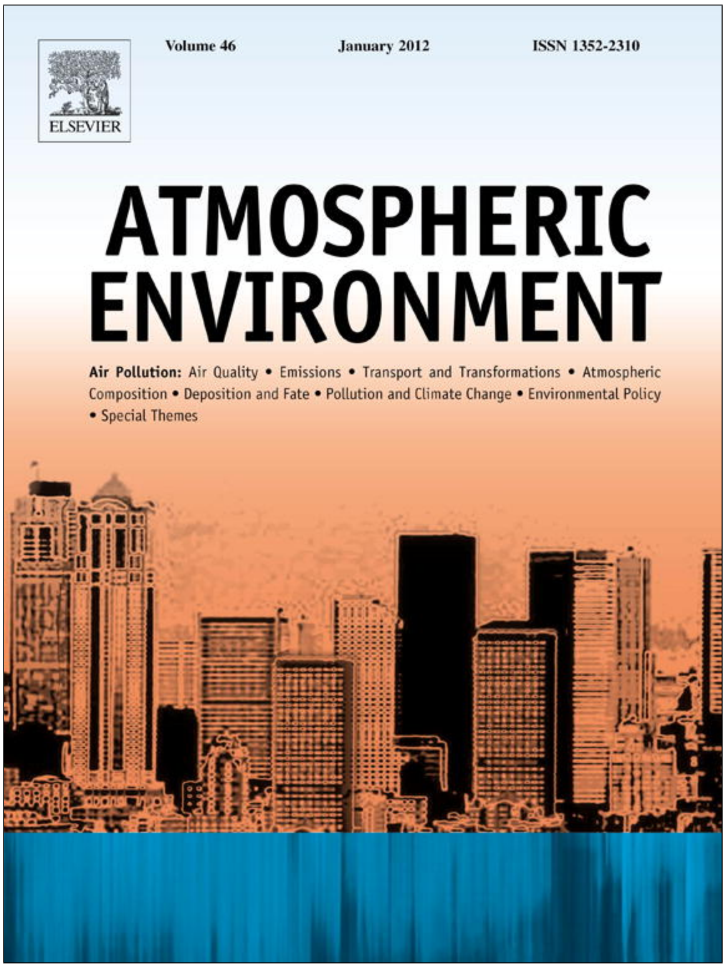
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# The effects of rapid urbanization on the levels in tropospheric nitrogen dioxide and ozone over East China

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## HIGHLIGHTS

- Tropospheric columns of $NO_2$ increased by 82–307% over East China during 1996–2011.
- Rapid urbanization plays a critical role in the long-term changes in tropospheric $NO_2$.
- Meteorological factors determine the seasonal patterns of tropospheric $NO_2$.
- Increase in tropospheric $NO_2$ over Beijing after the 2008 Olympic Games was larger than before.
- Tropospheric $O_3$ is relatively insensitive to urbanization and changes in tropospheric $NO_2$.

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## ABSTRACT

Over the past few decades, China has experienced a rapid increase in urbanization. The urban built-up areas (population) in Beijing, Shanghai, and Guangzhou increased by 197% (87%), 148% (65%), and 273% (25%), respectively, from 1996 to 2011. We use satellite retrieval data to quantify the effects of rapid urbanization on the yearly and seasonal changes in tropospheric nitrogen dioxide ($NO_2$) over East China. The results show that rapid urbanization has a profound effect on tropospheric columns of $NO_2$. During 1996–2011, the tropospheric columns of $NO_2$ over the surrounding areas of Guangzhou, Shanghai, and Beijing increased by 82%, 292%, and 307%, respectively. The tropospheric columns of $NO_2$ reach their maximum in winter and minimum in spring. The anthropogenic emissions related to urbanization are a dominant factor in the long-term changes in the yearly and seasonal mean tropospheric columns of $NO_2$, whereas meteorological conditions such as the prevailing winds and precipitation account for the unique spatial patterns. Around the time of the 2008 Beijing Olympic Games, the tropospheric columns of $NO_2$ over Beijing urban area significantly reduced by 48% in July, 35% in August, and 49% in September, relative to the same monthly averages over 2005–2007. However, this trend was reversed after the Games, and the increased rate was even larger than before. Our results show that the tropospheric $NO_2$ above the three regions increased at rates 1.3–8 times faster than the rates in a recent inventory estimate of $NO_x$ emissions for 2000–2010. We also discuss the influence of urbanization on tropospheric ozone and find that the Ozone Monitoring Instrument (OMI) retrieval tropospheric column shows that ozone levels are relatively insensitive to urbanization and changes in tropospheric $NO_2$.



## 1. Introduction

The dramatic economic development that China has experienced since the mid-1980s has been accompanied by a rapid increase in urbanization. The combined pace of economic growth and

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urbanization has led to tremendous increases in energy consumption and put millions of cars on the roads. As a consequence, many cities especially the megacities (with populations over 10 million), now suffer from severe air pollution. In Beijing, for instance, the China National Ambient Air Quality Standard Grade II for ozone (hourly average value of 100 ppb) was exceeded on 57 days during 2005, with a maximum hourly average concentration of 212 ppb (Hao and Wang, 2005; Fu et al., 2009), and the ground-level ozone concentrations have risen six-fold in the past three decades; and the daily average concentrations of $PM_{2.5}$ (airborne particles with diameter less than or equal to 2.5 μm) typically range from 100 to 150 $\mu g\ m^{-3}$, which is much higher than the US National Ambient Air Quality Standard value of 35 $\mu g\ m^{-3}$ (Qiu, 2012). The urban population in China has increased from 26% of the total population in 1990 to 47% in 2010 (UN ESCAP, 2011), and is expected to rise to nearly 70% by 2050 (Qiu, 2012). Therefore, an accurate assessment of the effects of urbanization on the atmospheric environment is essential for ensuring efficient energy use and air pollution mitigation.

Nitrogen oxides ($NO_x$, a mixture of NO and $NO_2$) are key substances contributing to the formation of ozone and aerosols (e.g., $PM_{2.5}$) in the troposphere. Changes in tropospheric $NO_x$ have important effects on air quality, acid deposition, and the balance of atmospheric radiation (Richter et al., 2005). $NO_x$ are emitted from soil and as a result of fossil fuel combustion, biomass burning, and lightning (Richter et al., 2005; Lin, 2012). While $NO_x$ levels have been decreasing in many industrialized countries, the recent rapid industrialization and urbanization in East Asia has resulted in significant increases in tropospheric nitrogen dioxide ($NO_2$) (Richter et al., 2005). Emission inventories show that China is the dominant source of anthropogenic emissions of $NO_x$, sulfur dioxide ($SO_2$), and carbon monoxide (CO) in Asia (Streets et al., 2003). $NO_x$ emissions in China increased by 280% from 1980 to 2003, and were predicted to undergo another stage of rapid increase from 2003 onwards (Ohara et al., 2007). Nevertheless, urbanization is associated with increased energy efficiency, and the central government of China has set a $NO_x$ emission reduction goal of 10% for the 12th 5-Year (2011–2015) implementation period (Wu et al., 2012). Therefore, an update on the changes in tropospheric $NO_2$ (a proxy of $NO_x$) at a regional level will provide an independent assessment of the inventory data and an objective means of evaluating the effectiveness of the government's emission control strategies in relation to the ongoing urbanization process.

Satellite retrieval data provide a feasible basis for revealing spatial and temporal variations in tropospheric columns of $NO_2$, and evaluating the effectiveness of emissions control measures (e.g., Richter et al., 2005; Witte et al., 2009). This is especially true for regions where there are limited surface observational data. Tropospheric columns of $NO_2$ ($TCNO_2$) can be retrieved from the ultraviolet/visible measurements observed by satellite instruments, such as the Global Ozone Monitoring Experiment (GOME) (Burrows et al., 1999) and the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY; Bovensmann et al., 1999). Richter et al. (2005) analyzed the retrieval data from the GOME and SCIAMACHY measurements and found decreasing trends in $TCNO_2$ over North America and Western Europe and increasing trends with accelerating growth rates over China from 1996 to 2002. Their findings are broadly consistent with bottom-up inventory studies (e.g., Zhang et al., 2007) showing a continuous and accelerating growth rate during 1996–2004 over East Central China. Witte et al. (2009) utilized the same satellite measurements and found a 43% reduction in the tropospheric columns of $NO_2$ over Beijing during July–September 2008 compared to the same months during 2005–2007. Wang et al. (2009b) analyzed the surface observations for several air pollutants at a rural site downwind of Beijing, and found that the mean daytime levels of $O_3$, $SO_2$, CO, and $NO_y$ ($NO_x$ plus other oxidized species such as $N_2O$, $N_2O_5$ and $HNO_3$) in August 2008 were 23%, 61%, 25%, and 21% lower, respectively, compared to the same months in 2006–2007. They attributed this change mainly to the strict short-term emissions control measures enforced in Beijing and neighboring provinces to improving air quality during the Beijing Olympic Games in August–September 2008. It is not known whether the reduction in tropospheric $NO_2$ had lasting effects after the Beijing Olympic Games.

Recently, Schneider and van der A (2012) used global nine-year (2002–2011) SCIAMACHY-derived $NO_2$ data to compare the trends in tropospheric $NO_2$ among the world's major megacities and found that Dhaka in Bangladesh had the largest relative increase. They also found a significantly decreasing trend in Europe and strong increasing trends in China and other countries in Asia. Nonetheless, it is still not clear how urbanization quantitatively influences the concentrations of tropospheric $NO_2$ and ozone.

In this study, we utilize the 1996–2011 retrieval data from both GOME and SCIAMACHY measurements to quantify the relationship between urbanization and changes in the tropospheric columns of $NO_2$ over East China. The existing related studies are limited to the annual average changes in tropospheric $NO_2$, and studies on seasonal mean changes and the influence of urbanization are relatively scarce. In this study, we characterize the temporal and spatial variations in the tropospheric columns of $NO_2$ in three regions of China that have undergone rapid economic growth and examine the factors that determine the temporal variation and spatial patterning of $NO_2$. We then assess the relationship between the anthropogenic emissions associated with urbanization and the changes in the levels of tropospheric ozone over East China.

## 2. Data and methodology

Monthly mean tropospheric excess columns of $NO_2$ ($TECNO_2$) derived from the GOME and SCIAMACHY satellite measurements (Richter et al., 2005) are used to quantify the changes in tropospheric $NO_2$. The gridded datasets used in this study were provided by the Institute of Environmental Physics (IEP), University of Bremen, Germany (data available at http://www.iup.uni-bremen.de/doas). $TECNO_2$ is the surplus of tropospheric column $NO_2$ in an area relative to that in a clean region over oceans at the same latitude. GOME was launched in April 1995 and provided global coverage from August 1995 to June 2003. SCIAMACHY was launched in March 2002 and took measurements from August 2002 to April 2012. Grid spacings of $0.5° \times 0.5°$ and $0.125° \times 0.125°$ are used for the GOME and SCIAMACHY data, respectively. The two datasets can be combined to investigate the long-term changes in tropospheric $NO_2$ as the time series of the two retrieval data fit almost seamlessly despite the different instruments and data resolution (Richter et al., 2005). A detailed evaluation of the resolution effects is given in Hilboll et al. (2013). The $TECNO_2$ products used in this study have been validated (Petritoli et al., 2004) and successfully applied to evaluating changes in tropospheric $NO_2$ in North America, Europe, and Asia (Richter et al., 2005; Wang et al., 2009a).

Tropospheric ozone ($O_3$) data retrieved from the Ozone Monitoring Instrument (OMI) are used to assess the influence of changes in $NO_2$ on that of $O_3$ in the troposphere. OMI is a nadir-viewing imaging spectrograph that measures the back-scattered solar radiation from the Earth's atmosphere and the surface in the ultraviolet and visible bands (Levelt et al., 2006). Launched in July 2004, the OMI monitors the total column ozone, ozone profiles, other trace gases (e.g., $NO_2$, HCHO, $SO_2$), and UV-absorbing aerosols and clouds (Tanskanen et al., 2007). The tropospheric column $O_3$ levels used in this study are monthly mean data with a spatial resolution of $1.25° \times 1.0°$ in the W–E and S–N directions, respectively (Ziemke et al., 2006) (data available at http://acd-ext.gsfc.nasa.gov/Data_services/cloud_slice/new_data.html).

We use MAM (March, April and May), JJA (June, July, and August), SON (September, October, and November), and DJF (December, January, and February) to represent spring, summer, autumn, and winter, respectively. The seasonal means of $TECNO_2$ are determined in terms of monthly averages of the same year, except for the mean of DJF which is calculated using the monthly mean of December in the current year and the monthly averages of January and February in the following year.

There are three distinct urban agglomerations in East China: Beijing–Tianjin–Tangshan in the Bohai Economic Rim (BER, 36.5–41.5°N, 114.0–119.0°E), Shanghai–Nanjing–Hangzhou in the Yangtze River Delta (YRD, 28.5–33.5°N, 117.5–122.5°E), and Guangzhou–Hong Kong–Macao in the Pearl River Delta (PRD, 21.5–24.0°N, 112.0–115.5°E). These three urban agglomerations are the most densely urbanized and economically dynamic regions in China. Six indices are used to evaluate the level of urbanization and the influence of urbanization on the atmospheric environment, namely, urban population, built-up area, gross domestic product (GDP), number of civilian vehicles, power consumption, and industrial exhaust gases. All data are obtained from the China Statistical Yearbooks Database at http://tongji.cnki.net/overseas/engnavi/navidefault.aspx. The changes in tropospheric $NO_2$ over the BER, YRD, and PRD regions demonstrate how urbanization influences air quality in megacities and provide scientific evidence on the effectiveness of emission control strategies.

## 3. Urbanization trends in Beijing, Shanghai and Guangzhou

Rapid population growth and the expansion of built-up area are two distinctive features of Chinese urbanization. Fig. 1a and b depicts the growth of the urban populations and built-up area in Beijing, Shanghai, and Guangzhou during 1996–2011. In 2011, the populations of the two megacities of Beijing and Shanghai were 20.2 million and 23.5 million, respectively, about 1.9 and 1.7 times their respective values in 1996. The urban population of Guangzhou increased from 6.5 million in 1996 to 8.1 million in 2011. Urban population growth in China is mainly the result of rural–urban migration and reclassification of rural towns to urban status. During 1996–2011, Beijing's population experienced three abrupt increases of 12.7% in 1997, 10.6% in 2000, and 11.7% in 2011, as

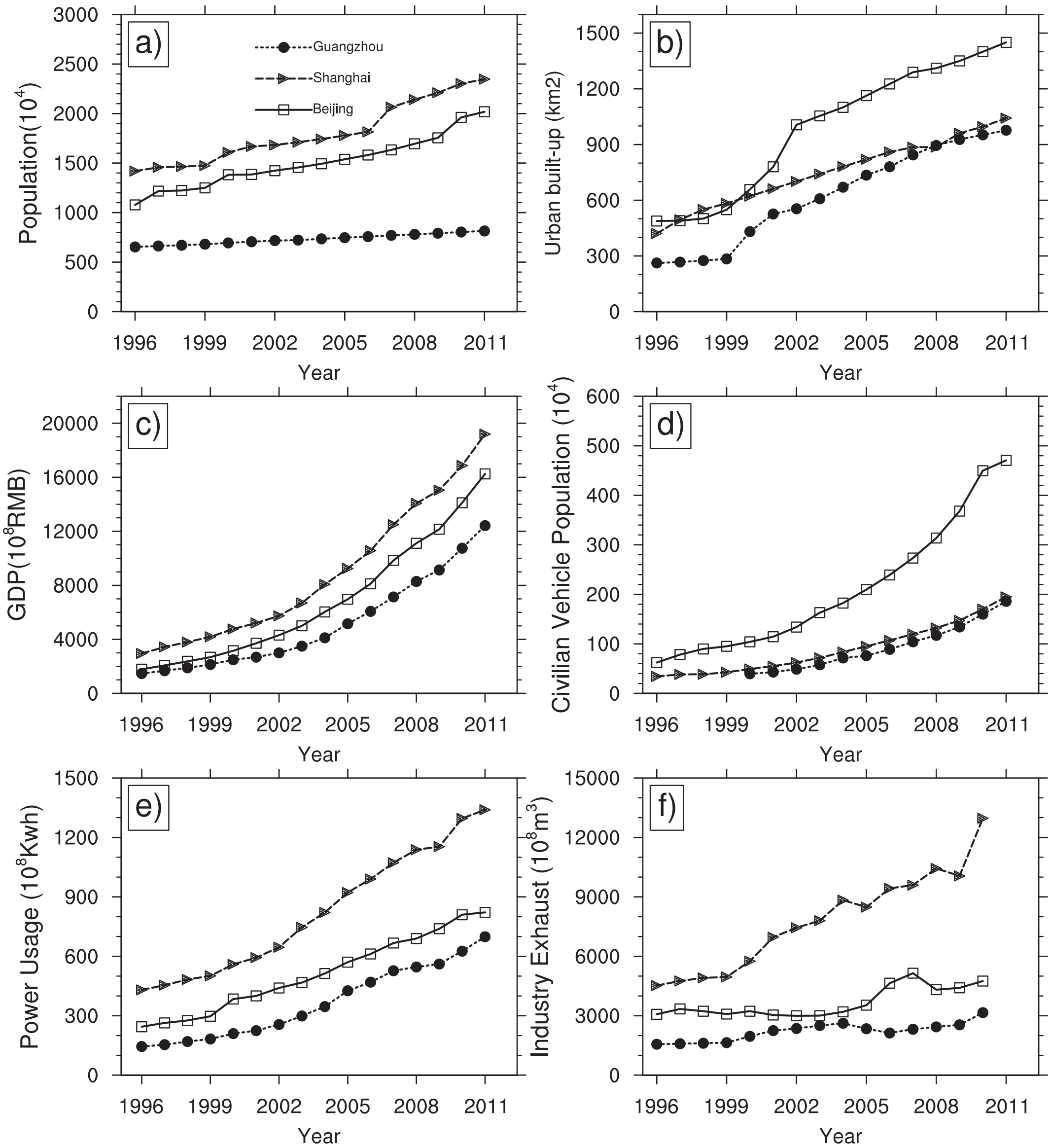


**Fig. 1.** The changes in a) urban population, b) built-up area, c) gross domestic product (GDP), d) civilian vehicle population, e) power usage, and f) industrial exhaust for Beijing (solid line with open square), Shanghai (dashed line with solid triangle), and Guangzhou (dotted line with solid circle) during 1985–2011.

compared to the values in the previous years. During the same period, Shanghai experienced two sharp increases of 9.1% in 2000 and 13.7% in 2007. In contrast, the population of Guangzhou showed a steadily increasing trend, with an average yearly growth rate of 1.5% during 1996–2011.

During urbanization, large amounts of agricultural and arable land are used for industrial, commercial, and residential development. As shown in Fig. 1b, during 1996–2011, the built-up areas of Beijing, Shanghai, and Guangzhou increased by 197%, 147%, and 273%, respectively. These rates are much faster than the corresponding increases in the urban populations. While Beijing has the largest built-up area, Guangzhou experienced the greatest level of expansion. Moreover, the built-up areas in Beijing and Guangzhou increased sharply during 1999–2002 and 2000–2001, respectively.

Urbanization in China is closely linked to industrialization and economic growth. About 85% of the country's economic production is generated in cities (Roberts and Kanaley, 2006). Over the past three decades, China's annual GDP has increased by between 7 and 10% (Hao and Wang, 2005). In contrast, the average GDP growth rates in Beijing, Shanghai, and Guangzhou were 17%, 14%, and 15% per year, respectively, during 1996–2011 (see Fig. 1c). In total, the GDP of Beijing increased by 44 times, that of Shanghai by 30 times, and Guangzhou by 63 times from 1996 to 2011.

The rapid urbanization and economic growth in China have created a range of environmental problems relating to high-consumption, especially in the megacities, some of which are ranked as the world's most polluted cities. Automobiles, power plants and industry are the three major emission sources of air pollutants. Fig. 1d–f shows the increases in number of civilian vehicles, electricity usage, and industrial exhaust in the three cities during the study period. The numbers of civilian vehicles and the consumption of energy and materials rose sharply, in close correlation with the urban growth of these megacities. As a result, the anthropogenic emissions of many air pollutants (e.g., $NO_x$, volatile organic compounds (VOC), and $PM_{2.5}$) increased significantly. As Fig. 1d–f also shows, Beijing had the most vehicles whereas Shanghai used the largest amount of electricity and emitted the most industrial exhausts. The China Statistics Yearbook contains no data for civilian vehicles in Guangzhou before 2001 or for industrial exhaust before 1996. Industrial exhaust is closely associated with the emission of air pollutants. It is noted that industrial exhaust was 16% lower in 2008 as compared to 2007. This reduction is the result of many of the factories with high pollutant emissions being shut down before or during the 2008 Beijing Olympic Games. We examine the association between this reduction and the change in tropospheric $NO_2$ in a later part of this paper. Notably, the industrial exhaust also reduced by 11% in 2004 and 9% in 2005 because of joint emission control efforts taken by the governments of Hong Kong and Guangdong province. For example, since 2000, a wide range of measures have been introduced to reduce the emissions from motor vehicles and power plants in Hong Kong. As a result, in 2005, the emissions of $NO_x$, VOC, and respirable suspended particulates (RSP) were 15%, 26%, and 36% lower, respectively, compared to 1997. These results provide a good example of how air quality can be improved during periods of increased urbanization.

## 4. Long-term changes in yearly mean tropospheric nitrogen dioxide levels and their driving factors

### *4.1. Long-term changes in yearly mean tropospheric nitrogen dioxide levels*

Fig. 2 compares the $TECNO_2$ levels between 1996 and 2011. The values are annual averages, calculated using the satellite-retrieved monthly mean data. Two features can be identified. First, while high levels of $TECNO_2$ were detected over the BER, YRD and PRD regions in 1996, the values were mostly low (less than $1.0 \times 10^{16}$ molecules $cm^{-2}$) during this period. Second, in 2011, the levels of $TECNO_2$ over East China were significantly greater than those recorded in 1996. The levels of $TECNO_2$ increased much faster over the BER than over the other two regions. The "hotspot" areas over the Northeastern China Plain expanded in 2011. Overall, the $TECNO_2$ over the PRD, YRD, and BER increased by 82%, 292% and 307%, respectively, from 1996 to 2011. Moreover, the high values of $TECNO_2$ are closely associated with these three economically dynamic regions, indicating that anthropogenic emissions have a major influence on the changes in $TECNO_2$ levels.

Fig. 3 shows the yearly averages of $TECNO_2$ over the three regions, BER, YRD, and PRD during 1996–2011 period. Of the three regions, BER has the highest levels of $TECNO_2$, and PRD the lowest. The changes in the $TECNO_2$ display different trends over the three regions. The $TECNO_2$ over the YRD increased steadily at an average yearly rate of 10.6% from 1996 to 2011. The BER experienced three stages of change: a steady increase, a slight decrease, and a period of sudden growth, which occurred before, during and after the 2008 Beijing Olympic Games, respectively. The yearly average changes relative to the previous year are 10.4%, −3.0%, and 14.1%, respectively, for the three stages. The reduction of the $TECNO_2$ stopped immediately after the Olympic Games were completed. Moreover, the yearly rates of increase during 2009–2011 are larger than the corresponding rates before the Beijing Olympic Games. The tropospheric $NO_2$ change trends for the PRD are very different from those for the other two regions. Although the level of $TECNO_2$ over the PRD increased yearly at an average rate of 11.3%, during 1996–2004, which is similar to the YRD and BER regions, it decreased at a rate of 2.7% after this period. This is likely due to the joint efforts to improve air quality in the PRD region. In 2002, Hong Kong and Guangdong province agreed to jointly reduce the emissions of four major pollutants ($SO_2$, $NO_x$, RSP and VOC) by 20–55% by 2010 compared to the base year 1997 (Hong Kong Environmental Department Annual Report, 2011).

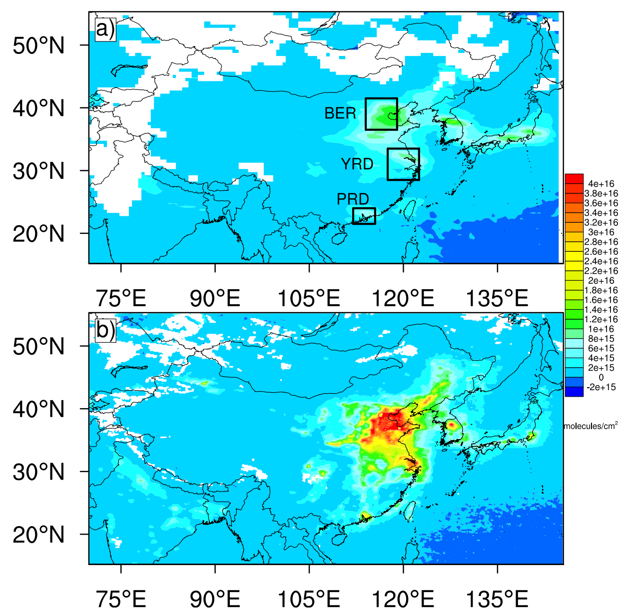


**Fig. 2.** Yearly mean tropospheric excess columns of nitrogen dioxide over China in a) 1996 and b) 2011. Boxes PRD, YRD, and BER represent the three studied subregions: the Pearl River Delta, the Yangtze River Delta, and the Bohai Economic Rim.

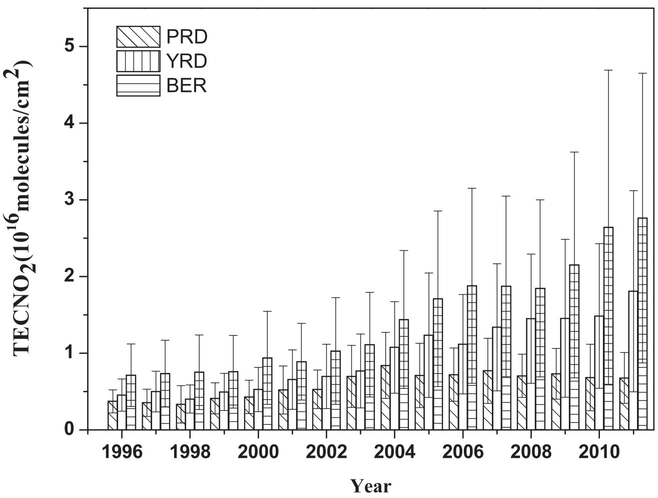


**Fig. 3.** Changes in yearly mean tropospheric excess columns of nitrogen dioxide over the PRD, YRD, and BER regions during 1996–2011.

### *4.2. Factors driving the changes in the tropospheric columns of nitrogen dioxide*

To better understand the changes in the tropospheric $NO_x$ levels, we first examine the effects of urbanization. In the preceding sections, we presented the trends of six urbanization indices and the yearly changes in the $TECNO_2$ over the three highly urbanized regions during 1996–2011. In this section, we compare these figures to reveal how urbanization influences the changes in tropospheric $NO_2$.

We use $R^2$ to describe the statistical relationship between the six urbanization indices of the three cities and the $TECNO_2$ over their corresponding regions. $R^2$ usually ranges from 0 to 1; a higher value of $R^2$ means that we can better predict one term from another. The $R^2$ values are determined through linear regression. A total of 16 yearly mean data are used for the calculations. There are three groups of $R^2$ in Table 1. The first column presents the $R^2$ between the $TECNO_2$ over BER and the six urbanization indices for Beijing. The second column is the $R^2$ between the $TECNO_2$ over YRD and the urbanization indices for Shanghai, and the third column is the $R^2$ between the $TECNO_2$ over PRD and the urbanization indices for Guangzhou. F-test shows that all $R^2$ are statistically significant at the 5% significance level. The $TECNO_2$ over the YRD are strongly associated with all the urbanization indices for Shanghai, with the $R^2$ for the six urbanization indices during 1996–2011 greater than or equal to 0.93. This implies that the urban development of Shanghai has a critical influence on the changes in the $TECNO_2$ over the YRD.

The $TECNO_2$ over the BER have similar magnitude of $R^2$ with Beijing's urbanization indices except for industrial exhaust. The lower $R^2$ (0.68) for industrial exhaust indicates that the industrial exhaust in Beijing is not major contributor of $NO_x$ emissions in the BER region.

The $TECNO_2$ over PRD have moderate values of $R^2$ with Guangzhou's urbanization indices, with values ranging from 0.42 to 0.76 except for the $R^2$ with civilian vehicle numbers (0.15). The $R^2$ between the $TECNO_2$ over the PRD and the urbanization indices for Guangzhou urbanization levels are much lower than those for BER and Beijing, and YRD and Shanghai. There are two reasons for this difference. First, the $NO_x$ emissions stemming from the urbanization of Guangzhou may not be the major source of emissions in the PRD. Second, the increased $NO_x$ emissions resulting from urbanization may have been mitigated by the emission control measures instituted across the PRD. Thus, the increased urbanization of the three cities had different effects on the levels of tropospheric $NO_2$ over the three different urban agglomerations in East China.

In addition, we calculate the correlations between the 2-m annual mean temperature and $TECNO_2$ over the three regions. We found much lower $R^2$ values (about 0.1–0.3), indicating that meteorological conditions have a minor influence on the long-term changes in $TECNO_2$. Therefore, the long-term changes of $TECNO_2$ are mostly the results of rapid urbanization and emission control.

**Table 1**
Relationship ($R^2$) between the tropospheric columns of $NO_2$ in BER, YRD and PRD and the urbanization indices for Beijing, Shanghai, and Guangzhou during 1996–2011.

| | BER | YRD | PRD |
|---|---|---|---|
| Urban population | 0.92 | 0.93 | 0.65 |
| Built-up area | 0.85 | 0.93 | 0.76 |
| Gross domestic product | 0.96 | 0.95 | 0.42 |
| Power consumption | 0.95 | 0.98 | 0.57 |
| Civilian vehicle population | 0.96 | 0.96 | 0.15 |
| Industrial exhaust | 0.68 | 0.93 | 0.60 |

## 5. Spatial and temporal changes in the seasonal mean levels of tropospheric nitrogen dioxide

### *5.1. Characteristics of the spatial patterns of the seasonal mean levels of tropospheric nitrogen dioxide*

In this section, we focus on the characteristics of seasonal mean levels of tropospheric $NO_2$. Fig. 4 shows spatial patterns of $TECNO_2$ over East Asia derived from the SCIAMACHY measurements for the four seasons of 2011. Distinct seasonal patterns are evident in the spatial distribution, with the maximum in winter and the minimum in summer. Various processes or factors may account for this distribution, especially, meteorological conditions, anthropogenic emissions, and the lifetime of $NO_2$. Under the influence of the Asian monsoons, the coastal regions of East China are dominated by continental flows in winter and marine air masses in summer (Fig. 5). In the summer, the prevailing winds bring air masses with lower concentrations of $NO_2$ from the ocean to the coastal regions, thereby diluting the $NO_2$ in the troposphere above the urban regions. Other meteorological conditions such as precipitation, and deep convection (i.e., a high tropospheric layer) also contribute to lower tropospheric columns of $NO_2$ in summer. In contrast, winter is characterized by drier (i.e., less cloud and precipitation), colder weather (i.e., lower temperature), and the lifetime of $NO_2$ is usually longer than in summer. Moreover, $NO_x$ emissions are usually higher in winter than in the other seasons due to more energy consumption for heating, especially in regions of northern China such as the BER (Fig. 6). In contrast, urbanization indices such as the size of urban and built-up areas, and the urban population do not have distinct seasonal variations. Therefore, the unique seasonal patterns of tropospheric $NO_2$ are predominantly influenced by meteorological conditions.

### *5.2. Long-term changes in the seasonal mean levels of tropospheric nitrogen dioxide*

As illustrated above, the spatial distribution of the $TECNO_2$ has a clear seasonal pattern. However, as few studies have examined changes in the seasonal mean levels of $TECNO_2$, relatively little is known of the characteristics of the seasonal changes. Therefore, in this section, we quantify the difference in the changes in the seasonal means and examine the possible reasons for such a difference.

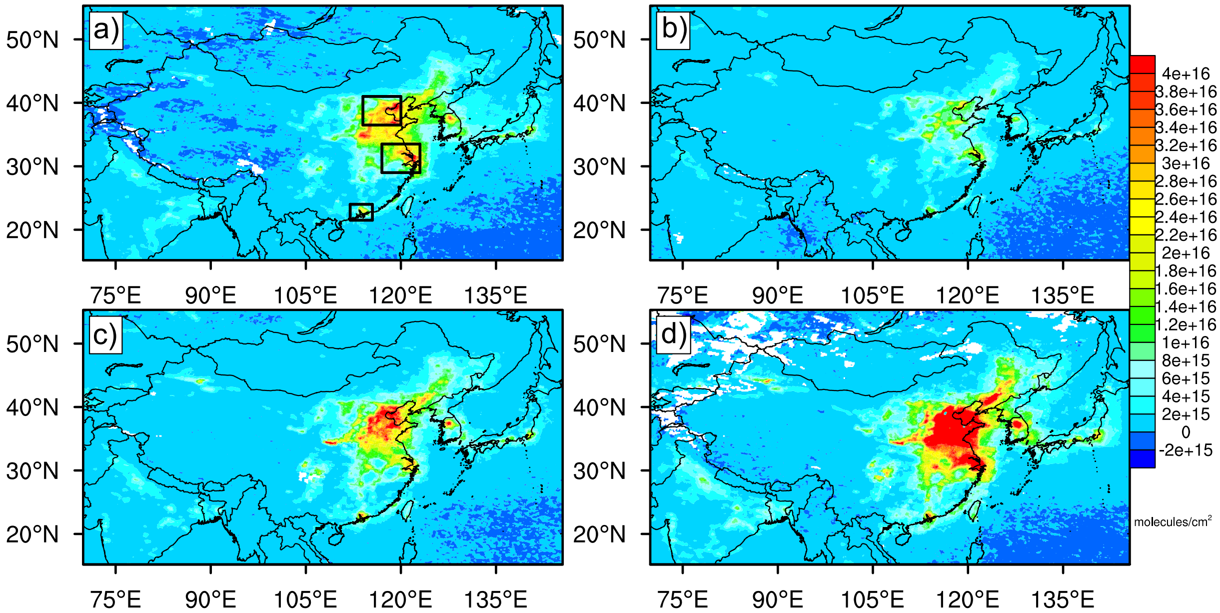


**Fig. 4.** Seasonal mean tropospheric columns of nitrogen dioxide retrieved from the SCIAMACHY measurements for the four seasons, a) MAM, b) JJA, c) SON, and d) DJF, 2011.

Fig. 7 illustrates the changes in the seasonal means of $TECNO_2$ levels for the three regions during 1996–2011. Similar to the spatial patterns, the time series show clear seasonal and regional differences. Regionally, the mean $TECNO_2$ in the BER are consistently higher over the four seasons than in other two regions. Seasonally, the mean $TECNO_2$ is consistently higher in winter in the three regions than in the other three seasons (Table 2). The same arguments relating to the long-term changes in the yearly mean and the characteristics of the spatial patterns, apply to the long-term changes in seasonal means. In other words, meteorological conditions such as prevailing winds, deep convection strength, and precipitation amount determine the differences of seasonal mean $TECNO_2$, whereas urbanization and the related anthropogenic emissions support the long-term changes in the yearly/seasonal mean $TECNO_2$.

In summary, the seasonal and the yearly means present similar change trends, although the seasonal mean time series have more detailed structure. The anthropogenic emissions accompanying

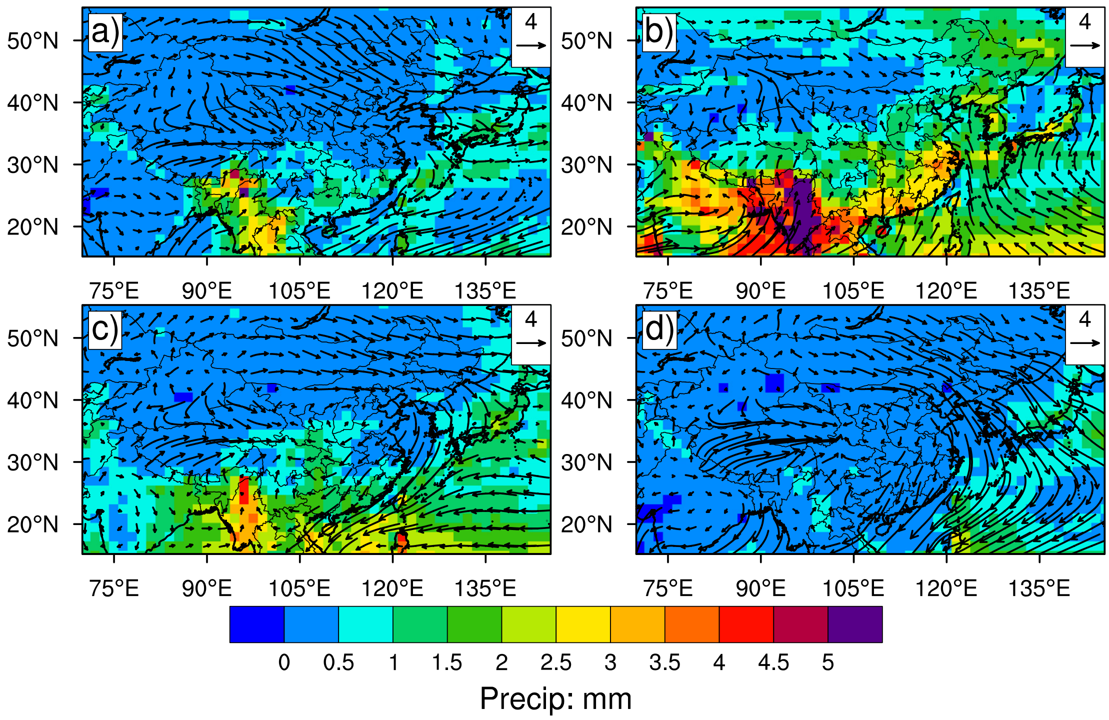


**Fig. 5.** Seasonal means of 10-m winds and precipitation based on ECMWF (European Centre For Medium-Range Weather Forecasts) Real-Analysis (ERA) data ERA-Interim (1.5° resolution) for a) MAM, b) JJA, c) SON, and d) DJF in 2011 (wind speed: m $s^{-1}$, precipitation: mm).

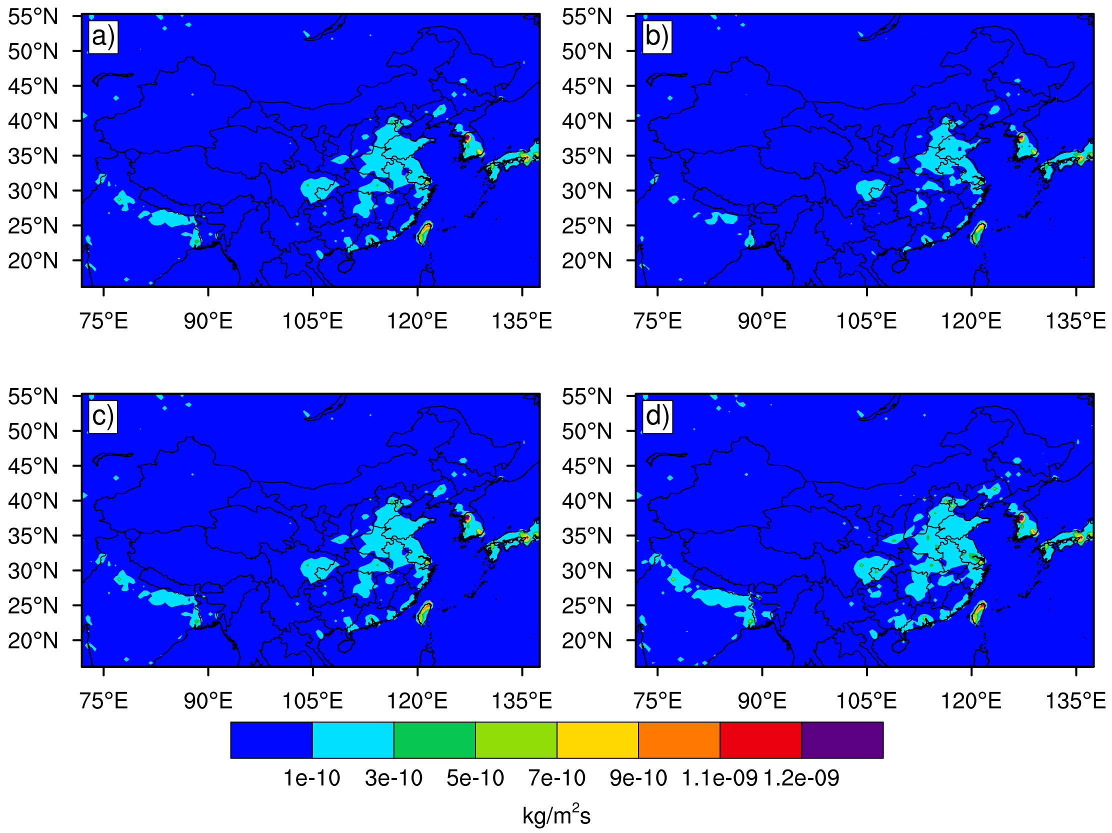


**Fig. 6.** Seasonal means of anthropogenic emissions of $NO_x$ from global emissions data (0.5° × 0.5°) of the REanalysis of TROpospheric chemical composition (RETRO) project for a) MAM, b) JJA, c) SON, and d) DJF in 2000.

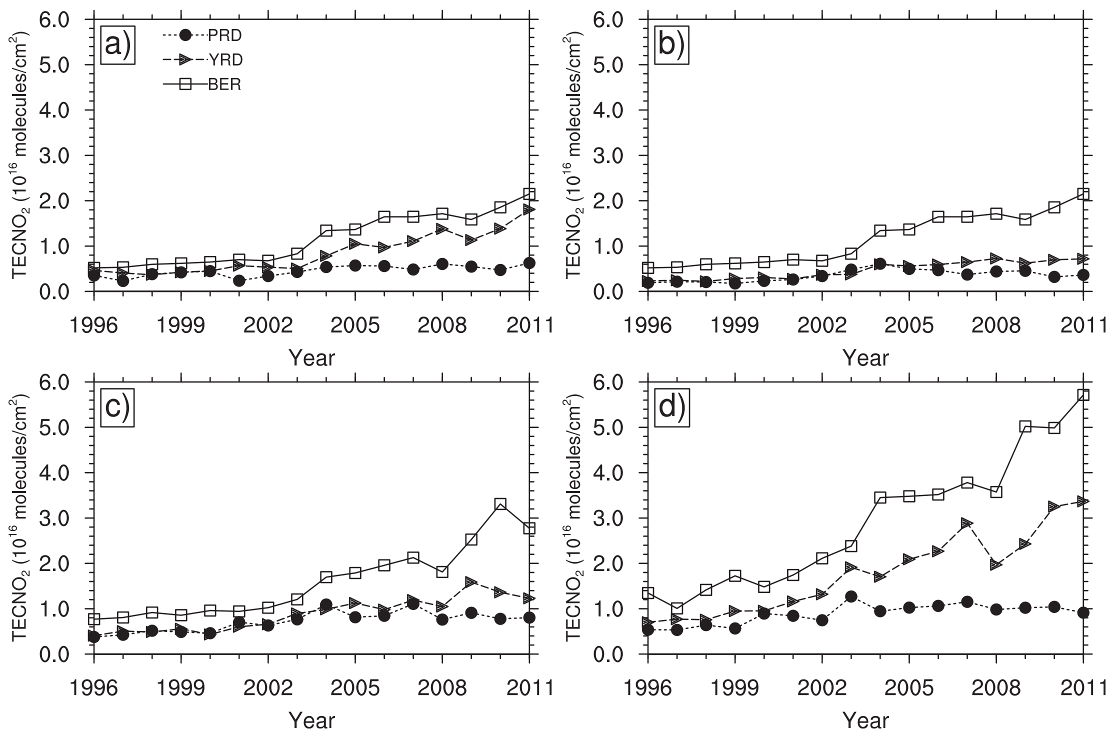


**Fig. 7.** Changes in seasonal mean tropospheric columns of nitrogen dioxide derived from the GOME and SCIAMACHY measurements for PRD, YRD, and BER in a) MAM, b) JJA, c) SON, and d) DJF during 1996–2011.

**Table 2**
Average growth rates of seasonal mean tropospheric excess columns of nitrogen dioxide relative to the previous year over the three regions during 1996–2011 (%/year).

| | MAM | JJA | SON | DJF | Annual |
|---|---|---|---|---|---|
| PRD | 8.0 | 6.5 | 8.1 | 9.5 | 7.1 |
| YRD | 11.3 | 9.3 | 9.7 | 12.7 | 10.7 |
| BER | 10.9 | 7.9 | 10.2 | 11.9 | 10.2 |

urbanization play the same important role in the changes of the seasonal mean as in changes in the yearly means. Moreover, meteorological conditions and the lifetime of $NO_2$ are responsible for the differences in the changes in seasonal means.

### 5.3. *The effect of emissions-reduction on the levels of tropospheric $NO_2$ over Beijing during the 2008 Olympic Games*

Fig. 8 illustrates the monthly mean tropospheric $NO_2$ levels over Beijing during the three periods, 2005–2007, 2008, and 2009–2011. In July, August, and September 2008, $TECNO_2$ over Beijing reduced by 48%, 35%, and 49%, respectively, as compared to their respective monthly means averaged over 2003–2007. The monthly mean percentage changes are more prominent than the calculations averaged over larger areas and longer time periods, i.e., seasonal or yearly means. The results of our calculations are comparable to those of other studies. For example, the OMI retrieval data show a 43% reduction between July and September 2008 compared to the previous three years (Witte et al., 2009) and in-situ measurements show a 36% reduction in $NO_x$ between 2008 and 2007 (Wang et al., 2009b). These significant reductions represent the immediate effects of the implementation of the strict emission-reducing measures in Beijing and neighboring provinces including Tianjin, Hebei, Shangdong, Henan, and Shanxi (UNEP, 2009). These strict emissions-reducing measures greatly improved the air quality in Beijing during the Games (Wang et al., 2009b).

However, the emissions levels grew dramatically after the Beijing 2008 Olympic Games. The monthly averages for July, August, and September during 2009–2011 increased by 95%, 79%, and 166%, respectively, compared to the corresponding months in 2008. This further demonstrates that the emission control measures during the 2008 Beijing Olympic Games had a significant effect on the level of tropospheric $NO_2$, and that the emission-reduction measures did not continue after that time.

## 6. Seasonal mean changes in tropospheric ozone

The change in the tropospheric $NO_2$ levels may exert important influence on the levels of ozone in the troposphere. In this section,

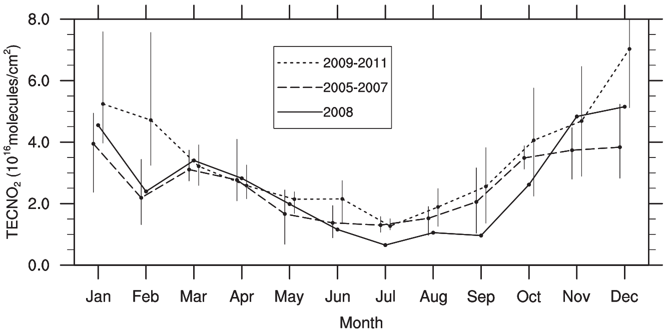


**Fig. 8.** Monthly mean comparison of the tropospheric excess columns of nitrogen dioxide over the Beijing area during 2005–2007, 2008, and 2009–2011.

we examine how urbanization and the resultant changes in tropospheric $NO_2$ influence the seasonal mean levels of tropospheric ozone.

Fig. 9 illustrates the seasonal changes in the mean tropospheric column of $O_3$ derived from the OMI measurements over the three regions during 2005–2011. The seasonal mean tropospheric columns of $O_3$ show a remarkable increase (the linear regression change is 0.5 Dobson year$^{-1}$) in spring and negligible changes (the linear regression changes less than 0.1 DU year$^{-1}$) in the other three seasons over BER. The corresponding seasonal mean changes in the tropospheric columns of ozone are 0.4, 0.3, 0.3 and 0.2 DU year$^{-1}$ for spring, summer, autumn, and winter, respectively, over the YRD. The large increases in tropospheric ozone during springtime over BER and YRD are most likely due to the intrusion of high concentration ozone through stratosphere–troposphere exchange since the springtime is not a period with large photochemical ozone formation in the troposphere. The seasonal mean changes in tropospheric ozone are 0.1, 0.2, 0.4, and 0.0 DU year$^{-1}$ for spring, summer, autumn, and winter, respectively over PRD. The greater increase in autumn is explained by the increased photochemical production associated with favorable weather conditions (e.g., strong solar radiation, prevailing northerly and northeasterly winds) and the increasing anthropogenic emissions over the PRD (e.g., Huang et al., 2005, 2006; Li et al., 2012) (the largest increase in surface ozone is also observed in autumn, although the figures are not shown here).

The seasonal mean tropospheric ozone does not display similar rapid growth to that found in the $TECNO_2$ over the BER and YRD regions. The difference between the ozone and $NO_2$ levels is a result of the two sources controlling tropospheric ozone levels: stratosphere–troposphere exchange and photochemical production. The changes in tropospheric ozone due to photochemical production may be counteracted by the influence of the ozone coming from stratosphere–troposphere exchange. In addition, the satellite retrievals may have difficulty detecting this due to the generally very low retrieval sensitivity to ozone near the surface and the relatively small portion of near surface ozone in tropospheric ozone columns.

We now turn our attention to the sensitivity of tropospheric ozone to the emission control measures implemented during the 2008 Beijing Olympics Games. Wang et al. (2009b) found significant decreases in the surface concentrations of $O_3$, CO, $NO_y$, and $SO_2$ during August 2008, relative to August 2006–2007. For example, the mean daytime mixing ratios of $O_3$ was reduced by 15 ppbv based on the measurements at a rural site in Beijing. The modeling results show that the emission restrictions reduced the ozone by 2–10 ppbv in the atmospheric boundary layer over the large regions of the North China Plain and northwestern China. However, our satellite retrieval data show a 3% reduction in the tropospheric column ozone occurred in SON over the BER in 2008 compared to 2007, but that increases occurred in the other three seasons (11% in MAM, 5% in JJA, and 14% in DJF). At the same time, the tropospheric column ozone decreased by 1.4 and 0.6 DU year$^{-1}$ in autumn and winter 2008, respectively, over the YRD region. Thus, the small changes observed in the tropospheric ozone columns during the emission controls indicate that the satellite retrievals of the tropospheric columns of ozone may be relatively lower for lower tropospheric ozone compared to middle tropospheric ozone due to the reduced retrieval sensitivity and the small contribution of the tropospheric ozone columns.

## 7. Discussion

Richter et al. (2005) discussed several potential factors influencing the observed changes in tropospheric $NO_2$ over China. They concluded that the changes in measurement sensitivity, $NO_2$/NO

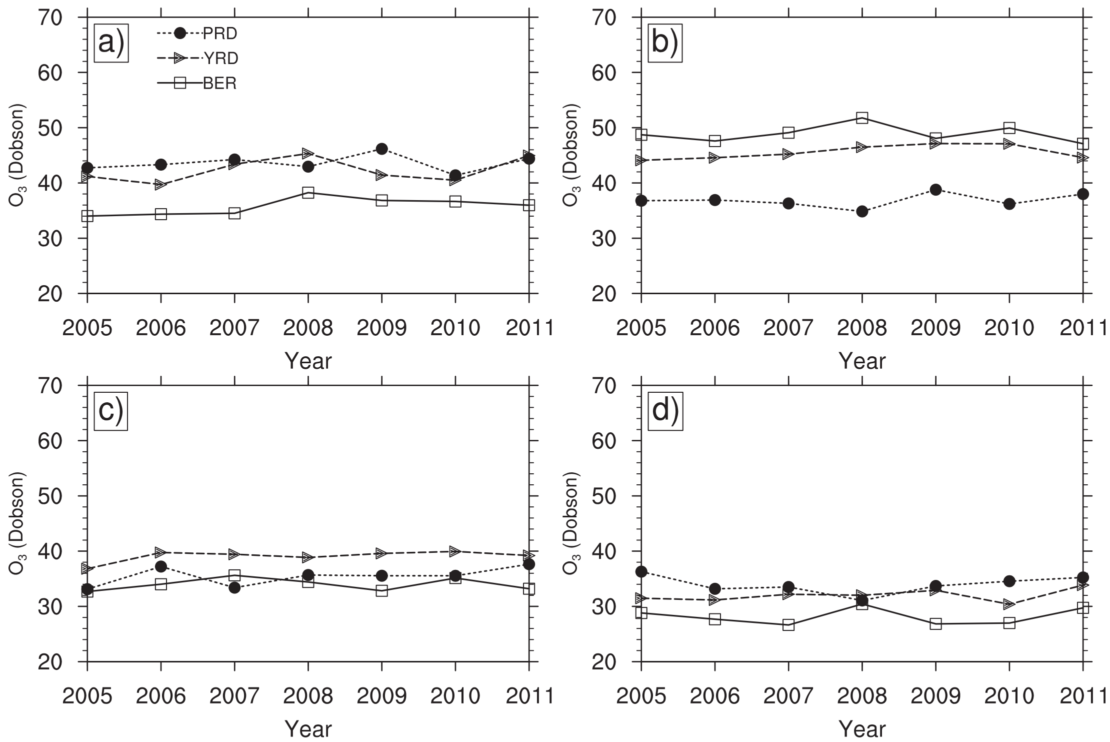


**Fig. 9.** Changes in the seasonal mean tropospheric columns of ozone retrieved from the OMI for PRD, YRD, and BER in a) MAM, b) JJA, c) SON, and d) DJF from 2005 to 2011.

partitioning, and the lifetime of $NO_2$ are not sufficient to explain the changes and that increased $NO_x$ emissions appear to be the most plausible explanation for increased tropospheric $NO_2$. Their analysis covered the period 1996–2002. However, China's annual mean GDP growth rate during 2002–2011 was almost 3 times that during 1996–2002. In this paper, we have updated the analysis of Richter et al. (2005) by using extended measurements. Recently, Ohara et al. (2007) presented an inventory dataset for Asia for 1980–2003 and projected the future emissions to 2020. According to their study, the $NO_x$ emissions in China increased dramatically (by 4 times) from 1980 to 2003. They also projected an increase of 25% by 2010 and 40% by 2020, compared to the emissions during the base year 2000. Our results show that the levels of tropospheric $NO_2$ over the PRD, YRD, and BER regions increased by 32%, 200%, and 180%, respectively, during 2000–2010. These changes in tropospheric $NO_2$, especially over the BER and the YRD, are much larger than the growth rates of $NO_x$ emissions suggested by the emission inventory study of Ohara et al. (2007). There are two possible reasons for these discrepancies. First, the three selected regions represent the most polluted regions in China, therefore their increase rates should be much higher than the national average. Second, the levels of $NO_x$ emissions are still underestimated in the emission inventory (Ohara et al., 2007; Zhang et al., 2007). It is believed that at the $NO_2$ levels currently observed in Eastern Central China, there is no longer a simple linear relationship in the $NO_2$ chemistry between the levels of $NO_x$ emissions and the tropospheric columns of $NO_2$ resulting from the process of urbanization. The lifetime of $NO_2$ is largely limited by OH radicals, and, at very high $NO_x$ concentrations, the OH itself is consumed leading to the amplification of $NO_2$. This factor was evaluated by Stavrakou et al. (2008).

## 8. Summary and conclusions

We used the China Statistical Yearbook Database to evaluate the urbanization of Beijing, Shanghai, and Guangzhou during 1996–2011. The results show that the three cities experienced a dramatic increase in urbanization during the study period. The urban and built-up areas (population) in Beijing, Shanghai, and Guangzhou increased by 197% (87%), 148% (65%), and 273% (25%), respectively, from 1996 to 2010 (2011). Other urbanization indices also show that these three cities increased significantly during 1996–2011.

We analyzed satellite retrieval data from the GOME and SCIAMACHY instruments to investigate the influence of urbanization levels on the temporal variations and spatial patterns of tropospheric $NO_2$ over the BER, YRD and PRD regions during 1996–2011. The tropospheric $NO_2$ levels were found to reflect the levels of economic growth in the regions. The maximum $NO_2$ levels were observed in the winter and the minimum values were in the summer. The analysis suggests that meteorological conditions such as prevailing winds and precipitation are responsible for the observed spatial and seasonal patterns. During 1996–2011, the tropospheric columns of $NO_2$ over the PRD, YRD, and BER regions increased by 82%, 292%, and 307%, respectively. The strong relationship ($R^2$) between the tropospheric excess column $NO_2$ and the six urbanization indices indicates that the anthropogenic emissions associated with the urbanization of Beijing and Shanghai played a critical role in determining the tropospheric columns of $NO_2$ over the BER and YRD regions. The influence of urbanization on tropospheric columns of $NO_2$ was counteracted by the effective emission control measures implemented in the PRD region.

Our results support the conclusion that a reduction in local emissions should result in reduced tropospheric $NO_2$ in the same region. The stringent emission control measures implemented around the time of the Beijing Olympic Games resulted in tropospheric $NO_2$ reductions of 48% in July, 35% in August, and 49% in September 2008, relative to the same months during 2005–2007. However, the trend was reversed quickly after the Games were completed. The joint emission control efforts between Hong Kong and Guangdong were found to be responsible for a slight decrease in the levels of tropospheric $NO_2$ over the PRD after 2004. The rapid increase in tropospheric $NO_2$ after 2008 in the YRD and the BER suggests that $NO_x$ emissions have been increasing rapidly in these two regions, at rates greater than those projected by the emission inventory study of Ohara et al. (2007).

The tropospheric $O_3$ measurements retrieved from the OMI show that the change trends of the seasonal mean tropospheric columns of $O_3$ are very different from those of the seasonal mean $TECNO_2$. While the largest increases in the $TECNO_2$ were detected in winter in the three regions, the greatest increases in the tropospheric columns of ozone were found in spring over the BER and YRD, and in autumn over the PRD. Overall, however, the tropospheric columns of ozone have relatively little sensitivity to the changes in tropospheric $NO_2$.

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## References

Bovensmann, H., Burrows, J.P., Buchwitz, M., Frerick, J., Noël, S., Rozanov, V.V., Chance, K.V., Goede, A.P.H., 1999. SCIAMACHY: mission objectives and measurement modes. J. Atmos. Sci. 56, 127–150.

Burrows, J.P., et al., 1999. The Global Ozone Monitoring Experiment (GOME): mission concept and first scientific results. J. Atmos. Sci. 56, 151–175.

Fu, J., Streets, D., Jang, D., Hao, J., He, K., Wang, L., Zhang, Q., 2009. Modeling regional/urban ozone and particulate matter in Beijing, China. J. Air Waste Manage. Assoc. 59, 37–44. http://dx.doi.org/10.3155/1047-3289.59.1.37.

Hao, J., Wang, L., 2005. Improving urban air quality in China: Beijing case study. J. Air Waste Manage. Assoc. 55, 1298–1305.

Hilboll, A., Richter, A., Burrows, J.P., 2013. Long-term changes of tropospheric $NO_2$ over megacities derived from multiple satellite instruments. Atmos. Chem. Phys. 13, 4145–4169. http://dx.doi.org/10.5194/acp-13-4145-2013.

Hong Kong Environmental Protection Department (HKEPD), 2011. Air Quality in Hong Kong 2011. Monitoring Report. Hong Kong Environ. Protect. Dep., Hong Kong Spec. Admin. Reg. Govt.. Available at: http://www.epd-asg.gov.hk/english/report/aqr.html.

Huang, J.P., Fung, J.C.H., Lau, A.K.H., 2006. Integrated processes analysis and systematic meteorological classification of ozone episodes in Hong Kong. J. Geophys. Res. 111, D20309. http://dx.doi.org/10.1029/2005JD007012.

Huang, J.P., Fung, J.C.H., Lau, A.K.H., Qin, Y., 2005. Numerical simulation and process analysis of typhoon related ozone episodes in Hong Kong. J. Geophys. Res. 110, D05301. http://dx.doi.org/10.1029/2004JD004914.

Levelt, P.F., et al., 2006. Science objectives of the ozone monitoring instrument. J. IEEE Trans. Geosci. Remote Sens. 44, 1199–1208.

Li, Y., Lau, A.K.H., Fung, J.C.H., Zheng, J.Y., Zhong, L.J., Louie, P.K.K., 2012. Ozone source appointment (OSAT) to differentiate local regional and super-regional source contributions in the Pearl River Delta region, China. J. Geophys. Res. 117, D15305. http://dx.doi.org/10.1029/2011JD017340.

Lin, J.T., 2012. Satellite constraint for emissions of nitrogen oxides from anthropogenic, lightning and soil sources over East China on a high-resolution grid. Atmos. Chem. Phys. 12, 2881–2898. http://dx.doi.org/10.5194/acp-12-2881-2012.

Ohara, T., Akimoto, H., Kurokawa, J., Horii, N., Yamaji, K., Yan, X., Hayasaka, T., 2007. An Asian emission inventory of anthropogenic emission sources for the period 1980–2020. Atmos. Chem. Phys. 7, 4419–4444.

Petritoli, A., et al., 2004. First comparison between ground-based and satellite-borne measurements of tropospheric nitrogen dioxide in the Po basin. J. Geophys. Res. 109, D15307. http://dx.doi.org/10.1029/2004JD004547.

Qiu, J., 2012. Megacities pose serious health challenge. Nature. http://dx.doi.org/10.1038/nature.2012.11495.

Richter, A., Burrows, J.P., Nüß, H., Granier, C., Niemeier, U., 2005. Increase in tropospheric nitrogen dioxide over China observed from space. Nature 437, 129–132. http://dx.doi.org/10.1038/nature04092.

Roberts, B., Kanaley, T., 2006. Urbanization and Sustainability in Asia: Good Practice Approaches in Urban Regional Development. Asian Development Bank, Manila.

Schneider, P., van der A, R.J., 2012. A global single-sensor analysis of 2002–2011 tropospheric nitrogen dioxide trends observed from space. J. Geophys. Res. 117, D16309. http://dx.doi.org/10.1029/2012JD017571.

Stavrakou, T., Müller, J.F., Boersma, K.F., De Smedt, I., van der A, R.J., 2008. Assessing the distribution and growth rates of $NO_x$ emission sources by inverting a 10-year record of $NO_2$ satellite columns. Geophys. Res. Lett., L10801. http://dx.doi.org/10.1029/2008GL033521.

Streets, D.G., et al., 2003. An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. J. Geophys. Res. 108, 8809. http://dx.doi.org/10.1029/2002JD003093.

Tanskanen, A., et al., 2007. Validation of daily erythemal doses from Ozone Monitoring Instrument with ground-based UV measurement data. J. Geophys. Res. 112, D24S44. http://dx.doi.org/10.1029/2007JD008830.

United Nations Economic and Social Commission for Asia and the Pacific, 2011. Statistical Yearbook for Asia and the Pacific 2011. Bangkok, Thailand. ISBN: 978-92-1-120629-6. ISSN: 0252 3655.

United Nations Environment Program (UNEP), 2009. Independent Environmental Assessment: Beijing 2008 Olympic Games. UN Environ. Programme, Nairobi, Kenya.

Wang, T., Wei, X.L., Ding, A.J., Poon, C.N., Lam, K.S., Li, Y.S., Chan, L.Y., Anson, M., 2009a. Increasing surface ozone concentrations in the background atmosphere of Southern China, 1994–2007. Atmos. Chem. Phys. 9, 6217–6227.

Wang, Y., Hao, J., McElroy, M.B., Munger, J.W., Ma, H., Chen, D., Nielsen, C.P., 2009b. Ozone air quality during the 2008 Beijing Olympics. Atmos. Chem. Phys. 9, 5237–5251.

Witte, J.C., Schoeberl, M.R., Douglass, A.R., Gleason, J.F., Krotkov, N.A., Gille, J.C., Pickering, K.E., Livesey, N., 2009. Satellite observations of changes in air quality during the 2008 Beijing Olympics and Paralympics. Geophys. Res. Lett. 36, L17803. http://dx.doi.org/10.1029/2009GL039236.

Wu, Y., et al., 2012. The challenge to $NO_x$ emission control for heavy-duty diesel vehicles in China. Atmos. Chem. Phys. Discuss 12, 18565–18604. http://dx.doi.org/10.5194/acpd-12-18565-2012.

Zhang, Q., et al., 2007. $NO_x$ emission trends for China, 1995–2004: the view from the ground and the view from space. J. Geophys. Res. 112, D22306. http://dx.doi.org/10.1029/2007JD008684.

Ziemke, J., et al., 2006. Tropospheric ozone determined from Aura OMI and MLS: evaluation of measurements and comparison with the Global Modeling Initiative's Chemical Transport Model. J. Geophys. Res. 111, D19303. http://dx.doi.org/10.1029/2006JD007089.