

## Tropospheric volatile organic compounds in China

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## Abstract

Photochemical smog, characterized by high concentrations of ozone (O<sub>3</sub>) and fine particles (PM<sub>2.5</sub>) in the atmosphere, has become one of the top environmental concerns in China. Volatile organic compounds (VOCs), one of the key precursors of O<sub>3</sub> and secondary organic aerosol (SOA) (an important component of PM<sub>2.5</sub>), have a critical influence on atmospheric chemistry and subsequently affect regional and global climate. Thus, VOCs have been extensively studied in many cities and regions in China, especially in the North China Plain, the Yangtze River Delta and the Pearl River Delta regions where photochemical smog pollution has become increasingly worse over recent decades. This paper reviews the main studies conducted in China on the characteristics and sources of VOCs, their relationship with O<sub>3</sub> and SOA, and their removal technology. This paper also provides an integrated literature review on the formulation and implementation of effective control strategies of VOCs and photochemical smog, as well as suggestions for future directions of VOCs study in China.

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**Keywords:** Volatile organic compounds; Ozone; Photochemical smog; China

## 1.1 Introduction

With rapid industrialization and urbanization in China, air pollution associated with photochemical smog and haze-fog, characterized by high levels of ozone (O<sub>3</sub>) and fine particulates (PM<sub>2.5</sub>), has become one of the most severe environmental pollution issues in many cities and regions of China (Zhang et al., 2008a, 2008b; Guo et al., 2009, 2013; Wang and Hao, 2012; Huang et al., 2014; Lee, 2015). The most polluted regions include the North China Plain (NCP; Beijing-Tianjin-Hebei region), Yangtze River Delta (YRD; Shanghai-Jiangsu-Zhejiang region) and Pearl River Delta (PRD; Guangdong-Hong Kong-Macau region) (Chan and Yao, 2008). Based on data collected at air monitoring stations in 74 cities throughout China (the largest and/or most polluted cities), it was found that the annual average concentration of PM<sub>2.5</sub> exceeded the national ambient air quality standard of 35 µg/m<sup>3</sup> in 71 cities, with the highest average value of 115 µg/m<sup>3</sup> (Liu et al., 2013a). The severity of PM<sub>2.5</sub> pollution has promoted the implementation of China's "Air Pollution Prevention and Control Action Plan", aimed at reducing the concentrations of PM<sub>2.5</sub> by 25%, 20% and 15% in the Beijing-Tianjin-Hebei region, the Yangtze River Delta and Pearl River Delta regions by 2017, respectively, compared to a 2012 baseline. High O<sub>3</sub> concentrations exceeding the national air quality standards have also been observed frequently in the aforementioned regions, with continuous increasing trends and the highest recorded 1-h O<sub>3</sub> mixing ratio of 286 ppbv, compared to the 1-h standard of 200 µg/m<sup>3</sup> or about 100 ppbv (Wang et al., 2006, 2009; Wang et al., 2014a, 2014b, 2014c, 2014d; Zhang et al., 2014). High concentrations of O<sub>3</sub> and PM<sub>2.5</sub> have detrimental effects on air quality, human health, visibility, climate change and ecological systems. Therefore, priority should be given to mitigating O<sub>3</sub> and PM<sub>2.5</sub> pollution in the most polluted cities and regions in order to affect a return to blue skies.

As key precursors of O<sub>3</sub> and secondary organic aerosols (SOA), (important constituents of PM<sub>2.5</sub>), volatile organic compounds (VOCs) are composed of hundreds of species, which are directly emitted into the atmosphere from a variety of natural and anthropogenic sources. The major anthropogenic emission sources of VOCs include vehicular exhaust, fuel evaporation, industrial processes, household products and solvent usage (Guo et al., 2011). Controlling VOCs emissions can be helpful to alleviate photochemical smog in cities and regions in China, especially because the production of O<sub>3</sub> in urban areas is usually limited by VOCs and because the loadings of SOA in PM<sub>2.5</sub> have become more significant in recent years (Huang et al., 2014; Cheng et al., 2010a, 2010b; Zhang et al., 2008a; Xu et al., 2008a, 2008b). Nevertheless, the development of an effective strategy to reduce photochemical smog in megacities based on the management of VOCs emissions is still problematic since each VOCs varies distinctly from others in its abundance and reactivity, which results in the nonlinear dependence of photochemical O<sub>3</sub> and SOA formation on VOCs. Furthermore, due to the dual roles of nitrogen oxides (NO<sub>x</sub>) in O<sub>3</sub> formation (fueling O<sub>3</sub> formation in low NO<sub>x</sub> environment and titrating O<sub>3</sub> in high NO<sub>x</sub> environment), VOCs reductions need to be considered in combination with patterns of NO<sub>x</sub> and the associated O<sub>3</sub>-VOCs-NO<sub>x</sub> sensitivities (Lyu et al., 2016a).

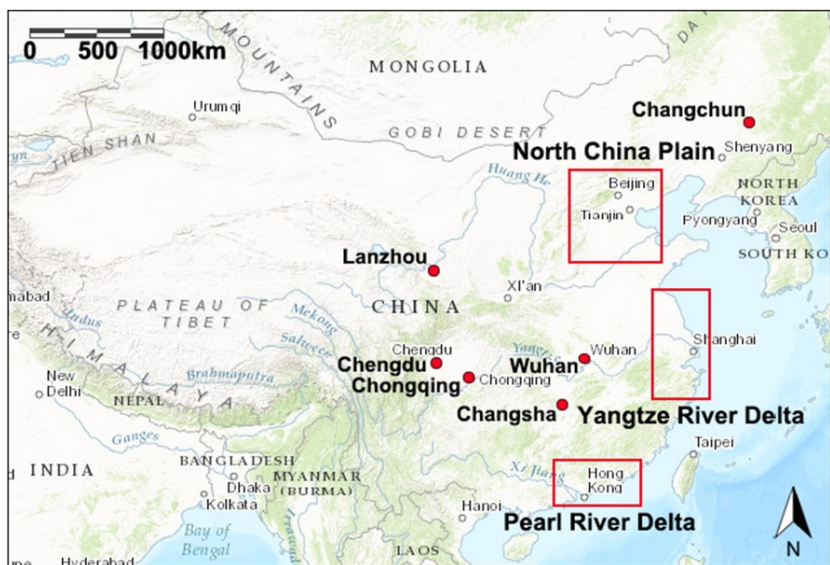
Photochemical smog in cities and regions will remain one of the top environmental concerns in the coming decades in China, especially since the emissions of VOCs and NO<sub>x</sub> are expected to increase in the near future (Ohara et al., 2007). To develop scientifically sound and effective control strategies on photochemical air pollution, a great deal of research sponsored by the Chinese central government and some local governments has been/is being conducted to investigate the characteristics of VOCs, including their abundances and sources, their roles in photochemical O<sub>3</sub> and SOA formation, and VOCs removal technology in different areas. The key research programs completed in Chinese cities in recent years include the "Campaigns of Air Quality Research in Beijing and Surrounding Regions (CARE-Beijing) (2006–2008)", the "Program of Regional Integrated Experiments of Air Quality over Pearl River Delta (PRIDE-PRD) (held biannually since 2004)", the "Synthesized Prevention Techniques for Air Pollution Complex and Integrated Demonstration in Key City Cluster Regions (3C-STAR) (2006–2011)", and the "Study of VOCs and Photochemical Ozone Pollution in the Pearl River Delta Region - Feasibility Study (2007–2010)" (Zhang et al., 2008b; Shao et al., 2009a; Louie et al., 2013). In addition, a number of research projects have been supported by the Ministry of Science and Technology (MOST) State Center and the Ministry of Environmental Protection (MEP) to help understand the current status of air pollution in China (Hao et al., 2007; Wang et al., 2010a, 2010b, 2010c; Wang and Hao, 2012). Therefore, it is timely to conduct a critical review on VOCs studies in Chinese cities

and regions. The cities selected in this review are situated in the most polluted and highly urbanized regions, *i.e.*, the NCP, YRD, and PRD. Although VOCs were also studied in some cities beyond the above regions, the number of these studies is relatively small compared to those in the aforementioned three regions. In addition, although hundreds of research papers on VOCs in the above regions are available in journals written in Chinese, this review mainly focuses on publications about tropospheric VOCs in the international peer-reviewed journals. Moreover, as the composition of VOCs in the atmosphere is complex, this paper only focuses on two categories of VOCs, *i.e.*, non-methane hydrocarbons (NMHCs) and carbonyl compounds, the main species contributing to the formation of photochemical O<sub>3</sub> and SOA. It should be noted that even though we have aimed to cover the major representative findings of VOCs in the above cities and regions, some studies may be not included in this review.

The contents of this review include the abundance and speciation of VOCs (Section 2), sources of VOCs (Section 3), the relationship of VOCs with O<sub>3</sub> and SOA (Section 4) and the development of the removal technology for VOCs (Section 5). Control strategies for VOCs/photochemical smog are reviewed in Section 6, together with their implications, while the future direction of VOCs studies is proposed in Section 7.

## 2.2 Abundance and speciation of VOCs

Since the properties of VOCs, such as toxicity, O<sub>3</sub> and SOA formation potentials depend strongly upon the concentrations and chemical compositions of VOCs, the abundance and speciation of VOCs have been extensively studied. One of the first speciated VOCs sampling campaigns in China was undertaken in 2001 (Barletta et al., 2005), in which VOCs were collected in 43 Chinese cities in the cold season (January and February). Since then, many efforts have been made to characterize the VOCs in various regions of China, particularly in the regions of NCP, YRD and PRD, as shown in Figure 1.



**Figure 1** Fig. 1 Geographic locations and extents of NCP, YRD and PRD in China.

alt-text: Fig. 1

Table 1 summarizes the main techniques used to analyze the chemical compositions of VOCs in air samples. Generally, the methods to obtain VOCs concentrations can be divided into online measurement and offline analysis. Whichever method is used, three units are integrated in the analysis system, *i.e.*, a pre-concentrator unit, a separation unit and a detection unit. With the pre-concentrator unit, VOCs are concentrated and the impurities, such as water and CO<sub>2</sub>, are removed. By thermal desorption, the concentrated VOCs sample is introduced into a gas chromatography (GC), where VOCs are separated by the columns. At last, the separated VOCs are sent to the detectors for quantification. Depending upon necessity, different columns are used, such as non-polar capillary columns and semi-polar columns. Mass spectrometric detector (MSD) and flame ionization detector (FID) are commonly used detectors, which can be separately applied or combined in the same system (see Table 1).

**Table 1** Table 1 Technique for VOCs analysis applied in previous studies.

alt-text: Table 1

instrument/system	Reference
Offline GC-MSD	Liu et al. (2005); Duan et al. (2008); Wang and Zhao (2008); Geng et al. (2009a, 2009b); Shao et al. (2009a); Cai et al. (2010); Han et al. (2015)
Offline GC-MS/FID	Song et al. (2007); Tang et al. (2007, 2009); Shao et al. (2009b); Guo et al. (2011); Zhu et al. (2016)
Online GC-MS/FID	Li et al. (2015)
Online GC-FID	An et al. (2014); Zou et al. (2015)
Online GC-FID/FID	Wang et al. (2008a, 2008b)

These analysis techniques provide information of mixing ratios of individual VOCs species, which are summed and defined as total VOCs (TVOCs) or total non-methane hydrocarbons (total NMHCs). Total NMHCs represent the sum of measured hydrocarbons except methane, regardless of the number of hydrocarbon species. For better comparison, the number of VOCs measured in each study was provided in this review.

## 2.1.2.1 Studies in the North China Plain region

The NCP region, with an area of ~ 300,000 ~~square kilometers~~ km<sup>2</sup>, is an important political and economic center in northern China (see Figure, 1). It lies between around 32°-41°N and 114°-121°E and stretches southward from the Yanshan Mountains to the Dabie Mountains. The NCP region has a typical temperate and monsoonal climate with four clearly distinct seasons (Fu et al., 2009). Due to the high population density and large amount of anthropogenic emissions, this region has been suffering from severe air pollution in recent years. Due to the adverse effects of VOCs on human health and their role in O<sub>3</sub> formation, numerous studies on VOCs have been carried out in this region (*e.g.*, Song et al., 2007; Shao et al., 2009b; Wang et al., 2012).

Table 3 summarizes the mixing ratios of total NMHCs reported by some representative studies in the NCP region. While VOCs concentrations are known to vary seasonally, typically with higher concentrations in winter and lower concentrations in summer, most of the studies presented in Table 3 were collected during a similar summer timeframe. Some studies reported results in units of ~~pg~~ µg/m<sup>3</sup> while others used ppbv, and we have provided unit conversions where possible. A study conducted during 2002-2003 reported an average total NMHCs concentration of 132.6 ± 52.2 µg/m<sup>3</sup> at six sites in Beijing (Liu et al., 2005). In August 2005, Song et al. (2007) detected the concentrations of 31 VOCs in central Beijing, which summed to 43.4 ppbv. Comparable mixing ratio of total NMHCs was observed in the northwest part of Beijing a year later (40.5 ppbv), according to Duan et al. (2008). Shao et al. (2009b) sampled VOCs at five urban sites in Beijing, where the mixing ratio of total NMHCs reached 33.2 ± 23.4 ppbv. A recent May 2014 study indicated that mixing ratios of total NMHCs in Beijing were 29.4 ppbv, higher than those in two adjacent cities in Hebei Province (Li et al., 2015). Furthermore, some long-term studies revealed the trends of VOCs in the atmosphere of Beijing. Wang et al. (2012) observed an increasing trend of total VOCs from 2000 to 2002, while they have tended to decrease since 2003. A reduction rate as high as 26.5% was recorded between 2006 and 2007. Consistently, the daytime VOCs levels in Beijing's summer were reduced by 1.8 ± 0.8 ppbv/year from 2005 through 2011 (Zhang et al., 2014). Although the number of vehicles remarkably increased in Beijing in these years, vehicular exhausts, particularly for gasoline vehicles, significantly decreased due to the continued implementation of control strategies (Wang et al., 2012; Zhang et al., 2014). In addition, studies were carried out in other cities in the NCP. For example, average mixing ratios of total NMHCs at an urban (92 ppbv) and a suburban site (174 ppbv) in Tianjin were measured by Han et al. (2015). The higher level at the suburban site was mainly due to stronger industrial emissions, which contributed 20% more to the total NMHCs than that at the urban site. In comparison, the concentration (16.1 ± 8.3 ppbv) was much lower at a rural site four years later in Yucheng, Shandong Province (Zhu et al., 2016). It is noticeable that anthropogenic emissions (*e.g.*, vehicular exhausts and industrial emissions) greatly elevated VOCs levels in the NCP region.

**Table 3.** Table 3 Mixing ratios (or concentrations) of total NMHCs in the North China Plain (NCP).

Sampling site	Site category	Sampling period	Mixing ratio (concentration) of total NMHCs	Number of VOCs species measured
Beijing <sup>a</sup>	Urban	March, July and November 2003	132.6 ± 52.2 µg/m <sup>3</sup>	108
Beijing <sup>b</sup>	Urban	August 2005	43.4 ppbv	31
Beijing <sup>c</sup>	Urban	August 2006	40.5 ppbv	57
Beijing <sup>d</sup>	Urban	August 2004-2006	33.2 ± 23.4 ppbv	20

Beijing <sup>e</sup>	Urban	May 2014	29.4 ppbv	56
Tianjin <sup>f</sup>	Urban	Summer 2009	92 ppbv	107
Tianjin <sup>f</sup>	Suburban	Summer 2009	174 ppbv	107
Yucheng <sup>g</sup>	Rural	June–July 2013	16.1 ± 8.3 ppbv	58

<sup>a</sup> Liu et al. (2005).

<sup>b</sup> Song et al. (2007).

<sup>c</sup> Duan et al. (2008).

<sup>d</sup> Shao et al. (2009b).

<sup>e</sup> Li et al. (2015).

<sup>f</sup> Han et al. (2015).

<sup>g</sup> Zhu et al. (2016).

Regarding the chemical compositions, Liu et al. (2005) reported that alkanes, aromatics and alkenes contributed 35%, 22% and 17% to the total 108 NMHCs in Beijing, respectively. Song et al. (2007) also found that alkanes were the most abundant group of VOCs in Beijing, contributing 43.7% to the sum of NMHCs. Shao et al. (2009b) measured 7 C<sub>3</sub>–C<sub>10</sub> alkanes, 8 C<sub>3</sub>–C<sub>8</sub> alkenes and 5 C<sub>6</sub>–C<sub>8</sub> aromatics, and found that VOCs in urban areas of Beijing were closely related to vehicular exhaust, as propane, propene and toluene were typical of the measured VOCs species. The study conducted by Li et al. (2015) in the Beijing-Tianjin-Hebei (BTH) region in May 2014 found that alkanes constituted > 50% of total NMHCs, with lower contributions of alkenes and aromatics. Specifically, the top 10 VOCs species among 28 alkanes, 12 alkenes and alkynes, and 16 carbonyls were C<sub>2</sub>–C<sub>5</sub> alkanes, C<sub>2</sub>–C<sub>3</sub> alkenes, benzene and toluene in this region. Among the carbonyl compounds, ketone was the most abundant species. Similarly, in the summer of 2013, 58 VOCs species were measured in Yucheng, a city in Shandong Province (Zhu et al., 2016). The results indicated that alkanes contributed the most (40.3%) of total VOCs, followed by halocarbons (29.1%), aromatics (13.6%), alkenes (11.2%) and alkynes (5.9%). In contrast, alkanes only ranked second in urban areas of Tianjin during a summer haze period (Han et al., 2015). Here, aromatics made the greatest contribution to total VOCs, accounting for 52%, while alkane and aromatic levels were comparable in suburban areas of Tianjin. Apart from the speciation in ambient air, chemical compositions of VOCs from different sources have also been studied. For example, Yuan et al. (2010) sampled and analyzed the VOCs emitted from painting applications and printing processes. They found that toluene and C<sub>9</sub> aromatics were the most abundant VOCs species in the emissions of painting applications, accounting for 76% of the total VOCs. In addition to aromatics, such as toluene and *m/p*-xylenes, heavy alkanes including *n*-nonane, *n*-decane and *n*-undecane were also important species in the emissions of printing processes. In terms of the on-road emissions of VOCs, Cao et al. (2016) stated that alkanes, aromatics and carbonyls were the dominant VOCs in the exhaust of light-duty gasoline vehicles, accounting for 36.4%, 33.1% and 17.4% of the total VOCs, respectively. In comparison, it was found that carbonyls dominated (42.7–69.2%) the VOCs emitted from three types of diesel trucks tested (Yao et al., 2015).

In summary, alkanes and aromatics were the most abundant VOCs in the NCP region, which implied high emissions of VOCs from vehicular exhausts and solvent use.

## 2.2.2.2 Studies in the Yangtze River Delta region

The YRD region, located in eastern China, is one of China's most economically developed regions. It consists of one megacity and two provinces, *i.e.*, Shanghai city, Jiangsu Province and Zhejiang Province. Approximately 158.9 million people (11.6% of the national population) live on the territory of 210,700 square kilometers km<sup>2</sup>, which is only 2.2% of China's total land area ([https://en.wikipedia.org/wiki/Yangtze\\_River\\_Delta](https://en.wikipedia.org/wiki/Yangtze_River_Delta)). The Gross Domestic Product (GDP) produced in this region is considerable. It contributed 20.25% of the total national GDP in 2014 (National Bureau of Statistics of the People's Republic of China, 2015). However, the dense population and rapid economic growth has also brought in severe air pollution into this region, such that photochemical pollution is becoming more and more outstanding. Since VOCs are key precursors of photochemical smog, they have been the subject of research in this region, particularly in recent years (Cai et al., 2010; An et al., 2014).

Table 4 lists the mixing ratios of total NMHCs reported in the YRD region. Based on the measurements in a commercial area of central Shanghai, Geng et al. (2009a) reported total NMHC mixing ratios of 30.3 and 38.7 ppbv in summer and winter, respectively. Consistently, another study carried out in the center of Shanghai from 2007 to 2010 found comparable level of total NMHCs (32.4 ppbv) (Cai et al., 2010). In contrast, the total NMHCs monitored at roadside sites in Nanjing (19.9 ppbv) were much lower than those measured in Shanghai (Wang and Zhao, 2008). It should be noted that only 11 VOCs were measured in the Nanjing study. In fact, An et al. (2014) measured 56 VOCs in an industrial area of Nanjing, which is the provincial capital of Jiangsu Province, and found that the mixing ratios of total NMHCs (43.5 ppbv) were higher than those in Shanghai. Additionally, studies were also conducted at a

rural/background site (Lin'an in Zhejiang province) in the YRD region. For example, Tang et al. (2009) quantified the mixing ratio of total NMHCs to be  $16.6 \pm 8.2$  ppbv at Lin'an. Note that the number of VOCs detected at Lin'an was the same or higher than that in other studies. Hence, the lower level of total NMHCs at this rural site implied the dominant emissions of anthropogenic sources in the YRD region (Geng et al., 2009a; An et al., 2014).

**Table 4.** Table 4 Mixing ratios of total NMHCs in the Yangtze River Delta (YRD).

alt-text: Table 4

Sampling site	Site category	Sampling period	Mixing ratio of total NMHCs	Number of VOCs measured
Shanghai <sup>a</sup>	Urban	2006–2008	Summer: 30.3 ppbv Winter: 38.7 ppbv	17
Shanghai <sup>b</sup>	Urban	April, July, October 2007–2010	32.4 ppbv	32
Nanjing <sup>c</sup>	Roadside	2006, and January 2007	19.9 ppbv	11
Nanjing <sup>d</sup>	Industrial	2011–2012	43.5 ppbv	56
Lin'an <sup>e</sup>	Rural	April–May 2004	$16.6 \pm 8.2$ ppbv	56

<sup>a</sup> Geng et al. (2009a).

<sup>b</sup> Cai et al. (2010).

<sup>c</sup> Wang and Zhao (2008).

<sup>d</sup> An et al. (2014).

<sup>e</sup> Tang et al. (2009).

The chemical compositions of VOCs in the YRD were also explored. Similar to those in the NCP region, ambient VOCs were dominated by alkanes and aromatics in the YRD. In central Shanghai, 6 C<sub>3</sub>–C<sub>6</sub> alkanes, 5 C<sub>6</sub>–C<sub>8</sub> aromatics and 6 C<sub>3</sub>–C<sub>5</sub> alkenes contributed 40–41%, 27–35%, and 8–11% to the total VOCs, respectively (Geng et al., 2009a). Similar results were also reported by Cai et al. (2010), with alkanes the most abundant group at 43% of total NMHCs, followed by aromatics (30%), halocarbons (14%) and alkenes (6%). Even though alkanes as a group were most abundant, toluene and propane exhibited the highest individual levels, reaching 4.81 and 4.70 ppbv on average, respectively. Several studies on the VOCs speciation in source emissions were also conducted in this region. For example, Huang et al. (2015a, 2015b) reported that single ring aromatics were mainly from diesel vehicles, while straight chain alkanes were the main components in the exhaust of gasoline vehicles. In addition, propane, *i*-pentane, *i*-butene and 1-pentene were the major species in gasoline evaporation, among which alkenes were of high proportion. Furthermore, VOCs speciation in the emissions of solvent usage was tightly related to the type of solvent products. Generally, aromatics and alkanes were the most abundant in the emissions of imported indoor solvents, while domestic indoor solvents had even higher emissions of aromatics (Huang et al., 2015a, 2015b). In addition, VOCs emitted from printing processes were mainly dominated by C<sub>2</sub>–C<sub>5</sub> hydrocarbons, as well as C<sub>8</sub>–C<sub>9</sub> aromatics (Wang et al., 2014a, 2014b, 2014c, 2014d).

### 2.3.2.3 Studies in the Pearl River Delta region

The PRD region, covering nine mainland cities and two special administrative regions (Hong Kong and Macau), is one of the most developed regions in China. It has a subtropical humid monsoon climate with average temperatures between 21.6 °C and 23.8 °C. With the land area of ~~more than 45 > 45,200 square kilometers~~ km<sup>2</sup>, around 57.7 million people live in this region. Since Chinese economic reform, the economy in the PRD has experienced booming growth. In 2014, GDP produced by this region accounted for 9.1% of the total national GDP (National Bureau of Statistics of the People's Republic of China, 2015). Almost without exception, environmental pollution is the consequence of rapid development in China. Industrial and vehicular emissions are causing severe photochemical pollution in the PRD region. As O<sub>3</sub> precursors, VOCs have been extensively and intensively studied in the PRD (Shao et al., 2009a; Guo et al., 2011; Zou et al., 2015).

The abundance of VOCs varies among different studies because of differences in sampling site, sampling period and VOCs species detected. Table 5 shows the mixing ratios or concentrations of total NMHCs in the PRD. Based on intensive field measurements of gaseous pollutants in summer and autumn in 2000, Shao et al. (2009a) reported the average VOCs concentration of 350 ppbC in the PRD. Wang et al. (2008a, 2008b) analyzed VOCs at an urban and rural site in autumn 2004, and found the average total NMHC values of 33.5 and 11.6 ppbv, respectively. In April 2005, VOCs at four sites in the PRD (*i.e.*, urban, suburban, rural and remote sites) were intensively sampled, and total

NMHCs were  $88.8 \pm 38.6$ ,  $60.8 \pm 31.5$ ,  $23.4 \pm 9.8$  and  $4.8 \pm 1.9$  ppbv, respectively (Tang et al., 2007). Another multi-site study was carried out in July 2006 by Yuan et al. (2012). The average total NMHCs were  $41.2 \pm 16.5$  and  $36.9 \pm 10.2$  ppbv at the two urban sites, much higher than at the suburban site ( $19.6 \pm 12.0$  ppbv) and the rural sites ( $13.9 \pm 9.1$  ppbv). Furthermore, Zou et al. (2015) measured 56 individual VOCs species in suburban Guangzhou with an online instrument for one year. The average mixing ratio of total NMHCs was 42.7 ppbv, varying from 34.6 ppbv in March to 63.6 ppbv in November. Inland PRD cities are adjacent to and often upwind of Hong Kong, and Guo et al. (2011) found that the total NMHC mixing ratio at a suburban site in inland PRD ( $42 \pm 9$  ppbv) was comparable to that in a downtown suburban site in Hong Kong ( $34 \pm 5$  ppbv). A long-term study at a suburban site in Hong Kong from 2005 to 2013 suggested that the concentration of total NMHCs increased with an average rate of  $0.34 \pm 0.02$  ppbv/year (Ou et al., 2015a).

**Table 5.** Table 5 Mixing ratios of total NMHCs in the Pearl River Delta (PRD).

alt-text: Table 5

Sampling site	Site category	Sampling period	Mixing ratio of total NMHCs	Number of VOCs measured
PRD <sup>*a</sup>	Urban	Summer and autumn 2000	350 ppbC	N.A.
PRD <sup>*b</sup>	Urban	October–November 2004	33.5 ppbv	10
	Suburban		11.6 ppbv	10
PRD <sup>*b</sup>	Urban	April 2005	$88.8 \pm 38.6$ ppbv	56
	Suburban		$60.8 \pm 31.5$ ppbv	56
	Rural		$23.4 \pm 9.8$ ppbv	56
	Remote		$4.8 \pm 1.9$ ppbv	56
PRD <sup>*c</sup>	Urban	July 2006	$41.2 \pm 16.5$ ppbv	56
	Urban		$36.9 \pm 10.2$ ppbv	56
	Suburban		$19.6 \pm 12.0$ ppbv	56
	Rural		$13.9 \pm 9.1$ ppbv	56
Guangzhou <sup>d</sup>	Suburban	June 2011–May 2012	42.7 ppbv	56
Wanqingsha <sup>e</sup>	Suburban	October–December 2007	$42 \pm 9$ ppbv	16
Tung Chung <sup>e</sup>	Suburban	October–December 2007	$34 \pm 5$ ppbv	16

N.A.: not available.

\* Refers to different cities in PRD.

<sup>a</sup> Shao et al. (2009a,b).

<sup>b</sup> Tang et al. (2007).

<sup>c</sup> Yuan et al. (2012).

<sup>d</sup> Zou et al. (2015).

<sup>e</sup> Guo et al. (2011).

In line with the other regions in China, alkanes and aromatics are the main components of VOCs in the PRD (Guo et al., 2006; Tang et al., 2007; Liu et al., 2008a; Louie et al., 2013). For example, a comparative study between Guangzhou and Dongguan (two cities in the PRD) in September 2005 indicated that propane (average of 6.8 ppbv) was the most abundant VOCs species among 50 detected NMHCs in Guangzhou of northwestern PRD, followed by toluene and ethyne. In contrast, toluene (average of 6.1 ppbv) was the most abundant in Dongguan of northern PRD, followed by ethyne and ethene (Barletta et al., 2008). Guo et al. (2011) conducted a field study on 16 VOCs in autumn



2007 in Wanqingsha, a suburban area in the central PRD, and found that ethene, ethyne, C<sub>2</sub>–C<sub>6</sub> alkanes, and toluene were the most abundant species. Based on a two-year grid study, Louie et al. (2013) measured oxygenated VOCs (OVOCs) in the PRD region. Formaldehyde, acetone, acetaldehyde, methylglyoxal, 2-butanone and glyoxal were the top five OVOCs, accounting for 87% of total OVOCs. In order to understand VOCs characteristics at roadsides sites, Lee et al. (2002) sampled VOCs at five roadside sites in Hong Kong from 1997 to 1999. Among the 12 VOCs detected, toluene was the highest. Benzene, toluene, ethylbenzene and xylenes constituted > 60% of the total detected VOCs. However, the C<sub>2</sub>–C<sub>5</sub> hydrocarbons were not measured in this study. Furthermore, Ho et al. (2004) confirmed that toluene was the most abundant VOCs based on measurements at an urban site and an industrial site in Hong Kong during 2000–2001 with average concentrations of ~ 6.3 ppbv and ~ 15.6 ppbv, respectively. Consistently, Guo et al. (2004a, 2004b) also reported the highest concentration of toluene in the atmosphere of urban and suburban Hong Kong in 2001, based on a study of 97 VOCs. A multi-site study involving an urban site, two suburban sites and a rural site also showed that toluene ranked the first in VOCs in Hong Kong, followed by the C<sub>2</sub>–C<sub>4</sub> hydrocarbons (ethane, ethene, ethyne, propane and *n*/*i*-butanes) (Guo et al., 2007). However, the VOCs sampled recently at a suburban site in Hong Kong revealed that the average mixing ratios of propane (3348 ± 239 pptv) and *n*/*i*-butanes (4370 ± 393 pptv/2597 ± 205 pptv) have now exceeded that of toluene (2548 ± 275 pptv) (Lam et al., 2013). This change was caused by the increased use of liquefied petroleum gas (LPG) as the main fuel of taxis and public light buses in Hong Kong since 2001. A long-term study of VOCs in Hong Kong also indicated that C<sub>3</sub>–C<sub>5</sub> alkanes slightly increased between 2005 and 2013 (Ou et al., 2015a). However, aromatics decreased with a rate of 0.23 ppbv/year in these years.

## 2.4.2.4 Studies in other regions in China

With the intensification of photochemical pollution, studies on VOCs have been progressively carried out in other regions/cities in China. Wuhan, a rapidly developing city in central China, is also suffering from severe photochemical pollution. Lyu et al. (2016b) found that the average mixing ratio of total NMHCs at an urban site in Wuhan was 23.3 ± 0.5 ppbv, in which ethane, ethene and toluene were the most abundant species, with mixing ratios of 5.2 ± 0.2, 3.3 ± 0.2 and 2.0 ± 0.1 ppbv, respectively. In Changsha in central China, aromatics showed the highest levels, representing 53% of the 48 NMHCs including 25 alkanes, 15 alkenes and 8 aromatics (Zhang et al., 2009). Toluene was the most abundant species (average mixing ratio of 2.51 ± 1.87 ppbv), followed by benzene (2.04 ± 1.30 ppbv). In the Chengdu-Chongqing Region (CCR) (Midwest China), Li et al. (2014a, 2014b) indicated that alkanes and methanol were the most abundant species in NMHCs and OVOCs, respectively, in a case study of biomass burning, with contributions of 59% and 42%, respectively. In Lanzhou, a city in western China, Jia et al. (2016) reported an average NMHC mixing ratio of 38.3 ppbv. Alkanes, alkenes and aromatics accounted for 57%, 23% and 20% of the total NMHCs, respectively, among which toluene (4.62 ppbv) and propane (4.56 ppbv) were the most abundant. Apart from the studies on VOCs composition in ambient air, the VOCs emitted from specific sources were also characterized. For example, coal-fired stationary sources in Liaoning province were studied by Shi et al. (2015). The results indicated that aromatics were the most abundant VOCs in heating station plants (69.1%), while ketones, alcohols and acetates comprised 45.0% of TVOCs in thermal power plants.

## 2.5.2.5 Comparison with other cities in the world

Table 6 lists the levels of total NMHCs in China and other countries reported in some studies. Though few studies showed comparable levels in cities in China and other countries, *e.g.*, 40.5 ppbv in Beijing in August 2006 (Duan et al., 2008) compared to 41.28 ppbv in Los Angeles in 2008 (Warneke et al., 2012), the levels of total NMHCs in China were generally higher than those in developed countries, regardless of the site categories. The mixing ratios of total NMHCs in rural areas of China (*e.g.*, 16.6 ± 8.2 ppbv and 23.4 ± 9.8 ppbv in eastern and southern China, respectively) (Tang et al., 2007, 2009) were much higher than those in rural Europe (4.01 ppbv in London and 6.04 ppbv at three French sites) (Sauvage et al., 2009; Von Schneidmesser et al., 2010). Furthermore, the total NMHCs in urban and suburban areas of developed countries, such as the United States (Mohamed et al., 2002), England (Von Schneidmesser et al., 2010) and Japan (Tiwari et al., 2010), were noticeably lower than those (*e.g.*, 132.6 ± 52.2 ppbv in urban Beijing) in Chinese cities (Liu et al., 2005; Tang et al., 2007; Han et al., 2015; Zou et al., 2015). The results revealed that China has been suffering from more serious air pollution than cities in the USA, Europe and Japan. It should be noted that considerable uncertainties exist in the comparison due to the differences in sampling site, sampling period, and number and species of VOCs analyzed.

**Table 6.** Comparison of total NMHCs levels **in cities** between China and **cities in** other countries. Bolded are the cities or regions in China.

Sampling site	Site category	Sampling period	Mixing ratio or concentration of total NMHCs	Number of VOCs species measured
Beijing <sup>a</sup>	Urban	March, July and November 2003	132.6 ± 52.2 μg/m <sup>3</sup>	108
Beijing <sup>b</sup>	Urban	August 2006	40.5 ppbv	57
Tianjin <sup>c</sup>	Urban	Summer 2009	92 ppbv	107
Shanghai <sup>d</sup>	Urban	April, July, October 2007–2010	32.4 ppbv	32



PRD <sup>*e</sup>	Urban	April 2005	88.8 <sub>±</sub> 38.6 ppbv	56
Tianjin <sup>c</sup>	Suburban	Summer 2009	174 ppbv	107
Guangzhou <sup>f</sup>	Suburban	June 2011–May 2012	42.7 ppbv	56
Nanjing <sup>g</sup>	Industrial	2011–2012	43.5 ppbv	56
Lin <sup>d</sup> an <sup>h</sup>	Rural	April–May 2004	16.6 <sub>±</sub> 8.2 ppbv	56
PRD <sup>*e</sup>	Rural	April 2005	23.4 <sub>±</sub> 9.8 ppbv	56
Northeastern and southern U.S. <sup>i</sup>	Urban	September 1996 to August 1997	11.93 ppbv	54
Los Angeles <sup>j</sup>	Urban	2008 whole year	41.28 ppbv	26
Houston <sup>k</sup>	Urban	August–September 2006	31.7 ppbv	60
Alberta, Canada <sup>l</sup>	Urban	2003–2009	65 µg/m <sup>3</sup>	> 70
London <sup>m</sup>	Urban	2008 whole year	22.1 ppbv	18
Tokyo <sup>n</sup>	Urban	April 2003–March 2005	43.4 ppbv	54
Yokohama, Japan <sup>o</sup>	Residential (suburban)	June 2007–November 2008	24.39 ppbv	38
Yokohama, Japan <sup>o</sup>	Industrial	June 2007–November 2008	47.93 ppbv	38
London <sup>m</sup>	Rural	2008 whole year	4.01 ppbv	18
3 French sites <sup>p</sup>	Rural	1997–2006	6.04 ppbv	46

\* Refers to different cities in PRD.

<sup>a</sup> Liu et al. (2005).

<sup>b</sup> Duan et al. (2008).

<sup>c</sup> Han et al. (2015).

<sup>d</sup> Cai et al. (2010).

<sup>e</sup> Tang et al. (2007).

<sup>f</sup> Zou et al. (2015).

<sup>g</sup> An et al. (2014).

<sup>h</sup> Tang et al. (2009).

<sup>i</sup> Mohamed et al. (2002).

<sup>j</sup> Warneke et al. (2012).

<sup>k</sup> Leuchner and Rappengluck (2010).

<sup>l</sup> McCarthy et al. (2013).

<sup>m</sup> Von Schneidemesser et al. (2010).

<sup>n</sup> Hoshi et al. (2008).

° [Tiwari et al. \(2010\)](#).

p [Sauvage et al. \(2009\)](#).

## 3.3 Sources of VOCs

The sources of VOCs are important references for formulating and implementing effective control measures. Generally, the ratios between specific VOCs and receptor models, such as positive matrix factorization (PMF), principal component analysis - absolute principal component score (PCA-APCS) and chemical mass balance (CMB), are tools commonly used for source identification and/or apportionment. As a bottom-up approach, emission inventories can also quantify the source contributions to VOCs.

### 3.1.3.1 The North China Plain region

Based on measurements at six sites in Beijing from 2002 to 2003, [Liu et al. \(2005\)](#) analyzed the potential sources of VOCs using CMB. Vehicular exhaust contributed 57.7% to the total VOCs, followed by painting operations (12.4%), gasoline vapor (11.3%), and LPG (5.8%). In August 2005, VOCs collected in Beijing were apportioned to eight sources by PMF, among which gasoline-related emissions, petrochemicals and LPG were the main contributors, with the contribution of 52%, 20% and 11%, respectively ([Song et al., 2007](#)). [Yuan et al. \(2009\)](#) conducted a comparative study using PMF to distinguish the VOCs sources at an urban and a rural site in Beijing in 2006. Vehicle-related emissions made the greatest contribution to VOCs at both sites, *i.e.*, 62% at the urban site and 38% at the rural site, followed by LPG (13% and 37%, respectively) and paint & industrial coatings (16% and 14%, respectively). Using data collected in August 2006, [Duan et al. \(2008\)](#) qualitatively identified the sources of VOCs in the northwest part of Beijing using PCA. The results indicated that combustion activities, solvent usage and biogenic emissions were the main sources of NMHCs, while vehicle emissions, cooking and biogenic sources mainly contributed to the carbonyls. Furthermore, PMF for source apportionment was applied to long-term measurements of VOCs in Beijing every August from 2004 to 2012 ([Wang et al., 2015a, 2015b](#)). Four sources including gasoline evaporation, vehicle exhausts, LPG and natural gas usage and background, and paint and solvent use and industry were resolved. From 2004 to 2012, gasoline evaporation and vehicle exhaust decreased significantly over years, while there were no significant changes in the paint, solvent use and industry source. Apart from the source apportionment of TVOCs, some studies focused on the sources of the individual VOCs ([Liu et al., 2008b](#); [Liu et al., 2009a, 2009b](#)). For example, [Liu et al. \(2009a, 2009b\)](#) quantified the source contributions to C<sub>2</sub>-C<sub>3</sub> alkenes, isoprene and C<sub>1</sub>-C<sub>3</sub> aldehydes in Beijing, and found that secondary formation contributed nearly 50% to C<sub>1</sub>-C<sub>3</sub> aldehydes.

Consistent with its high contributions in Beijing, vehicular exhaust was also identified as the main VOCs source in Tianjin, contributing 60% and 42% to VOCs at urban and suburban sites, respectively, based on a study in 2009, while 36% and 16% of VOCs were emitted from industries, respectively ([Han et al., 2015](#)). By contrast, the emission inventories indicated that industrial activities emitted 44.9% of VOCs, even higher than the vehicle emissions (23.8%) in Tianjin ([Li et al., 2015](#)).

It should be noted that different models can produce different results in source apportionment. Hence, several studies compared the results acquired from more than one models ([Song et al., 2008](#); [Yuan et al., 2009](#); [Liu et al., 2016a, 2016b](#)). For example, [Song et al. \(2008\)](#) used PMF, CMB and UNMIX models to define the sources of VOCs in Beijing. The results indicated that gasoline-related sources, petrochemical production, and LPG were identified as the major contributors by all three models. The source profiles and contributions were fairly similar between PMF and UNMIX. However, the contributions of gasoline-related sources and LPG estimated by CMB (60.7% and 26.4%, respectively) were higher than those estimated by PMF (51.5% and 11.0%, respectively) and UNMIX (48.3% and 19.9%, respectively), while petrochemical emissions were lower.

In conclusion, though sampling site and period, VOCs species selected, and models or techniques utilized might all influence the results of VOCs source apportionments, the common finding was that vehicle-related emissions were the most predominant contributor to VOCs in the NCP region. It should be noted that most of the studies reviewed for the NCP were conducted in Beijing, where the weather conditions and emission sources might be different from those in other cities in the NCP. Further studies are necessary, particularly in the surrounding cities of Beijing, such as those highly industrialized cities in Hebei Province.

### 3.2.3.2 The Yangtze River Delta region

To understand the sources of VOCs in the YRD, [Cai et al. \(2010\)](#) used PMF to resolve the sources of the measured VOCs from 2007 to 2010 in central Shanghai. The results indicated that vehicle related emissions contributed 25% to the total NMHCs, followed by industrial emissions (17%), fuel evaporation (15%), paint solvent usage (15%), steel related industrial production (12%), biomass/biofuel burning (9%) and coal burning (7%). Similarly, for source apportionment PCA-APCS was applied to the VOCs data collected between 2006 and 2008 in the center of Shanghai, and four sources were identified, including fuel leakage and evaporation, vehicle exhaust, solvent usage and industrial production, and biomass/biofuel/coal burning and other natural sources ([Geng et al., 2009a](#)). Solvent usage and industrial production together made the highest contribution to VOCs, *i.e.*, 35% and 48% in summer and winter, respectively. These contributions were comparable to the sum (46%) of the contributions of industrial emissions, paint solvent usage and steel related industrial production reported by [Cai et al. \(2010\)](#). In an industrial area of Nanjing, [An et al. \(2014\)](#) found that industrial emissions accounted for 45-63% of the VOCs, with the remainder from automobile emissions (34-50%). In addition to studies in urban and industrial areas, [Guo et al. \(2004c\)](#) explored the sources

of VOCs sampled at a rural site in Lin'an, Zhejiang province. The results indicated that  $71 \pm 5\%$  of VOCs could be attributed to the combination of vehicle emissions and biofuel burning, followed by biomass burning ( $11 \pm 1\%$ ), industrial emissions ( $11.00 \pm 0.03\%$ ), and gasoline evaporation and solvent emissions ( $7 \pm 3\%$ ).

On the basis of emission inventories, Huang et al. (2011a, 2011b) stated that industrial sources, including power plants and other fuel combustion facilities, and non-combustion processes contributed about 69% of the TVOCs emissions in 2007. By contrast, vehicle emissions only accounted for 12.4%. However, based on a different emission inventory from 2010, emissions from industrial process only accounted for 33.7% of the total NMVOCs (Fu et al., 2013). The large discrepancy might be due to the differences in VOCs species measured, activity levels, emission factors and VOCs emission sectors considered.

Overall, vehicular emission was an important source of VOCs in the YRD, similar to that in the NCP. However, industrial emissions played more critical role in this region. It is noteworthy that the extent of previous studies was still insufficient to fully understand the sources of VOCs in the YRD region (Cai et al., 2010; An et al., 2014). The need for further studies is urgent.

### 3.3.3.3 The Pearl River Delta region

With the aid of the CMB model, Liu et al. (2008a) extracted 12 sources from 134 VOCs measured at seven sites in the PRD in the fall of 2004. Overall, vehicular exhaust was the most predominant source at the urban sites, contributing to > 50% of the VOCs. This is in contrast to solvent usage, which played an important role ( $\sim 30\%$  of VOCs) at an industrial and a non-urban site. Additionally, LPG leakage represented  $8 \pm 16\%$  of VOCs in PRD. Zheng et al. (2009) established a speciated VOCs emission inventory in the PRD, in which the exhausts of gasoline vehicles, diesel vehicles and motorcycles made the highest contribution ( $45.5 \pm 51.5\%$ ) to VOCs emissions. In Dongguan (a highly industrialized city), 28.2% VOCs were emitted from solvent usage, comparable to that ( $\sim 30\%$ ) quantified by a receptor model. However, the contribution of LPG ( $0.2 \pm 0.6\%$ ) to total VOCs as determined by emission inventory was much lower. Besides the inherent uncertainties of both methods, the long lifetimes of LPG related VOCs (propane and *n*-butanes) might enlarge their fractions among the total VOCs, because the reactive species (*e.g.*, alkenes and aromatics) were significantly consumed through photochemical reactions (Zheng et al., 2009). The problem lies in the fact that the receptor models quantify the source contributions in ambient air, rather than in emission strength, which is the basis of emission inventory. In 2007, Ling et al. (2011) analyzed the sources of VOCs in the central PRD with the PMF model, and found that solvent usage and vehicular emissions were the most significant sources, with contributions of  $\sim 51\%$  and  $\sim 37\%$ , respectively. At the same site, similar results were reported by Guo et al. (2011) in 2007, that solvent usage and vehicular emission contributed  $46 \pm 1$  and  $26 \pm 1\%$  to the ambient VOCs.

Hong Kong, as the most developed area in the PRD, has made great efforts in air quality improvement. Numerous studies have focused on the sources of VOCs, which are the key precursors of photochemical smog. Using the technique of PCA-APCS, Guo et al. (2004a) probed the sources of VOCs sampled at an urban and a suburban site in Hong Kong in 2001. Vehicle exhaust made the highest contributions to total NMHCs (39% and 48% at the urban and suburban site, respectively), followed by solvent usage, LPG/natural gas leakage and industrial emissions. In 2002–2003, a concurrent sampling campaign was conducted at four sites (an urban site, two suburban sites and a rural site) in Hong Kong (Guo et al., 2007). This study again demonstrated the important role of vehicular emissions to ambient VOCs in urban ( $65 \pm 36\%$ ) and suburban ( $50 \pm 28\%$  and  $53 \pm 41\%$ ) Hong Kong. At these same four sites, source apportionment was conducted on the VOCs collected between 2006 and 2007 (Lau et al., 2010). It was found that emissions from traffic sources were the largest contributor to ambient VOCs, followed by solvent usage and aged air masses. Furthermore, they found that the contributions of LPG increased by  $118 \pm 184\%$  from 2002–2003 to 2006–2007. Based on the sampling at a suburban site in autumn 2010, Ling and Guo (2014) found that gasoline vehicle emissions, LPG usage and diesel exhaust were the main contributors, accounting for  $30 \pm 3$ ,  $21 \pm 2$  and  $20 \pm 2\%$  of TVOCs, respectively. A long-term study covering the period of 2005–2014 was conducted at another suburban site in Hong Kong (Ou et al., 2015a). The results showed that vehicular exhaust, gasoline evaporation and LPG usage, consumer product and printing, architectural paints, and biogenic emissions on average accounted for  $20.2 \pm 6.2\%$ ,  $25.4 \pm 6.3\%$ ,  $32.6 \pm 5.8\%$ ,  $21.5 \pm 4.5\%$ , and  $3.3 \pm 1.5\%$  of total NMHCs, respectively, and no significant changes were found for the solvent-related and traffic-related sources over the period.

Consistent with the findings in the NCP and YRD regions, vehicular exhaust was the dominant source of VOCs in the PRD region. Furthermore, solvent usage also made considerable contribution to VOCs, particularly in inland PRD where industries with solvent usage such as furniture manufacturing and shoes making, emitted a large amount of VOCs to the atmosphere.

### 3.4.3.4 Other regions in China

In recent years source apportionment studies on the sources of VOCs in other regions/cities in China have also been carried out. In Wuhan, capital of Hubei Province in central China, Lyu et al. (2016b) identified the sources of VOCs with the PMF model, and found that vehicular exhaust ( $27.8 \pm 0.9\%$ ) and coal burning ( $21.8 \pm 0.8\%$ ) were the main contributors to VOCs. Still in central China, Zhang et al. (2009) reported that vehicle exhaust was the dominant source of NMHCs in Changsha, capital of Hunan Province, including a large portion of propane due to the use of LPG as vehicle fuel. Similar results were also found in Changchun (an industrial city in northeastern China) showing that vehicle exhausts were the main contributors to VOCs (Liu et al., 2000). PCA associated with multiple linear regressions (MLR) was applied to identify the dominant emission sources of VOCs in downtown Lanzhou (capital of Gansu Province in western China) (Jia et al., 2016). Vehicle emission, solvent usage and industrial activities were major sources, accounting for 58.3%, 22.2% and 19.5% of the total monitored NMHCs, respectively.

## 4.4 Relationship of VOCs with O<sub>3</sub> and SOA

In the atmosphere, O<sub>3</sub> is produced *via* a series of photochemical reactions involving VOCs and nitrogen oxides (NO<sub>x</sub>). Photochemical O<sub>3</sub> formation is a non-linear function dependent on the relative concentrations of VOCs and NO<sub>x</sub> and the mix of reactive VOCs in the atmosphere. This has been classified into two categories: VOC-limited and NO<sub>x</sub>-limited. In the VOC-limited regime (the relative ratio of [NO<sub>x</sub>]/[VOC] is high), photochemical O<sub>3</sub> formation decreases with the decreasing VOCs levels (resulting from the control of VOCs emissions), while in the NO<sub>x</sub>-limited regime (low [NO<sub>x</sub>]/[VOC] ratio), any reduction in the NO<sub>x</sub> concentration would shorten the O<sub>3</sub> formation chain length and reduce photochemical O<sub>3</sub> formation (Sillman, 1999; Jenkin and Clemitshaw, 2000). In this section, the relationship between O<sub>3</sub> and its precursors, the reactivity of VOCs and the contribution of VOCs to SOA formation in Chinese cities and regions are discussed.

#### **4.1.4.1 VOC-limited or NO<sub>x</sub>-limited O<sub>3</sub> formation**

It is important to determine whether photochemical O<sub>3</sub> formation is VOC- or NO<sub>x</sub>-limited in order to develop appropriate control measures. Hence, efforts have been made to investigate the relationship between O<sub>3</sub> and its precursors in different regions of China.

##### **4.1.1.4.1.1 The North China Plain region**

Many intensive studies on photochemical pollution have been undertaken in Beijing and its surrounding cities in the NCP to improve the air quality (Shao et al., 2009b; Wang et al., 2010a; Wang et al., 2010a, 2010b, 2010e; Ma et al., 2011; Wang et al., 2012; Lu et al., 2010a, 2010b; Gao and Zhang, 2012; Zhang et al., 2014). Consistent with the results in the urban environments in the PRD and YRD regions, the photochemical O<sub>3</sub> formation at urban sites in Beijing was VOC-limited. For example, Xu et al. (2008a,b) used a 3D air quality model to show that the Beijing urban area was in a VOC-limited regime, while O<sub>3</sub> formation in the downwind area changed gradually to a NO<sub>x</sub>-controlled process. In addition to model simulation, a concept of initial mixing ratios of VOCs, followed by multi-regression, was proposed and used in Beijing to investigate the O<sub>3</sub>-precursor relationship (Shao et al., 2009b). The results suggest that the photochemical O<sub>3</sub> formation at the urban site (PKU) was a VOC-controlled process, while it was sensitive to both emissions of VOCs and NO<sub>x</sub> at the rural site (Yufa). However, based on the same data set, Lu et al. (2010a, 2010b) used an OBM to evaluate the O<sub>3</sub>-precursor relationship at the PKU and Yufa sites, yet found different results. Even though the ratios of L<sub>N</sub>/Q (fraction of radicals removed by reaction with NO<sub>x</sub> compared to total radical production rates) and RIR values extracted from the OBM demonstrated that both NO<sub>x</sub>-sensitive and VOC-sensitive chemistry frequently existed at both sites, O<sub>3</sub> production on high-O<sub>3</sub> days was mostly characterized by a NO<sub>x</sub>-sensitive condition, suggesting that the O<sub>3</sub> formation and its related photochemistry should be investigated individually in different areas in Beijing (Wang et al., 2015a, 2015b). Moreover, by studying the reactivity of TVOCs, NO, the diurnal variations of modeled O<sub>3</sub> production, and the model-derived L<sub>N</sub>/Q values, Lu et al. (2010a, 2010b) reported that the OBM had a tendency to over-predict the conditions of VOC-sensitive chemistry, which needs further investigation.

On the other hand, in Tianjin, another important city in the NCP region, Ran et al. (2011) reported that O<sub>3</sub> enhancement resulted from increasing NO emissions, indicating the NO<sub>x</sub> limitation of O<sub>3</sub> photochemistry based on the empirically observed VOCs/NO<sub>x</sub> ratios and the results of an OBM model (National Center for Atmospheric Research (NCAR)-MM) using the observed data collected at Wuqing, Tianjin, nearly 80 km southeast of Beijing and 30 km northwest of Tianjin.

##### **4.1.2.4.1.2 The Yangtze River Delta region**

There are relatively few studies on the O<sub>3</sub>-precursor relationships in the YRD region compared to the NCP and PRD regions. Most of the studies were conducted in Shanghai, the largest city in eastern China, and Nanjing, capital of Jiangsu Province. Li et al. (2012) conducted a process analysis of photochemical O<sub>3</sub> formation in the YRD region using the CMAQ modeling system with the Carbon Bond 05 (CB05) chemical mechanism. The results suggested that in urban areas of Shanghai and Hangzhou, the O<sub>3</sub> formation from vehicles was more sensitive to VOCs because of the high NO<sub>x</sub> emissions, while the O<sub>3</sub> formation was likely to be NO<sub>x</sub>-sensitive in the oil and chemical industrial region and the rural areas of the YRD region, such as the Jinshan district of southwestern Shanghai.

In Shanghai, both measurement and modeling results have indicated that O<sub>3</sub> formation was clearly under the VOC-sensitive regime in urban environments, while it tended to be NO<sub>x</sub> sensitive in rural areas (Geng et al., 2007, 2008, Geng et al., 2009a,b; Tang et al., 2008; Tie et al., 2009; Cai et al., 2010; Li et al., 2010; Li et al., 2011a, 2011b). For example, based on measurements at Xujiahui in Shanghai, the average ratios of VOCs/NO<sub>x</sub> were 4.55 on weekends and 4.73 on weekdays, indicating that O<sub>3</sub> formation was limited by VOCs, which was further confirmed by the results of the Ozone Isopleth Plotting Package Research (OZIPR) model with different initial concentrations of VOCs and NO<sub>x</sub> as input (Tang et al., 2008). Using the same method, Ran et al. (2009) reported that photochemical O<sub>3</sub> production at another urban site in Shanghai was also situated in a NMHC-limited regime. In addition, based on another weekend/weekday experiment, the large reduction in the daytime NO<sub>2</sub> concentration was found to be mainly responsible for the higher O<sub>3</sub> production during the weekend, suggesting that O<sub>3</sub> formation in Shanghai was under a VOC-sensitive regime (Geng et al., 2008), which was further confirmed by the ratios of CH<sub>2</sub>O/NO<sub>y</sub> and the results of sensitivity analysis by the NCAR Master Mechanism (NCAR-MM) model (Geng et al., 2008). Similar results were found at a suburban site in Shanghai using the photochemical box model with master chemical mechanism (PBM-MCM) (Xue et al., 2014).

Consistent with the O<sub>3</sub>-precursor relationship in Shanghai, photochemical O<sub>3</sub> formation at urban and suburban areas in Nanjing was VOC-limited, based on only a few studies (An et al., 2015; Ding et al., 2013). Correlations of

CO-NO<sub>y</sub>-O<sub>3</sub> indicated a VOC-limited regime for photochemical production of O<sub>3</sub> in Nanjing based on the 1-year data collected at the station for Observation of Regional Processes of the Earth System (SORPES) in Nanjing University in 2011–2012 (Ding et al., 2013). From the data in a sampling campaign conducted at four sampling sites in 2013 in Nanjing, including industrial area, traffic area, residential area, and commercial area, An et al. (2015) investigated the difference in O<sub>3</sub> photochemical characteristics between Nanjing and its surrounding areas. The VOC/NO<sub>x</sub> ratios indicated a generally VOC-limited regime in the industrial area, with the exception that most VOC/NO<sub>x</sub> ratios exceeded 8 during a NO<sub>x</sub>-limited regime from 13:00–15:00, perhaps due to low NO<sub>x</sub> emissions in this time period. A sensitivity study performed with an OBM confirmed that O<sub>3</sub> formation was limited by VOCs, and high NO concentrations suppressed O<sub>3</sub> formation in the industrial area of Nanjing.

### **4.1.3.4.1.3 The Pearl River Delta region**

Different approaches have been used to demonstrate that O<sub>3</sub> formation in urban areas of Hong Kong and the inland PRD region is generally VOC-limited (Zhang et al., 2008a; Cheng et al., 2010a; Zheng et al., 2010; Ou et al., 2016). For example, based on air quality monitoring data from 2006 and 2007 collected by the PRD regional air quality monitoring network, the diurnal variations in NO<sub>x</sub> and O<sub>3</sub> indicated a negative response of NO<sub>x</sub> emission increases to O<sub>3</sub> photochemistry, implying VOC-limited regime in the metropolitan urban areas, whereas a slightly positive response in rural areas of the PRD region, suggesting that photochemical O<sub>3</sub> production was possibly limited by NO<sub>x</sub> in the northern or northeastern rural area in PRD (Zheng et al., 2010).

However, investigating the O<sub>3</sub>-precursor relationship based only on the observed ratios of photochemical pollutants has uncertainties because: 1) The observed ratios are varying with the emissions of O<sub>3</sub> precursors from different sources and substantial photochemical processing; 2) the environments at different sampling sites may be different. Therefore, different models have been developed to investigate the O<sub>3</sub>-precursor relationship by assembling the photochemical reactions related to O<sub>3</sub> and its precursors, as well as observed and/or simulated data of air pollutants and meteorology. In addition, such models play a central role in policy development and implementation. Two kinds of models, including emission-based and observation-based models have been used extensively in the PRD region (Huang et al., 2005; Zhang et al., 2007; Zhang et al., 2008a; Cheng et al., 2010a, 2010b; Zheng et al., 2010; Wei et al., 2012; Liu et al., 2013a, 2013b, 2013c; Ou et al., 2016).

In Hong Kong, Huang et al. (2005) used the Pollutants in the Atmosphere and their Transport over Hong Kong (PATH) model to investigate the photochemical evolution from one type of O<sub>3</sub> episode related to tropical cyclones in 1999–2003 with the emission inventory from U.S. Emission Modeling System (EMS-95) and meteorological conditions from meteorological model (MM5). By reducing the VOCs and NO<sub>x</sub> emissions by specific ratios, sensitivity analysis found that O<sub>3</sub> formation over Hong Kong was within the VOC-limited regime. In another study, coupling the emission inventory of Hong Kong and the inland PRD region, Wang et al. (2010a, 2010b, 2010c) simulated an O<sub>3</sub> episode during October 2004 for the inland PRD, Pearl River estuary (PRE), and southern coastal areas using the Community Multiscale Air Quality (CMAQ) model. Through sensitivity analysis, it was found that O<sub>3</sub> formation was VOC-limited in the central inland PRD, PRE and surrounding coastal areas, where the air masses were less chemically aged, while it was NO<sub>x</sub>-limited in the rural southwestern inland PRD where the air masses were photochemically aged. By using a validated O<sub>3</sub> modeling system and the latest regional emission inventory, Ou et al. (2016) reported that VOC-focused controls are more efficient for O<sub>3</sub> reduction in urban and industrial areas, but significant NO<sub>x</sub> emission reductions and a subsequent transition to a NO<sub>x</sub>-limited regime are required for O<sub>3</sub> attainment.

In contrast to the emission-based models, the observation-based model (OBM) requires high resolution measurements of gaseous pollutants and meteorological conditions to perform simulations of O<sub>3</sub>-precursor relationships. This avoids the uncertainties associated with emission inventories and the simulated boundary layer dynamics. However, the OBM usually adopts a number of simplifying assumptions. One of the critical assumptions is the neglect of horizontal transport in solving the concentrations of the unspecified species. Another assumption is that an O<sub>3</sub> precursor is reduced by a certain amount in the OBM. The critical parameter is the change in O<sub>3</sub> production that occurs between the cases with and without the reduction of precursors. The difficulty arises because there are no real-world situations that represent the second case (*i.e.*, with reduction of precursors): an O<sub>3</sub> episode in which an O<sub>3</sub> precursor is reduced by a certain amount while all other conditions remain unchanged. Based on the daily VOCs concentrations, Zhang et al. (2007) used the OBM for the first time to evaluate the O<sub>3</sub>-precursor relationship at four monitoring sites operated by the Hong Kong Environmental Protection Department (HKEPD). The large positive values of relative incremental reactivity (RIR) for anthropogenic hydrocarbons (AHCs) and the negative RIRs for NO<sub>x</sub> suggested that photochemical O<sub>3</sub> formation at these sites were controlled by VOCs. In 2006 in Guangzhou, Zhang et al. (2008a) used the same model to evaluate the O<sub>3</sub>-precursor relationship at an urban site and a rural site. The RIR values suggested that O<sub>3</sub> photochemistry was usually in the VOC-limited regime at both sites, where reducing NO<sub>x</sub> could result in O<sub>3</sub> increase. The O<sub>3</sub> formation at both sites was mainly attributable to a small number of VOCs, including propene, toluene, *m,p*-xylenes and *o*-xylene. However, although AHCs had the highest RIR value at another urban site in Guangzhou, NO<sub>x</sub> also had a positive RIR value (Shao et al., 2009a), suggesting the important contributions of NO<sub>x</sub> to the O<sub>3</sub> production, which was different from other urban environments in Guangzhou (Zhang et al., 2008a). The above studies only considered the relationship of O<sub>3</sub> with hydrocarbons, NO<sub>x</sub> and CO. Therefore, to further investigate the O<sub>3</sub>-precursor relationship in the PRD region, high resolution measurements were conducted at an urban site (Tung Chung, TC) in Hong Kong and a downwind site (Wanqingsha, WQS) in the inland PRD region in 2007 (Cheng et al., 2010a). In contrast to previous studies, hourly data of carbonyls, including formaldehyde, acetaldehyde and acetone were input into the OBM. The simulated RIR values suggested that O<sub>3</sub> formation at the two sites were VOC-limited, and formaldehyde, acetaldehyde, *m,p*-xylene and isoprene were the major VOCs responsible for O<sub>3</sub> production at the two sites. Similar findings were obtained at another urban site of Hong Kong (Tsuen Wan, TW) by Ling and Guo (2014) and at TC using 10-year data by Wang et al. (2016a, 2016b).

In summary, the emission-based and observation-based models have identified both VOC- and NO<sub>x</sub>-limited regimes in the PRD, and the local governments have used this information to formulate the most appropriate O<sub>3</sub> control strategies.

Apart from the NCP, YRD and PRD, research has shown that other urban areas of China are often VOC-limited. For example, O<sub>3</sub> formation was found to be VOC-limited in the urban areas of Wuhan, a city of central China (Lyu et al., 2016a, 2016b), while the O<sub>3</sub> production was NO<sub>x</sub>-limited in suburban mountainous areas in Lanzhou, western China (Xue et al., 2014), consistent with the O<sub>3</sub>-precursor relationship identified by O<sub>3</sub>-isopleth plots (Jia et al., 2016).

Overall, based on the observed variations of O<sub>3</sub> and its precursors, and the results of model simulations, it can be concluded that O<sub>3</sub> production in the urban areas of cities and regions is generally VOC-limited, while O<sub>3</sub> production is possibly limited by NO<sub>x</sub> in the rural areas.

## 4.2.4.2 The roles of VOCs in O<sub>3</sub> formation

VOCs photochemical reactivity is a measure of how much each VOCs species reacts in the atmosphere and contributes to the formation of O<sub>3</sub>, which is an important consideration when policymakers aim to prevent and control O<sub>3</sub> and/or photochemical smog through controlling VOCs emission sources. There are some frequently used scales for the evaluation of the VOCs photochemical reactivity and/or O<sub>3</sub> formation potential (OFP) of VOCs, including the calculations of Propene-Equivalent concentration of species (j) (Pro-Equiv (j)) (Chameides et al., 1992), the OFP with maximum incremental reactivity (MIR) values (Carter, 1994, 1995, 2008) and OH radical loss rate (L<sub>OH</sub>) (Shao et al., 2009a). The above parameters are calculated *via* the following equations (Equations (1)–(3)):

$$\text{Prop-Equiv}(j) = [\text{VOC}]_j \times \frac{k_{\text{OH}}(j)}{k_{\text{OH}}(\text{C}_3\text{H}_6)} \quad (1)$$

$$\text{OFP}(j) = [\text{VOC}]_j \times \text{MIR}(j) \quad (2)$$

$$L_{\text{OH}} = [\text{VOC}]_j \times k_{\text{OH}}(j) \quad (3)$$

where [VOC]<sub>j</sub> is the concentration of the VOCs species (j), k<sub>OH</sub> is the reaction rate of VOCs with OH radical, and C<sub>3</sub>H<sub>6</sub> is propene. However, these methods simply estimate the contributions of VOCs to O<sub>3</sub> formation based on the assumption that all the VOCs in the atmosphere are attacked by OH radical and form O<sub>3</sub> (Ling and Guo, 2014). In addition, the above methods for evaluating the contributions of VOCs to O<sub>3</sub> formation are only valid when the chemical regime of the O<sub>3</sub> formation process is sensitive to VOCs in the specific areas being studied. Hence, different models incorporating various photochemical mechanisms have been intensively applied to study the photochemical reactivity of VOCs in the PRD, YRD and NCP regions, including the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem) or the Community Multiscale Air Quality model (WRF-CMAQ), the OBM and/or OBM-MCM, photochemical trajectory model with master chemical mechanism (PTM-MCM) and so on (Xu et al., 2008a,b; Cheng et al., 2010b; Li et al., 2012; Xue et al., 2014; Shao et al., 2009a).

### 4.2.1.4.2.1 The Pearl River Delta region

In the PRD region, earlier observations of hydrocarbons did not include OVOCs, and photochemical reactivity analysis revealed that toluene, ethene, propene and xylenes were the leading contributors to the photochemical reactivity in urban areas while isoprene dominated in rural areas (Tang et al., 2007; Barletta et al., 2008; Liu et al., 2008a; Lai et al., 2009; Tan et al., 2012; Wu et al., 2016). For example, Barletta et al. (2008) reported that ethene and toluene were among the top compounds in terms of O<sub>3</sub> formation in urban centers in the PRD, due to their high mixing ratios and MIR values (3.97 for toluene and 9.07 for ethene). Tan et al. (2012) also found that the leading contributors to OFP and Prop-Equiv in Foshan were ethene, toluene, propene, *i*-pentane and *m/p*-xylene. In Hong Kong, isoprene was found to have the highest OH-reactivity and OFP at rural sites, and toluene, propene and xylenes were the leading contributors in urban sites (Zhang et al., 2007; Cheng et al., 2010a, 2010b).

In addition to the observed mixing ratios, the contributions of VOCs to O<sub>3</sub> formation have been calculated based on the speciated VOCs emission inventory in the PRD region. The top 10 NMHCs contributing to OFP in the inland PRD region were isoprene, *m,p*-xylene, toluene, ethene, propene, *o*-xylene, 1,2,4-trimethylbenzene, 2-methyl-2-butene, 1-butene, and  $\alpha$ -pinene (Zheng et al., 2009). For the biogenic emission inventories (Tsui et al., 2009; Zheng et al., 2010), isoprene and monoterpenes together contributed 70% and 59% of the total biogenic VOCs in Hong Kong and the inland PRD region, respectively. The latest bulk speciated VOCs and OVOCs emission inventories have recently been established for the PRD (Ou et al., 2015b). Based on OFP values calculated from the emissions and MIR values of VOCs and OVOCs, aromatics and alkenes were responsible for 59.4% and 25.8% of the OFP in 2010 (Ou et al., 2015b). Among them, ethene, *m,p*-xylene, toluene and 1,2,4-trimethylbenzene were the top 4 individual VOCs contributing to the OFPs. The loss of isoprene in the top 4 VOCs reflected the rapid urbanization and industrialization in the PRD region.

In recent years more and more OVOCs data have become available in the PRD region as previous studies suggested that the contributions of OVOCs were also important in this region. Lü et al. (2010) reported that formaldehyde, acetaldehyde, valeraldehyde, butyraldehyde, and propionaldehyde contributed 89–96% of the total OFP of carbonyls. Yuan et al. (2012) measured 47 hydrocarbons and 3 carbonyls at six sites in the PRD in July 2006 and in October–November 2008. Carbonyls contributed 19.1%–50.5% of the total L<sub>OH</sub> at suburban/rural sites, and their significant contributions further confirmed the box modeling results of Lou et al. (2010). In addition, a large-

scale spatio-temporal sampling campaign of VOCs and OVOCs was conducted throughout the PRD region in September 2008–December 2009 (Louie et al., 2013). Compared to toluene, the mixing ratios of the most abundant OVOCs species, *i.e.*, formaldehyde, acetone, acetaldehyde and 2-butanone, were lower by about 0.6, 0.6, 0.26, and 0.19 times the mixing ratio of toluene. Altogether, the OFP of OVOCs was **more than 1** /3 of that of VOCs alone, demonstrating the important roles of OVOCs in O<sub>3</sub> formation in the PRD region (Louie et al., 2013).

Identifying the sources of VOCs and investigating their contributions to O<sub>3</sub> formation are of critical importance for formulating control strategies for photochemical pollution. Therefore, a new reactivity-based parameter, namely, a RIR-weighted value, which combines the RIR values with the observed mixing ratios of VOCs from different sources using positive matrix factorization (PMF) and OBM models, has been used to determine the contribution of sources of VOCs to O<sub>3</sub> formation (Ling et al., 2011; Lam et al., 2013; Ling and Guo, 2014). Toluene and *m/p*-xylene from solvent usage and ethene from biomass burning and diesel vehicular emissions were found to be the most important contributors to O<sub>3</sub> formation based on data collected at the downwind rural site in the inland PRD region (Wanqingsha), while xylenes and ethylbenzene in paint and sealant solvents, toluene in gasoline exhaust, *i/n*-butane, ethene, propene and propane in LPG usage and *n*-butane and ethene in diesel exhaust were the significant contributors to the O<sub>3</sub> formation at the urban site in Hong Kong (Tung Chung).

#### **4.2.2.4.2.2 The Yangtze River Delta region**

In the YRD region, aromatics play dominant roles in O<sub>3</sub> production at urban sites in Shanghai, followed by alkenes and alkanes. However, different from the PRD region, aldehydes, ketones and alcohol contributed **less than 10** % of photochemical O<sub>3</sub> formation (Geng et al., 2007, 2008). Among all the species, toluene, xylenes, 1,3,5-trimethylbenzene, ethylbenzene, 1-butene, propene, 1,2,4-trimethylbenzene and *i*-pentane were the top 8 species responsible for the photochemical O<sub>3</sub> formation in Shanghai, with total contributions of 77% to the summed MIR values of all VOCs based on the samples collected at an urban site (Ran et al., 2009). Similarly, by multiplying the emissions of different VOCs estimated from the emission inventory by their photochemical reactivity, it was found that chemical industry, domestic use of paint and printing, and gasoline vehicles were the three most important sources of VOCs contributing to O<sub>3</sub> formation in the YRD region. Among them, ethene, xylenes, toluene and 1,2,4-trimethylbenzene, 2,4-dimethylpentane, ethylbenzene, propene, 1-pentene, and isoprene were the key VOCs for O<sub>3</sub> production, contributing 77% to the total OFP of VOCs (Huang et al., 2011a, 2011b). It is noteworthy that this result is different from the findings by Geng et al. (2007, 2008) for Shanghai where ethene was not in the top 8 species. This was mainly caused by different datasets used in these two studies, of which Geng et al. (2007, 2008) used measurement data while Huang et al. (2011a, 2011b) relied on emission inventory data.

In Nanjing, the relative importance of VOCs to O<sub>3</sub> formation was evaluated by RIR values extracted from the OBM (An et al., 2015). Alkenes had the highest RIR value compared to other VOCs groups, and so were the largest contributor to O<sub>3</sub> formation in urban Nanjing, followed by aromatics (An et al., 2015), consistent with the results simulated by the NCAR-MM at a suburban site of northern Nanjing (Shao et al., 2016). Similar results were also found in an industrial area in Nanjing, where alkenes had the highest values, followed by aromatics and alkanes using the propylene-equivalent method (An et al., 2014).

#### **4.2.3.4.2.3 The North China Plain region**

In the NCP, alkenes and aromatics were two major VOCs groups contributing to the O<sub>3</sub> formation based on the calculation of OFP, Prop-Equiv concentrations and L<sub>OH</sub> values, together with the results of sensitivity analysis by model simulations (Wang et al., 2010a, 2010b, 2010e). Of the above two groups, ethene, propene, toluene and xylenes were the major VOCs species responsible for O<sub>3</sub> formation (Duan et al., 2008). For example, Wang et al. (2016a, 2016b) investigated the differences in the characteristics and sources of VOCs before and after the Asia-Pacific Economic Cooperation (APEC) meeting held in Beijing in November 2014, based on canister samples collected at a suburban site in Beijing on 1–25 November 2014. The OFP of VOCs on the days before the APEC meeting (1–2 November and 13–25 November), when there were no emission-reduction measures, was 1.6 times higher than on the days during the APEC meeting (3–12 November), when a series of emission-reduction measures including industrial enterprises, vehicle sources and fugitive dust were carried out in Beijing and surrounding cities and regions, *i.e.*, Hebei Province, Shandong Province, Shanxi Province, Inner Mongolia Autonomous Region, and Tianjin city. Furthermore, the OFP values indicated that alkenes including propene, 1-butene and *trans/cis*-2-butene, and aromatics including toluene and xylenes, were the major VOCs contributing to O<sub>3</sub> formation. By considering the contributions of both NMHCs and OVOCs, Shao et al. (2009b) found that alkenes and OVOCs were the two major VOCs groups for the total OH reactivity, accounting for about 71–85% of the L<sub>OH</sub> of VOCs at the urban site (PKU) and rural site (Yufa) in Beijing. Formaldehyde and acetaldehyde were the major species contributing to the L<sub>OH</sub> of OVOCs, while ethene and propene dominated the L<sub>OH</sub> of alkenes. The emission-based measurements further confirmed that carbonyls from the emissions of diesel trucks and alkenes from light-duty gasoline vehicles made dominant contributions to O<sub>3</sub> formation in Beijing (Yao et al., 2015; Cao et al., 2016).

Tianjin is another important megacity in the Beijing-Tianjin-Hebei region, where air samples were collected at an urban site, *i.e.*, Tieta, and a rural site, *i.e.*, Wuqing in July–September 2009 (Han et al., 2013). Through the sensitivity analysis from the NCAR-MM model, alkenes were the primary contributors to O<sub>3</sub> production (53.5%), followed by aromatics (35.1%) and alkanes (9.2%). The key species associated with photochemical O<sub>3</sub> formation at the Wuqing site were *trans/cis*-2-butene, isoprene, trimethylbenzenes, xylenes, 3-methylhexane, *n*-hexane and toluene (Ran et al., 2011). Similar results were also found in the study of Li et al. (2015) based on sampling campaigns at three sites, *i.e.*, Beijing, Gucheng and Quzhou in the NCP region.



In other areas of the NCP, [Zhu et al. \(2016\)](#) found that toluene, isoprene, ethene, propene and *n*-hexane were the top 5 species responsible for OFP in the rural area of Shandong Province.

Considering other areas of China apart from the NCP, YRD and PRD regions, [Lyu et al. \(2016b\)](#) combined PMF and PBM-MCM to evaluate the effects of VOCs on O<sub>3</sub> production in Wuhan, central China. Ethene and toluene were the primary species contributing to O<sub>3</sub> production, while vehicular exhaust (23.4%) and LPG usage (23.1%) were the two major VOCs sources to O<sub>3</sub> production. In another study conducted in Lanzhou, the calculated MIR values suggested that *cis*-2-butene, propene and *m/p*-xylene were the top three compounds contributing to OFP in downtown areas of Lanzhou, whereas ethane, propene and *trans*-2-butene played more important roles in O<sub>3</sub> formation at the suburban site of Lanzhou ([Jia et al., 2016](#)). The difference in top VOCs species between the two sites was related to the fact that vehicular exhausts and solvent usage were major sources in city center while petrochemical industry was dominant in suburban area in Lanzhou.

### 4.3.4.3 The roles of VOCs in SOA formation

In the atmosphere both homogenous and heterogeneous reactions of VOCs can result in the formation of SOA ([Claeys et al., 2004](#); [Jang et al., 2002](#)). As SOA precursors, global emissions of anthropogenic VOCs (*e.g.*, aromatics) were very minor compared to those of biogenic VOCs (terpenes) ([Piccot et al., 1992](#); [Guenther et al., 1995](#)), about 90% of global SOA were believed to be caused by biogenic VOCs ([Kanakidou et al., 2005](#)). However, recent field studies suggested that anthropogenic SOA might be more significant than previously thought. Based on the observation in Mexico City and extrapolation of the results to the other urban areas, [Volkamer et al. \(2006\)](#) estimated that global anthropogenic SOA accounted for one third of global SOA. In the United States, the secondary organic matter (SOM) produced by urban VOCs were estimated to dominate over biogenic SOM ([de Gouw et al., 2008](#)). The dominant role of anthropogenic secondary organic carbon (SOC) was also observed in the urban areas in the United States, such as Birmingham ([Ding et al., 2008](#)) and Cleveland, Detroit, and Riverside ([Stone et al., 2009](#)). Moreover, anthropogenic emissions in urban regions might accelerate oxidation of biogenic VOCs ([Weber et al., 2007](#); [Carlton et al. \(2010\)](#)). These findings suggest important contributions of anthropogenic sources to SOA particularly in the polluted regions. Previous studies have identified that terpenes, aromatics, alkenes (including isoprene), carbonyls, and alkanes with **more than 5 > 5** carbon atoms were the main VOCs that could form SOA through photo-oxidation ([Piccot et al., 1992](#); [Guenther et al., 1995](#); [Kanakidou et al., 2005](#); [Volkamer et al., 2006](#); [Weber et al., 2007](#); [de Gouw et al., 2008](#); [Ding et al., 2008](#); [Stone et al., 2009](#); [Carlton et al., 2010](#)). In the past decade, different methods have been developed to evaluate the roles of VOCs in SOA formation in China, including smog chamber studies, on-site measurements of SOA-tracers (tracer-based method), and model simulations.

Smog chamber studies can provide detailed information on the mechanism of SOA formation through the photo-oxidation of VOCs, as well as the SOA yields ([Liu et al., 2015](#); [Liu et al., 2016a, 2016b](#); [Wang et al., 2014a, 2014b, 2014c, 2014d](#)). For example, [Liu et al. \(2015\)](#) investigated the SOA formation from the emissions of two idling light-duty gasoline vehicles under specific reaction conditions using a recently configured smog chamber at the Guangzhou Institute of Geochemistry. By considering the mass of reacted organic precursors identified by GC-MS and their reactivity, the predicted SOA production was obtained. It was found that traditional single-ring aromatic precursors, including benzene, toluene, ethylbenzene, 1,2,3-methylbenzene, *m*-ethyltoluene as well as naphthalene (a two-ring system) could explain 51–90% of the formed SOA, while the unexplained SOA was associated with unspiciated VOCs by the GC-MS system.

However, smog chamber studies investigate the pathways of individual VOCs and/or the mixture of VOCs to SOA formation under specific conditions, which is conceptually different from the real atmosphere. By combining the concentrations of VOCs, the related SOA-tracers and measured SOA/SOC (secondary organic carbon) ratios, the contributions of VOCs to SOA can be better determined ([Zhang et al., 2016](#); [Ding et al., 2012](#)). This tracer-based method was first developed by [Kleindienst et al. \(2007\)](#). Several molecular markers of SOA have been found, such as the tracers for SOA from the photo-oxidation of isoprene (2-methylthreitol and 2-methylerythritol) ([Claeys et al., 2004](#); [Edney et al., 2005](#)),  $\alpha$ -pinene (3-hydroxyglutaric acid, 3-hydroxy-4,4,-dimethylglutaric acid and 3-methyl-1,2,3-butane-tricarboxylic acid) ([Offenberg et al., 2007](#); [Kourtchev et al., 2008](#); [Szmigielski et al., 2007](#)),  $\beta$ -caryophyllene ( $\beta$ -caryophyllinic acid) ([Jaoui et al., 2007](#)) and toluene (2,3-dihydroxy-4-oxopentanoic acid) ([Jaoui et al., 2007](#); [Kleindienst et al., 2007](#)). Generally, the contributions of the photo-oxidation of biogenic VOCs to SOA formation are higher than those of anthropogenic precursors at suburban/rural sites because of the higher emissions of biogenic VOCs ([Ding et al., 2014, 2016](#)). In addition, higher contributions of biogenic VOCs to SOA formation were found in summer than in winter because of the higher temperatures in summer ([Shen et al., 2015](#)).

In Hong Kong, [Hu et al. \(2008\)](#) analyzed the levels of SOA-tracers of isoprene, monoterpenes,  $\beta$ -caryophyllene and toluene at four sites in summer in 2006. The tracer-based method indicated that monoterpenes and  $\beta$ -caryophyllene were the major contributors to SOA in fine particles in summer due to the high emissions of these biogenic hydrocarbons, contributing about 49% and 21% to the ambient organic compound concentrations, respectively. However, a different phenomenon was observed in the inland PRD region, where higher contributions of anthropogenic VOCs to SOA formation were found. For example, [Ding et al. \(2012\)](#) measured the typical SOA tracers from significant biogenic (isoprene, monoterpenes, and sesquiterpenes) and anthropogenic (aromatics) precursors at a rural site located in the downwind areas of the highly industrialized PRD region during summer-winter 2008. The tracer-based method indicated that the photo-oxidation of anthropogenic precursors and isoprene were responsible for 76% and 18% of the estimated SOC in summer, respectively, while aromatic precursors contributed 76% of the estimated SOC in fall-winter, confirming the dominant role of aromatics from anthropogenic emissions in the production of SOA in the industrial areas of the PRD region. Similarly, compared to isoprene, monoterpenes and toluene had much higher contributions to SOA formation at the suburban and urban sites in Shanghai ([Feng et al., 2013](#)). In Beijing, contributions of isoprene and  $\alpha/\beta$ -pinene photo-oxidation were higher at the upwind suburban site than at the urban site ([Yang et al., 2016](#)).

For the rural areas, Wang et al. (2008a, 2008b) analyzed the biogenic SOA tracers in four forested areas in China, including Mt. Changbai of Jilin Province, Chongming of Shanghai, Mt. Dinghu of the PRD region, and Mt. Jianfengling of Hainan Province. Photo-oxidation of isoprene contributed an estimated 0.32, 0.03, 0.16 and 0.27  $\mu\text{gC}/\text{m}^3$  to the SOC in fine particles ( $\text{PM}_{2.5}$ ), respectively, consistent with the results of a recent study conducted in the Central Tibetan Plateau, which found that the annual average biogenic SOC (sum of isoprene, monoterpenes and  $\beta$ -caryophyllene) accounted for about  $0.17 \pm 0.22 \mu\text{gC}/\text{m}^3$  of total SOC (Shen et al., 2015). Similarly, Fu et al. (2010) measured biogenic SOA tracers at the summit of Mountain Tai, Central East China in summer of 2006. The estimation of biogenic precursors to SOA by the tracer-based method showed that isoprene-derived SOC accounted for 58% and 63% of total SOC during the daytime and nighttime, respectively, suggesting greater importance of isoprene in SOA formation than  $\alpha/\beta$ -pinene and  $\beta$ -caryophyllene at high altitudes in central eastern China.

Different from the measurement-based analysis, model simulations of SOA are useful for investigating the importance of different pathways/potential mechanisms of photo-oxidation of VOCs and the factors that affect SOA formation (Situ et al., 2013). For example, Li et al. (2013) used the regional air quality model (CMAQ) to simulate organic aerosol concentrations over the PRD region in 2009. The model performance was improved by incorporating an additional source of SOA, *i.e.*, the aqueous reactive uptake of dicarbonyls (glyoxal and methylglyoxal). Isoprene was the most important precursor to SOA formation in the PRD region, accounting for about 75% of the simulated SOA. On the other hand, to improve the predicted SOA and SOC concentrations, an approach with chemical aging mechanism was incorporated into another regional air quality model system (RAQMS) that studied SOA formation over eastern China in April 2009 (Han et al., 2016). Photo-oxidation of aromatics contributed to 55% of SOA formation, whereas the contributions of biogenic VOCs were only 14%. In addition to RAQMS, box modeling has been developed to investigate the contributions of VOCs to SOA formation (Wang et al., 2013). For example, a 0-D box model with the Carbon Bond 05 (CB05) mechanism was developed to estimate relative contributions of isoprene, monoterpenes, toluene and xylenes to SOA formation in Hong Kong and Guangzhou. Reasonable agreement was found between the model simulation results and those calculated by the tracer-based method (Ding et al., 2012; Hu et al., 2008), with the dominant contributions from biogenic VOCs in Hong Kong but higher contributions of anthropogenic VOCs in Guangzhou. Though different models have been developed to simulate SOA formation, the predicted SOA concentrations are frequently lower than those measured. This discrepancy is associated with the limited knowledge of the mechanisms of SOA formation, the uncertainty of the production rates and/or reactivity of precursors, and the unspecified precursors (de Gouw and Jimenez, 2009; Pye and Seinfeld, 2010; Dzepina et al., 2011; Hodzic et al., 2010).

## 5.5 Removal technology

The removal techniques of VOCs can be broadly divided into three categories, *i.e.*, physical, chemical and biological methods. The physical methods, making use of the physical properties of VOCs (*e.g.*, solubility and boiling points), mainly include absorption, adsorption, membrane separation and condensation (Godish, 2003). In general, the physical removal processes only involve the phase conversion of the contaminants or their transfer between the mediums. As such, secondary pollution is one of the main disadvantages of the physical methods. The chemical treatment of VOCs in waste gas generally means reactions between VOCs and oxidants or radiation (Noel de Nevers, 1995). Through these approaches, the VOCs are often degraded to carbon oxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ). Incineration, catalytic combustion, ozone oxidation, plasma treatment and photochemical catalytic oxidation (PCO) are the commonly used methods in chemical removal of VOCs. The biological technologies to treat VOCs mainly consist of biofiltration and botanical purification (Godish, 2003). The three categories are discussed in more detail below.

### 5.1.5.1 Physical methods

Adsorption has been successfully applied for retaining contaminants on the surface of an adsorbent material, such as activated carbon (AC), zeolites, silica gel, activated alumina, mineral clay, and some polymers. To date, AC and hydrophobic zeolites are most commonly used, due to their large surface area and high adsorption capacity (Zhao et al., 1998; Li et al., 2011a, 2011b). To examine the adsorption performance of the AC derived from sewage sludge on the removal of formaldehyde, Wen et al. (2011) found that formaldehyde was effectively removed *via* adsorption on an AC filter with an initial efficiency of  $\sim 84\%$  and  $\sim 90\%$ , respectively. Even higher efficiency ( $> 90\%$ ) was confirmed by Jo and Yang (2009) when they applied the AC adsorption technique to the removal of aromatics. However, the drawbacks of this method are as follows. Firstly, the removal efficiency depends strongly upon the working conditions (*e.g.* relative humidity, compound species and initial concentrations). In addition, the already adsorbed VOCs could be re-emitted in to the atmosphere without regular replacement of the adsorbent (Liebana and Calleja, 1998).

Apart from adsorption, membrane separation is also widely used in VOCs treatment. Semipermeable membranes with high VOCs selectivity are the key units of such purification systems, such as zeolite-based membranes, polymeric moisture permeable membranes, polyvinyl alcohol with lithium chloride as an additive, polyvinylpyrrolidone and polyacrylamide membranes, *etc.* Aguado et al. (2004) and Zhang et al. (2012) both reported high efficiencies of the membrane separation method in the removal of VOCs including ethane, benzene, toluene, formaldehyde and acetaldehyde. However, there are many defects inhibiting the commercialization of membrane separation techniques. With the interception of the pollutants on one side of the semipermeable membrane, the pressure drop of the system increases, increasing mechanical resistance during operation. In addition, the cleaning and reuse of semipermeable membrane is a critical issue which needs to be addressed in the field of membrane technology.

### 5.2.5.2 Chemical methods

Incineration and catalytic combustion are the traditional ways to degrade waste gases (Khan and Ghoshal, 2000; Li et al., 2009). However, the byproducts during combustion lead to secondary pollution and can pose harm to the environment. Additives are often needed to support the combustion or catalyze the reactions, consequently raising the cost. Furthermore, not all pollutants are removed efficiently by these methods.

In contrast to the traditional catalytic thermal oxidation, which requires high temperatures (200–1200 °C), photocatalytic oxidation (PCO) allows the degradation and mineralization of VOCs at room temperature. Catalysis and irradiation are the main components of the PCO system. Generally, a semi-conductor is used as the catalyst, and is activated in the presence of ultraviolet (UV) radiation, generating pairs of positive charged holes ( $H^+$ ) and electrons ( $e^-$ ). The reactions of  $H^+$  and  $e^-$  with water,  $OH^-$  and  $O_2$  provide the oxidation agents (hydroxyl radical, OH) for the VOCs degradation.  $TiO_2$ , ZnO, ZnS, CdS,  $Fe_2O_3$  and  $SnO_2$  are the commonly used catalysts (Mo et al., 2009). As an example, Ao et al. (2004) tested the removal of formaldehyde by this method, and found that the removal efficiency reached 80% and up to 85% in the presence of NO. Moreover, it was reported that 99.7% of *n*-heptane could be converted to the intermediates,  $CO_2$  and  $H_2O$ , by PCO treatment (Shang et al., 2002). Deactivation of the catalyst is the main drawback of the PCO method.

An improved PCO method with vacuum UV (VUV) as the radiation source has been proposed in recent years (Huang et al., 2011a, 2011b; Huang et al., 2015a, 2015b). The wavelength range of 100–200 nm VUV is of higher energy than the commonly used 254 nm UV. VUV can destroy VOCs in two ways. First, VUV directly destroys the VOCs molecules with energetic photons. Second, OH and oxygen species ( $O(^1D)$ ,  $O(^3P)$  and  $O_3$ ) generated from the reactions of VUV irradiation with water and/or  $O_2$  can oxidize and degrade the VOCs. In traditional PCO method, 254 nm UV is generally used, however, the VUV-PCO system makes full use of the irradiation of both 100–200 nm and 254 nm wavelengths. Therefore, the VUV-PCO method significantly improves the removal efficiency of VOCs. In addition, the productions of toxic byproducts are reduced in the VUV-PCO system. A comparative study conducted by Huang et al. (2011a, 2011b) indicated that the removal efficiency of toluene reached 80% with the VUV-PCO method, followed by VUV photolysis (60%) and 254 nm PCO (15%). However,  $O_3$  was still produced. Although the generated  $O_3$  has some potential in VOCs degradation, it is also the main problem with this method, because the residual  $O_3$  is harmful to the environment and human health.

Plasma, a collection of electrons, positive ions and neutral particles (atoms and/or molecules) in the highly ionized gas, is also used to treat VOCs waste gases. It is produced by high voltage electrical discharges, which promote the generation of UV radiation, free radicals and oxidation species. These species further participate in the degradation of VOCs. Using this approach, several studies (Ding et al., 2005; Chang and Lee, 1995) reported high removal efficiencies of toluene under the treatment of dielectric barrier discharge. However, undesirable byproducts, such as formic acid and carboxylic acids, are generated during the process. Apart from these species,  $O_3$  is the most common byproduct of the plasma technique. Indeed, this is a main disadvantage of the plasma method, as  $O_3$  formation is unavoidable in high voltage discharge.

Although  $O_3$  is often an undesirable byproduct in the removal processes of VOCs, it also serves as an effective reagent in VOCs degradation. In a UV-irradiated and non-thermal plasma-driven photocatalyst system, Huang et al. (2010) found that active oxygen generated from  $O_3$  decomposition played a vital role in the removal of toluene.

### 5.3.5.3 Biological methods

The biological treatment of VOCs in waste gas generally makes use of the degradation of volatile organic pollutants by microorganisms. Actually, the organic pollutants are treated as the nutrients to support the growth and reproduction of microorganisms (Edwards and Nirmalakhandan, 1996; Lü et al., 2010). Biofiltration is the main type of biological treatment technique, in which the VOCs transfer from the gas phase to biofilm, and are further metabolized by the microorganisms. The commonly used bioreactors include packed bed bioreactors, bioscrubbers, biotrickling filters (BTFs) and membrane bioreactors. In a study of the removal of indoor VOCs, Lu et al. (2010a, 2010b) indicated that formaldehyde, benzene, toluene and xylenes were reduced by 100%, 65–70%, 93% and 85–90% by a BTF system, respectively, under the gaseous flow rate of 600 L/h, pH of 6–7 and temperature of 30 °C. In addition, Liu et al. (2009a, 2009b) found that biofiltration treatment achieved a VOCs removal efficiency of 20% to 95% from biostabilization processing of municipal solid waste, and was particularly effective for alkylated benzenes (> 80%). To improve the biofiltration method, Xi et al. (2005) indicated that adding large size inert spheres in the packing media remarkably increased the toluene removal capacity and reduced the pressure drop of the system. Another type of biological treatment system was botanical purification, which used the plant's root bed to absorb and/or adsorb the VOCs in the waste gas. Furthermore, the intercepted VOCs became a potential nutrient source for bacterial communities in the soil. Although this method was confirmed to be effective in laboratory studies, it has not been commercially used in the treatment of VOCs in industrial waste gas or indoor air (Xi et al., 2005).

### 5.4.5.4 Hybrid systems for VOCs treatment

Since nearly all the removal techniques have inherent drawbacks, and the separation method cannot always meet the requirements of emission standards of VOCs, they are often combined to achieve a better performance in VOCs treatment. Typically, the widely used combined systems include plasma-catalytic hybrid systems, biological and photocatalytic oxidation hybrid systems, biological process and adsorption hybrid systems, adsorption and photocatalysis hybrid systems, and systems combining VUV with other techniques (*e.g.* ozone oxidation and PCO). For example, the combination of plasma and catalyst not only increases the removal efficiency of VOCs, but also reduces the production of undesirable by-products (Delagrangue et al., 2006). An experiment of the removal of low-concentration of benzene, toluene and *p*-xylene (BTX) in air indicated that the plasma-catalytic hybrid system rendered much higher removal efficiencies for benzene (94%), toluene (97%) and *p*-xylene (95%) than the separate non-thermal plasma system (removal efficiency of 2%, 19% and 49% for benzene, toluene and *p*-xylene, respectively) (Fan et al., 2009). In combining the biological methods with PCO, an intention is to broaden the selectivity of the treatment system to VOCs with different characteristics. Generally, the BTF system performs well in the treatment of hydrophilic

VOCs, while the selectivity of PCO is much weaker. Using BTF as a pre-treatment of a PCO system, He et al. (2012) found that the removal efficiencies ranged from 79.4–99.8% (95.6% on average) for paint-related VOCs (ethyl acetane, toluene, ethylbenzene, xylene and trimethylbenzene isomers), higher than that in the separate PCO (88.7% on average) and BTF system (73.7% on average). The BTF system prolonged the catalyst lifetime in PCO, and the PCO ensured the excellent performance of the system, even for the hydrophobic VOCs. In a comparative study of toluene removal in air, the VUV-PCO system performed much better with higher efficiency (82.3% *versus* 14.5%) and lower O<sub>3</sub> production (1.8 ppm *versus* 30 ppm), as compared to a conventional PCO system (Huang and Leung, 2011). Apart from these combined systems, the adsorption and photocatalysis hybrid system was utilized to treat formaldehyde, toluene and other aromatics (Jo and Yang, 2009; Ao and Lee, 2005). Not only did the removal efficiencies increase, but also the productions of intermediates reduced.

In China, VOCs are extensively emitted from various industries, such as coating and painting, packaging, printing, shoes making, artificial leather manufacturing and petrochemical industry. To reduce VOCs emissions, removal techniques have been selectively applied under different situations. Overall, absorption, adsorption and incineration are traditional methods. In recent years, new techniques including membrane filtration, PCO, plasma and biological processes have drawn much attention of scientific communities, due to their advantages over traditional methods in removal efficiency, operating conditions and some other aspects. However, the traditional methods, particularly the adsorption technique, still occupy most of the markets in China. Instead, many new techniques such as UVU-PCO system are still in the stage of laboratory experiments. Further improvement and modification are needed for their industrial application, where the operational conditions are more complicated. In addition, high cost of many new techniques is another factor constraining their practical application. What is more, new techniques with high removal efficiencies are not urgently needed by industrial employers at this stage, because there are no national VOCs emission standards in China. Nevertheless, with increasing concerns about photochemical pollution, it is expected that detailed VOCs emission standards will be formulated and enacted in China. Subsequently, in near future the new removal techniques of VOCs will blossom throughout China. In particular, the biological processes with high removal efficiency, few undesirable byproducts and moderate operating conditions, are of great potential in VOCs removal.

## 6.6 Control policy for VOCs and/or photochemical smog

Since air pollution problems are becoming increasingly complicated and entangled from a regional perspective, air pollution policies, including air pollution prevention and control measures, have been/are being implemented to effectively control the emissions of air pollutants and improve the air quality in China. The policy on VOCs and/or photochemical smog in China contains different types of measures, including laws, standards, regulation, action plans and others. As a developing country, Chinese government follows a strict “command-control” management strategy from the central government to local governments. Considering the nationwide variations and differences, environmental control policies are often formulated first in a general way, by the central government and the Ministry of Environment, while specific control measures are implemented by local governments, within the framework of the central government, according to local conditions. In addition, swift but short-term control measures can be implemented by local governments when mega-events are held in specific cities, such as the 2014 APEC meeting in Beijing, the 2010 Asian Games in Guangzhou, the 2010 Expo in Shanghai, and the 2008 Olympic Games in Beijing (Zhou and Elder, 2013). In this section, we mainly focus on the current status and/or the development of national control policies of VOCs and/or photochemical smog in China, which can provide useful information on the direction and the strength of the control strategies of VOCs and/or photochemical smog.

### 6.1.6.1 The development of control policies on VOCs and/or photochemical smog

#### 6.1.1.6.1.1 Laws

The regulations for atmospheric pollution control in China were first proposed in 1979 as the trial version of the Environmental Protection Law (EPL). The first formal version of the regulation, *i.e.*, the Law of the Prevention and Control of Atmospheric Pollution, was enacted in 1987, and amended in 1995 and 2000. As the air pollution has been shifting from typical coal smoke pollution to combined vehicle and coal pollution, major atmospheric pollutants have been changing from SO<sub>2</sub> and PM<sub>10</sub>, to PM<sub>2.5</sub> and O<sub>3</sub> and its precursors. The Atmospheric Pollution Prevention and Control Law (APRCL 2016) was amended on 29 August 2015 and was enacted on 1 January 2016. Compared to the 2000 version, the current version of APRCL has expanded the scope for atmospheric pollution prevention and control, including coal combustion, industrial emissions, vehicular and vessel emissions, dust, agriculture and other emissions, which has placed PM<sub>2.5</sub> and O<sub>3</sub> and its precursors in a core position in the prevention and control of air pollution in China, in addition to SO<sub>2</sub> and smoke dust (CCICED, 2014). In addition, the joint prevention and control mechanisms for regional air pollution were improved in the aspects of emission standards, regional economic distributions and development, traffic management, and the development of clean fuel. Furthermore, the penalties for violations were strengthened and the cost of atmospheric environment illegalities was increased in APRCL 2016 as compared to APRCL 2000.

#### 6.1.2.6.1.2 Air Quality Standards

6.1.2.1.6.1.2.1 **National ambient air quality standard** To strengthen the control of atmospheric pollution, the National Ambient Air Quality Standard (NAAQS), which limits the ambient levels of selected air pollutants and sets clear reduction goals for air quality planners and regulators, was revised on 29 February 2012 and enacted on 1 January 2016 (Table 7). The grades of NAAQS were revised, with Grade III (the limits for special industrial areas) merged into Grade II for residential commercial, normal industrial and rural areas. In addition, the levels of PM<sub>2.5</sub> and a short-term 8-hour standard of O<sub>3</sub> concentrations have been added in the current NAAQS. The annual average level of PM<sub>2.5</sub> in Grade II of the current NAAQS is 35 µg/m<sup>3</sup>.

consistent with the WHO's recommended interim target-1 standard, while the 8-hour average concentration of O<sub>3</sub> is 160 µg/m<sup>3</sup>, indicating that more effective controls on O<sub>3</sub> precursors should be implemented to meet the stringent standards. Furthermore, the limits for PM<sub>10</sub> and NO<sub>2</sub> are more rigorous in the new NAAQS, with the annual average concentrations of 70 and 40 µg/m<sup>3</sup>, respectively, compared to 100 and 80 µg/m<sup>3</sup> in the NAAQS enacted in 2000.

**Table 7** National ambient air quality standards in China (unit: µg/m<sup>3</sup>)

alt-text: Table 7

Pollutant	Averaging time	Grade III level of China ambient air quality standard (GB 3095-1996 & amendment in 2000) <sup>a</sup>	Grade II level of China ambient air quality standard (GB 3095-1996 & amendment in 2000) <sup>a</sup>	Grade I level of China ambient air quality standard (GB 3095-1996 & amendment in 2000) <sup>a</sup>	Grade II level of China ambient air quality standard (GB 3095-2012) <sup>b</sup>
Sulfur dioxide (SO <sub>2</sub> )	1-hr	700	500	150	500
	24-hr	250	150	50	150
	Annual	100	60	20	60
Respirable suspended particulates (PM <sub>10</sub> )	24-hr	250	300	50	150
	Annual	150	200	40	70
Fine suspended particulates (PM <sub>2.5</sub> )	24-hr	N/A	N/A	35	75
	Annual	N/A	N/A	15	35
Nitrogen dioxide (NO <sub>2</sub> )	1-hr	240	240	200	200
	24-hr	120	120	80	80
	Annual	80	80	40	40
Ozone (O <sub>3</sub> )	1-hr	200	200	160	200
	8-hr	N/A	N/A	100	160
Carbon monoxide (CO)	1-hr	20,000	10,000	10,000	10,000
	24-hr	6,000	4,000	4,000	4,000

<sup>a</sup> China ambient air quality enacted on 6 Jan. 2000 (GB 3095-1996 & amendment in 2000).

<sup>b</sup> China ambient air quality enacted on 1 Jan. 2016 (GB 3095-2012).

**6.1.2.2 Industrial emission standards** Many emission standards for the VOC-related industries have been revised and/or newly established in the recent years. In addition to the existing standards for different industries, new standards including the emission standards of pollutants for the petroleum chemical industry (GB 31571-2015), the petroleum refining industry (GB 31570-2015), and the synthetic resin industry (GB 31572-2015) were implemented by the central government on 01 July 2015 (Table 8). It should be noted that the revised standard for thermal power plants (GB 13223-2011) is more stringent than that in the US, Canada and Europe. The VOCs species that are included under these standards are the total NMHCs, benzene, toluene, xylenes, ethylbenzene, 1,3-butadiene, formaldehyde, acetaldehyde, acetone and acrolein.

**Table 8** Emission standards for different industries implemented by the central government.

alt-text: Table 8

Standard	Number	Enacted date
Integrated emission standard of air pollutants	GB 16297-1996	1 Jan. 1997
Emission standards for odor pollutants	GB 14554-1993	15 Jan. 1994

Emission standards of cooking fume	GB 18483-2001	1 Jan. 2002
Emission standard of air pollutant for bulk gasoline terminals	GB 20950-2007	1 Aug. 2007
Emission standard of air pollutant for gasoline transport	GB 20951-2007	1 Aug. 2007
Emission standard of air pollutant for gasoline filling station	GB 20952-2007	1 Aug. 2007
Emission standard of pollutants for synthetic leather and artificial leather industry	GB 21902-2008	01 Aug. 2008
Emission standard of pollutants for rubber products industry	GB 27632-2011	01 Jan. 2012
Emission standard of air pollutants for thermal power plants	GB 13223-2011	01 Jan. 2012
Emission standard of pollutants for coking chemical	GB 16171-2012	01 Oct. 2012
Emission standard of air pollutants for steel rolling industry	GB 28665-2012	01 Oct. 2012
Emission standard of pollutants for battery industry	GB 30484-2013	01 Mar. 2014
Emission standard of pollutants for petroleum chemistry industry	GB 31571-2015	01 Jul. 2015
Emission standard of pollutants for petroleum refining industry	GB 31570-2015	01 Jul. 2015
Emission standard of pollutants for synthetic resin industry	GB 31572-2015	01 Jul. 2015

Emission standards for other specific industries have been implemented by local governments according to the development status of local industries. For example, to strengthen the control and management of VOCs emission industries, emission standards including VOCs from the furniture manufacturing operations (DB 44/814-2010), the printing industries (DB44/815-2010), the surface coating of automobile manufacturing (DB44/816-2010) and the shoe-making industry (DB44/804-2010) have been implemented by Guangdong Province. Standards of integrated VOCs emissions for the bio-pharmaceutical industry, semiconductor industry, and surface coating of automobile industry were implemented in Shanghai, and standards of integrated VOCs emissions, surface coating of automobiles, industrial surface coatings, vehicle maintenance and repair, wooden furniture manufacturing, petroleum refining and manufacturing and printing industries were implemented in Beijing.

**6.1.2.3.6.1.2.3 Vehicular emission standards** Controlling VOCs emissions from vehicles is a top priority in China, especially given that the major air pollution sources have been shifting from coal burning to a mix of coal burning and vehicle emissions in many cities and regions (Wang and Hao, 2012). In China, the emission standards for new vehicles and engines were developed based on the European Union's standards, with five stages of vehicular emission standards implemented since 1999. Since 1 July 2011, all the light-duty gasoline cars, dual-fuel cars, and single-fuel cars for retail sale should meet the 4th phase of vehicle emission standards. On 1 February 2013, Beijing adopted the 5th phase of vehicle emission standards in China. Although the 5th phase of vehicle emission standards was the same as the 4th phase on the emissions of total hydrocarbons for the cars (*e.g.*, 0.1 g/km for cars with maximum mass (MM) larger than 2,500 kg and for cars with reference mass (RM)  $\leq 1,305$  kg; 0.13 g/km for cars with  $1,305 \text{ kg} < \text{RM} \leq 1,760$  kg; and 0.16 g/km when  $1,760 < \text{RM}$ ), the 5th phase of vehicle emission standards further limited total emission of NMHCs. The standard of total NMHC emissions was 0.068 g/km for car with  $\text{MM} > 2,500$  kg and  $\text{MV} \leq 1,350$  kg, 0.090 g/km with  $1,350 \text{ kg} < \text{RM} \leq 1,760$  kg, and 0.108 g/km with  $\text{RM} > 1,760$  kg. Furthermore, the regulations specified that new vehicles that did not meet the 5th phase standards should not be manufactured. In addition, light-duty gasoline cars and heavy-duty diesel vehicles for public transportation and cleaning purposes that did not meet the 5th phase emission standards could not to be registered and sold (IGES, 2014). Since then, both the PRD region and Shanghai have gradually adopted the 5th phase vehicle emission standards on 31 December 2015 and 30 April 2014, respectively. It is expected that the 5th phase vehicle emission standards will be implemented throughout China on 1 January 2018 (MEP, 2013).

For the emissions of vehicles in use, a supervision and management system is being implemented in China, with an annual environmental protection attainment examination. The standard monitoring methods for the vehicle emissions are based on the documents of "Limits and measurement methods for exhaust emissions from motorcycles and mopeds at dual idle speed (GB 14621-2011)" and "Guideline for air quality assessment of passenger cars (GB/T 27630-2011)", while the standard measurement method for the 5th phase emission standards is "Limits and measurement methods for emissions from light-duty vehicles (China 5)" (IGES, 2014). Cars which fail the attainment examination will be marked with a yellow label, meaning "outdated". The cars with high exhaust emissions will be phased out mandatorily according to the standards implemented on 1 May 2013.

### **6.1.3.6.1.3 Joint prevention and control of regional air pollution**

The levels of air pollutants, especially the secondary air pollutants (O<sub>3</sub> and SOA) and their precursors with relatively low reactivity (*i.e.*, the low-reactivity VOCs) at a specific location are influenced by the local emissions and the transport from upwind areas. The complex air pollution in China is not just a local issue but a domestic regional cross-boundary problem. In addition to the efforts made on the control of local emissions, regional coordination to

control cross-boundary air pollutants is necessary to reduce the impact of atmospheric pollution on downwind locations, and improve the regional air quality. Until now, nine regions, including the Beijing-Tianjin-Hebei region, the PRD region, the YRD region, central Liaoning region, Shandong Peninsula, Western Taiwan Straits Metropolitan region, Cheng-Yu Metropolitan region, Wuhan Metropolitan region, and Cheng-Zhu-Tan region, have been designated as pilot regions for the joint prevention and control of regional air pollution (Zhou and Elder, 2013). The APRCL 2016 improved the mechanism for joint prevention and control of regional air pollution through the principles of joint monitoring, joint supervision, joint assessment, and joint coordination, and the APRCL designated VOCs as one of the key air pollutants.

### 6.2.6.2 Actions for the control of VOCs by local governments

In China, after the target of the total emission control of air pollutants has been implemented by the central government (the Ministry of Environmental Protection), the government of each administrative region implements different programs/plans to achieve the reduction goal. Table 9 summarizes the programs/plans for the control of VOCs from different industries in megacities in China in recent years, such as Beijing, Shanghai, Guangdong, Zhejiang and Jiangsu.

**Table 9:** Programs/plans for the control of VOCs from different industries in Beijing, Shanghai, Guangdong, Zhejiang and Jiangsu.

alt-text: Table 9

Location	Year	Action
Beijing	2006–2010	The 12th–16th phases of air pollution control measures
	2013	The clean air plan (2013–2017)
Shanghai	2012	Strengthening the prevention and control of the emissions of VOCs from typical industries
	2013	Specialized control measures on the VOCs emissions from dry cleaning
	2013	The clean air plan (2013–2017)
	2014	Strengthening the prevention and control of the VOCs emitted from typical VOC-emission enterprises
	2015	The program for the control of VOCs emitted from industries/the guidelines for the support for the VOC-emitted enterprises to reduce VOCs emissions
Guangdong	2009	The program for the control of the emissions of VOCs from typical industries in Guangzhou
	2010	Clean air plan in the PRD region
	2011	Control measures on the VOCs emissions from furniture manufacturing in Shenzhen
	2012	Strengthening the prevention and control of the VOCs emitted from typical VOC-emission enterprises in the PRD region
	2013	The air clean plan for the PRD region-phase II (2013–2015)
	2014	The program for the control of VOCs emitted from printing
Zhejiang	2010	The clean air plan
	2011	Standardization of production management in chemical industries
	2012	Strengthen the emissions of chemical industries
	2012	The improvement for the control for the missions of printing and dyeing, paper making, and chemical industries
	2013	The integrated program for the VOCs emissions
Jiangsu	2011	The survey for the VOCs emissions from the chemical industries
	2012	Strengthen the prevention and control of VOCs pollution
	2013	Strengthen the prevention and control of VOCs emitted from typical industries in chemical industrial park



2014	The plan for the prevention and control of air pollutants
2015	The program for the control of VOCs emitted from typical industries

Based on the above programs/plans, different measures were implemented to control VOCs emissions, in addition to the strict standards described above (Zhong et al., 2013). The measures mainly focused on vehicular emissions, vessel emissions, and industrial emissions by the following means, which include routine rules and aggressive measures during mega-events (Kelly and Zhu, 2016): 1) controls on new industrial projects and implementation of strengthened environmental impact assessment; 2) elimination of slow production capacity for different industries (CCICED, 2014); 3) optimizing industrial locations; 4) providing funding to enterprises to improve the control equipment, covering about 30–50% of the control fees; 5) strengthening the monitoring of VOCs emissions from typical industries; 6) limiting the amount of coal-fired and fuel-fired power plants; 7) expanding the use of nuclear power and the use of hydroelectric power; 8) introducing environmental friendly cars and clean fuel for vehicles and vessels; 9) limiting the number of vehicles and the amount of vehicles on the road; 10) strengthening the labeling system for vehicles in use and developing monitoring methods for the emissions of vehicles in use; 11) installing special equipment at gas stations, oil storage tanks and oil tank trucks to control/recover the fuel evaporation; 12) phasing out the high VOCs content products such as synthetic resin, petroleum refining industry and rubber products listed in Table 8, and replacing them with low-VOCs ones; and 13) developing taxation policies conducive to VOCs control in the coating industries.

### 6.3.6.3 Studies on the effectiveness of control policies on ambient VOCs

Long-term variations of VOCs can provide useful information on the effectiveness of the policies on the control of VOCs emissions. Most long-term VOCs studies have been based on the investigation of variations of VOCs emission inventories. For example, Lu et al. (2013) investigated emission trends and variations in source contributions of VOCs in the PRD region from 2000 to 2009 based on the emission inventories developed in this region. On-road mobile sources, the largest VOCs contributor, had a slight declining trend from 58% to 53% from 2000 to 2009, while industrial solvent usage increased from 18% to 33%. Among the on-road mobile sources, the contributions of motorcycles decreased from 57% in 2005 to 45% in 2009 because of the restriction or prohibition on motorcycles in urban areas in most cities of the PRD region, while the contributions of passenger cars increased from 17% 2000 to only 41% in 2009, even though the number of passenger cars increased by 530% in last decade, mainly because of the implementation of stricter vehicle emission standards. Different from on-road mobile sources, the VOCs emissions from industrial solvent use sources have tripled from 2000 to 2009, due to the limitations of control technology, ineffective operations, or less supervision. Based on observational data collected from 2005–to 2013, long-term variations of NMHCs sources were investigated by the PMF model and compared with those of the emission inventories in Hong Kong (Ou et al., 2015b). The PMF-resolved contributions of traffic-related sources and solvent-related sources did not change from 2005 to 2013, different from those in the emission inventory, which indicated an increasing trend of traffic-related sources and a decreasing trend of solvent-related sources. The difference between the PMF-resolved results and the emission inventory was related to the different mechanisms and performance of the two approaches (Ling and Guo, 2014), of which the PMF model investigated the characteristics of VOCs based on measurement data at the receptor sites and the emission inventory estimated the emission loadings based on bottom-up survey (Yu et al., 2011; Zheng et al., 2009).

Other studies have been conducted to investigate the effectiveness of aggressive measures taken during mega-events, *i.e.*, the 2010 Guangzhou Asian Games and the 2008 Beijing Olympic Games. For example, after the eight steps of the abatement strategy for the Guangzhou Asian Games 2010, the VOCs emissions were reduced by 39.7% during 12–27 November 2010 (Liu et al., 2013a). In Beijing, the influence of the measures during 2008 Olympic Games was investigated by several research groups, and all indicated that the aggressive control measures can reduce the anthropogenic emissions of VOCs significantly (Wang et al., 2014a, 2014b, 2014c, 2014d; Shao et al., 2011; Li et al., 2010; Wang et al., 2010a, 2010b, 2010e). For example, Liu et al. (2009a, 2009b) analyzed the variations of benzene, toluene, ethylbenzene and xylenes in Beijing urban area during July–October 2008, covering the periods of the 2008 Olympic Games and Paralympic Games. Together these compounds were reduced by 36–53% because of the aggressive measures for the 2008 Olympic Games. In addition, by using the emission inventory with the revised emission factors for traffic emissions due to the transportation control measures, Zhou et al. (2010) compared traffic emissions before and after the 2008 Olympic Games in Beijing. Urban traffic emissions of VOCs were reduced by 55.5% when the aggressive measures for vehicles, including travel restriction by odd-even numbered license plates, truck operational restrictions and removal of yellow-labeled vehicles, were implemented.

Overall, from the review of the policies on the control of VOCs and/or photochemical smog, the stricter and aggressive measures help to alleviate air pollutants. Even though the atmospheric pollution is likely to be persistent because of on-going urbanization and industrialization, it is possible that the air quality can be gradually improved if appropriate measures are undertaken.

### 6.4.6.4 Implication for the control strategies of VOCs and/or photochemical pollution

From the 12th five-year plan (2011–2015), the Chinese government began to attach great importance to controlling VOCs emissions, regarding VOCs as a top priority among atmospheric pollutants for effectively improving air quality. Even though laws, regulations, standards and measures to control VOCs and/or photochemical smog have been introduced in recent years, they still need to be further strengthened and standardized, and should include the following aspects:

- 1) Developing evidence-based air quality management in a regional perspective. In recent years, different research groups have studied the characteristics of VOCs and its secondarily photochemical products, providing valuable insights and implications for control policies. However, the interaction of atmospheric pollution and control policies between regions, which could help to shape the management of joint prevention and control of VOCs and photochemical smog, still needs further investigation, especially given the momentum of economic growth all over the country (Zhong et al., 2013). This evidence-based air quality management could act as a supplementary means for the traditional command-control air quality management. It should be noted that the monitoring networks already established do provide strong data supports for the studies on VOCs and photochemical smog, which should be very helpful to bridge science and policy.
- 2) Accelerating the implementation of the regulation of major VOC-related industries. Until now, the control policies of VOCs have only focused on a small number of VOC-related industries as stated above, while standards for other industries are still being implemented or even not implemented. The lack of these standards has resulted in “no legal basis” for the environmental protection departments at various levels to regulate the VOC-related industries, limiting the prevention and control of VOCs from industries. In addition, in the implemented standards of VOCs industries, only the limits of a small number of VOCs, as well as the total VOCs were provided. Further reduction of these species may be less effective because other reactive VOCs species from the same industry were not controlled. For example, the emission standards of VOCs for the printing industry (DB44/815-2010) only limit the emissions of benzene, toluene, xylene and total VOCs, while other highly reactive species emitted from the printing industry are not included (Ou et al., 2015b; Ling and Guo, 2014).
- 3) Adopting reactivity-based methods for the control of VOCs emissions. Most of the reduction strategies are mass-based, meaning that the weight of total emitted VOCs should be controlled without considering the reactivity of individual VOCs. Replacing heavier VOCs, with lower photochemical reactivity, by lighter VOCs with higher photochemical reactivity could result in the deterioration of photochemical smog in specific regions where O<sub>3</sub> formation is VOC-limited. VOCs with high photochemical reactivity should be placed in a core position in the prevention and control of VOCs emissions. Furthermore, it is well documented that cutting VOCs and NO<sub>x</sub> in a specific ratio can optimize the reduction of O<sub>3</sub>. Therefore, not only the abundance and reactivity of VOCs, but also the abundance of NO<sub>x</sub> should be considered in the control of photochemical smog.
- 4) Developing more credible analysis systems and removal technology for VOCs. As VOCs are a group including hundreds of species, and each one reacts at a different rate and with a different reaction mechanism, developing more credible analysis systems and removal technology for VOCs is required for the prevention and control of VOCs and photochemical smog.
- 5) Conducting substantial regulation and evaluation for the effectiveness of the policies. The government should evaluate the effectiveness of the policies based on whether the levels of air pollutants meet the standards and/or the reduction goals after the implementation of policies. Furthermore, the reduction of air pollutants is related to the integrated implementation of a series of policies, of which the effectiveness varies. Given this, substantial regulation and evaluation of the effectiveness of individual policies should include timely revisions of the original policies in order to devise more appropriate policies to face the on-going changes in air pollutant challenges.

## 7.7 Future directions for VOCs studies

Improving air quality has become paramount in China for many years. Specifically controlling secondary pollutants, *e.g.* O<sub>3</sub> and SOA, as well as their precursors is one of the top priorities of the central government. Over the past decades, the capacity for tropospheric VOCs measurement and analysis in China has increased significantly. There is also a growing interest on the chemical degradation and regeneration pathways of VOCs and other radical species in various regions. The number of publications and new findings related to tropospheric VOCs in China has grown exponentially in the past 10 years, mainly investigating their abundance, composition and sources, as well as the chemical processes responsible for the generation of O<sub>3</sub> and SOA, and VOCs control strategies in the cities and regions of China. Such progress is achieved through the combination of laboratory analysis, field observations, numerical simulations and policy studies. However, future research is still needed to obtain a more complete and comprehensive picture of the roles of VOCs and their impact on atmospheric chemistry in China.

### 7.1.7.1 Strengthening measurements

Tremendous efforts have been made to investigate tropospheric VOCs in China. Government departments, scientists and the public have always been open and adaptable to new ideas and advanced technology. It is recommended that the scientific community continues this tradition, to provide high-quality monitoring data. It is anticipated that a large amount of VOCs data will be generated from advanced ground based, aircraft and satellite measurements in the coming years. These data will help researchers to better characterize the tropospheric VOCs composition in China, monitor the variations in VOCs levels, and validate and improve model performance. Data quality and transparency are keys for future tropospheric VOCs studies in China. Appropriate monitoring programs, which can provide the needed data for better understanding the characteristics of VOCs and their roles in atmospheric chemistry, are one of the most important prerequisites for effective control strategies. Even though local governments have benefited from different monitoring programs and have implemented policies accordingly, most of the data and/or sampling campaigns have mainly occurred over limited time periods. Long-term measurements of VOCs with more monitoring locations and more species detected, can provide a robust databases and significant insights in terms of emissions, photochemical reactions, transport and other physical processes, and are still limited (Louie et al., 2013; Ou et al., 2016), especially given that the emission standards are being improved, the structures of industrial enterprises and energy use are being adjusted, and emission control measures are being strengthened (Zhang et al., 2013; Yuan et al., 2013). For example, the combination of economic development and implementation of different control measures can cause VOCs emissions and composition to change in complex ways that are sometimes difficult to predict (*e.g.*, Lyu et al., 2016a, 2016b). Therefore, comprehensive monitoring programs on the characteristics of

VOCs emissions, including composition, emission factors/rates, and source profiles, which are essential for top-down and bottom-up estimates of VOCs abundance, are urgently needed (Ou et al., 2015b).

Apart from VOCs other species including radicals, intermediates of photochemical reactions, and photochemical products need to be monitored because the formation of O<sub>3</sub> and SOA through photooxidation of VOCs involves various reactions and species (Hua et al., 2008; Hofzumahaus et al., 2009; He et al., 2010). In addition, detailed photooxidation mechanisms of certain categories/species of VOCs are still not fully elucidated such as organic nitrates (Lyu et al., 2015). Monitoring these species can provide meaningful data for the in-depth investigation and prediction of photochemical behavior of VOCs in the atmosphere.

It is important to continuously develop measurement techniques, though the mass spectrometric technology for real-time speciated VOCs measurements has been significantly improved in recent years. Instruments like the Proton Transfer Reaction–Time-of-Flight–Mass Spectrometer (PTR-ToF-MS), the Time-of-Flight Chemical Ionization Mass Spectrometer (ToF-CIMS), and the Thermal Desorption Aerosol Gas Chromatography–Time-of-Flight–Aerosol Mass Spectrometer (TAG-ToF-AMS) have become affordable and available to deploy for field measurements (Jordan et al., 2009; Williams et al., 2014; Yuan et al., 2016). Compared to the standard and classical whole air samples collected by canisters, the new technology will provide a much finer temporal resolution in VOCs concentration, much more VOCs species, as well as offering finer precision, which will improve the air quality model inputs and therefore model outcomes.

### **7.2.7.2 Combining laboratory studies, field measurements and model simulations**

Laboratory studies provide an effective means to directly explore the rates and mechanisms of the oxidation of various VOCs. However, it is clearly not feasible to study the degradation of VOCs based only on laboratory studies because reaction conditions in the chamber are different from those in the real atmosphere, where there is a continuous supply of VOCs and the meteorological conditions substantially vary. On the other hand, though field measurements can help investigate the evolution of VOCs in the real atmosphere, limitations still exist in the exploration of detailed mechanisms and the quantification of numerous pathways (de Gouw et al., 2008; Brock et al., 2008). Although model simulations can provide detailed information on the processes that form O<sub>3</sub> and SOA *via* VOCs oxidation, large discrepancies are frequently determined between measurement and simulation, which are related to missing mechanisms, inappropriate parameterization and unstudied species (de Gouw and Jimenez, 2009; Pye and Seinfeld, 2010). These limitations can be minimized by combining high-resolution data from field measurements and detailed parameterization from laboratory studies for model input.

Regarding the chemical processes, one of the most important concerns is that the degradation mechanisms for certain classes of VOCs are still uncertain such as organic nitrates (Lyu et al., 2015), while most of the present databases only provide the reactivity of unstudied VOCs based on structure-reactivity correlations (Atkinson, 2007). Furthermore, although the aromatic hydrocarbons and terpenes have been identified as important SOA precursors, the detailed chemical and physical processes leading to SOA formation, together with their environmental and climate feedbacks, are almost certainly another major current challenge in atmospheric photochemical pollution research (Carlton et al., 2009; Pye and Seinfeld, 2010). In addition to homogeneous reactions between species, the influence of heterogeneous and multi-phase chemical processes on the formation and destruction of O<sub>3</sub>, SOA and other photochemical pollutants is also important in the atmosphere (Ervens and Volkamer, 2010; Knote et al., 2014; Li et al., 2014a, 2014b), which will be an active research area for future studies of VOCs and their roles in O<sub>3</sub> and SOA formation.

For the physical processes, meteorological conditions indeed have significant influence on the reaction and distributions of VOCs, while deposition of specific VOCs and their photochemical products, as well as the interaction between deposition and emissions/abundance of VOCs should not be ignored (Li et al., 2014a, 2014b).

### **7.3.7.3 Assessment of VOCs control strategies**

Following from the increasing recognition of the critical roles of VOCs in the formation of photochemical smog and haze-fog, various control measures have been/will be implemented in China. The most important criterion for evaluating their success is whether the VOCs reductions result in air pollutant levels that meet the air quality standards. As VOCs consist of hundreds of species emitted from various sources, the control policies on VOCs should vary according to their characteristics including abundance, emissions and reactivity. The assessment of each policy based on sound scientific knowledge is essential given the continuous economic development and the increasing recognition of human and environmental health issues (Zhong et al., 2013). Furthermore, policy development has a strong correlation with other issues, including community acceptance, human health, policy transparency and other socio-economic processes. In short summary the following questions remain to be answered: 1) How will the policies implemented by government at different levels work co-operatively? 2) Which policy will work best for the reduction of VOCs and other photochemical pollutants, by considering the balance between the implementation cost and social benefits? (Crane and Mao, 2015; Qiu et al., 2015; Gao et al., 2016) 3) What is the degree of community acceptance of these policies? and, 4) What feasible is the ongoing development of these policies? Overall, China has a solid foundation for VOCs monitoring and control, and the strategies proposed here will help China to best meet evolving air quality challenges in the future.

## **Acknowledgements**

This study was supported by the Research Grants Council of the [Hong Kong Special Administrative Region](#) via grants [PolyU5154/13E](#), [PolyU152052/14E](#), [CRF/C5004-15E](#) and [CRF/C5022-14G](#). This study is partly supported by the [Hong Kong PolyU Hong Kong Polytechnic University](#) internal grant ([1-ZVCX](#) and [4-BCAV](#)) and the [National Natural Science Foundation of China](#) (No. [41275122](#)). The authors are grateful to the Australia-China Centre for Air Quality Science and Management (ACC-AQSM) for helpful discussions in preparing the manuscript.

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## Graphical abstract

