tends to be VOCs-limited in dry season, when the values of T2 greater than 302 K, SSR greater than 1.15 × 10^7 J/m^2, TCW greater than 55 kg/m^2, SP less than 100,250 Pa, respectively. In GBA, the seven significant meteorological factors that with the greatest influences on OFS is TCW, SSR, T2 and SP. The LUT classification can reflect the intensity of human activities, and it has great relationships with OFS. The “Urban areas” are mostly distributed in central cities, however, the “Sub-urban areas” and “Rural areas” are principally distributed in the peripheral cities. The FNR displays obvious differences on different LUTs, with the largest in “Rural areas”, the second in “Suburban areas” and the smallest in “Urban areas”. The proportion changes of OFS in “Urban areas”, “Suburban areas” and “Rural areas”, from 2012 to 2016, indicate that the OFS tended to be more sensitive to NOx, no matter in which LUTs. In GBA, high ozone concentrations generally occur in summer and autumn. In order to effectively reduce ozone in these two seasons, some detailed strategies can be suggested in GBA according to the seasonal variation characteristics of OFS. The OFS is principally NOx-limited in seasons (summer and autumn) with higher T2, SSR, TCW and lower SP, whether in central cities (predominantly urban) or peripheral cities (predominantly suburban and rural). Therefore, in summer and autumn, it is better to control NOx emissions to inhibit ozone formation in GBA. But in the long run, the OFS will gradually tend to be VOCs-limited regime as the strengthening of VOCs emission reduction. Whereas, considering the climate change, the OFS will tend to be NOx-limited regime as the temperature gradually increases (Stocker et al., 2013). Thus there will be an equilibrium point of changes in OFS and finally probably the transitional regime will be dominate. If so, determining the optimal emission reduction ratio of ozone precursors is the ultimate strategy to solve the ozone issues.

This work has analyzed finer spatial and temporal variations of OFS in central cities and peripheral cities of GBA, and the relationships of OFS with the precursors emissions, meteorological factors and the LUTs. This study can be combined with meteorological forecast and sources emission simulation to comprehensively evaluate and predict the OFS on different regions, and the methods used in this study can be applied to other regions. We are further studying the localized FNR threshold division criteria in GBA and other regions of China, in an effort to establish a set of FNR localized threshold criteria in China. Based on that, the overestimation of OFS derived from satellite data will be optimized.

Declaration of Competing 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.

Acknowledgments

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.04.005.

REFERENCES


