



## Ozone pollution in China: A review of concentrations, meteorological influences, chemical precursors, and effects



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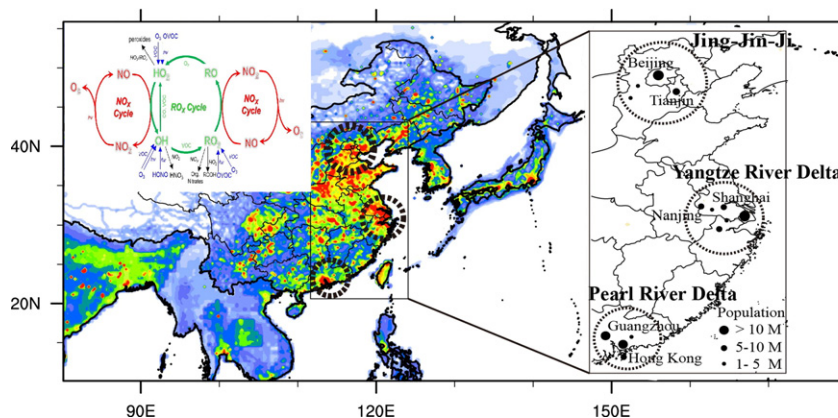
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### HIGHLIGHTS

- Studies of atmospheric ozone in urban and rural areas of China are reviewed.
- Topics include abundance, chemical and meteorological processes, and effects.
- Available data reveals serious and worsening ozone pollution in major areas of China.
- Data from national network are needed to get a full picture of ozone pollution and to evaluate its impact.
- Strategies for control ozone precursors need to be developed.

### GRAPHICAL ABSTRACT



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### ABSTRACT

High concentrations of ozone in urban and industrial regions worldwide have long been a major air quality issue. With the rapid increase in fossil fuel consumption in China over the past three decades, the emission of chemical precursors to ozone—nitrogen oxides and volatile organic compounds—has increased sharply, surpassing that of North America and Europe and raising concerns about worsening ozone pollution in China. Historically, research and control have prioritized acid rain, particulate matter, and more recently fine particulate matter (PM<sub>2.5</sub>). In contrast, less is known about ozone pollution, partly due to a lack of monitoring of atmospheric ozone and its precursors until recently. This review summarizes the main findings from published papers on the characteristics and sources and processes of ozone and ozone precursors in the boundary layer of urban and rural areas of China, including concentration levels, seasonal variation, meteorology conducive to photochemistry and pollution transport, key production and loss processes, ozone dependence on nitrogen oxides and volatile organic compounds, and the effects of ozone on crops and human health. Ozone concentrations exceeding the ambient air quality standard by 100–200% have been observed in China's major urban centers such as Jing-Jin-Ji, the Yangtze River delta, and the Pearl River delta, and limited studies suggest harmful effect of ozone on human health and agricultural crops; key chemical precursors and meteorological conditions conducive to ozone pollution have been investigated, and inter-city/region transport of ozone is significant. Several recommendations are given for future research and policy development on ground-level ozone.

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## 1. Introduction

Ozone (O<sub>3</sub>) in the troposphere plays a central role in the oxidation of chemically and climatically relevant trace gases, thereby regulating their lifetime in the atmosphere. As a strong oxidant, O<sub>3</sub> at ground level is detrimental to human health and vegetation. Tropospheric O<sub>3</sub> is also the third most important greenhouse gas. Because of its importance to air quality and climate change, O<sub>3</sub> has received continuous attention in the past three decades from both the scientific and regulatory communities (e.g., Monks et al., 2015; NARSTO, 2000; NRC, 1991).

Photochemical smog—characterized by elevated concentrations of O<sub>3</sub>, other gases, and particulates—results from chemical reactions between nitrogen oxides (NO<sub>x</sub>) and volatile organic compounds (VOCs) in the presence of sunlight (NRC, 1991). This type of air pollution, first discovered in the 1950s in Los Angeles, has been found in major urban and industrial regions throughout the world. Extensive research, mostly in North America, has investigated the chemical and meteorological processes responsible for ozone formation and transport, and these findings have been comprehensively reviewed (Hidy, 2000; Jenkin and Clemitshaw, 2000; Kleinman, 2000; NARSTO, 2000; NRC, 1991; Solomon et al., 2000). Although research on urban ozone pollution began in the early 1980s in a western city, little systematic research and coordinated ozone monitoring was performed in China until the mid-2000s, partly because research and control efforts during that period were focused on sulfur (acid rain) and particulate matter. Nonetheless, intensive field measurements have revealed very high concentrations of ozone in or near some large Chinese cities. For instance, an hourly mixing ratio of up to 286 ppbv was observed in summer 2005 at a rural mountain site north of Beijing (Wang et al., 2006a), and summer peak ozone concentrations increased from 1980 to 2003 at a sub-urban (now urban) site in Beijing (Shao et al. 2006). In the past decade, particularly the past 5 years, extensive ozone monitoring has been carried out in urban and rural locations by national and local environmental and meteorological agencies. The available data reveal that ambient ozone concentrations in major urban areas have continued to increase despite recent reductions in the emissions of SO<sub>2</sub> (since 2006) and NO<sub>x</sub> (since 2011) (<http://www.mep.gov.cn>). According to monitoring results from 74 Chinese cities, the mean daily 8-hour maximum concentrations increased from approximately 69.5 ppbv in 2013 to approximately 75.0 ppbv in 2015 while the percentage of non-compliant cities increased from 23% to 38%, whereas the metrics on other pollutants improved from 2013 to 2015 (China Environment Report 2014 and 2015, available at <http://www.mep.gov.cn>, in Chinese). It has been suggested that elevated ozone levels in China adversely affect agricultural crops (Chameides et al., 1999; Feng et al., 2015 and references therein) and human health (Brauer et al., 2016; Li et al., 2015b). Current projections indicate that ozone pollution is likely to worsen in future (Wang et al., 2013). A review of known factors that determine ozone formation and distribution in China is therefore needed to aid in formulating a mitigation policy and to guide future research.

This review focuses on ground-level ozone in urban and polluted rural areas of mainland China and Hong Kong, and is structured as follows. Section 2 gives a brief review of chemical mechanisms for ozone formation; Section 3 reviews the field measurements of ozone and ozone precursors; Section 4 summarizes the typical meteorological conditions associated with high ozone events; Section 5 examines the use of observations to identify ozone formation regimes, including several indicators and observation-constrained model studies; Section 6 reviews the emission-based model results on the sources of ozone; Section 7 covers the effects of ozone on agricultural crops and human health; and Section 8 provides a summary and some recommendations for future research and control. The review focuses on findings which have been published in English-language literature.

## 2. Brief review of ozone formation mechanism

This section gives a condensed review of the chemical mechanisms of ozone production and loss and non-linear chemistry to lay down the foundation for discussion of the studies of the complex relationship between ozone and its precursors. Ozone in the Earth's atmosphere is ultimately formed from the combination reaction of atomic oxygen (O<sup>3</sup>P) and molecular oxygen (O<sub>2</sub>) (R1). In the stratosphere, photolysis of O<sub>2</sub> by the short-wavelength ultraviolet (UV) radiation (λ ≤ 240 nm) supplies atomic oxygen and facilitates the formation of the O<sub>3</sub> layer (Chapman, 1930). In the troposphere with little UV radiation, photolysis of NO<sub>2</sub> at wavelengths ≤ 424 nm (R2) becomes the primary source of O<sup>3</sup>P atoms and prompts O<sub>3</sub> formation. Once formed, O<sub>3</sub> readily reacts with NO to regenerate NO<sub>2</sub> (R3). The (R1–R3) reactions result in a null cycle when no other chemical species are involved.



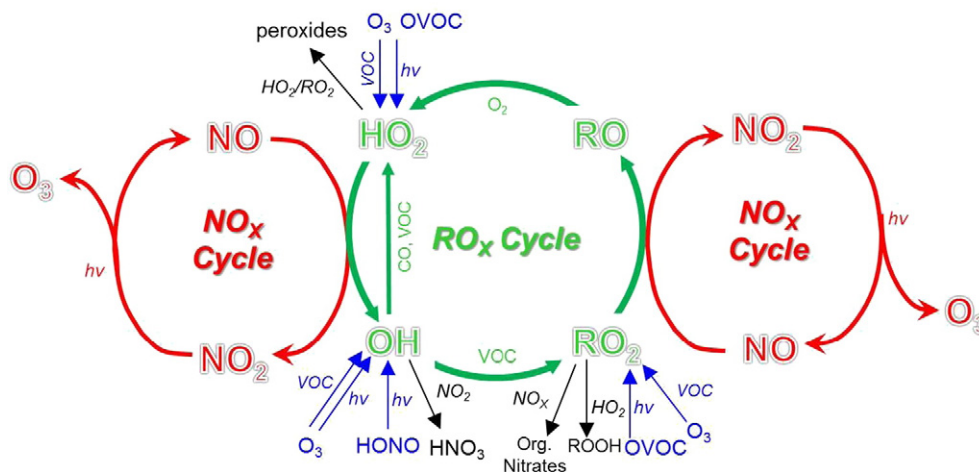
However, in reality, the troposphere contains alternative oxidants (i.e., HO<sub>2</sub> and RO<sub>2</sub>) that efficiently convert NO to NO<sub>2</sub> (R4 and R5), resulting in the accumulation of O<sub>3</sub>. The R4, R5, and R2 reactions establish an efficient “NO<sub>x</sub> cycle” that produces O<sub>3</sub> without consumption of NO<sub>x</sub> (see Fig. 1). The other important chemistry cycle that affects O<sub>3</sub> formation is the so-called “RO<sub>x</sub> (RO<sub>x</sub> = OH + HO<sub>2</sub> + RO<sub>2</sub>) radical cycle” that continuously supplies HO<sub>2</sub> and RO<sub>2</sub> to oxidize NO to NO<sub>2</sub>. It generally starts from the OH-initiated degradation of VOCs that produce RO<sub>2</sub> radicals (R7), followed by R5 converting RO<sub>2</sub> to RO, R7 converting RO to HO<sub>2</sub>, and finally R4 to regenerate OH from HO<sub>2</sub>. Each RO<sub>x</sub> cycle oxidizes two molecules of NO to NO<sub>2</sub>, which then produces two molecules of O<sub>3</sub> through the “NO<sub>x</sub> cycle” and recycles NO. The coupling of both chemistry cycles and the photochemical formation of O<sub>3</sub> are illustrated in Fig. 1.



The RO<sub>x</sub> and NO<sub>x</sub> cycles are terminated by the cross reactions of RO<sub>x</sub> and/or NO<sub>x</sub>. At high NO<sub>x</sub> conditions, the termination process is dominated by the reactions of NO<sub>2</sub> with OH (R8) and RO<sub>2</sub> (R9), which form nitric acid and organic nitrates (the so-called NO<sub>z</sub> species). At low NO<sub>x</sub> conditions, the dominant termination processes are self-reactions of HO<sub>2</sub> (R10) and cross-reactions of HO<sub>2</sub> and RO<sub>2</sub> (R11), producing hydrogen peroxides (H<sub>2</sub>O<sub>2</sub>) and organic peroxides. As such, the relative abundances of NO<sub>z</sub> and peroxides (e.g., H<sub>2</sub>O<sub>2</sub>/HNO<sub>3</sub>) can reflect the ambient atmospheric conditions, i.e., low-NO<sub>x</sub> or high-NO<sub>x</sub>, and are usually adopted as indicators to infer the O<sub>3</sub> formation regimes (e.g., NO<sub>x</sub>-limited or VOC-limited; see Section 5.1).



Another key process of O<sub>3</sub> formation is the primary production of RO<sub>x</sub> radicals from the closed-shell molecules. It initiates the aforementioned RO<sub>x</sub> cycle and hence plays a central role in ozone production.



**Fig. 1.** Sketch of photochemical ozone formation mechanism and coupling of “RO<sub>x</sub> cycle” and “NO<sub>x</sub> cycle.” Reaction pathways shown in red, green, blue, and black refer to “NO<sub>x</sub> cycle,” “RO<sub>x</sub> cycle,” radical initiation, and termination processes, respectively.

In the polluted troposphere, the RO<sub>x</sub> radicals arise mainly from the photolysis of O<sub>3</sub>, HONO, and carbonyls, but also from the ozonolysis reactions of unsaturated VOCs, and the relative contribution of each source may vary from one place to another (Xue et al., 2016). New sources of atmospheric radicals (and radical precursors) have been revealed, including unknown daytime source(s) of HONO (e.g., Kleffmann, 2007) and the nocturnal formation of nitryl chloride (ClNO<sub>2</sub>) with subsequent release of chlorine atoms the next day. Reactions between Cl and VOCs enhance the photochemical formation of ozone via a gas-phase mechanism similar to that of OH (e.g., Riedel et al., 2014).

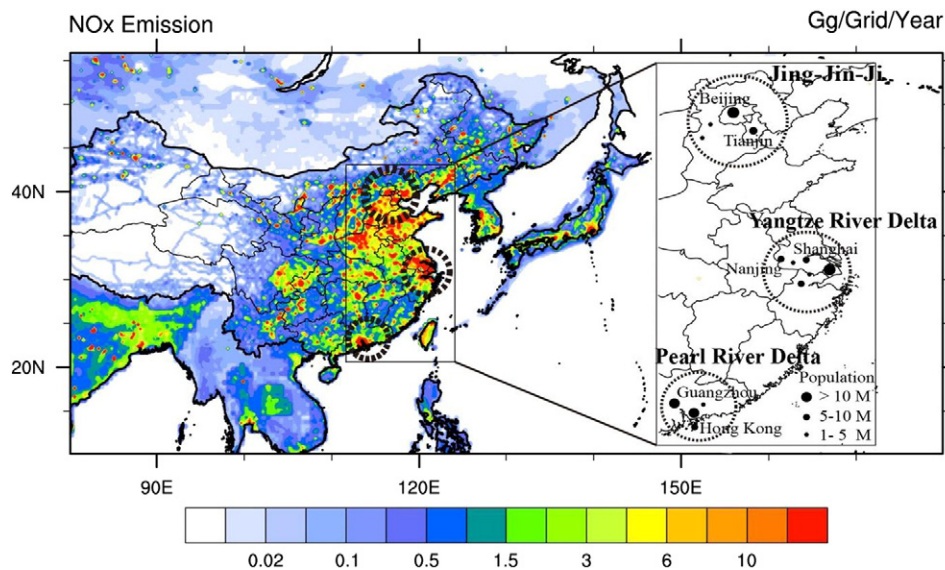


A common feature of O<sub>3</sub> formation is the non-linear dependence of O<sub>3</sub> production on its precursors, i.e., NO<sub>x</sub> and VOCs. With low NO<sub>x</sub>/VOCs, the intensity of the “NO<sub>x</sub> cycle” is weaker than that of the “RO<sub>x</sub> cycle”, and hence it becomes the limiting factor in O<sub>3</sub> production. Such a scenario is commonly known as the NO<sub>x</sub>-limited O<sub>3</sub> formation regime. With high NO<sub>x</sub>/VOCs, in contrast, O<sub>3</sub> production is mainly limited by the intensity of the “RO<sub>x</sub> cycle”, and is known

as VOC-limited. If NO levels are much higher, the usual case in polluted urban zones, O<sub>3</sub> production is suppressed by the R3 reaction and falls into a “NO<sub>x</sub> titrated regime.” Therefore, identifying the O<sub>3</sub> formation regime is a fundamental step in the science-based regulation of O<sub>3</sub> air pollution and has been a major area of O<sub>3</sub> pollution research in China (e.g., Wang et al., 2010; Xue et al., 2014b; Zhang et al., 2007; Zhang et al., 2008c).

### 3. Field measurements of ozone and ozone precursors in China

The majority of the Chinese population lives in the eastern part of China, especially in the three most developed regions, “Jing-Jin-Ji” (Beijing-Tianjin-Hebei), the Yangtze River Delta (YRD; including Shanghai-Jiangsu-Zhejiang-Anhui), and the Pearl River Delta (PRD; including Guangzhou, Shenzhen, and Hong Kong). These regions consistently have the highest emissions of anthropogenic precursors (Fig. 2), which have led to severe region-wide air pollution. As indicated earlier, ozone measurements before year 2000 were scarce in mainland China. Although ozone was included in China’s first ambient air quality standards in 1996 (which adopted an hourly concentration of 240 μg/m<sup>3</sup>



**Fig. 2.** Map of China showing the three most developed regions—Jing-Jin-Ji (Beijing-Tianjin-Hebei), Yangtze River Delta (including Shanghai), and Pearl River Delta (including Guangzhou and Hong Kong—Shenzhen)—and NO<sub>x</sub> emission intensity for 2013 with resolution of 0.25° × 0.25°. Emission data is from Tsinghua University available at <http://meicmodel.org/>. Also shown are major cities in three regions.



[~112 ppbv at 273 K, 101.3 kPa] for urban and industrial areas), it was not regularly monitored or reported by environmental agencies until 2012, after China revised its O<sub>3</sub> standards to hourly and 8-hourly maximum values of 200 µg/m<sup>3</sup> and 160 µg/m<sup>3</sup>, respectively (<http://www.mep.gov.cn>). The China Meteorological Administration (CMA) began to continuously monitor surface ozone in 2005 at its three regional background air monitoring stations (i.e., Longfengshan in Heilongjiang province in the northeast, Shangdianzi to the north of Beijing, and Lin'an to the southwest of Shanghai). Historical ozone data from the two government networks currently are not openly accessible, although partially quality controlled hourly data are being reported in real-time online by the China Environmental Monitoring Center (<http://www.cnemc.cn>).

In Hong Kong, the Hong Kong Environmental Protection Department (HKEPD) began to measure ozone at several air quality monitoring stations in early 1990s, but only in densely populated urban areas. In 1993, the Hong Kong Polytechnic University established the first regional station (Hok Tsui) in South China, which has been operational ever since (Wang et al., 2009a). In 1997 and 1999, two non-urban stations were set up by the HKEPD, one to the northeast and the other to the southwest of the city center. Hourly data from this network are available at <http://epic.epd.gov.hk/EPICDI/air/station/>. The Hong Kong Observatory has been launching ozonesonde since 1993 initially on a monthly basis (with enhanced weekly releases in 1993–1994 and 2000–2001), and the frequency was increased to weekly release since April 2003 (<http://www.weather.gov.hk/publica/reprint/r1173.pdf>). The data are publically assessable at the World Ozone and Ultraviolet radiation Center (<http://woudc.org/data/stations/?id=344>).

Because of the lack of nationwide ozone monitoring data in earlier years, the ozone pollution situation can only be discerned from limited campaign-type measurements. Tables 1a–1d summarizes the ozone field studies in the three most developed regions and other areas of mainland China and Hong Kong. It should be noted that although the references listed (a total of 91) may not be exhaustive and do not cover Chinese-language literature, we believe that they should represent comprehensive field studies in mainland China. The first study of photochemical pollution in China was conducted in the early 1980s in Lanzhou, a city situated in a valley in western China with a large petrochemical facility (Tang et al., 1989). Ozone was measured sporadically in Beijing during the summers of 1982 through 2003 (Shao et al. 2006) and in Guangzhou in southern China (Zhang et al., 1998). In

Lin'an, ozone (and ozone precursors) was measured for a full year in 1994 (Yan et al., 1997) and again from 1999 to 2010, as part of the China Map project (Guo et al., 2004b; Wang et al., 2002; Wang et al., 2001a). In Hong Kong, aircraft measurements of ozone and several pollutants were taken in 1994 along the Hong Kong border (Kok et al., 1997); surface measurements of ozone, ozone precursors, and other pollutants were taken at a pollution-receptor site in western Hong Kong in 2001 and 2002 (Guo et al., 2006; Wang et al., 2003; Zhang et al., 2007). In the summers of 2004, 2005, and 2006, ozone and ozone precursors were measured downwind of four major cities (Beijing, Shanghai, Guangzhou, and Lanzhou) (Wang et al., 2006a; Xue et al., 2014a; Zhang et al., 2009). A major international field program was also conducted during the fall of 2004 in the PRD region (Zhang et al., 2008b and references therein).

Since 2005, the number of photochemical studies has increased drastically in mainland China, especially in the PRD region in the south, the Jing-Jin-Ji region in the north, and the YRD region in the east. Many of these studies were international joint efforts, some of which were conducted to improve air quality for the Beijing 2008 Summer Olympics. The findings of these studies are given in the sections below.

According to the published data, the Beijing area has the highest peak ozone concentrations of the three most developed regions. Wang et al. (2006a) conducted field measurements for 6 weeks at a rural site 50 km north of Beijing city center in June and July 2005 and frequently observed hourly O<sub>3</sub> close to 200 ppbv; the highest value was 286 ppbv, a level unsurpassed in the available literature. Even during the first 2 weeks of emission control for the Beijing Olympic Games, hourly ozone mixing ratios in the range of 160 to 180 ppbv were observed in urban Beijing (Wang et al., 2010). In comparison, the highest hourly O<sub>3</sub> level reported in the YRD region was 140 to 167 ppbv, and hourly O<sub>3</sub> mixing ratios of up to 200 to 220 ppbv were reported in the PRD region, which includes Hong Kong (Zhang et al., 2007; Guangdong EPD reports, available at: <http://www.gdep.gov.cn/hjce/kqjc/>). Data from the national networks, once available, would give a full picture of the severity of ozone pollution across the country.

Seasonal variations in ozone pollution in the three regions are clearer. In the north and in the YRD, the highest seasonal mean ozone occurs from late May to July (Ding et al., 2013; Ding et al., 2008; Li et al., 2007; Wang et al., 2001a; Xu et al., 2008), like many other mid-latitude locations in the Northern Hemisphere. In contrast, the PRD region peaks in

**Table 1a**  
Summary of field measurements of ozone and ozone precursors in the Jing-Jin-Ji region.

Site	Measurement period	Type	Ozone precursors	Maximum O <sub>3</sub> (ppbv)	Reference
Zhongguancun, Beijing	1982–2003 (summer, sporadic)	Suburban	–	>200	Shao et al. (2006)
Shangdianzi, Beijing	Sep 2003–Dec 2006	Rural	NO <sub>x</sub> (NO + NO <sub>2</sub> ), CO	~175	Meng et al. (2009), Lin et al. (2008)
Changping, Beijing	2004–2015 Jun–Jul 2005 (downwind)	Rural	NO, CO, NMHCs	286	Ma et al. (2016) Wang et al. (2006a), Wang et al. (2010)
Miyun, Beijing	Jul–Aug 2008 (downwind)	Rural	NO <sub>x</sub> , CO, NMHCs	~170	Wang et al. (2010)
PKU <sup>a</sup> , Beijing	Jun–Aug 2006, 2007, 2008 Aug–Sep 2006	Urban	NO, CO NO, NO <sub>2</sub> , VOCs	123	Wang et al. (2009c) Chou et al. (2009) Shao et al. (2009a)
Tianjin	Aug–Sep 2008	Urban	NO, NO <sub>2</sub> , CO, NMHCs	117	Chou et al. (2011) Han (2011)
Gucheng, Hebei	Sep–Oct 2006	Urban	NO, NO <sub>2</sub>	162	Lin et al. (2009)
Aircraft measurement, NCP <sup>a</sup>	Jul 2006–Sep. 2007 2007–2010	Regional	NO, NO <sub>2</sub> , CO	60–120	Chen et al. (2013)
Multiple, Beijing	Jun–Sep 2007	Urban-rural, 4 sites	NO, NO <sub>2</sub> , CO, NMHCs	171–275	Xu et al. (2011)
CMA <sup>a</sup> , Beijing	Nov 2007–Mar 2008	Urban	NO, NO <sub>2</sub> , CO	70	Lin et al. (2011)
Multiple, Beijing	Jun–Aug 2008	Urban-rural, 2 sites	NO, NO <sub>2</sub> , CO	~150–180	Ge et al. (2012)
Aoyuncun, Beijing	Jul–Aug 2008	Urban	NO, NO <sub>2</sub>	180	Gao and Zhang (2012)
Multiple, Beijing	Jul–Aug 2008	Urban-rural, 3 sites	CO, NO <sub>x</sub> , NMHCs	190	Wang et al. (2010)
IAP, CAS <sup>a</sup> , Beijing	Jul–Sep 2008	Urban	NO, NO <sub>2</sub>	128	Sun et al. (2011)
Wuqing, Tianjin	Jul–Aug 2009	Urban	NO, NO <sub>2</sub> , VOCs	~200	Ran et al. (2012)
Multiple, Beijing	Jul 2010–Aug 2011	Urban-suburban, 4 sites	NO, NO <sub>2</sub> , CO, VOCs	175	Wei et al. (2015)

<sup>a</sup> PKU: Peking University; NCP: Northern China Plain; CMA: China Meteorological Administration; IAP, CAS: Institute of Atmospheric Physics, Chinese Academy of Sciences;

**Table 1b**  
Summary of field measurements of ozone and ozone precursors in the YRD region.

Site	Measurement period	Type	Ozone precursors	Maximum O <sub>3</sub> (ppbv)	Reference
Shanghai	1990–1994	Urban	NO <sub>x</sub>	~100	Xu et al. (1997)
Lin'an	1991–2006 (non-continuous) Aug 1994–Aug. 1995 Jun 1999–Apr. 2001	Rural	NO <sub>x</sub> NO, NO <sub>2</sub> , VOCs NO <sub>x</sub> , CO, NMHCs	156 112 145	Xu et al. (2008) Luo et al. (2000) Cheung and Wang (2001), Wang et al. (2001a), Wang et al. (2002), Wang et al. (2004), Guo et al. (2004b)
Multiple, YRD	May 1999–Jun 2000	Rural, 6 sites	NO, NO <sub>2</sub> , CO	116	Wang et al. (2005)
Nanjing	Jan 2000–Feb 2003 Aug 2011–Jul 2012 Jun 2013–Aug 2013	Urban Suburban Urban, 4 sites	NO, NO <sub>2</sub> , CO, NMHCs NO, CO NO, NO <sub>2</sub> , CO, VOCs	125 ~177 135	Tu et al. (2007) Ding et al. (2013) An et al. (2015)
SEMC <sup>a</sup> , Shanghai	Jan 2001–Dec 2004 Mar 2004–Dec 2005	Urban	NO <sub>2</sub>	~126 (8-hour)	Zhang et al. (2006) Huang et al. (2009)
Taicang, Jiangsu	May–Jun 2005	Rural	NO, NO <sub>2</sub> , CO, NMHCs	127	Xue et al. (2014b)
Downtown, Shanghai	Jun 2006–Jun 2007	Urban	NO <sub>x</sub> , CO, NMVOCs	128	Ran et al. (2009)
Aircraft measurement, YRD	30 Sep–11 Oct. 2007	Regional	NO <sub>x</sub> , CO, VOCs	60	Geng et al. (2009)
Fudan University, Shanghai	Jan–Dec 2013	Urban	NO <sub>2</sub> , CO	179	Shi et al. (2015)

<sup>a</sup> SEMC: Shanghai Environmental Monitoring Center.

the fall (October) (Wang et al., 2009a; Zheng et al., 2010). This feature can be explained by the interplay of chemistry and meteorology that contributes to a different seasonal maximum of ozone in southern China than in the north. The different seasonal peaks of surface ozone have implications for assessment of its effects on crops.

Long-term (>10 years) changes of ozone pollution have been reported based on limited data. In Hong Kong, where a continuous record is available, both background and urban ozone (O<sub>x</sub> = O<sub>3</sub> + NO<sub>2</sub> in urban areas) have increased since the early 1990s (at a rate of 0.27 to 0.58 ppbv/year) (Wang et al., 2009a; Xue et al., 2014a). In the PRD, O<sub>3</sub> was found to increase at a rate of 0.86 ppbv/year from 2006 to 2011 (Li et al., 2014). In the YRD region, the mean monthly highest 5% ozone at Lin'an increased at a rate of 1.8 ppbv/year during 1991–2006

(Xu et al., 2008). In the Northern China Plain (NCP), aircraft data from the MOZAIC program showed a large increase (2%/year) in the summer-time boundary-layer ozone during 1995–2005; the surface daily 1-hour maximum ozone in urban Beijing also increased at rate of 1.3%/year during 2001–2006 (Tang et al., 2009) and the daily 8-hour maximum O<sub>3</sub> at rural Shangdianzi rose at a rate of 1.1 ppbv/year during 2003–2015 (Ma et al., 2016). Non-continuous measurements at Mt. Tai, the highest peak in the NCP, showed an increase of 1.7–2.1%/year during the summer months from 2003 to 2015 (Sun et al., 2016). All of these results point to worsening photochemical pollution in China's major developed regions. According to available emission and satellite data (Duncan et al., 2016; <http://data.stats.gov.cn/>; Krotkov et al., 2016; Kurokawa et al., 2013; Mijling et al., 2013; Ohara et al., 2007; Richter et al., 2005;

**Table 1c**  
Summary of field measurements of ozone and ozone precursors in the PRD region.

Site	Measurement period	Type	Observed ozone precursors	Maximum O <sub>3</sub> (ppbv)	Reference
Hok Tsui, Hong Kong	1994–2007	Rural	NO <sub>x</sub> , CO, VOCs <sup>a</sup>	~200	Wang et al. (1998), Wang et al. (2003), Wang et al. (2009a)
Multiple, Hong Kong	1994–1999	Urban-rural, 10 sites	NO <sub>2</sub>	167	Lee et al. (2002)
Aircraft measurement, Hong Kong	Oct–Nov 1994	Regional	NO, CO	115	Kok et al. (1997)
Tung Chung, Hong Kong <sup>a</sup>	2001–2013	Suburban	NO, NO <sub>2</sub> , CO, NMHCs	~200	Zhang et al. (2007), Guo et al. (2009), Cheng et al. (2010), Xue et al. (2014a), Xue et al. (2016), Zhang et al. (2016), Guo et al. (2014)
Tai O, Hong Kong	Aug 2001–Dec 2002	Rural	CO, NO, NMHCs	203	Wang et al. (2003), Wang and Kwok (2003), Zhang et al. (2007), Guo et al. (2006)
Aircraft measurement, PRD	Oct 2004	Regional	NO <sub>x</sub>	~100	Wang et al. (2008)
Xinken, Guangzhou	Oct–Nov 2004	Rural	NO, NO <sub>2</sub> , CO, NMHCs	163	Zhang et al. (2008b)
Downtown, Guangzhou	Oct–Nov 2004 Jul 2006	Urban	NO, NO <sub>2</sub> , CO, NMHCs	~210	Zhang et al. (2008b) Lu et al. (2010b)
Wanqingsha, Guangzhou	Apr–May 2004 Oct 2004 Oct–Dec 2007 Nov–Dec 2007, Nov–Dec 2008	Suburban	NO <sub>x</sub> , NMHCs NO, NO <sub>2</sub> , CO, NMHCs, NO, CO, NMHCs NO, NO <sub>2</sub> , CO, NMHCs,	212	Xue et al. (2014b) Zhang et al. (2008a) Guo et al. (2009), Cheng et al. (2010) Zhang et al. (2012)
Multiple, PRD	2006–2007	Urban–Rural, 16 sites	NO, CO	31 (monthly)	Zheng et al. (2010)
Backgarden, Qianguan	Jul 2006	Suburban	NO, NO <sub>2</sub> , CO, NMHCs	~200	Lu et al. (2010b), Lu et al. (2012)
Tai Mo Shan, Hong Kong	Oct–Nov 2010 Nov–Dec 2013	Suburban mountain top	NO, NO <sub>2</sub> , CO, NMHCs	~118	Guo et al. (2012) Wang et al. (2016), Brown et al. (2016)

<sup>a</sup> Regular monitoring station with intensive studies.

**Table 1d**  
Summary of field measurements of ozone and ozone precursors in other regions of China.

Site	Measurement period	Type	Observed ozone precursors	Maximum O <sub>3</sub> (ppbv)	Reference
Multiple, Chongqin	1993–1996	Urban-rural, 20 sites		93	Zheng et al. (1998)
Longfengshan, Heilongjiang	Aug 1994–Jul 1995	Rural	NO <sub>x</sub> , CO, NMHCs	~85	Li et al. (1999)
Waliguan, Qinghai	Aug 1994–Dec 1995	Remote continental	NO <sub>x</sub> , CO, NMHCs	130	Li et al. (1999)
(global baseline station with intensive studies)	Aug 1994–Dec. 2013		/	~65 (monthly)	Xu et al. (2016)
	Apr–May 2003,		NO, CO, VOCs	~80	Wang et al. (2006b),
	Jul–Aug 2003				Xue et al. (2014b)
	Jun–Jul 2006		CO	91	Zhang et al. (2009)
	Jul–Aug 2006		NO, NO <sub>2</sub> , CO	~62	Xue et al. (2011)
Mt. Tai, Shandong	Jul–Nov 2003	Rural mountain top	CO	160	Gao et al. (2005)
	Mar 2004–May 2007		NO, NO <sub>2</sub> , CO		Kanaya et al. (2013)
	May 2004		/		Wang et al. (2006c)
	Jun. 2006		NO, NO <sub>x</sub> , CO, NMVOCs		Kanaya et al. (2009),
					Kanaya et al. (2013),
					Li et al. (2007)
	Jun 2006–Jun 2009		NO, NO <sub>2</sub> , CO		Sun et al. (2016)
	Jun–Aug 2014				
	Jun–Aug 2015				
Ji'nan, Shandong	Jun 2003–Oct 2004	Urban	/	144	Shan et al. (2009a),
					Shan et al. (2009b)
Mt. Huang, Anhui	May 2004	Rural mountain top	/	114	Wang et al. (2006c)
Lanzhou, Gansu	Jun–Jul 2006	Suburban	NO <sub>x</sub> , CO, NMHCs	161	Zhang et al. (2009),
					Xue et al. (2014b)
	Jun–Jul. 2013	Urban-Suburban, 2 sites	NO <sub>x</sub> , CO NMHCs	186	Jia et al. (2016)
Aircraft measurement, Jilin	Jun–Jul 2007	Regional	CO, VOCs	~140	Ding et al. (2009)
Xi'an, Shan'xi	Mar 2008–Jan 2009	Urban	/	140	Wang et al. (2012a)
Wuhan, Hubei	Feb 2013–Oct 2014	Urban	NO <sub>x</sub> , CO, VOCs	~85 (daytime average)	Lyu et al. (2016)

Streets et al., 2001; Zhao et al., 2013), NO<sub>x</sub> emission increased since 1980s, peaked in 2011 and decreased since in the three major regions due to implementation of NO<sub>x</sub> control in China's 12th Year Plan (2011–15) and a slowdown in manufacturing activities. Emission of VOCs have also increased in mainland China since the 1980s (Lu et al., 2013; Ohara et al., 2007), with no turning point up to 2014 according to satellite data on formaldehyde vertical column (De Smedt et al., 2015). For Hong Kong which is located in the PRD region, NO<sub>x</sub> and VOC emissions have been reduced by 28% and 65%, respectively, during 1997–2014 (<http://www.epd.gov.hk/>). The paradox increase in ambient ozone levels in Hong Kong have been attributed largely to the increasing concentrations in air transported into the territory (Xue et al., 2014a). It will be of great interest to see whether the continuing NO<sub>x</sub> emission reduction and long-awaited VOC control in China will affect the ambient ozone levels in the near future.

The ozone precursors—NO<sub>x</sub> (NO + NO<sub>2</sub>) and VOCs, including CO, non-methane hydrocarbons (NMHC), and oxygenated organics—were measured initially in ad hoc field studies. With large increases in research funding and increasing awareness of the importance of VOCs, speciated VOCs have been measured in many recent field studies and also by governments' agencies. The ozone precursor data and other concurrently measured pollutants have been used to characterize site environments, identify sources, elucidate ozone-forming potentials and regimes, apportion sources of VOCs, and validate model simulations. For instance, field measurements at Lin'an revealed that biomass burning (biofuel and crop residues) was an important source of ozone precursors in rural areas in the YRD region (Cheung and Wang, 2001; Guo et al., 2004b). Reactive aromatics were found to dominate ozone production in Hong Kong and in the PRD region (So and Wang, 2004; Xue et al., 2014a; Xue et al., 2014b; Zhang et al., 2007; Zhang et al., 2008c), and source apportionment studies show that solvent use and vehicle exhausts are the main source of these compounds (Guo et al., 2006; Guo et al., 2004a). Detailed discussions on the use of these data are given in later sections of this review.

#### 4. Meteorological influence on ozone episodes

Meteorological conditions conducive to photochemical episodes in China have been extensively studied. Tropical cyclones and continental

anticyclones are the main meteorological systems related to ozone episodes. Anticyclones (i.e., high pressure systems) create favorable conditions at the center, e.g., sunny weather and low wind velocity, for pollution accumulation and O<sub>3</sub> production (Ding et al., 2013; Gao et al., 2005). Ozone episodes in the PRD region (including Hong Kong) are often influenced by tropical cyclones in the western Pacific. Due to large-scale subsidence at the outskirts of the low-pressure systems, the PRD region often has fine weather with intense sunlight, high temperatures, and light winds (Ding et al., 2004; So and Wang, 2003).

A number of studies have examined the local meteorological parameters during ozone episodes, including solar radiation, temperature, relative humidity, wind speed and direction, and cloud cover. Similar to findings in other parts of the world, elevated ozone concentrations generally occurs on days with strong sunlight and low winds, which favor the photochemical production of ozone and the accumulation of ozone and its precursors. Wind direction is also important because it affects pollution transport, giving rise to high ozone in downwind locations. For instance, in Beijing, northwesterly airflows bring relatively clean air masses from the region of the Inner Mongolia region, but southerly winds can carry ozone and ozone precursors from Hebei and Shandong Provinces to Beijing (Duan et al., 2008; Han, 2011; Ma et al., 2011; Wang et al., 2010). In the coastal cities like Hong Kong, ozone episodes are often associated with weak northwesterly winds which transport pollution from the inner PRD cities to the coastal areas (e.g., Wang et al., 2001b; Wang et al., 2001c).

Mountain-valley winds have been shown to be an important dynamic feature in mountainous areas. Upslope winds bring pollutants including ozone from low-lying areas to the peak of Mt. Tai (1534 m a.s.l.) in Shandong (Gao et al., 2005) and to the top of Mt. Tai Mo Shan (957 m a.s.l.) in Hong Kong (Guo et al., 2013), contributing to the elevated daytime concentrations of ozone and other pollutants observed at these sites. Beijing is surrounded by mountains from the northeast to the west. In summer, upslope winds transport O<sub>3</sub> and other pollutants to the northern mountainous areas in the afternoon and valley winds return them to the flat southern areas at night (Gao and Zhang, 2012; Wang et al., 2006a; Wang et al., 2009c).

Sea-land breezes are another important meteorological phenomena that distribute ozone and its precursors in coastal cities such as those in the YRD and PRD. Ding et al. (2004) simulated the sea-land breezes

during a multiday episode in the PRD region. On episode days, from midnight to noon of the following day, the land breezes and offshore synoptic winds brought the ozone precursors from inland and coastal cities to areas over the ocean, where air pollutants accumulated due to a low mixing height and calm wind. In the afternoon, the ozone-laden air masses were recycled to the coast by onshore sea breezes, with most sites receiving the highest levels of ozone between 13:00 and 14:00 local time. Shan et al. (2010) observed a similar pattern at a coastal site in Jinshan District, Shanghai. The ozone levels were much higher during the sea breeze than the land breeze. Tie et al. (2009) found that the sea breeze is noticeable in the city of Shanghai under calm conditions. The sea breeze changes the southerly wind to an easterly direction, resulting in a cycling wind pattern in which the weak surface wind and the sea breeze trap O<sub>3</sub> in the city, giving rise to high ozone concentrations in the afternoon.

## 5. Observation-based analysis of ozone-precursors relationship

Several observation-based approaches have been developed to diagnose the O<sub>3</sub>-precursor relationships from the field measurement data. Overall, these methods can be divided into two categories—indicator species correlation and observation-based kinetic calculations (e.g., the chemical box model and steady state calculation). In this section, we describe several widely used methods and their applications in studies of ozone pollution in China.

### 5.1. Observed indicators of O<sub>3</sub> formation regimes

#### 5.1.1. Ozone production efficiency

Ozone production efficiency (OPE =  $\Delta O_3 / \Delta NO_2$ ) is one of the most widely used indicators to infer the O<sub>3</sub> formation regimes, partly due to the simple measurements of O<sub>3</sub> and NO<sub>2</sub> (NO<sub>2</sub> = NO<sub>y</sub> – NO<sub>x</sub>). It is defined as the number of O<sub>3</sub> molecules produced per oxidation of a NO<sub>2</sub> molecule to a NO<sub>z</sub> species (Trainer et al., 1993) and can be realized as the number of “NO<sub>x</sub> (or RO<sub>x</sub>) cycles” that occur before termination. Lower OPE values (e.g.,  $\leq 4$ ) indicate inefficient radical recycling (see Fig. 1), in which the supply of VOCs is the limiting factor, and thus points to the VOC-controlled O<sub>3</sub> formation regime. In contrast, higher OPE values (e.g.,  $\geq 7$ ) suggest that radical cycling is efficient and that O<sub>3</sub> formation is mainly controlled by the availability of NO<sub>x</sub> (i.e., NO<sub>x</sub>-limited). OPE values in the medium range (e.g.,  $4 < OPE < 7$ ) indicate that O<sub>3</sub> production is controlled by both NO<sub>x</sub> and VOCs in a so-called mixed (or transition) regime.

Technically, the OPE can be derived from the regression slope of the scatter plots of O<sub>3</sub> versus NO<sub>z</sub> (e.g., Xue et al., 2011). In addition to the formal definition of  $\Delta O_3 / \Delta NO_2$ , several derivatives are used to determine the OPE according to the specific conditions. In urban atmospheres with high NO<sub>x</sub> levels, for instance, total oxidants (O<sub>x</sub> = O<sub>3</sub> + NO<sub>2</sub>) are usually adopted instead of O<sub>3</sub> to take into account the O<sub>3</sub> titration by NO, and OPE can then be estimated as the  $\Delta O_x / \Delta NO_2$  ratio (e.g., Wang et al., 2010). In rural areas where the air masses are relatively aged, i.e., with lower NO<sub>x</sub>/NO<sub>y</sub> ratios, NO<sub>y</sub> (or NO<sub>x</sub>\* that includes NO<sub>x</sub> and some NO<sub>z</sub> species) has been used to deduce the OPE values (as  $\Delta O_3 / \Delta NO_y$  or  $\Delta O_3 / \Delta NO_x^*$ ), in the absence of NO<sub>z</sub> measurements (e.g., Wang et al., 2006a). All of these indicator species pairs can be selected to estimate the OPE according to the specific atmospheric and experimental conditions, although the derived exact values may differ slightly.

Table 2 summarizes some OPE values reported over China in the past decade. A glance at this table reveals several noticeable features. First, most OPE investigations has been conducted around Beijing and to a lesser extent in the PRD region in south China, with sparse efforts in other areas. Second, the observationally derived OPE values vary widely (from 1.1 to 20.2) from place to place, and even case by case in the same locale, suggesting spatial and temporal heterogeneity in O<sub>3</sub> formation regimes. Third, a nonlinear relationship between O<sub>3</sub> and O<sub>3</sub> precursors is clearly illustrated in the O<sub>3</sub> (or O<sub>x</sub>) versus NO<sub>z</sub> scatter plot. For

example, Wang et al. (2010) examined OPE at both suburban and rural sites in Beijing and found larger OPE values of 7.7 and 6.5, corresponding to a NO<sub>x</sub>-limited or transition regime during low NO<sub>x</sub> conditions (i.e., NO<sub>z</sub> < 10 ppbv) compared to 2.7 and 4.0 (VOC-limited) at high NO<sub>x</sub> conditions (NO<sub>z</sub> > 10 ppbv). Analysis of OPE is a relatively easy way to identify the ozone formation regime from field observations.

An appropriate data set forms the basis for high-quality OPE analysis. The data usually chosen for OPE calculation include either afternoon data while maximum photochemistry is occurring (e.g., Wang et al., 2010) or a specific pollution plume with strong ozone production (e.g., Wang et al., 2006a). The former provides an overall average estimation of the OPE for a longer period, although the mixing of various air plumes may raise some uncertainty for analysis. The latter case ideally derives the OPE for a polluted plume and is hence capable of providing the most accurate estimation, but it is solely relevant to a specific pollution event. In addition, the location of study sites plays an important role in determining the regional-scale O<sub>3</sub> formation regime by the OPE method. As mentioned above, the observed OPE values show large spatial variations within a given area. Taking Beijing as an example, the OPE-derived O<sub>3</sub> formation regimes at different sites vary significantly from highly VOC-limited (OPE = 1.1) to highly NO<sub>x</sub>-limited (OPE = 20.2; Table 2). Obviously, it is impossible to formulate a universal mitigation strategy for regional O<sub>3</sub> pollution based on results from a single locale. To obtain a holistic understanding of the O<sub>3</sub> formation regime at a regional scale, representative regional monitoring networks should be developed to determine OPE at high spatial (and temporal) resolutions. Built on this, a strict statistical analysis can be enforced to achieve more robust results.

#### 5.1.2. H<sub>2</sub>O<sub>2</sub>/NO<sub>z</sub> ratio

Another indicator of the chemistry regime of O<sub>3</sub> formation is the H<sub>2</sub>O<sub>2</sub>/NO<sub>z</sub> (or H<sub>2</sub>O<sub>2</sub>/HNO<sub>3</sub>) ratio. For VOCs-limited regimes (i.e., high NO<sub>x</sub>/VOCs conditions), RO<sub>x</sub> + NO<sub>x</sub> reactions forming NO<sub>z</sub> species dominate the termination process and one would expect lower H<sub>2</sub>O<sub>2</sub>/NO<sub>z</sub> ratios. In comparison, higher H<sub>2</sub>O<sub>2</sub>/NO<sub>z</sub> ratios indicate the dominance of radical cross-reactions (e.g., HO<sub>2</sub> + HO<sub>2</sub>) in the radical termination processes, corresponding to the high VOCs/NO<sub>x</sub> conditions and a NO<sub>x</sub>-limited regime. Transition values for the H<sub>2</sub>O<sub>2</sub>/NO<sub>z</sub> ratio also occur, implying a transition in O<sub>3</sub> production from a VOC-limited to a NO<sub>x</sub>-limited regime (Hammer et al., 2002; Millard and Toupance, 2002).

Compared to the O<sub>3</sub>/NO<sub>z</sub> indicator, the H<sub>2</sub>O<sub>2</sub>/NO<sub>z</sub> ratio has rarely been used in previous studies in China, partly owing to a lack of concurrent measurements of H<sub>2</sub>O<sub>2</sub> and NO<sub>z</sub>. Fig. 3 presents both O<sub>3</sub>-NO<sub>z</sub> and H<sub>2</sub>O<sub>2</sub>-NO<sub>z</sub> scatter plots during two groups of O<sub>3</sub> pollution episodes observed at a polluted suburban site in Hong Kong (Tung Chung) in fall 2011. We can clearly see the consistency between both indicators in determining the O<sub>3</sub> formation chemistry. Given the wider measurements of O<sub>3</sub> compared to H<sub>2</sub>O<sub>2</sub>, OPE should remain the preferred indicator of the relationship between O<sub>3</sub> and precursors, with the H<sub>2</sub>O<sub>2</sub>/NO<sub>z</sub> ratio as an important supplement.

### 5.2. Measurement-constrained model analysis of O<sub>3</sub> sensitivity to various precursors

The observation-based model (OBM) combines in-situ field observations and chemical box modeling. It is built on widely-used chemistry mechanisms (e.g., MCM, Carbon Bond, RACM or SAPRC), and applied to the observed atmospheric conditions to simulate various atmospheric chemical processes, including the in-situ O<sub>3</sub> (usually considered as O<sub>x</sub>) production rate. As mentioned in Section 2, O<sub>x</sub> production is primarily facilitated by the oxidation of NO to NO<sub>2</sub> by HO<sub>2</sub> and RO<sub>2</sub> radicals (R4 and R5), and the O<sub>x</sub> production rate ( $P(O_x)$ ) can be computed with Eq. (E1). The chemical loss of O<sub>x</sub> results mainly from the photolysis of O<sub>3</sub> (R13 and R14); reactions of O<sub>3</sub> with OH (R15), HO<sub>2</sub> (R16) and unsaturated VOCs (R17); reactions of NO<sub>2</sub> with OH (R8) and RO<sub>2</sub> (R9), reactions of



**Table 2**  
Summary of the OPE evaluation studies over China.

Region	Site <sup>a</sup>	Period	Site type	Indicator species	OPE Values	Reference
Beijing	Changping	Jun–Jul 2005 (episodes)	Rural downwind	O <sub>3</sub> /NO <sub>y</sub>	3–6	Wang et al. (2006a)
		Jul–Aug 2008		O <sub>x</sub> /NO <sub>z</sub>	6.5 ± 0.54 (NO <sub>z</sub> < 10) 4.0 ± 0.80 (NO <sub>z</sub> > 10)	Wang et al. (2010)
	PKU <sup>a</sup>	Aug–Sep 2006 (episodes)	Urban	O <sub>x</sub> /NO <sub>z</sub>	3.9–9.7	Chou et al. (2009)
	CMA <sup>a</sup>	Nov 2007–Mar 2008	Urban	O <sub>x</sub> /NO <sub>z</sub>	1.1 ± 1.6	Lin et al. (2011)
	CRAES <sup>a</sup>	Jul–Aug 2008	Suburban	O <sub>x</sub> /NO <sub>z</sub>	7.7 ± 0.78 (NO <sub>z</sub> < 10) 2.7 ± 0.49 (NO <sub>z</sub> > 10)	Wang et al. (2010)
	Shangdianzi	Jul–Aug 2008 (episodes)	Rural background	O <sub>x</sub> /NO <sub>z</sub>	4.0 ± 0.32 5.3 ± 0.55	Ge et al. (2012)
Pearl River Delta	IAP, CAS <sup>a</sup>	Jul–Aug 2008 (background)				Sun et al. (2011)
	Guangzhou	Aug 2, 2008 (episode)	Urban	O <sub>x</sub> /NO <sub>z</sub>	6.9	
		Aug 24, 2008 (episode)			20.2	
Back garden	Summer 2006	Urban	O <sub>x</sub> /NO <sub>z</sub>	2.1	Lu et al. (2010b)	
	Summer 2006	Suburban		7.8		
Dinghushan	Oct 29–30 2008 (episodes)	Rural	O <sub>x</sub> /NO <sub>z</sub>	>10	Sun et al. (2010)	
Yangtze River Delta	Lin'an	Summer 2001	Rural	O <sub>3</sub> /NO <sub>x</sub> *	~8	Wang et al. (2001a)
North China Plain	Mt. Tai	Jun 2006	Rural	O <sub>3</sub> /NO <sub>z</sub>	5.8 ± 0.5	Kanaya et al. (2013)
		Jun 2006–2015		O <sub>3</sub> /NO <sub>2</sub> *	3.9–14.9	Sun et al. (2016)
	Jul–Aug 2006–2015			3.6–15.0		
Qinghai-Tibetan Plateau	Waliguan	Jul–Aug 2006 (episodes)	Remote	O <sub>3</sub> /NO <sub>z</sub>	7.7–11.3	Xue et al. (2011)

<sup>a</sup> PKU: Peking University; IAP, CAS: Institute of Atmospheric Physics, Chinese Academy of Sciences; CMA: China Meteorological Administration; CRAES: Chinese Research Academy of Environmental Science.

NO<sub>3</sub> with VOCs (R18) and the heterogeneous loss of N<sub>2</sub>O<sub>5</sub> on particles (R19) (Xue et al., 2014b). Thus the loss rate of O<sub>x</sub> can be described as Eq. (E2). The difference between E1 and E2 then gives the net O<sub>x</sub> production rate.

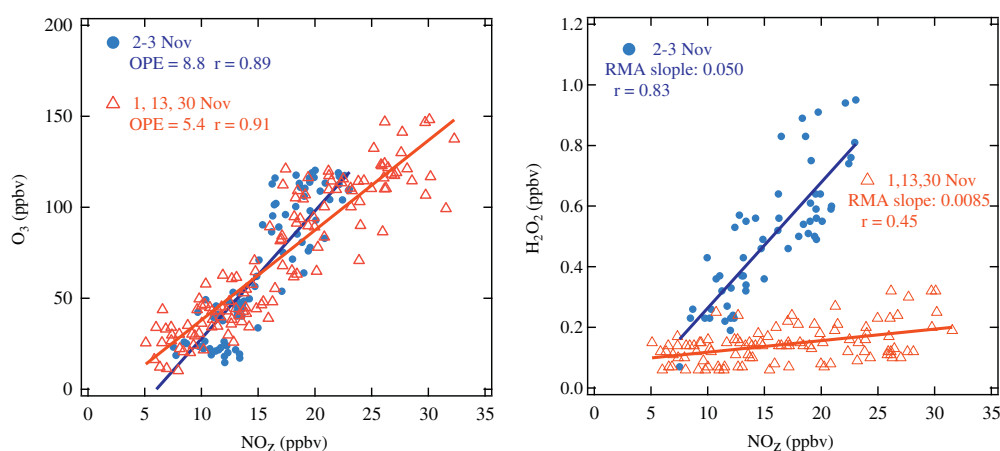


$$P(\text{O}_x) = k4 [\text{HO}_2][\text{NO}] + \sum (k5[\text{RO}_2][\text{NO}]) \quad (\text{E1})$$

$$L(\text{O}_x) = k14[\text{O}(^1\text{D})][\text{H}_2\text{O}] + k15[\text{O}_3][\text{OH}] + k16[\text{O}_3][\text{HO}_2] + \sum (k17[\text{O}_3][\text{VOC}]) + k8[\text{OH}][\text{NO}_2] + k9[\text{RO}_2][\text{NO}_2] + 2\sum (k17[\text{NO}_3][\text{VOC}]) + 3k19[\text{N}_2\text{O}_5] \quad (\text{E2})$$

The sensitivity of ozone production to various O<sub>3</sub> precursors, including NO<sub>x</sub>, VOCs, and even individual VOC species, can be quantified by conducting sensitivity modeling analyses with an assumed reduction in the concentration of target precursors. A key parameter that infers the O<sub>3</sub> formation regime is the relative incremental reactivity (RIR), which is defined as the ratio of the decrease in O<sub>x</sub> production rate to a given reduction in the precursor concentration (Cardelino and Chameides, 1995). Higher positive RIR values indicate the compounds to which O<sub>3</sub> production is more sensitive, and the species with negative RIR play a negative role (i.e., O<sub>3</sub> titration) in ozone formation (Xue et al., 2014a). Therefore, RIR has important implications for developing a science-based control strategy for O<sub>3</sub> pollution.

In the past decade, OBM has been widely applied to assess the O<sub>3</sub>-precursors relationship in China. The available results from previous studies are summarized in Table 3. Most work has been conducted in the PRD, the YRD, and the NCP, with only few studies in other areas.



**Fig. 3.** Scatter plots of (a) O<sub>3</sub> vs. NO<sub>2</sub> and (b) H<sub>2</sub>O<sub>2</sub> vs. NO<sub>2</sub> during two sets of photochemical episodes at Tung Chung, Hong Kong, in fall 2011 (unpublished data). The slopes were calculated based on the Reduced Major Axis method. (RMA) (e.g., Wang et al., 2010).



In terms of the O<sub>3</sub> formation regime, most of the study areas (e.g., the PRD, YRD and the urban areas in the NCP) are found in VOCs-limited zones, with anthropogenic VOCs (i.e., reactive aromatics and alkenes) playing a dominant role. Nonetheless, some variations were found in the chemistry regime of O<sub>3</sub> formation in different regions in China. Xue et al. (2014b) examined the O<sub>3</sub>-precursors relationship and VOC reactivity in four major Chinese cities (i.e., Beijing, Shanghai, Guangzhou and Lanzhou) and found that O<sub>3</sub> formation was governed mainly by NO<sub>x</sub> at a rural site in Beijing, by aromatics in Guangzhou, by aromatics and alkenes in Shanghai, and by NO<sub>x</sub> and alkenes in Lanzhou. More observation-based modeling studies are still needed, especially in the less-tapped regions and rural areas, to achieve a thorough understanding of ozone formation chemistry across China. It should be noted that the OBM analysis requires measuring NO at sub-ppb levels and > 50 number of VOCs; care must be taken to ensure accurate determination of these critical chemicals, especially VOCs which are difficult to measure.

## 6. Processes analysis of ozone and source attribution

### 6.1. Ozone source apportionment

Severe O<sub>3</sub> air pollution events over highly urbanized areas have prompted the development of emission-driven photochemical grid modeling to better understand the pollution sources/sinks, formation mechanisms, and regional source contribution, and to help develop effective control strategies. Techniques applied in these models include the factor separation technique, ozone source apportionment technology, integrated process analysis, and response surface modeling (Li et al., 2012a; Liu et al., 2010; Qu et al., 2014; Xing et al., 2011).

#### 6.1.1. The Jing-Jin-Ji region

Regional air quality models such as CAMx, CMAQ, and WRF-Chem have been applied to analyze the source contribution of ozone. Wang et al. (2009b) investigated high ozone events in Jing-Jin-Ji using Ozone Source Apportionment Technology (OSAT) with Geographic Ozone Assessment Technology (GOAT). They found that the main contribution to high afternoon ozone levels in June 2000 was from the urban and southern Beijing areas, which accounted for 31.6% and 12.6%, respectively. Furthermore, they found a significant contribution of precursor emissions from southern Hebei Province and Tianjin, which were estimated at 16.9% and 12.6%, respectively. This result is consistent with an early study by Streets et al. (2007) using CMAQ, which found that ozone air pollution in Beijing was derived partially from regional emissions outside of Beijing (e.g., Hebei), reportedly 20% to 30% in July 2001 and 35% to 65% during the high ozone episodes. Mijling et al. (2013) indicated that Hebei province is one of the nation's top three NO<sub>x</sub> emissions. The high local emissions in Jing-Jin-Ji have rendered the contribution of long-range transport from other continents (e.g., Europe) insignificant (Fu et al., 2012). In general, urban Jing-Jin-Ji is found to be VOC-limited, due to the abundance of NO<sub>x</sub> emissions from local industrial and traffic sources, whereas the rural area of Jing-Jin-Ji tends to be NO<sub>x</sub> limited (Chou et al., 2009; Wang et al., 2010). This finding is further supported by a model study by Liu et al. (2010) that found P(H<sub>2</sub>O<sub>2</sub>)/P(HNO<sub>3</sub>) ratios below 0.2 in urban Beijing and Tianjin during summer with CMAQ (Tonnesen and Dennis, 2000). Additional analysis by Wang et al. (2009b) using OSAT source category analysis suggested that the relative ozone contributions from various sources in Beijing are 31.6% (mobile), 20% (industrial), 13% (point) and 12% (biogenic).

In terms of regional emission control, Qu et al. (2014) applied multi-“brute force” CMAQ model simulations (August 2007) with a factor

**Table 3**  
Summary of the OBM studies over China.

Region	Site	Sampling period	Site type	Chemical Mechanism	O <sub>3</sub> Formation Regime	Dominant VOCs <sup>a</sup>	References
Pearl River Delta (including Hong Kong)	PRD (8 sites)	Summer, autumn 2000	Urban/suburban	–	VOCs-limited (Guangzhou)	AHC	Shao et al. (2009b)
	Hong Kong (5 sites)	Oct 1–Dec 31, 2002	Urban/suburban	CB-IV	VOCs-limited	R-AROM	Zhang et al. (2007)
	Tung Chung	Autumn 2002–2013	Suburban	MCM3.2/CB-IV	VOCs-limited	R-AROM	Cheng et al. (2010), Xue et al. (2014a), Xue et al. (2014b)
	Guangzhou	2004 Nov./2006 Jul	Urban	CB-IV	VOC-limited	AHC	Lu et al. (2010b), Zhang et al. (2008c)
	Xinken Back garden	2004 Nov 2006 Jul	Rural Suburban	GIT-OBM CB-IV	VOC-limited transition	AHC –	Zhang et al. (2008c) Lu et al. (2010b)
	Wan Qing Sha	Oct 23–Dec 1 2007	Suburban	CB-IV	VOCs-limited	R-AROM	Cheng et al. (2010), Ling et al. (2011)
Yangtze River Delta	Tsuen Wan	Autumn 2010	Urban	MCM3.2	VOCs-limited	R-AROM	Guo et al. (2013), Ling et al. (2014)
	Tai Mo Shan	Sep–Nov 2010	Semirural site	MCM3.2	transition	–	Guo et al. (2013)
	Taicang	Apr 4–Jun 1, 2005	Urban	MCM3.2	VOCs-limited	R-AROM	Xue et al. (2014b)
	Shanghai (5 sites)	Nov 15–Nov 26 2005 Jan 2006–May 2007	Urban Urban/suburban/rural	NACR-MM NACR-MM	VOCs-limited VOCs-limited (urban)	R-AROM R-AROM	Geng et al. (2007) Geng et al. (2008)
	Jiangsu	May 15–Jun 24 2010	Rural	RACM	VOC-limited (morning) to NO <sub>x</sub> -limited (afternoon)	–	Pan et al. (2015)
North China Plain	Nangjing (4 sites)	Jun–Aug. 31, 2013	Urban/suburban	CB-IV	VOCs-limited	Alkenes	An et al. (2015)
	Mount Tai	Jun 2006	Mountain	RACM	NO <sub>x</sub> -limited (mainly)	–	Kanaya et al. (2009)
	Peking University	Aug–Sep 2006/Aug 2007	Urban	CBM4/SAPRC-07	transition/VOCs-limited	–	Liu et al. (2012), Lu et al. (2010a)
	Yufa	Aug–Sep 2006	suburban	CBM4	Mixed-limited	–	Lu et al. (2010a)
	Wuqing	Summer 2009	Suburban	NACR-MM	NO <sub>x</sub> -limited	–	Ran et al. (2011)
	Yanshan	Jul–Aug of 2010 and 2011	Industrial	NACR-MM	NO <sub>x</sub> -limited	–	Wei et al. (2015)
Western and Central China	Tieta	Jun–Oct, 2010/Jul–Aug 2010 and 2011	Urban	NACR-MM	transition/VOCs-limited	–	Ran et al. (2012), Wei et al. (2015)
	Lanzhou	Jun 19–Jul 16 2006	Urban	MCM3.2	NO <sub>x</sub> -limited	–	Xue et al. (2014b)
	Wuhan	Feb 2013–Oct 2014	Urban	MCM3.2	VOCs-limited	AHC	Lyu et al. (2016)

<sup>a</sup> AHC represents anthropogenic hydrocarbons; R-AROM represents reactive-aromatics; AHC represents anthropogenic hydrocarbons.

separation technique to identify the effects of individual emission source types. They found that power plant emissions play an important role in peak ozone levels in southwestern Jing-Jin-Ji. Moreover, a 30% across-the-board reduction in industrial and transportation emissions would result in a maximum reduction of 20 ppbv in the Jing-Jin-Ji area. In another study, Xing et al. (2011) examined multiple emission reduction options using the CMAQ response surface model and found that solely reducing local NO<sub>x</sub> or VOC emissions in the Beijing area (even by 90%) would be insufficient to meet the ozone Class 2 Ambient Air Quality Standard of China. It is recommended that synchronous regional reductions in VOC and NO<sub>x</sub> by 60% to 80% are needed across the entire Jing-Jin-Ji region.

### 6.1.2. The PRD

In the PRD region, with its different emission characteristics and meteorological conditions, the regional and source category contributions to high O<sub>3</sub> differ from those in Beijing. Using the CAMx model implemented with OSTA, Li et al. (2012c) reported that between 7 and 10 November 2006, the top sources of average daytime ozone in the PRD were mobile (28%), area (14%), point (5%), marine (2%), and biogenic sources (5%), respectively, and in summer (24 and 25 July 2006), they were 30% (mobile), 12% (area), 16% (point), 3% (marine), and 8% (biogenic), respectively. Li et al. (2013) further extended the ozone contribution estimates for Hong Kong and the PRD to all four seasons and established a full precursor contribution matrix for ozone concentration in all PRD cities. They suggested that during ozone episodes, the top contributors to the ozone in PRD cities were mobile, point, and area sources, and that local and PRD regional sources accounted for 68% to 80% of ozone concentrations in summer, 35% to 55% in fall, and 19% to 32% in spring and winter (Li et al., 2013). These values could be even higher with the recent findings of an ozone production pathway from HONO chemistry, which further enhanced the local ozone production by 6% to 12% in Hong Kong and major PRD cities (Zhang et al., 2016).

In terms of regional emission control, it is suggested that the PRD government should focus on the local emissions reduction, particularly in the mobile source category, to maximize the effectiveness of control policies for long-term ozone reduction. Ou et al. (2016) suggested that 43% of NO<sub>x</sub> and 40% of anthropogenic VOCs reduction in the mobile sources can be achieved by applying Stage V of the Vehicle Emission Standards in the PRD areas. They also suggested a VOC-focused control with a reduction ratio of 1:2 (anthropogenic VOC to NO<sub>x</sub>) to effectively reduce the peak O<sub>3</sub> levels in urban and industrial areas.

### 6.1.3. The YRD

Compared with the two regions mentioned above, source apportionment studies for the YRD are relatively limited. Using CAMx with OSAT, Li et al. (2015a) and Wang et al. (2014) reported in August 2010 and July 2013 that the top sources of the 8-hour maximum ozone were mobile (19% to 23%), point (5.7% to 9.8%), industrial (38.3% to 53.0%), and biogenic (6.6% to 17%). Li et al. (2015a) found that the regional contributions of non-YRD emissions to the averaged ozone in the Shanghai, Jiangsu and Zhejiang areas were 43%, 49%, and 60%, respectively, indicating a large influence of emissions from outside the YRD. On high ozone days, the contributions from local and northern Zhejiang to the average ozone in Shanghai were suggested to be 29% and 20%, respectively, which are consistent with the results (13% to 21%) of CMAQ process analysis by Li et al. (2012a). Using the WRF-Chem model coupled with an ozone tagging method, Gao et al. (2016) studied the source regions for ozone pollution in the YRD and showed that the region was affected by surrounding upwind provinces such as Anhui, Shandong, and Henan-Hebei, with average contributions of 16.2%, 13.6%, and 9.0%, respectively, during the study period.

## 6.2. Impact of HONO and ClNO<sub>2</sub> on ozone formation in China

Photolysis of emitted and secondarily formed HONO during the daytime could significantly increase the levels of OH radicals that accelerate ozone formation (Aumont et al., 2003). However, early modeling studies of ozone mostly underestimated daytime HONO sources and thus their contributions to ozone production (Zhang et al., 2016). Elevated levels of HONO (0.15 to 3.24 ppbv) have been observed across the Jing-Jin-Ji (mostly Beijing), YRD, and PRD regions (Hendrick et al., 2014; Hou et al., 2016; Li et al., 2012b; Su et al., 2008; Xu et al., 2015) and were suggested to considerably enhance the ROx concentrations and accelerate the ROx cycles in these regions (Liu et al., 2012; Tang et al., 2015). Regional model simulations have suggested that elevated HONO in China could lead to an increase of 3 to 10 ppbv in the 8-hour maximum surface O<sub>3</sub> concentrations in most areas of the Jing-Jin-Ji region (An et al., 2013; Li et al., 2011), an increase of 60% to 250% in OH, HO<sub>2</sub>, and RO<sub>2</sub> levels in China's coastal regions, including the YRD (Tang et al., 2015), and an increase of 6% to 12% enhancement in the daily ground-level ozone concentration over the urban areas of the PRD region (Zhang et al., 2016).

ClNO<sub>2</sub> is formed at night via heterogeneous reactions of N<sub>2</sub>O<sub>5</sub> on aerosols that contain chloride. During the daytime, ClNO<sub>2</sub> is photolyzed to release chlorine atoms (Cl) and NO<sub>2</sub>, both of which affect ozone production (Osthoff et al., 2008; Thornton et al., 2010). Recent field measurements in the Jing-Jin-Ji and PRD (Hong Kong) regions found high levels of ClNO<sub>2</sub> (0.35–4.7 ppbv) that contribute 10% to 30% of primary ROx production in the morning hours and enhance the integrated daytime net ozone production by up to 13% at a rural site in the NCP and up to 41% at a mountain site in Hong Kong (Tham et al., 2016; Tham et al., 2014; Wang et al., 2016; Xue et al., 2015). Regional model simulations by Sarwar et al. (2014) suggest that ClNO<sub>2</sub> in China could reach up to 0.8 ppbv and lead to an increase of 7 ppbv in the 8-hour maximum ozone concentration. Li et al. (2016) suggested that across the PRD region the ClNO<sub>2</sub>, which was mostly concentrated within the residual layer (~300 m above the surface), increased O<sub>3</sub> by up to 16% within the PBL. These findings suggest a potentially important contribution of 'new' radical or radical sources to O<sub>3</sub> formation in polluted atmospheres such as in the eastern part of China. Photochemical air quality models should consider these sources and processes.

## 7. Effect of ozone on crops and human health

### 7.1. Effect on crops

Ozone is widely distributed in the troposphere, which means that its presence is found well beyond the more polluted cores of large cities. Thus it has the potential to damage crops and vegetation or affect human health in populations dispersed over continental areas. Ozone affects vegetation through a range of mechanisms (Bhatia et al., 2012), and its effects on crops in China have recently been reviewed by Feng et al. (2015). The interaction between vegetation and air pollution begins with the transfer to vegetation via turbulent diffusion. High ozone concentrations are found in spring, and typically in the afternoon when the wind speed is often low; i.e., conditions that limit the transfer of ozone. The phytotoxicity of ozone is largely due to its oxidative capacity and the generation of oxidizing entities such as OH, O<sub>2</sub><sup>-</sup> and H<sub>2</sub>O<sub>2</sub>. These attack the composition, structure, and function of the plasma membrane, and peroxide can be transported through the membrane and generate species that affect the signal chains via messenger molecules. Common symptoms of foliar injury are: changes in pigmentation, chlorosis and premature senescence; the effects on water use make crops appear to wilt (Feng et al., 2014). These processes affect plant growth, and McKee and Long (2001) suggested that the changes to allocation and development ozone causes are more important than its effects on photosynthesis and biomass accumulation.

Chameides et al. (1999) suggested that ozone concentrations across China were sufficiently enough to affect winter wheat production. More recently, Wang et al. (2012b) and Feng et al. (2015) argued that rising ozone concentrations pose problems for China's food security. These concerns are heightened by the possibility that changes in climate and precursor emissions seem likely to continue to increase and have led to a number of experimental studies, especially on the effect of ozone on wheat and rice (Feng et al., 2003; Wang et al., 2012b). Exposure to 62 ppb of ozone gives a yield reduction in China's field-grown rice of 14% to 20%, although wheat is more sensitive than rice (Wang et al., 2012b). Although a range of methods are available to estimate the yield loss, they can give very different values. In the case of spring wheat across China (which is more affected than winter wheat), the predicted losses in yield for 2020 vary between 2% and 29%. In the case of rice, the losses may be between 3.7% and 10%. Losses of summer corn may be as much as 64% and soybeans 45% by 2020, although these estimates are also highly variable (Feng et al., 2015).

Clearly more work is needed given the large uncertainties in the likely impact of ozone on food crops, but such studies may contribute to the development of air quality standards for crops. Although it is desirable to reduce ambient ozone concentrations in agricultural areas, a more immediate approach may be to choose more resistant crop varieties (e.g., Feng et al., 2015).

### 7.2. Effects on human health

Human health is also affected by exposure to ozone and epidemiological studies have demonstrated an association between ambient ozone levels and premature mortality. Ozone is a pulmonary irritant that affects respiratory mucous membranes and other lung tissues. A reduction in lung function means that exposure to elevated concentrations can lead to increased hospital admissions for pneumonia, chronic obstructive pulmonary disease, asthma, allergic rhinitis, and other respiratory diseases. There is likely a causal relationship between cardiovascular outcomes and short-term exposure (<30 days), with indications of biological disease mechanisms below the air quality standard of 75 ppbv (Goodman et al., 2015). It is now recognized that short-term exposures to ozone is also linked to childhood asthma, but the causality has yet to be established (Sousa et al., 2013). It has often been suspected that ozone has a synergistic relationship with other pollutants, and in line with this there are recent observations of this in relationship to asthma (Alexis and Carlsten, 2014).

The ozone standards set by the WHO (2005) are based on the small but convincing, associations between daily mortality rates and ozone concentrations, which suggested the need for a downward revision of the earlier value of  $120 \mu\text{g m}^{-3}$  to  $100 \mu\text{g m}^{-3}$  for the 8-hour maximum concentration. New regulations in China reflect these changes, suggesting that ozone air quality standards (GB 3095-2012) for class 1 (remote) areas mandate daily 8-hour and 1-hour maxima of 100 and  $160 \mu\text{g m}^{-3}$ , respectively, whereas for class 2 (urban/industrial and surrounding rural) areas, these values are 160 and  $200 \mu\text{g m}^{-3}$ , respectively. There is little evidence of a threshold, and recent work supports sensitivity even to low concentrations. The absence of a threshold argues for more stringent regulations (Goodman et al., 2015; WHO, 2005), and this must be especially true for class 2 urban areas.

However, appropriate metrics (Li et al., 2015b) and the difference between indoor and outdoor concentrations (ozone is readily deposited on indoor surfaces) can make exposure estimates problematic and likely health impacts uncertain (e.g. Chen et al., 2012). Although numerous studies have been done on the epidemiology of ozone (e.g. Bell et al., 2007; Bell et al., 2004), they are less common in China (e.g. Yang et al., 2012). Some have examined the acute effects of ambient ozone and ozone metrics in Guangzhou (Li et al., 2015b) and Suzhou (Yang et al., 2012). In cities in the PRD region, increases of  $10 \mu\text{g m}^{-3}$  in ozone concentrations over the prior 2 days were associated with a 0.81% increase in the mortality rate (Tao et al., 2012). In Hong Kong, Wong et al. (2006)

suggested that the greatest respiratory effects of air pollution are on relatively chronic obstructive pulmonary diseases, with ozone having the greatest effect at 1.034 for a  $10 \mu\text{g m}^{-3}$  increase in concentration. More recently, Liu et al. (2013) observed a seasonal sensitivity to ozone exposure in Guangdong, with the effects of ozone lasting longer on cold days with a 3.34% increase for  $10 \mu\text{g m}^{-3}$  accumulating over a 6 day lag period. Shanghai showed a shorter 2-day lag during the cold season, with a 0.45% increase (Zhang et al., 2006).

Studies of the regional distribution of the global disease burden (e.g. Brauer et al., 2016) have indicated significant risks from exposure to outdoor air pollutants in China, drawing particular attention to particulate matter and ozone. Throughout China, the financial burden of air pollution in terms of medical expenses and wage and leisure loss is seven times higher for particulate matter than for ozone (Matus et al., 2012). However, any future increases in ozone will tend to elevate the importance of ozone, because as a secondary pollutant it is generally more difficult to regulate. A key obstacle to understanding the health effects of ozone is the paucity of studies in China that explore the effects across the breadth and geographical diversity of the country. In addition, the strong gradient between indoor and outdoor ozone concentrations influences human exposure.

### 8. Summary and recommendations

This review focuses on published research findings in English-language literature on surface ozone processes in China, including ozone abundance and its relationship to atmospheric dynamics and chemical processes. We offer the following conclusions and recommendations:

- The available data have clearly shown serious ozone pollution in China's major cities, especially in the three most developed regions, namely "Jing-Jin-Ji," the YRD, and the PRD. Data from other populated and fast-developing regions are needed to get the full picture of ozone pollution in China. In this regard, it is strongly suggested that the ozone data from nation-wide air monitoring networks be made available for such assessments.
- Measurements and modeling studies have revealed that in most urban and industrial regions in the eastern half of China, ozone production is limited by VOCs. However, more studies in forested areas downwind of urban/industrial centers are needed to determine the transition to NOx dominated regimes and to develop ozone precursor control strategies. In view of successful NOx control in coal fired power plants since 2010 but delayed actions in reducing VOCs emissions, it is likely that some regions will change to NOx-limited regimes. It is recommended that implementation of measures to control VOCs along with NOx should be speeded up.
- Reactive aromatics are found to be the predominant contributor to ozone formation in many urban areas in China. Control measures targeting solvent use along with vehicular emissions are advised.
- Cross-boundary transport has been shown to be an important cause of high ozone events in Beijing, Shanghai, and Hong Kong, highlighting the need to control precursors not only in the jurisdiction concerned but also over larger regions.
- Despite a good understanding of the overall ozone formation mechanism, recent research has revealed some new sources of radicals (e.g., additional sources of HONO and chlorine from the photolysis of ClNO<sub>2</sub>) that require better understanding to improve the predictive capability of current photochemical models. Some processes involve heterogeneous reactions (such as the uptake of N<sub>2</sub>O<sub>5</sub> on aerosol surfaces), which could be particularly important in China in view of the high aerosol loading in China's atmosphere.
- In recent years, numerous VOCs measurement programs have been undertaken by both the research community and government agencies. Inter-comparison of the measurement techniques of different groups is needed to ensure data comparability in view of the technical difficulties in sampling, identifying, and quantifying hundreds of VOCs.



- Most previous field studies were conducted at surface sites, and more vertical measurements of chemical and meteorological parameters are needed to understand the processes in the whole boundary layer and the exchanges with the free troposphere.
- Research on the effects of ozone on human health and crops is limited relative to that on atmospheric processes. It is recommended that more research be conducted on the effects of ozone and consideration be given to further lowering the guideline values for Class 2 areas.

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