Ambient air benzene at background sites in China's most developed coastal regions: Exposure levels, source implications and health risks

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HIGHLIGHTS

- Background benzene had higher cancer risk in China's developed regions.
- Coal/biofuel burning for heating increased benzene levels in winter in north China.
- Industrial emission contributed substantially to benzene in the Yangtze River Delta.
- Vehicle exhaust was the main source of benzene in the Pearl River Delta.

ARTICLE INFO

ABSTRACT

Benzene is a known human carcinogen causing leukemia, yet ambient air quality objectives for benzene are not available in China. The ambient benzene levels at four background sites in China's most developed coastal regions were measured from March 2012 to February 2013. The sites are: SY_{NECP}, in the Northeast China Plain (NECP); YC_{NCP}, in the North China Plain (NCP); TH_{YRD}, in the Yangtze River Delta (YRD) and DH_{PRD}, in the Pearl River Delta (PRD). It was found that the mean annual benzene levels (578–1297 ppt) at the background sites were alarmingly higher, especially when compared to those of 60–480 pptv monitored in 28 cities in the United States. Wintertime benzene levels were significantly elevated at both sites (SY_{NECP} and YC_{NCP}) in northern China due to heating with coal/biofuels. Even at these background sites, the lifetime cancer risks of benzene (1.7–3.7E−05) all exceeded 1E−06 set by USEPA as acceptable for adults. At both sites in northern China, good correlations between benzene and CO or chloromethane, together with much lower toluene/benzene (T/B) ratios, suggested that benzene was largely related to coal combustion and biomass/biofuel burning. At the DH_{PRD} site in the PRD, benzene revealed a highly significant correlation with methyl tert-butyl ether (MTBE), indicating that its source was predominantly from vehicle emissions. At the TH_{YRD} site in the YRD, higher T/B ratios and correlations between benzene and tetrachloroethylene, or MTBE, implied that benzene levels were probably affected by both traffic-related and industrial emissions.

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1. Introduction

Benzene has been classified as a known Group I human carcinogen by the International Agency for Research on Cancer (IARC) (WHO, 1999). It has been estimated that a lifetime exposure of 1 μg/m³ of benzene leads to about 6 cases of leukemia per 1,000,000 inhabitants (WHO, 2000). Benzene may also cause central nervous system depression, cardiac arrhythmias, respiratory irritation and aplastic anemia (USEPA, 2002). As one of the most important hazardous air pollutants

with adverse health effects, benzene in ambient air is widely regulated in many countries, or regions, to protect public health. For example, an annual limit of 5 μg/m³ was recommended for benzene in ambient air by the European Union (EU, 2008), and the Inhalation Minimal Risk Level (MRL, at a cancer risk of 1 in 10,000) of 4.0 ppbv was established by the United States Environmental Protection Agency for benzene (USEPA, 2009a). These guidelines, or limits, for ambient benzene levels, however, are not available in China.

Since benzene has been forbidden to be used in solvents, the main emission sources are from combustion processes, including biomass/biofuel burning and fossil fuel combustion (Andreae and Merlet, 2001; Moreira dos Santos et al., 2004; Liu et al., 2008). The rapid economic growth in recent decades has resulted in coal consumption in China

reaching 2.41 billion tons Standard Coal Equivalent (SCE) by 2012, the number of vehicles surging to over 100 million with 37.5 million tons of gasoline, and 107 million tons of diesel being consumed by the transportation sector (NBSC, 2013a). Besides fossil fuels, it was estimated that 110–158 million tons per year of agricultural residues were burned in situ (Streets et al., 2003; Yan et al., 2006), and 522–568 million tons of stalks and firewood were used for cooking and heating in rural areas in China (NBSC, 2008). This huge fuel consumption induces a large amount of primary air pollutants, including benzene, being emitted into the atmosphere (Klimont et al., 2002; Wei et al., 2008, 2014). As estimated by Wei et al. (2014), total emissions of benzene in China were up to 1.06 million tons in 2005. With these massive benzene emissions, there are serious concerns for public health, and the regulation of ambient benzene level is of high importance in China.

More importantly, China's east–west imbalance in economic status and population density makes the health risks of ambient benzene a more alarming problem. The ten developed coastal provinces or municipalities, including Liaoning, Hebei, Beijing, Tianjin, Shandong, Jiangsu, Shanghai, Zhejiang, Fujian and Guangdong, covered 10.9% of China's land area. However, together they contained 40.6% of China's population in 2012, and they accounted for 61.3% of the Gross Domestic Product (GDP); 68.6% of the Gross Industrial Output; 27.9% of grain production; 54.8% of vehicle numbers and 50.5% of fossil fuel consumption (NBSC, 2013a). This implies that a larger portion of China's benzene emissions are concentrated in the densely populated coastal regions and, therefore, a large proportion of the population is exposed to elevated benzene levels in the ambient air. Previous studies in urban areas of this region, such as Beijing (Liu et al., 2009; Zhang et al., 2012a,b; Li et al., 2014) and Guangzhou (Wang et al., 2002; Barletta et al., 2008; Zhang et al., 2013), showed much higher benzene levels when compared to those reported in Europe, or in the United States. Even early in January–February 2001, benzene was found to pose potential health risks from a survey of volatile organic compounds (VOCs) in 43 Chinese cities (Barletta et al., 2005), mostly in the eastern areas. In China, the leukemia incidence rate was 4.3 per 100,000 in 2012 (Ferlay et al., 2013), with urban areas showing a higher occurrence than rural areas (Chen et al., 2012; Liu et al., 2013). In 2012, leukemia cases reported in China reached 65,778, accounting for 18.7% of the world's total leukemia occurrences (Ferlay et al., 2013). It is of high importance to investigate whether benzene exposure levels in China is a factor contributing to leukemia incidence.

To date, a systematic health risk assessment for benzene exposure has not been undertaken in China, and very few health risk studies are available with a focus on urban environments (Zhou et al., 2011; Zhang et al., 2012a; Li et al., 2014). The results of previous studies in urban areas cannot be regarded as representative of those in the whole developed coastal regions because field measurements were conducted at sites close to emission sources, and conducted over very short time spans. Monitoring of benzene levels at more background sites would, therefore, not only reveal background exposure levels, but also reflect the impact of regional social–economic changes. Unfortunately, monitoring at background or remote locations is scarce and sporadic in China (Guo et al., 2004; Tang et al., 2009; Suthawaree et al., 2010; Xue et al., 2013; Zhang et al., 2014). To fully understand the exposure levels and the potential health risks, long-term measurements are needed. Furthermore, identifying major sources of benzene is crucial to reducing emissions.

In this study, we monitored benzene levels at four background sites in China's most developed coastal regions concurrently for a one-year period. The sites were located in the Northeast China Plain (NECP), the North China Plain (NCP), the Yangtze River Delta (YRD) region, and in the Pearl River Delta (PRD) region. The purposes of this study are: (1) to investigate the background exposure levels of benzene in the most developed coastal regions; (2) to explore the main emission sources of benzene and their spatiotemporal patterns; and (3) to estimate the potential health risks of benzene in these developed regions.

2. Methodology

2.1. Description of sampling sites

The geographical locations of the sampling sites are shown in Fig. 1. The sites are all research stations included in the Chinese Ecosystem Research Networks (CERN, available at: http://www.cern.ac.cn/0index/index.asp/; last access: 19 June 2014). They are all located at rural or remote areas without factories and workshops in the neighborhood, and they are suitable sites to monitor regional background atmospheric compositions.

The SY$_{NECP}$ site (Shenyang; 41.50°N, 123.40°E) is located in the Northeast China Plain (NECP), which has long been a famous base of China's heavy industry and a center of mining industry since 1953. Located in the center of the Liaoning Province, the SY$_{NECP}$ site can receive air pollutants from the surrounding industrial cities. The site is 35 km south of the provincial capital Shenyang, 38 km northwest of Benxi, 32 km to the northeast of Liaoyang and 55 km to the northeast of Anshan, making it a good regional monitoring station.
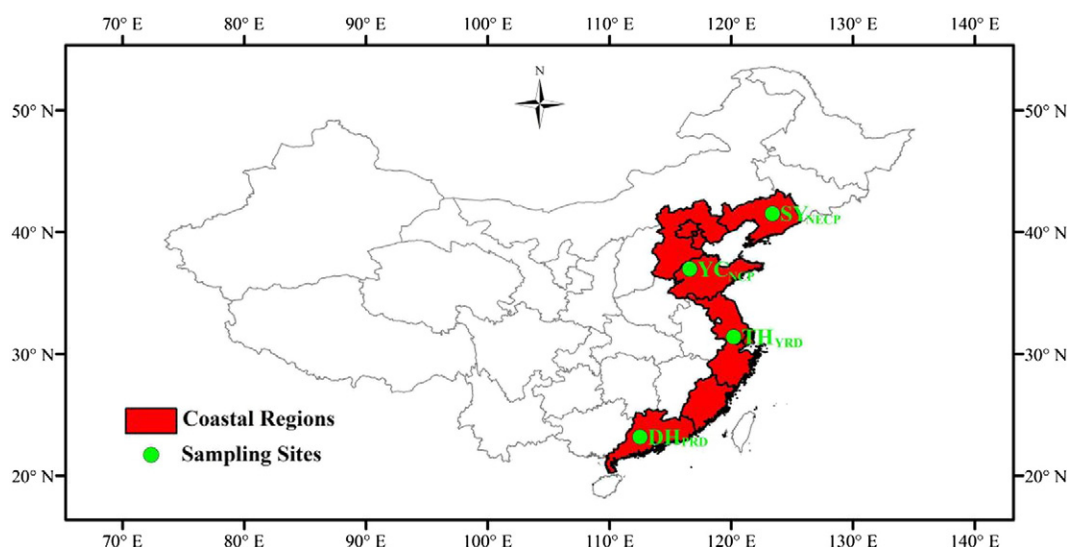

Fig. 1. Locations of the four sampling sites (green cycle) in China's most developed coastal regions (red colored areas).

The YC$_{NCP}$ site (Yucheng; 36.95°N, 116.60°E) is located in the NCP region, which geographically includes Beijing and Tianjin Municipalities, Hebei and Shandong Provinces, and some parts of Shanxi and Henan Provinces. The YC$_{NCP}$ site is located at CERN's Yucheng Integrated Agricultural Experimental Station (available at: http://www.cern.ac.cn/ssyz/ detail1.asp?sid=yucheng&tsortid=1&gjgl=1; last access: 19 June 2014), being 325 km to the south of Beijing and 56 km to the northwest of Jinan. The sampling site was surrounded by farmlands and small villages.

The TH$_{YRD}$ site (Taihu; 31.40°N, 120.22°E) is adjacent to the northeastern coast of Tai Lake in the YRD region, having a typical southeast–northwest monsoon climate (Cai et al., 2010). The TH$_{YRD}$ site is 153 km to the southeast of Nanjing, 120 km to the west of Shanghai and 120 km to the north of Hangzhou. The nearest city, Wuxi, is located 15 km northeast of the TH$_{YRD}$ site.

The DH$_{PRD}$ site (Dinghu; 23.17°N, 112.53°E) is located in the northwest of the PRD region, and in the northeastern suburb of Zhaoqing City, about 80 km away from Guangzhou City. The site is on a hill top in Dinghushan National Natural Reserve with a total area of 11.55 km^2 of monsoon evergreen broad-leaved forests. The DH$_{PRD}$ site is also a regional background station among the Baseline Air Pollution Monitoring Stations of Chinese Academy of Sciences (http://www.cas.cn/zt/kjzt/ywtz/; last access: 19 June 2014).

2.2. Field sampling and lab analysis

From March 2012 to February 2013, ambient air samples were collected at the four background sites every Wednesday, at approximately 14:00 local time, when the benzene levels were expected to be relatively lower due to its diurnal variation (Tang et al., 2007; Zhang et al., 2012a,b). Ambient air was compressed into cleaned and evacuated 1 L Silonite-treated stainless steel canisters (Entech Instruments Inc., California, USA), to approximately 30 psi in about 60 min using high-purity oil-free pumps. A total of 179 samples were collected during all sampling. These samples were transported back to the laboratory and analyzed within one month after sample collection.

The samples were analyzed with a Model 7100 Preconcentrator (Entech Instruments Inc., California, USA) coupled with an Agilent 5973N gas chromatography-mass selective detector/flame ionization detector (GC-MSD/FID, Agilent Technologies, USA). Detailed cryogenically concentration steps are described elsewhere (Zhang et al., 2012c). In summary, 500 mL air samples were firstly drawn through a liquid-nitrogen cryogenic trap with glass beads at −160 °C. After trapping, this primary trap was heated to 10 °C, and then all target compounds were transferred, by pure helium, to the secondary trap at −50 °C with Tenax-TA as adsorbents. The redundant H$_2$O and CO$_2$ were removed through this micro-Purge-and-Trap step. The secondary trap was then heated to get VOCs transferred by helium to a third cryo-focus trap at −170 °C. After the focusing step, the trap was rapidly heated and the VOCs were transferred to the GC-MSD/FID system. The mixture was firstly separated by a DB-1 capillary column (60 m × 0.32 mm × 1.0 μm, Agilent Technologies, USA), with helium as the carrier gas, at a constant rate of 4.0 mL/min, and then split into two ways controlled by a splitter: one is a 0.35 m × 0.10 mm I.D. stainless steel line followed by MSD detection, and another is a HP PLOT-Q column (30 m × 0.32 mm × 20.0 μm, Agilent Technologies, USA) followed by FID detection. The GC oven temperature was programmed to be initially at 10 °C, holding for 3 min; this then increased to 120 °C at 5 °C/min, and then to 250 °C at 10 °C/min with a final holding time of 20 min. The MSD was operated in selected ion monitoring (SIM) mode, and the ionization method was electron impacting (EI, 70 eV). Carbon monoxide (CO) in the air samples was analyzed by an Agilent 6890 gas chromatograph equipped with an FID and a packed column (5Å Molecular Sieve 60/80 mesh, 3 m × 1/8 in.). After separation by the packed column, CO was converted by a Ni-based catalyst to CH$_4$ and was then detected by FID.

2.3. Quality control and quality assurance (QA/QC)

Before sampling, all canisters were cleaned at least five times by repeated filling and evacuating of humidified zero air. In order to check if there was any contamination in the canisters, all vacuumed canisters, after the cleaning procedure, were re-filled with humidified zero air and stored in the laboratory for at least 24 h, and then analyzed by the same methods as the field samples, thus ensuring that all the target VOC compounds were not present.

Target compounds (benzene and other specific tracers) were identified based on their retention times and mass spectra, and quantified by external calibration methods. The calibration standards were prepared by dynamically diluting the PAMS standard mixture and TO-14 standard mixture (100 ppbv, Spectra Gases Inc., New Jersey, USA) to 0.5, 1, 5, 15 and 30 ppbv, respectively. The calibration curves were obtained by running the five diluted standards, plus the humidified zero air, the same way as the field samples. The correlation coefficients were 0.992–0.999. Each day, before sample analysis, the precision of analytical system was assessed initially with humidified zero air to ensure that the analytical system was clean, and then with a one-point (typically 1 ppbv) calibration. If the response was beyond ± 10% of the initial calibration curve, recalibration was performed. The method detection limit for benzene was 3 pptv.

3. Results and discussion

3.1. Background benzene levels

Mixing ratios of benzene measured at SY$_{NECP}$, YC$_{NCP}$, TH$_{YRD}$ and DH$_{PRD}$ sites averaged 1297 ± 491, 1008 ± 249, 1167 ± 302, and 578 ± 123 pptv, respectively (Table 1). Benzene at the DH$_{PRD}$ site was significantly lower ($p < 0.01$, two tailed t-test) than those at the other three sites, while no significant difference ($p > 0.05$) was observed among the SY$_{NECP}$, YC$_{NCP}$ and TH$_{YRD}$ sites. The highest mixing ratios of benzene at SY$_{NECP}$, YC$_{NCP}$, TH$_{YRD}$ and DH$_{PRD}$ reached 8274 pptv, 3898 pptv, 5287 pptv and 1716 pptv, respectively.

Seasonal patterns at the four background sites are depicted in Fig. 2. At both SY$_{NECP}$ and YC$_{NCP}$ in northern China, mixing ratios of benzene in winter were 3210 ± 1613 pptv and 1204 ± 809 pptv, respectively, significantly higher ($p < 0.05$) than those recorded in other seasons. At the TH$_{YRD}$ site, benzene levels showed no significant seasonal difference ($p > 0.05$), although they tended to be higher in spring (1961 ± 1509 pptv). At the DH$_{PRD}$ site, the mixing ratios of benzene were significantly lower ($p < 0.01$) in summer (256 ± 126 pptv) than in other seasons, while no significant differences ($p > 0.05$) were observed among spring (740 ± 254 pptv), autumn (522 ± 168 pptv) and winter (832 ± 361 pptv).

A comparison of mixing ratios of benzene from this study with those previously reported at other rural or remote sites is summarized in Fig. 3. Average mixing ratios of 578–1297 pptv for benzene at the four sites fell within that of 570–1914 pptv reported at other rural sites in China's developed regions, such as NCP (Suthawaree et al., 2010, 2012; Yuan et al., 2013), YRD (Guo et al., 2004; Tang et al., 2009), PRD

Table 1
Statistics of benzene mixing ratios (pptv), exposure levels and health risks at the four background sites. Number in parentheses indicates the total number of samples at each site. The orders (i–iv) were ranked by their lifetime cancer risks.

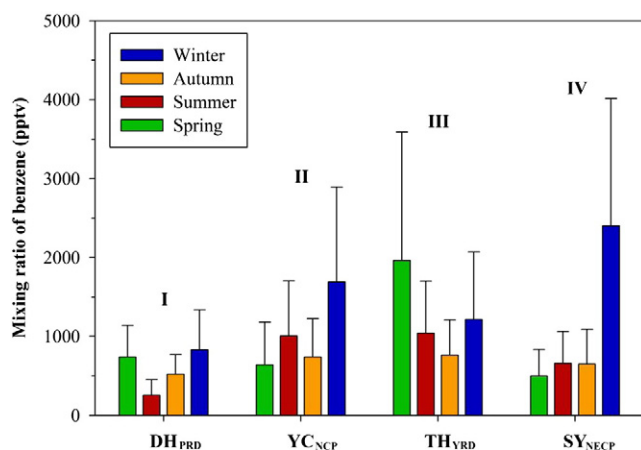| Sampling site	SY$_{NECP}$ (46)	TH$_{YRD}$ (41)	YC$_{NCP}$ (47)	DH$_{PRD}$ (45)
Mean ± 95% C.I.	1297 ± 491	1167 ± 302	1008 ± 249	578 ± 123
Range	154–8274	204–5287	92–3898	60–1716
Daily exposure (mg/kg·day)	1.29E−03	1.16E−03	1.00E−03	5.76E−04
Lifetime cancer risk (LTCR)	3.73E−05	3.36E−05	2.90E−05	1.66E−05
Hazard quotient (HQ)	0.14	0.13	0.11	0.06
Rank order	i	ii	iii	iv

Fig. 2. Seasonal variations of benzene measured at the four background sites in China from March 2012 to February 2013. Error bars represent 95% C.I. The orders (I–IV) indicated the increased annual averaged mixing ratios of benzene.

(Tang et al., 2007; Zhang et al., 2013) and Hong Kong (Guo et al., 2011). Benzene at the SY_{NECP} site (1297 ± 491 pptv) showed significantly lower mixing ratios when compared to those observed at rural Changchun in the NECP (2949 ± 1890 pptv; Liu et al., 2000). The near ground benzene levels observed at the background sites in the present study were apparently higher than those observed at high mountains in China, such as 87 ± 48 pptv at Mt. Waliguan (Xue et al., 2013), 130 ± 90 pptv at Mt. Jianfeng or 240 ± 70 pptv at Mt. Tengchong (Tang et al., 2009). As shown in Fig. 3, benzene levels at the four background sites were much higher than the surface benzene levels reported at rural or remote sites in USA, Canada and European countries (114–300 pptv). Moreover, the mean annual benzene levels at the four background sites (578–1297 pptv) were alarmingly higher even compared to that of 60–480 pptv monitored in 28 cities in the United States (Baker et al., 2008).

Fig. 4 shows the cumulative distribution of benzene mixing ratios. Although ambient benzene is not regulated in China, they can be compared with guidelines in other countries, or regions. Even at the four background sites, the annual average mixing ratios of benzene were 1.09–2.45 times the limit of 530 pptv set by Thailand (CAI-Asia, 2009). Furthermore, over 52.8%, 61.3%, 74.8% and 47.8% of samples at SY_{NECP}, YC_{NCP}, TH_{YRD} and DH_{PRD} sites, respectively, had benzene levels exceeding this limit. Annual averaged benzene levels at SY_{NECP}, YC_{NCP} and TH_{YRD} sites were 7.2%–38.0% higher than Japan's annual limit of 940 pptv (CAI-Asia, 2009). When compared to the widely used limit of 1540 pptv or 5 μg/m³ in the European Union (EU, 2008), South Africa (Government Gazette Republic of South Africa, 2009), India and South Korea (CAI-Asia, 2009), 26.1%, 23.4%, 26.8% and 4.4% of samples collected at SY_{NECP}, YC_{NCP}, TH_{YRD} and DH_{PRD} sites, respectively, had benzene levels above this limit. Additionally, four samples at the SY_{NECP} site, and one sample at the TH_{YRD} site, had benzene levels even higher than the Inhalation Minimal Risk Level (MRL, at a cancer risk of 1 in 10,000) of 4000 pptv established by the United States Environmental Protection Agency for benzene (USEPA, 2009a). The relatively higher benzene levels at these regional background sites are therefore alarming for benzene exposure in China's most developed coastal regions.

3.2. Source implications

Fig. 5a shows the correlation between benzene and carbon monoxide (CO), a typical tracer of emissions from incomplete combustion of biomass/biofuel or fossil fuel (Parrish et al., 2009). The highly significant correlations between benzene and CO at SY_{NECP}, YC_{NCP} and DH_{PRD} sites ($r = 0.96, 0.92$ and 0.77, respectively; $p < 0.001$) suggested that benzene at these sites was largely combustion-related. The toluene to benzene

ratio (T/B) can be further used to differentiate various combustion sources (Barletta et al., 2005; Zhang et al., 2013). As shown in Fig. 5b, although fairly good correlations ($r > 0.7$, $p < 0.001$) between toluene and benzene were observed at SY_{NECP}, YC_{NCP} and DH_{PRD} sites, the T/B slopes were quite different. They were 0.20 and 0.40 respectively at SY_{NECP} and YC_{NCP} sites within that of 0.23–0.68 for biomass/biofuel burning (Andreae and Merlet, 2001; Liu et al., 2008; Li et al., 2009; Wang et al., 2009; Akagi et al., 2011) or 0.13–0.71 for coal combustion (Tsai et al., 2003; Liu et al., 2008), implying input from biomass/biofuel burning and coal combustion at the two sites. Contrastingly, the T/B slope of 1.66 at DH_{PRD} site was close to that of ~1.6 for vehicle emissions (Perry and Gee, 1995; Gelencser et al., 1997; Wang et al., 2002; Barletta et al., 2005; Tang et al., 2007; Liu et al., 2008; Gentner et al., 2013), indicating the contribution of traffic-related sources. This difference in combustion sources was also confirmed by the significant correlations between benzene and chloromethane, a commonly used biomass/biofuel burning indicator (de Gouw et al., 2004; Suthawaree et al., 2010), at the SY_{NECP} and YC_{NCP} sites ($r = 0.66$ and 0.78, respectively; $p < 0.001$; Fig. 5c), and by the significant correlation between benzene and methyl tert-butyl ether (MTBE), an exclusive indicator for traffic-related emissions (Chang et al., 2003), at the DH_{PRD} site ($r = 0.75$, $p < 0.001$; Fig. 5d). As shown in Fig. 5b, three samples at the DH_{PRD} site had extremely high T/B ratios (>4), suggesting occasional input by non-combustion sources, mostly likely industrial emissions.

Correlations between benzene and these typical tracers at each site were further calculated for different seasons (Table 2). At the YC_{NCP} site, summer samples showed a substantially improved correlation ($r = 0.91$, $p < 0.001$; Table 2) between benzene and chloromethane with a slope of 0.60, which was within that of 0.24–0.91 for open burning of agricultural residues (Andreae and Merlet, 2001; Liu et al., 2008), and also close to that of 0.72 derived for biomass burning episodes at Mt. Tai in June 2006 (Suthawaree et al., 2010). As shown in Fig. S1, fire spot counts by the Moderate Resolution Imaging Spectroradiometer (MODIS), aboard the Terra and Aqua satellites (https://firms.modaps.eosdis.nasa.gov/firemap/; last access: 24 May 2014), confirmed the widespread active burning of agricultural residues during the 2012 summer harvest season in the NCP. In wintertime, good correlations between benzene and chloromethane were also observed at YC_{NCP} ($r = 0.92$, $p < 0.001$) and SY_{NECP} ($r = 0.70$, $p < 0.05$). However, winter is not the harvest season, and few fire counts in winter were observed in northern China (Fig. S1). Therefore, at SY_{NECP} and YC_{NCP} sites the significantly higher benzene levels in winter (Fig. 2) could be largely attributed to combustion sources other than open burning of agricultural residues. In northern China, domestic heating supply generally starts in mid-November and lasts until mid-March the following year. In 2012, 14.6% of the 0.182 billion tons of coal consumed in the Liaoning Province, and 11.4% of the 0.402 billion tons coal consumed in the Shandong Province were used for heating supply (NBSC, 2013b). This increase in coal consumption for domestic heating supply has been assumed to be the major reason for elevated benzene levels in winter, as coal combustion is an important source of benzene (Tsai et al., 2003; Moreira dos Santos et al., 2004; Liu et al., 2008). In fact, a recent study in Beijing revealed that coal combustion contributed significantly more to ambient VOCs in the winter (19%) than in the summer (4%) (Wang et al., 2014). As shown in Table 2, improved correlation between benzene and CO ($r = 0.84$, $p < 0.01$), as well as between benzene and chloromethane ($r = 0.83$, $p < 0.01$), was also observed in the winter at the TH_{YRD} site (Table 2), suggesting that the influence of a heating supply also existed. At DH_{PRD}, as vehicle emissions was the major source for benzene, the correlations revealed much less seasonal changes (Table 2).

It should also be noted that benzene levels at SY_{NECP} and YC_{NCP} were more than double in winter than in other seasons. This increase was higher than that of coal consumption. One possible reason is that the reported benzene emission factor of 25.8–1050 mg/kg for rural residential coal combustion (Tsai et al., 2003) is extremely high when compared to
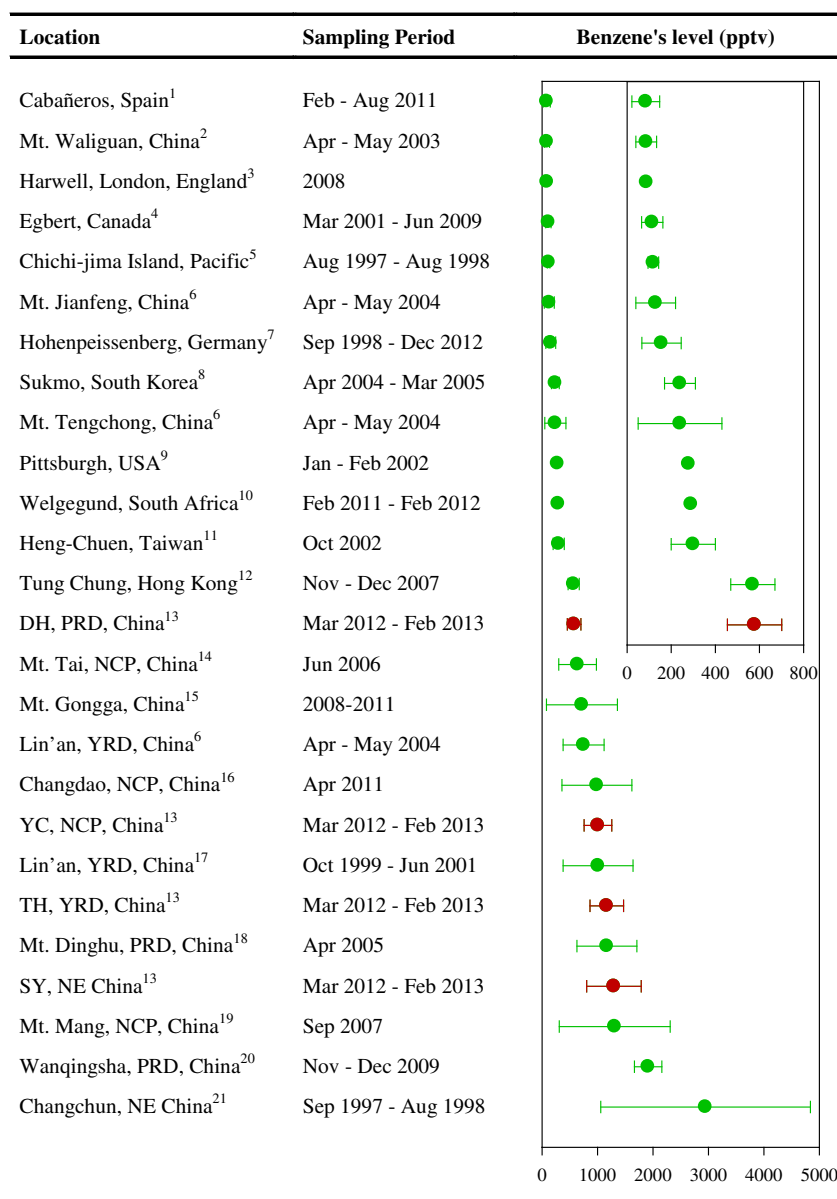
Location	Sampling Period	Benzene's level (pptv)
Cabañeros, Spain[1]	Feb - Aug 2011	
Mt. Waliguan, China[2]	Apr - May 2003	
Harwell, London, England[3]	2008	
Egbert, Canada[4]	Mar 2001 - Jun 2009	
Chichi-jima Island, Pacific[5]	Aug 1997 - Aug 1998	
Mt. Jianfeng, China[6]	Apr - May 2004	
Hohenpeissenberg, Germany[7]	Sep 1998 - Dec 2012	
Sukmo, South Korea[8]	Apr 2004 - Mar 2005	
Mt. Tengchong, China[6]	Apr - May 2004	
Pittsburgh, USA[9]	Jan - Feb 2002	
Welgegund, South Africa[10]	Feb 2011 - Feb 2012	
Heng-Chuen, Taiwan[11]	Oct 2002	
Tung Chung, Hong Kong[12]	Nov - Dec 2007	
DH, PRD, China[13]	Mar 2012 - Feb 2013	
Mt. Tai, NCP, China[14]	Jun 2006	
Mt. Gongga, China[15]	2008-2011	
Lin'an, YRD, China[6]	Apr - May 2004	
Changdao, NCP, China[16]	Apr 2011	
YC, NCP, China[13]	Mar 2012 - Feb 2013	
Lin'an, YRD, China[17]	Oct 1999 - Jun 2001	
TH, YRD, China[13]	Mar 2012 - Feb 2013	
Mt. Dinghu, PRD, China[18]	Apr 2005	
SY, NE China[13]	Mar 2012 - Feb 2013	
Mt. Mang, NCP, China[19]	Sep 2007	
Wanqingsha, PRD, China[20]	Nov - Dec 2009	
Changchun, NE China[21]	Sep 1997 - Aug 1998	

Fig. 3. Comparison of mixing ratios of benzene at various rural or remote sites. Error bars represent ± 1 standard deviation (or 95% C.I.) for studies with available data. Reference: [1]Villanueva et al., 2014; [2]Xue et al., 2013; [3]von Schneidemesser et al., 2010; [4]Environment Canada, 2012; [5]Kato et al., 2001; [6]Tang et al., 2009; [7]DWD Germany, 2013; [8]Choi et al., 2010; [9]Millet et al., 2005; [10]Jaars et al., 2014; [11]Chang et al., 2005; [12]Guo et al., 2011; [13]This study; [14]Suthawaree et al., 2010; [15]Zhang et al., 2014; [16]Yuan et al., 2013; [17]Guo et al., 2004; [18]Tang et al., 2007; [19]Suthawaree et al., 2012; [20]Zhang et al., 2013; [21]Liu et al., 2000.

that of 0.59 mg/kg for controlled power plant's and industrial coal combustion (Garcia et al., 1992; USEPA, 1995). Additionally, biofuel could account for about two thirds of the total energy used for cooking and heating in China's rural areas (Yan et al., 2006; Wei et al., 2008; Tang et al., 2009), so more benzene emissions from biofuel-stoves in rural areas in the winter could also result in the higher ambient benzene levels (Tsai et al., 2003; Wang et al., 2009). A cleaner energy supply for heating, therefore, should be an effective way to lower the exposure to benzene, particularly in rural areas in winter time.

At the TH_{YRD} site, benzene showed poor correlations ($r < 0.5$; Fig. 5) with CO, chloromethane and MTBE, suggesting that benzene might have sources other than those already mentioned. The T/B ratios at the TH_{YRD} site ranged from 0.32 to 7.10, with an average of 2.66 ± 0.57, this being larger than those typical ratios of combustion sources including biomass/biofuel burning, coal burning and vehicle emissions. The average ethylbenzene to benzene ratio (E/B) and xylenes to benzene ratio (X/B) at the TH_{YRD} site were 1.29 ± 0.37 and 1.45 ± 0.48, also much

higher than that of 0.31 ± 0.09 and 0.69 ± 0.22 at SY_{NECP}, 0.14 ± 0.03 and 0.24 ± 0.06 at YC_{NCP}, or 0.45 ± 0.10 and 0.60 ± 0.14 at DH_{PRD}, respectively. As toluene, ethylbenzene and xylenes are widely used in industrial solvents, much higher ratios of T/B, E/B and X/B are indicative of industrial emissions (Chan et al., 2006; Barletta et al., 2008). Furthermore, if we further divide samples into two groups by their T/B ratios, Group I with T/B < 2 and Group II with T/B > 2, we find closer correlations between benzene and tetrachloroethylene (C_2Cl_4), a marker of industrial emissions (McCulloch et al., 1999; Zhang et al., 2012c), for Group II samples ($r = 0.81$, $p < 0.001$) than for Group I samples ($r = 0.18$, $p > 0.05$; Fig. 6a). Group I samples showed a substantially improved correlation ($r = 0.76$, $p < 0.001$; Fig. 6b) between benzene and MTBE, the tracer for traffic-related emissions, when compared with all samples at the TH_{YRD} site pooled together ($r = 0.04$, $p > 0.05$; Fig. 5d). Therefore, benzene at the TH_{YRD} site was probably affected by both traffic-related sources and industrial emissions. Although benzene has been forbidden to be used as a solvent in industrial processes, it is still being produced
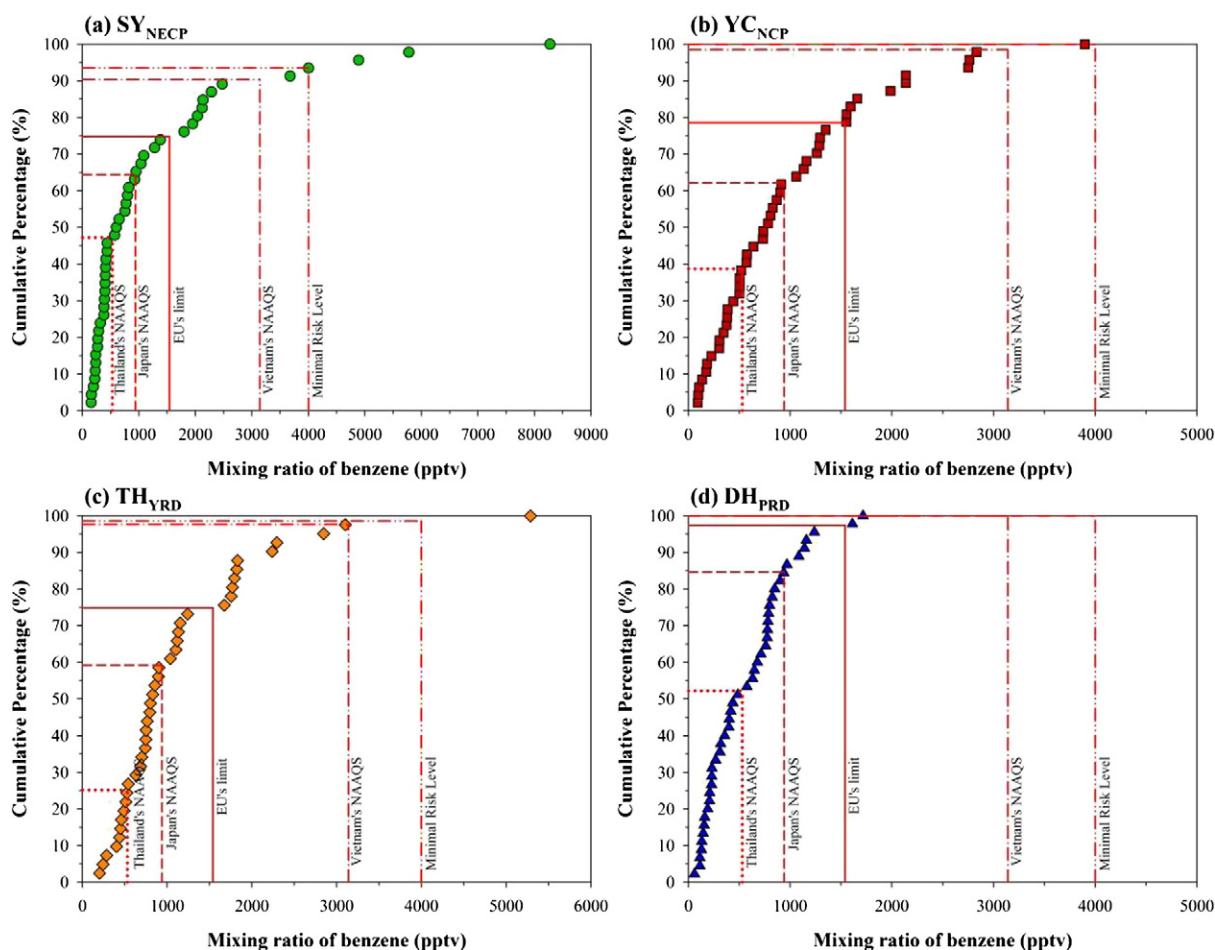
Fig. 4. Cumulative percentages of benzene's levels at the four background sites in China. The red drop lines are guidelines for benzene in various countries or regions: Thailand's NAAQS of 530 pptv (dotted; CAI-Asia, 2009), Japan's NAAQS of 940 pptv (dash; CAI-Asia, 2009), European Union's limit as well as India, South Korea and South Africa's NAAQS of 1540 pptv (solid; EU, 2008; CAI-Asia, 2009; Government Gazette, 2009), Vietnam's NAAQS of 3140 pptv (dash-dot; CAI-Asia, 2009), and the Inhalation Minimal Risk Level (MRL, at a cancer risk of 1 in 10,000) of 4000 pptv (dash–dot–dot; USEPA, 2009a).

and used as a raw material for synthesizing chemicals such as styrene, phenol and cyclohexane. In fact, 2.06 million tons of benzene, 28.6% of China's total annual benzene production, was produced in Shanghai, Jiangsu and Zhejiang in the YRD region in 2013 (http://www.chyxx.com/data/201402/230083.html; last access: 4 July 2014).

3.3. Exposure and health risk assessment

Daily exposure E in mg/kg per day of an individual by inhalation can be calculated as:

$$E = C \times I_{ra} \times D_a / B_{wa} \tag{1}$$

where C (mg/m^3) is the concentration of benzene, I_{ra} is the inhalation rate of an adult (0.83 m^3/h; USEPA, 1998), D_a is the exposure duration of an adult (24 h/day) and B_{wa} is the body weight of an adult (65 kg; USEPA, 1998).

The lifetime cancer risk (LTCR) is then calculated as:

$$LTCR = E \times SF \tag{2}$$

where SF is the slope factor of inhalation unit risk for toxics when the exposure-carcinogenic effect is considered as linear. Here we adopt SF of 2.89E − 02 kg·day/mg for benzene by USEPA (2009b).

The non-cancer risk of benzene is measured by the hazard quotient (HQ):

$$HQ = C/RfC \tag{3}$$

where C is the yearly average daily received concentration, and RfC is the inhalation reference concentration, which is 0.03 mg/m^3 for benzene (USEPA, 2002).

Based on the collected data, the average daily exposure, LTCR and HQ at the four background sites are estimated and listed in Table 1. Although benzene levels in the present study were observed at background sites and at time when relatively lower levels occurred during the day (Tang et al., 2007; Zhang et al., 2012a,b), the calculated LTCR, ranging from 1.66E − 05 (DH$_{PRD}$) to 3.73E − 05 (SY$_{NECP}$), all exceeded the acceptable LTCR of 1E − 06 for adults (USEPA, 2009b). This implies that the potential cancer risks due to ambient benzene exposure should be a health concern in the densely populated coastal regions of China. For the non-cancer risk, the calculated HQs of benzene were in the range of 0.06–0.14. According to USEPA, if the HQ value is lower than 1, the pollutant has no obvious non-cancer risk (USEPA, 2009b). Hence, calculated HQs at the four background sites indicated that the non-cancer risk of benzene was not as distinctive as its cancer risk.
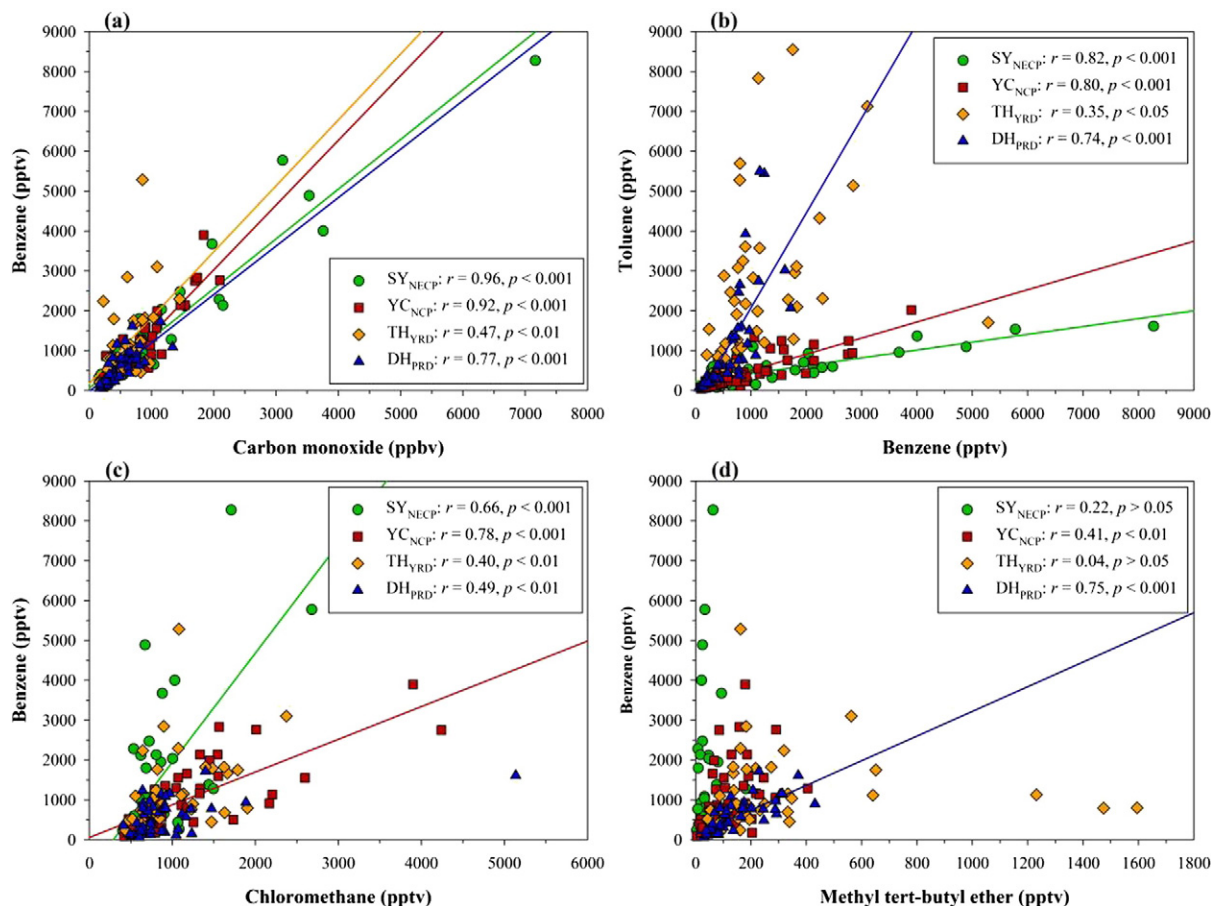
Fig. 5. Scatter plots of benzene versus (a) carbon monoxide; (b) toluene; (c) chloromethane; and (d) methyl tert-butyl ether (MTBE) at the four background sites. r is the correlation coefficient and p is the significance level. $r > 0.5$ and $p < 0.05$ were used as critical values for significant correlations.

4. Conclusions

In this study, the results of ambient air samples from four background sites in China's most developed coastal regions, from March 2012 to February 2013, were presented. These results have shown ambient benzene levels to be higher than those previously observed at

urban areas in the US or Europe, and that the life time cancer risk due to exposure to ambient benzene at these sites all exceeded the acceptable level of $1E-06$ by USEPA. As benzene concentrations at these background sites represent the lowest levels in the developed coastal regions, health concerns of benzene exposure should be seriously considered, particularly during winter in the North. For the protection

Table 2

Pearson's correlations between benzene and typical tracers of emission sources at each sampling site during the four seasons. r is the correlation coefficient and p is the significance level. $r > 0.5$ and $p < 0.05$ were used as critical values for significant correlations.

| Site	Season	CO		Toluene		MTBE		Chloromethane	
		r	p	r	p	r	p	r	p
SY_{NECP}	Spring	0.71	<0.05	0.87	<0.01	0.37	>0.05	0.26	>0.05
	Summer	0.93	<0.001	0.57	<0.05	0.47	>0.05	0.44	>0.05
	Autumn	0.94	<0.001	0.41	>0.05	0.13	>0.05	0.74	<0.01
	Winter	0.95	<0.001	0.83	<0.01	0.47	>0.05	0.70	<0.05
YC_{NCP}	Spring	0.83	<0.01	0.96	<0.001	0.64	<0.05	0.64	<0.05
	Summer	0.93	<0.001	0.89	<0.001	0.12	>0.05	0.91	<0.001
	Autumn	0.81	<0.01	0.74	<0.01	0.48	>0.05	0.41	>0.05
	Winter	0.94	<0.001	0.84	<0.01	0.78	<0.01	0.92	<0.001
TH_{YRD}	Spring	0.35	>0.05	−0.20	>0.05	−0.38	>0.05	−0.09	>0.05
	Summer	0.17	>0.05	0.69	<0.05	0.66	<0.05	0.31	>0.05
	Autumn	0.51	>0.05	0.51	>0.05	0.11	>0.05	0.64	<0.05
	Winter	0.84	<0.01	0.68	<0.05	0.44	>0.05	0.83	<0.01
DH_{PRD}	Spring	0.78	<0.01	0.78	<0.01	0.76	<0.01	0.30	>0.05
	Summer	0.88	<0.001	0.93	<0.001	0.84	<0.01	−0.14	>0.05
	Autumn	0.89	<0.001	0.69	<0.05	0.83	<0.01	0.25	>0.05
	Winter	0.66	<0.05	0.75	<0.05	0.86	<0.01	0.68	<0.05
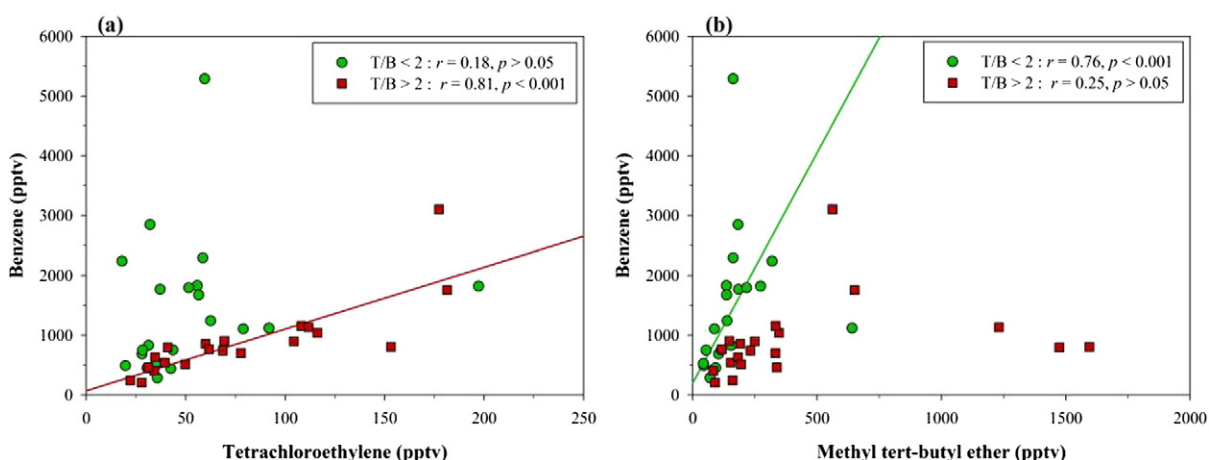
Fig. 6. Scatter plots of benzene versus (a) tetrachloroethylene; and (b) methyl tert-butyl ether at TH_YRD site. Samples were separated by the toluene to benzene (T/B) ratios.

of public health, China should set an ambient air quality standard for benzene, and the relationship between ambient benzene levels and leukemia incidence should be investigated further.

We have also provided diagnostic analysis about sources of benzene in the regions through correlations between benzene and typical source tracers or markers. We found that benzene at these sites was largely originating from combustion sources, and at the site in the Yangtze River Delta region industrial emissions might also be an important source. Among the combustion sources, coal burning was the dominant source at sites in the north (NECP and NCP regions), and vehicle emissions was the dominant source at sites in the south (YRD and PRD regions). Open burning of agricultural residues may also contribute substantially during the harvest season in the north. It is also worth noting that the wintertime heating supply in the north greatly enhances ambient benzene levels due to increased coal consumption, and the less stringent emission control in domestic coal burning, particularly in the rural areas. This information about sources of benzene would benefit its emission control in the regions. For example, apart from tightening emission control for benzene from motor vehicles and industry, a cleaner energy supply in the residential sector is also of great importance to reduce benzene emissions, and the ban of open burning of agricultural residue, or the promotion of cleaner ways to dispose of crop residue, would also help lower ambient benzene levels during harvest seasons.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.01.003.

References

Akagi, S.K., Yokelson, R.J., Wiedinmyer, C., Alvarado, M.J., Reid, J.S., Karl, T., et al., 2011. Emission factors for open and domestic biomass burning for use in atmospheric models. Atmos. Chem. Phys. 11, 4039–4072.
Andreae, M.O., Merlet, P., 2001. Emission of trace gases and aerosols from biomass burning. Glob. Biogeochem. Cycles 15, 955–966.
Baker, A.K., Beyersdorf, A.J., Doezema, L.A., Katzenstein, A., Meinardi, S., Simpson, I.J., et al., 2008. Measurements of nonmethane hydrocarbons in 28 United States cities. Atmos. Environ. 42, 170–182.
Barletta, B., Meinardi, S., Rowland, F.S., Chan, C.Y., Wang, X.M., Zou, S.C., et al., 2005. Volatile organic compounds in 43 Chinese cities. Atmos. Environ. 39, 5979–5990.
Barletta, B., Meinardi, S., Simpson, I.J., Zou, S.C., Rowland, F.S., Blake, D.R., 2008. Ambient mixing ratios of nonmethane hydrocarbons (NMHCs) in two major urban centers of the Pearl River Delta (PRD) region: Guangzhou and Dongguan. Atmos. Environ. 42, 4393–4408.
Cai, C.J., Geng, F.H., Tie, X.X., Yu, Q.O., An, J.L., 2010. Characteristics and source apportionment of VOCs measured in Shanghai, China. Atmos. Environ. 44, 5005–5014.
Chan, L.Y., Chu, K.W., Zou, S.C., Chan, C.Y., Wang, X.M., Barletta, B., et al., 2006. Characteristics of nonmethane hydrocarbons (NMHCs) in industrial, industrial-urban, and industrial-suburban atmospheres of the Pearl River Delta (PRD) region of south China. J. Geophys. Res. 111. http://dx.doi.org/10.1029/2005jd006481 (D11304).
Chang, C.C., Lo, S.J., Lo, J.G., Wang, J.L., 2003. Analysis of methyl tert-butyl ether in the atmosphere and implications as an exclusive indicator of automobile exhaust. Atmos. Environ. 37, 4747–4755.
Chang, C.-C., Chen, T.-Y., Lin, C.-Y., Yuan, C.-S., Liu, S.-C., 2005. Effects of reactive hydrocarbons on ozone formation in southern Taiwan. Atmos. Environ. 39, 2867–2878.
Chen, W.Q., Shan, B.E., Zheng, R.S., Lin, G.Z., Chen, J.Z., Chen, J.G., et al., 2012. Analysis of incidence and mortality of leukemia in registration areas of China from 2003 to 2007 (in Chinese). Tumor 32, 251–255.
Choi, E., Heo, J.B., Yi, S.M., 2010. Apportioning and locating nonmethane hydrocarbon sources to a background site in Korea. Environ. Sci. Technol. 44, 5849–5854.
Clean Air initiative for Asian Cities (CAI-Asia) Center, 2009. Ambient Air Quality Standards in Asia Survey Report (Philippines).
de Gouw, J.A., Cooper, O.R., Warneke, C., Hudson, P.K., Fehsenfeld, F.C., Holloway, J.S., et al., 2004. Chemical composition of air masses transported from Asia to the U.S. West Coast during ITCT 2K2: fossil fuel combustion versus biomass-burning signatures. J. Geophys. Res. 109, D23. http://dx.doi.org/10.1029/2003jd004202.
DWD, Germany, 2013. World Data Centre for Greenhouse Gases. World Meteorological Organization (Available at: http://ds.data.jma.go.jp/gmd/wdcgg/pub/ata/current/dvocs/benzene/monthly/hpb647n00.dwd.as.cn.benzene.nl.mo.dat(last access: 29 May 2014)).
Environment Canada, 2012. World Data Centre for Greenhouse Gases. World Meteorological Organization (Avaiable at: http://ds.data.jma.go.jp/gmd/wdcgg/pub/data/current/vocs/benzene/monthly/egb444n01.ec.as.cn.benzene.nl.mo.dat (last access: 29 May 2014)).
European Union (EU), 2008. Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. Available at:, http://eur-lex.europa.eu/ (last access: 26 May 2014).
Ferlay, J., Soerjomataram, I., Ervik, M., Dikshit, R., Eser, S., Mathers, C., Rebelo, M., et al., 2013. GLOBOCAN 2012 v1.0, Cancer Incidence and Mortality Worldwide: IARC CancerBase No. 11. Internet, International Agency for Research on Cancer, Lyon, France (Available from: http://globocan.iarc.fr, accessed on 26/06/2014 (last access: 3 July 2014)).
Garcia, J.P., Beyne-Masclet, S., Mouvier, G., Masclet, P., 1992. Emissions of volatile organic compounds by coal-fired power stations. Atmos. Environ. 26A (9), 1589–1597.
Gelencser, A., Siszler, K., Hlavay, J., 1997. Toluene–benzene concentration ratio as a tool for characterizing the distance from vehicular emission sources. Environ. Sci. Technol. 31, 2869–2872.
Gentner, D.R., Worton, D.R., Isaacman, G., Davis, L.C., Dallmann, T.R., Wood, E.C., et al., 2013. Chemical composition of gas-phase organic carbon emissions from motor vehicles and implications for ozone production. Environ. Sci. Technol. 47, 11837–11848.
Government Gazette Republic of South Africa, 2009. 24 December 2009, No. 32816, National Ambient Air Quality Standards. Available at:, http://faolex.fao.org/docs/pdf/saf122986.pdf (last access: 27 May 2014).

Guo, H., Wang, T., Simpson, I.J., Blake, D.R., Yu, X.M., Kwok, Y.H., et al., 2004. Source contributions to ambient VOCs and CO at a rural site in Eastern China. Atmos. Environ. 38, 4551–4560.

Guo, H., Cheng, H.R., Ling, Z.H., Louie, P.K.K., Ayoko, G.A., 2011. Which emission sources are responsible for the volatile organic compounds in the atmosphere of Pearl River Delta? J. Hazard. Mater. 188, 116–124.

Jaars, K., Beukes, J.P., van Zyl, P.G., Venter, A.D., Josipovic, M., Pienaar, J.J., Vakkari, V., Aaltonen, H., Laakso, H., Kulmala, M., Tiitta, P., Guenther, A., Hellén, H., Laakso, L., Hakola, H., 2014. Ambient aromatic hydrocarbon measurements at Welgegund, South Africa. Atmos. Chem. Phys. 14, 7075–7089.

Kato, S., Pochanart, P., Kajii, Y., 2001. Measurements of ozone and nonmethane hydrocarbons at Chichi-jima island, a remote island in the western Pacific: long-range transport of polluted air from the Pacific rim region. Atmos. Environ. 35, 6021–6029.

Klimont, Z., Streets, D.G., Gupta, S., Cofala, J., Fu, LX., Ichikawa, Y., 2002. Anthropogenic emissions of non-methane volatile organic compounds in China. Atmos. Environ. 36, 1309–1322.

Li, X.H., Wang, S.X., Duan, L., Hao, J.M., 2009. Characterization of non-methane hydrocarbons emitted from open burning of wheat straw and corn stover in China. Environ. Res. Lett. 4, 044015. http://dx.doi.org/10.1088/1748-9326/4/4/044015.

Li, L., Li, H., Zhang, X., Wang, L., Xu, L., Wang, X., et al., 2014. Pollution characteristics and health risk assessment of benzene homologues in ambient air in the northeastern urban area of Beijing, China. J. Environ. Sci. 26, 214–223.

Liu, C.M., Xu, Z.L., Du, Y.G., Guo, H.C., 2000. Analyses of volatile organic compounds concentrations and variation trends in the air of Changchun, the northeast of China. Atmos. Environ. 34, 4459–4466.

Liu, Y., Shao, M., Fu, L., Lu, S., Zeng, L., Tang, D., 2008. Source profiles of volatile organic compounds (VOCs) measured in China: part I. Atmos. Environ. 42, 6247–6260.

Liu, J.F., Mu, Y.J., Zhang, Y.J., Zhang, Z.M., Wang, X.K., Liu, Y.J., et al., 2009. Atmospheric levels of BTEX compounds during the 2008 Olympic Games in the urban area of Beijing. Sci. Total Environ. 408, 109–116.

Liu, Y.Q., Zhao, F.J., Chen, W.Q., 2013. An analysis of incidence and mortality of leukemia in China, 2009 (in Chinese). China Cancer 22, 528–534.

McCulloch, A., Aucott, M.L., Graedel, T.E., Kleiman, G., Midgley, P.M., Li, Y.-F., 1999. Industrial emissions of trichloroethene, tetrachloroethene, and dichloromethane: Reactive Chlorine Emissions Inventory. J. Geophys. Res. 104, 8417–8427. http://dx.doi.org/10.1029/1999JD900011.

Millet, D.B., Donahue, N.M., Pandis, S.N., Polidori, A., Stanier, C.O., Turpin, B.J., et al., 2005. Atmospheric volatile organic compound measurements during the Pittsburgh Air Quality Study: results, interpretation, and quantification of primary and secondary contributions. J. Geophys. Res. 110. http://dx.doi.org/10.1029/2004jd004601 (D7).

Moreira dos Santos, C.Y., de Almeida Azevedo, D., de Aquino Neto, F.R., 2004. Atmospheric distribution of organic compounds from urban areas near a coal-fired power station. Atmos. Environ. 38, 1247–1257.

National Bureau of Statistics of China (NBSC), 2008. China Energy Statistical Yearbook, 2008. China Statistics Press, Beijing.

National Bureau of Statistics of China (NBSC), 2013a. China Statistical Yearbook, 2013. China Statistics Press, Beijing.

National Bureau of Statistics of China (NBSC), 2013b. China Energy Statistical Yearbook, 2013. China Statistics Press, Beijing.

Parrish, D.D., Kuster, W.C., Shao, M., Yokouchi, Y., Kondo, Y., Goldan, P.D., et al., 2009. Comparison of air pollutant emissions among mega-cities. Atmos. Environ. 43, 6435–6441.

Perry, R., Gee, I.L., 1995. Vehicle emissions in relation to fuel composition. Sci. Total Environ. 169, 149–156.

Streets, D.G., Yarber, K.F., Woo, J.H., Carmichael, G.R., 2003. Biomass burning in Asia: annual and seasonal estimates and atmospheric emissions. Glob. Biogeochem. Cycles 17, 1099.

Suthawaree, J., Kato, S., Okuzawa, K., Kanaya, Y., Pochanart, P., Akimoto, H., et al., 2010. Measurements of volatile organic compounds in the middle of Central East China during Mount Tai Experiment 2006 (MTX2006): observation of regional background and impact of biomass burning. Atmos. Chem. Phys. 10, 1269–1285.

Suthawaree, J., Kato, S., Pochanart, P., Kanaya, Y., Akimoto, H., Wang, Z.F., et al., 2012. Influence of Beijing outflow on Volatile Organic Compounds (VOC) observed at a mountain site in North China Plain. Atmos. Res. 111, 46–57.

Tang, J.H., Chan, L.Y., Chan, C.Y., Li, Y.S., Chang, C.C., Liu, S.C., et al., 2007. Characteristics and diurnal variations of NMHCs at urban, suburban, and rural sites in the Pearl River Delta and a remote site in South China. Atmos. Environ. 41, 8620–8632.

Tang, J.H., Chan, L.Y., Chang, C.C., Liu, S., Li, Y.S., 2009. Characteristics and sources of non-methane hydrocarbons in background atmospheres of eastern, southwestern, and southern China. J. Geophys. Res. 114. http://dx.doi.org/10.1029/2008jd010333 (D03304).

Tsai, S.M., Zhang, J., Smith, K.R., Ma, Y., Rasmussen, R.A., Khalil, M.A.K., 2003. Characterization of non-methane hydrocarbons emitted from various cookstoves used in China. Environ. Sci. Technol. 37, 2869–2877.

United States Enivironmental Protection Agency (US EPA), 2009b. Risk assessment guidance for superfund volume I: human health evaluation manual (part F, supplemental guidance for inhalation risk assessment): final [EPA Report] (EPA/540/-R-070/002).

Available at:, http://www.epa.gov/oswer/riskassessment/ragsf/index.htm ((last access: 9 June 2014). Washington, DC).

United States Environmental Protection Agency (US EPA), 2009a. Agency for Toxic Substances and Diseases Registry (ATSDR). Minimal Risk Levels List. available at:, http://www.atsdr.cdc.gov/mrls/mrllist.asp#14tag ((last access: 9 June 2014). Washington, DC).

United States Environmental Protection Agency (USEPA), 1995. Compilation of Air Pollutant Emission Factors (AP42). Chapter 1, Fifth Edition. (available at: http://www.epa.gov/ttn/chief/ap42/ch01/index.html (last access: 9 June 2014). Washington, DC).

United States Environmental Protection Agency (USEPA), 1998. Integrated Risk Information System (IRIS). Carcinogenic effects of benzene: an update (EPA/600/P-97/001F). Available at:, http://www.epa.gov/iris/supdocs/0276index.html ((last access: 9 June 2014). Washington, DC).

United States Environmental Protection Agency (USEPA), 2002. Integrated Risk Information System (IRIS). Toxicological review of benzene (non-cancer effects) (EPA/635/R-02/001F). Available at:, http://www.epa.gov/iris/toxreviews/0276tr.pdf ((last access: 9 June 2014). Washington, DC).

Villanueva, F., Tapia, A., Notario, A., Albaladejo, J., Martínez, E., 2014. Ambient levels and temporal trends of VOCs, including carbonyl compounds, and ozone at Cabañeros National Park border, Spain. Atmos. Environ. 85, 256–265.

von Schneidemesser, E., Monks, P.S., Plass-Duelmer, C., 2010. Global comparison of VOC and CO observations in urban areas. Atmos. Environ. 44, 5053–5064.

Wang, X.M., Sheng, G.Y., Fu, J.M., Chan, C.Y., Lee, S.C., Chan, L.Y., et al., 2002. Urban roadside aromatic hydrocarbons in three cities of the Pearl River Delta, People's Republic of China. Atmos. Environ. 36, 5141–5148.

Wang, S., Wei, W., Du, L., Li, G., Hao, J., 2009. Characteristics of gaseous pollutants from biofuel-stoves in rural China. Atmos. Environ. 43, 4148–4154.

Wang, M., Shao, M., Chen, W., Yuan, B., Lu, S., Zhang, Q., Zeng, L., Wang, Q., 2014. A temporally and spatially resolved validation of emission inventories by measurements of ambient volatile organic compounds in Beijing, China. Atmos. Chem. Phys. 14, 5871–5891.

Wei, W., Wang, S.X., Chatani, S., Klimont, Z., Cofala, J., Hao, J.M., 2008. Emission and speciation of non-methane volatile organic compounds from anthropogenic sources in China. Atmos. Environ. 42, 4976–4988.

Wei, W., Wang, S., Hao, J., Cheng, S., 2014. Trends of chemical speciation profiles of anthropogenic volatile organic compounds emissions in China, 2005–2020. Front. Environ. Sci. Eng. 8, 27–41.

World Health Organization (WHO), 2000. Air Quality Guidelines for Europe. WHO Regional Publication, European Series World Health Organization, Regional Office for Europe, Copenhagen Available at: http://apps.who.int/iris/bitstream/10665/107335/1/E71922.pdf (last access: 26 May 2014).

World Health Organization (WHO) International Agency for Reserach on Cancer (IARC), 1999. Some Industrial Chemicals and Dyestuffs. vol. 29. WHO Regional Publication, European Series World Health Organization, Regional Office for Europe, Copenhagen (Available at: http://monographsiarc.fr/ENG/Monographs/vol29/wolume29.pdf (last access: 26 May 2014)).

Xue, L.K., Wang, T., Guo, H., Blake, D.R., Tang, J., Zhang, X.C., et al., 2013. Sources and photochemistry of volatile organic compounds in the remote atmosphere of western China: results from the Mt. Waliguan Observatory. Atmos. Chem. Phys. 13, 8551–8567.

Yan, X., Ohara, T., Akimoto, H., 2006. Bottom-up estimate of biomass burning in mainland China. Atmos. Environ. 40, 5262–5273.

Yuan, B., Hu, W.W., Shao, M., Wang, M., Chen, W.T., Lu, S.H., et al., 2013. VOC emissions, evolutions and contributions to SOA formation at a receptor site in eastern China. Atmos. Chem. Phys. 13, 8815–8832.

Zhang, Y., Mu, Y., Liu, J., Mellouki, A., 2012a. Levels, sources and health risks of carbonyls and BTEX in the ambient air of Beijing, China. J. Environ. Sci. 24, 124–130.

Zhang, Y.J., Mu, Y.J., Liang, P., Xu, Z., Liu, J.F., Zhang, H.X., et al., 2012b. Atmospheric BTEX and carbonyls during summer seasons of 2008–2010 in Beijing. Atmos. Environ. 59, 186–191.

Zhang, Y.L., Wang, X.M., Blake, D.R., Li, L.F., Zhang, Z., Wang, S.Y., et al., 2012c. Aromatic hydrocarbons as ozone precursors before and after outbreak of the 2008 financial crisis in the Pearl River Delta region, south China. J. Geophys. Res. 117. http://dx.doi.org/10.1029/2011JD017356 D15306.

Zhang, Y.L., Wang, X.M., Barletta, B., Simpson, I.J., Blake, D.R., Fu, X.X., et al., 2013. Source attributions of hazardous aromatic hydrocarbons in urban, suburban and rural areas in the Pearl River Delta (PRD) region. J. Hazard. Mater. 250, 403–411.

Zhang, J., Sun, Y., Wu, F., Sun, J., Wang, Y., 2014. The characteristics, seasonal variation and source apportionment of VOCs at Gongga Mountain, China. Atmos. Environ. 88, 297–305.

Zhou, J., You, Y., Bai, Z., Hu, Y., Zhang, J., Zhang, N., 2011. Health risk assessment of personal inhalation exposure to volatile organic compounds in Tianjin, China. Sci. Total Environ. 409, 452–459.