Sources and Fates of BTEX in the General Environment and Its Distribution in Coastal Cities of China

Xiaoyong Duan¹,²* and Yanxia Li³

¹Key Laboratory of Marine Hydrocarbon Resources and Environmental Geology, Ministry of Land and Resources, Qingdao Institute of Marine Geology, Qingdao, China
²Laboratory for Marine Mineral Resources, Qingdao National Laboratory for Marine Science and Technology, Qingdao, China
³Qingdao National Laboratory for Marine Science and Technology, Qingdao 261000, China

*Corresponding Author: Xiaoyong Duan, Key Laboratory of Marine Hydrocarbon Resources and Environmental Geology, Ministry of Land and Resources, Qingdao Institute of Marine Geology, Qingdao, China, Tel: +86-532-85720830; E-mail address: duan-x@foxmail.com

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Abstract
Benzene, toluene, ethylbenzene and xylene (BTEX) are the most abundant volatile organic compounds (VOCs) in the urban atmosphere. In this paper, fates and possible sources of BTEX in general atmosphere were reviewed. A fairly comprehensive review of BTEX in atmosphere of China’s coastal cities was presented. In the general environment, BTEX partitions mainly into air. Higher atmospheric concentrations of BTEX were observed in the cities of south China than in north China and in winter than in summer. The atmospheric BTEX concentrations were significantly reduced over the past two decades. Vehicle emission and coal burning were the most important sources in North China. In south China, the other sources could make remarkable contribution to atmospheric BTEX concentrations.

Keywords: Benzene compounds; temporal variation; spatial variation; source; Fate

1. Introduction
China is facing serious air pollution [1]. Ozone has been the second most important cause of air pollution after PM$_{2.5}$ in recent years. Over high ozone content in the lower atmosphere has a significantly negative effect on the human-living environment [2]. The ozone formation was closely related to the anthropogenic volatile organic chemicals
(VOCs) that were originated from vehicle exhaust, industrial emission, petroleum and its products, coal and biomass burning [3].

Benzene, toluene, ethylbenzene and xylene (collectively called BTEX) are typical VOCs. They have been identified as potent carcinogens by World Health Organization. BTEX, the indispensable industrial materials, are used widely in building material, rubber and as additive in paint, dyestuff and pesticide [4]. BTEX in the industrial products can easily enter the environment [5]. And now they can be widely found in the general environment [6]. BTEX were the most abundant VOCs species in the atmosphere and surface water [4, 7, 8].

BTEX in coastal cities of China have been widely studied [4, 7, 8]. There were big differences in the BTEX concentrations, sources and variations between different regions, especially between north and south. Therefore, this review was focused on the regional and temporal distribution patterns of BTEX on a large scale. A fairly comprehensive review of BTEX in atmosphere of Chinese coastal cities was presented. Fates and possible sources of BTEX in urban atmosphere were also reviewed.

2. Sources and Fates of BTEX in the Environment

VOCs in the environment were generally originated from the leakage of petroleum and its products, vehicle exhaust, coal and biomass burning, painting and petrochemical industry [4, 9]. BTEX were the most abundant species in the emissions (Table 1).

<table>
<thead>
<tr>
<th>Source</th>
<th>VOCs species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vehicle exhaust</td>
<td>Pentane, 2-methylpentane, 3-methylpentane ethylene, acetylene, ethane, 1,3-butadiene*, Ethylene, propylene*, n-heptane, methylcyclohexane, n-nonane, n-decane, n-undecane, benzene*, toluene*, m,p-xylene</td>
</tr>
<tr>
<td>Painting</td>
<td>Benzene*, toluene*, ethylbenzene*, m,p-xylene*, o-xylene*, propane, pentane, n-butane</td>
</tr>
<tr>
<td>Gasoline/Diesel fuel evaporation</td>
<td>iso-pentane, isobutene, pentane*, propane, n-butane*, trans-2-pentene, cis-2-pentene, 2-methyl-1-butene, n-heptane, methylcyclohexane, benzene, toluene, m,p-xylene</td>
</tr>
<tr>
<td>Coal/Biomass burning</td>
<td>Ethylene*, acetylene*, ethane, propane*, naphthalene, Methyl chloride, ethylene, ethane, acetylene, propylene, 1,3-butadiene, benzene*, toluene*, ethylbenzene*</td>
</tr>
<tr>
<td>Petrochemical industry</td>
<td>benzene, toluene*, ethylbenzene*, m,p-xylene*, o-xylene*, 1,2,4,-trimethylbenzene*, 3-methylheptane</td>
</tr>
</tbody>
</table>

Table 1: The potential VOCs tracers for various emission sources ("**"indicate the relatively abundant VOCs species, "_"indicate the relatively abundant BTEX species [4, 7-9].

2.1 Leakage of Petroleum and its Products

During the Deepwater Horizon oil spill in 2010, concentrations of mono-aromatic hydrocarbon in samples collected from within the plume was >50 μg/L. This means about 5.5 tons mono-aromatic hydrocarbons were input to the
region per day, which is more than double the total source rate of the mono-aromatic hydrocarbons all natural seeps in the northern Gulf of Mexico [10]. The most abundant petroleum hydrocarbons larger than C1-C5 in the water samples collected within the hydrocarbon-enriched plume were BTEX at concentrations up to 78 μg/L [11]. And the background BTEX concentrations in the surface coastal waters of the Gulf of Mexico have been reported in the range of 0.02 to 0.45 μg/L [12]. Concentrations of BTEX in the oilfield produced water in the State of Sergipe ranged from 96.7 to 1397 μg/L [13]. Therefore, natural and man-made oil seeps were important sources of BTEX in the environment. And BTEX contents were important indicators of oil exploration and petroleum source identification [14].

BTEX concentrations ranged from 0 to 169.5mg/kg in petroleum products (gasoline, diesel and etc. [15]). They dominated the water-soluble fraction of crude oil and their derivatives products [16]. Therefore, BTEX was abundant in the groundwater of sites near gasoline station [15] and in the waters with very heavy traffic.

2.2 Vehicle exhaust
Vehicle emissions were considered the major contributor to ambient VOCs in urban areas. Ethylene, benzene, and toluene were the main species in exhaust emissions [4]. According to Oudejans et al. [17], diesel generator cold start-ups and warm restarts resulted in sharp peak emissions (such as benzene) that were up to a factor of 90 and 2.5 higher than the predominately constant concentrations observed during steady-state operation, respectively. According to Gullett et al. [18], emissions (e.g., benzene) of cold- and warm-start from a medium duty diesel engine exceed 15 times their steady state levels. In urban areas of Bari (Italy), vehicular traffic was the top source of BTEX in ambient air [19]. Nearly half of the total non-methane hydrocarbons mass concentration measured at Hong Kong were originated from vehicle emissions [20].

In HoChiMinh, high correlations between BTEX concentrations and the volume of on-road motorcycles indicate that the motorcycle-exhaust was the source of BTEX species [21]. According to Lan and Binh [22], Vietnam and Malaysia were more polluted by BTEX than China, Japan and Singapore. High BTEX levels in Vietnam and Malaysia (87, 52, 32, 23, 13, 12 and 48 μg/m³ for benzene in HoChiMinh, Hanoi, Cantho, Danang, Hue, Vung Tau and Kuala Lumpur, respectively) were due to high number and high emission factor of motorcycles. BTEX levels were significantly higher at garages where only natural ventilation was used (e.g. 127–1101 μg/m³ for toluene), the higher BTEX levels posed a potential risk for the workers [23]. In addition, concentrations of benzene were 29-99 mg/L, and those of other BTEX compounds were higher (500-2000 mg/L) in used motor oil [24]. Therefore, used motor oil was also an important source of BTEX to the environment.

The use of biofuel as an alternative fuel has a promising potential worldwide. The results using compression ignition engine with the addition of an alternative biofuel (biodiesel) to a traditional fuel (diesel) showed a reduction in the pollutants emissions (14.5–24.5%). BTEX emissions were also lower with ethanol blends compared to the traditional fuel [25]. Therefore, push to expand the use of biofuels might help to reduce the air pollution.
2.3 Painting and printing
The aromatics benzene, toluene and $m,p$-xylene were the most important VOC species emitted from architectural or furnishing coatings [4, 9], accounting for 7%, 19% and 13% of total VOCs (wt.%) from building coatings in China, respectively [4]. In printing factory of Beijing, 31.6% of the VOC emissions were aromatic compounds [26]. Some consumer products, such as whiteout, oil-based ballpoint pen, shoe polish and leather cleaner, were also contained higher levels BTEX [27]. BTEX were detected at high levels in workplaces such as photocopy centers and automotive paint shops [28]. Toluene was the most abundant species among BTEX in paint [8, 9]. Therefore, toluene was always present in indoor air in detectable levels caused by indoor source emissions (such as paint organic solvent and household cleaning chemicals), which range from 1.3 to 75.6 µg/m$^3$ in living room [29]. In Spain, the indoor concentrations of BTEX were approximately 2.5 times higher than those observed outdoors [30]. According to the national wide survey in Canada conducted in 2009-2011, the mean level of BTEX in Canadian residences was 43.8 µg/m$^3$ (2.0 µg/m$^3$, 19.2 µg/m$^3$, 4.1 µg/m$^3$, 14.4 µg/m$^3$ and 4.2 µg/m$^3$ for benzene, toluene, ethylbenzene, $m,p$-xylenes, and $o$-xylene, respectively), renovation in the past month, use of paint remover and use of fragrance were the significant predictors of BTEX presence [31].

2.4 Coal and biomass burning
Coal combustion contributed 28%–39% to ambient VOCs during winter in Beijing [32]. BTEX accounted for about 61.1%–94.8% in total mass of VOC discharged from coal or wood incomplete combustion [33]. In rural sites of the North China Plain, the outdoor and indoor concentrations of BTEX were 25.8–236.0 µg/m$^3$ and 254.5–1552.9 µg/m$^3$ during winter in 2011, respectively [34]. The indoor concentrations far exceeded the limit levels of Chinese Indoor Air Quality Standard (110 µg/m$^3$, 200 µg/m$^3$ and 200 µg/m$^3$ for benzene, toluene and xylenes, respectively). The serious BTEX pollution was mainly ascribed to domestic coal combustion for heating during the winter season. Toluene was one of the most abundant specie in the coal-burning factories (such as thermal power plant and coke production) in the Liaoning Province, China [35]. And in heating station, approximately 70.0% of non-methane hydrocarbons were contributed by trimethylbenzene, $n$-propylbenzene and $o,m$-ethyltoluene [35]. In previous studies [8, 9, 36, 37], benzene was identified as the most abundant VOC specie from coal-burning. The ratios of benzene/toluene (B/T) in most case of coal combustions were found to be greater than 1[8, 9, 34, 36, 37], which was considered as the marker of coal-burning emissions.

2.5 Petrochemical industry
In Daegu, Korea [38], residential and commercial areas have high BTEX concentrations during daytime, while industrial areas have high concentrations during nighttime. And the highest toluene concentration was in the industrial areas. BTEX levels in the downwind ambient air of petrochemical industrial areas were higher. This indicated that the sources of BTEX in industrial areas were totally different from sources in other areas. The study in a petrochemical plant in Kaohsiung, Taiwan showed that 12% VOCs contributed by aromatics [39]. More than 90% of VOCs came from 10% equipment components [39]. In the oily sewerage system and tank farm area of an oil refinery [40], most of VOCs were BTEX. In the boundaries of industrial parks in southern Taiwan, VOCs were
dominated by benzene and toluene [41]. In the urban area of Shanghai, ~36% VOCs contributed by aromatics, chemical and petrochemical industry contributed 22.3% of the VOCs [42].

3. Environmental Fate of BTEX

BTEX were easily transported to the atmosphere due to the high vapor pressure [43]. According to currently published papers [44-46], the fate of BTEX in the general environment can be summarized as Figure 1.

![Figure 1: Fates of BTEX in the general Environment (based on [44-46]).](image)

3.1 BTEX in soil

Soil and sediment were considered as the most important reservoirs of some semi- and non-volatile pollutants. However, only a very small percentage of VOCs, including BTEX of course, released into the environment were stored in soil and sediment [43].
In natural environment, BTEX compounds can migrate quickly through soil, with benzene being the fastest followed by toluene, m-, p- and o-xylenes and ethylbenzene [47]. According to Tan et al. [48], benzene were not detected in soil samples around three representative pesticide factories collected in Hebei Province, China. And there was an increasing trend of BTEX from soil to dust, and from living area to production area in the factories [49]. In Amman–Zarqa Basin [50], concentrations of BTEX in groundwater varied between no-detection to 6.6mg/L. BTEX group tend to partition between sediments and soil rather than leach into groundwater. They tend as well to volatize to atmosphere rather than stick to soil particles.

In a gasoline-contaminated aquifer [51], BTEX biodegradation appears to be occurring using both oxygen and nitrate as terminal electron acceptors. Toluene, ethylbenzene, and m-, p-xylenes were removed very rapidly and o-xylene and benzene were removed much slower.

3.2 BTEX in water

Oil leak, sewage discharge and water transport were the most important sources of BTEX in natural waters. The levels of BTEX in natural waters were influenced by many factors. In waters of Mediterranean coast [52], temperature and precipitations were related on the BTEX levels. Lower levels of contaminants were observed when the discharges of water and temperatures increased. In surface waters of Irish Sea [53], the highest concentrations were found near the river mouths and close to the port activities. BTEX concentrations were highly variable in the same station between different times, the highest concentrations of BTEX were coincident with high solar irradiation and low wind speeds. According to the results of long-term observation in the southern North Sea [54], the occurrence of BTEX in the surface waters was attributed to anthropogenic emissions and discharges from shipping and oil-related activities in coastal areas.

BTEX were nearly impossible to sorb onto suspended particulate matter. In an oil impacted river of State Nigeria [55], the concentration of BTEX markedly decreases as time increases due to evaporation and other factors. In the Scheldt Estuary and the Southern North Sea [56], VOC levels in many sediment samples were at or below the detection limits. According to the study conducted at a former coke plant [57], benzene concentrations decreased almost five orders of magnitude 70 m downgradient the source. Benzene could never be detected near the river which is about 160 m downgradient the main source. Within the water column, at most 5% of BTEX was predicted to be adsorbed under the most favorable environmental conditions [58].

Based on mesocosm experiments with 14C-model compounds [59], aromatic hydrocarbons in seawater were subject to both volatilization and biodegradation, with mineralization dominating in summer. BTEX do not undergo direct photolysis in natural waters. However, direct photolysis could be an important removal pathway for BTEX in snow-covered regions because they undergo significant red-shifts in their absorption spectra when they were present at air-ice interfaces [46]. In groundwater, dispersion is not a very effective natural attenuation process. Because of the relative abundance of anaerobic electron acceptors (such as Fe3+, NO3) as compared with dissolved oxygen, most of BTEX in groundwater is attenuated by anaerobic biodegradation [45].
Therefore, BTEX levels in natural water were highly variable between different times or locations. And surely, BTEX dispersion was mainly controlled by volatilization and degradation rather than sedimentation.

### 3.3 BTEX in atmosphere

In the general environment, benzene partitions mainly into air (99.9%; [60]). The levels were influenced by several factors, such as distance from sources, ambient temperature and air diffusive condition. Similar diurnal and seasonal profiles were presented by different researchers of the world. In Windsor (Canada; [61]), lower concentrations were observed in the warmer months. Similar seasonal profiles were also observed in Beijing [62] and Delhi [63]. The average concentrations of BTEX in the upper atmosphere around Beijing in November were about 1.5 times larger than those in July [64]. The daily variations were also evident. In Beijing, BTEX concentrations in the morning and evening were higher than that at noontime [65]. The peaks were mainly contributed by the emissions from vehicles. And more notably, BTEX can be easily accumulated in the air due to the weak photochemical reaction with lower temperature and low light intensity in cloudy day. In comparison with non-haze days, remarkable accumulation of BTEX was found under haze days, with enhancement factors of 1.9-5.7 [66].

In urban storm water in the United States [67], toluene and total xylene were the most frequently detected BTEX compounds and the most frequently detected VOCs in the investigations during 1991-1995. However, BTEX did not show any correlation between rainfall amount and concentrations. Rainwater was not an effective removal mechanism of BTEX, only 0.1% of BTEX in the atmosphere was removed by rainwater [68]. But the amount of BTEX species retained in water were significantly higher than suggested by theoretical predictions indicating that dissolution is not the major mechanism of gaseous BTEX uptake in aqueous phase [69].

Their results indicated that the main atmospheric sink for these mono-aromatic hydrocarbons was chemical oxidation primarily by the ·OH radical rather than wet depositional removal by precipitation. In waters of Mediterranean coast [52], BTEX levels were influenced by temperature and precipitations. In surface waters of Greece, not only industrial and agricultural activity within the Greek territory, but also transboundary pollution deriving from neighbouring countries consisted important sources of VOCs [70].

In conclusion, atmospheric BTEX was probably an important source of BTEX in the surface waters. But surely, most of BTEX were probably ended in the atmosphere rather in other medium.

### 4. BTEX in the Ambient Air of China

#### 4.1 Spatial and seasonal variation

The temporal and spatial distribution patterns of atmospheric BTEX in coastal cities of China were shown in Figure 2. The locations of Chinese cities mentioned in this paper were given in supplemental material Figure S1.
As shown in Figure 2a, the composition characteristics of BTEX in different regions were significantly different. Generally, high atmospheric concentrations of BTEX were observed in the cities of south China. The annual average atmospheric BTEX concentration was 20.0 μg/m³ and 46.7 μg/m³ for the cities in north and south China, respectively. Toluene was the most abundant species varying from 21.8–81.3% (accounted for an average 33.8% and 17.3% of the total BTEX in the north and south, respectively) of the total BTEX followed by benzene (8.9–44.8%; accounted for an average 35.6% and 59.9% of the total BTEX in the north and south, respectively). The concentrations of BTEX measured in Shenyang, Tianjin, Nanjing and Wenzhou were higher than in other cities (Figure 2). Those cities are important industrial cities in China. Therefore, industrial emissions played important roles on maintaining high BTEX levels in those cities.

There was marked seasonal changes of atmospheric BTEX concentrations (Figure 2b). The atmospheric concentrations of BTEX were higher in winter than in summer. The lowest BTEX levels related to summer with a mean concentration of 24.5 μg/m³. On the other hand, the highest levels of BTEX compounds were measured in
winter, with a mean concentration of 44.6 μg/m\(^3\). The difference was more apparent in south than in north, as in average 29.8μg/m\(^3\) in summer and 64.0μg/m\(^3\) in winter was reported in cities of south China versus 18.1μg/m\(^3\) in summer and 20.3μg/m\(^3\) in winter was reported in north China (Figure 2b).

As shown in Table 2, the reported BTEX levels in China were comparable with the concentrations observed in Mexico (59.0 μg/m\(^3\);[88]), Italy (63.7 μg/m\(^3\);[89]) and Egypt (49.2 μg/m\(^3\);[90]), but much lower than the concentrations observed in HoChiMinh (285.0 μg/m\(^3\);[21]), Delhi (371.3 μg/m\(^3\);[91]) and Bangkok (118.3 μg/m\(^3\);[92]), and much higher than the concentrations observed in developed countries such as Korea and Canada (Table 2). This might reveal that atmospheric BTEX concentrations were influenced by the social and economic development of the country. Although domestic airs of China were less contaminated with BTEX than some Southeast Asian countries, this problem should not be ignored.

<table>
<thead>
<tr>
<th>Sampling Site</th>
<th>Sampling Date</th>
<th>Sampling Method</th>
<th>B</th>
<th>T</th>
<th>E</th>
<th>X</th>
<th>BTEX</th>
<th>B/T</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada</td>
<td>Windsor</td>
<td>2004-2006</td>
<td>0.8</td>
<td>2.8</td>
<td>0.5</td>
<td>1.8</td>
<td>5.8</td>
<td>0.28</td>
<td>[61]</td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td>Jeddah</td>
<td>2011-2012</td>
<td>1.3</td>
<td>4.5</td>
<td>1.6</td>
<td>8.0</td>
<td>15.4</td>
<td>0.29</td>
<td>[93]</td>
</tr>
<tr>
<td>Iran</td>
<td>Ahvaz</td>
<td>2012-2013</td>
<td>1.8</td>
<td>5.2</td>
<td>0.5</td>
<td>1.1</td>
<td>8.6</td>
<td>0.34</td>
<td>[94]</td>
</tr>
<tr>
<td>Mexico</td>
<td>Monterrey</td>
<td>2011-2012</td>
<td>3.0</td>
<td>10.8</td>
<td>0.7</td>
<td>3.8</td>
<td>18.4</td>
<td>0.28</td>
<td>[95]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2013</td>
<td>38.2</td>
<td>12.9</td>
<td>4.7</td>
<td>3.1</td>
<td>59.0</td>
<td>2.95</td>
<td>[88]</td>
</tr>
<tr>
<td>Poland</td>
<td>Gdansk</td>
<td>2013</td>
<td>0.7</td>
<td>1.6</td>
<td>0.7</td>
<td>2.9</td>
<td>5.9</td>
<td>0.40</td>
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<tr>
<td></td>
<td></td>
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<td>1.0</td>
<td>0.3</td>
<td>1.2</td>
<td>3.2</td>
<td>0.71</td>
<td>[97]</td>
</tr>
<tr>
<td>Turkey</td>
<td>Aliaga</td>
<td>2009-2010</td>
<td>2.7</td>
<td>7.7</td>
<td>0.6</td>
<td>3.5</td>
<td>14.5</td>
<td>0.35</td>
<td>[98]</td>
</tr>
<tr>
<td>Nigeria</td>
<td>Lagos</td>
<td>2010-2011</td>
<td>6.8</td>
<td>6.9</td>
<td>7.9</td>
<td>23.6</td>
<td>45.2</td>
<td>0.99</td>
<td>[99]</td>
</tr>
<tr>
<td>Italy</td>
<td>Caserta</td>
<td>2005</td>
<td>25.2</td>
<td>6.3</td>
<td>14.0</td>
<td>18.2</td>
<td>63.7</td>
<td>4.00</td>
<td>[89]</td>
</tr>
<tr>
<td>Spain</td>
<td>NW of Spain</td>
<td>2006</td>
<td>1.6</td>
<td>2.2</td>
<td>0.6</td>
<td>1.4</td>
<td>5.8</td>
<td>0.75</td>
<td>[100]</td>
</tr>
</tbody>
</table>
As found in many studies [66, 94], several factors, such as photochemical removal, atmospheric dispersion and sources, affect the seasonal and regional variations of BTEX in the atmosphere.

### 4.1.1 Photochemical removal:

The chemical removal by OH radical in the atmosphere is the most important degradation pathway of VOCs in the environment. There was a significant association between BTEX atmospheric concentration and atmosphere oxidizing capacity. In central Tokyo [104], the average concentrations of OH in summer is at least five times the concentrations in winter. According to Su et al. [105], up to ~30% of the primary OH radical production is attributed to the photolysis of nitrous acid (released from soil nitrite) in the lower atmosphere. Thus, agricultural activities and land-use changes may strongly influence the oxidizing capacity of the atmosphere. In general, higher OH radical concentration resulted by more sunlight and higher temperatures in warmer seasons. Agricultural activities in warmer season are also playing a big role. Therefore, the low atmospheric BTEX levels in summer can be attributed to the fast chemical removal in summer caused by high OH radical concentration. OH radical reactions were also the major removal pathway for persistent organic pollutants from the atmosphere [106].

### 4.1.2 Atmospheric dispersion:

The atmospheric levels also can be significantly influenced by the atmospheric mixing. The mixing layer in warmer seasons is much higher than in cooler seasons [107]. The dilution of airborne pollutants from ground source emissions in warmer seasons is stronger than in cooler seasons. Based on previous
studies [108-110], atmospheric particles collected in Hawaii, Korea and Japan reveal strong influxes of Asian dust in the spring of each year. Therefore, the wind directions may influence atmospheric pollutant levels. Generally, the wind was blowing from ocean to land and land to ocean in summer and winter, respectively [111]. Thus, polluted air in coastal cities was continuously blown away by the wind from the South China Sea and the west Pacific Ocean in summer. The meteorological conditions were advantageous for mixing and dissipation of the pollutants leading to lower BTEX levels in the atmosphere in summer. However, in winter, only heavily polluted air from inland areas can reach this region.

Although coal-fired heating was an important source of BTEX in north China, the concentrations during winter and summer were comparable in some cities of north China, such as Beijing and Tianjin (Figure 2b). In Beijing [112], the highest wind speeds occur in the spring (~3m/s), with slightly weaker winds in the winter and significantly lower wind speeds in the summer and autumn (<2m/s). Therefore, the atmospheric BTEX can easily spread in north China during winter.

4.1.3 Changes of emission sources: In North China, the high BTEX concentration in winter also is because the emissions associated with coal-fired heating. In Beijing [64], the average concentrations of BTEX after 15 November (winter heating season began in 15 November) were about 1.5 times larger than those in July and before 15 November, indicating extra sources (coal-fired heating) in late November.

Another factor to consider is the influence of rainfall on atmospheric pollutants concentrations. The rainy days are mainly concentrated in summer. Although rainwater was not considered as an effective removal mechanism of BTEX in atmosphere [68], the fates of pollutants in the land surface were strongly impacted by rainfall, such as leaching to deep layer or washing into river [113]. Therefore, the emissions of BTEX to atmosphere may reduce in summer.

4.2 Yearly variation

During the past decades, Chinese environment has changed significantly, such as air pollution was getting more and more serious. Here, we summarized the reported BTEX concentrations in the urban atmosphere of China (Figure 3). As far as we know, the highest BTEX concentration was observed in in Guangzhou in 2002 (285 μg/m³ [73]). In 1996, the reported concentration was 218.2 μg/m³ in urban atmosphere of Guangzhou [71]. However, the reported peak concentrations in other cities were only about 100 μg/m³ (Figure 3). Generally, a significant decreasing trend was presented in Figure 3. In recent years, Chinese government has adopted a range of policies to narrow the gap between different cities in the level of industrialization and urbanization. Accordingly, the regional differences were significantly reduced and the concentrations were stay at lower levels (~30 μg/m³). This phenomenon may associate with China's economic development.

Although the BTEX concentrations were significantly reduced, the concentrations were still well above levels observed in urban atmosphere of developed countries (such as Canada and Korea; showed in Table 2).
5. Source Identification

The ratio of B/T has been widely used as an indicator to provide information about the different emission sources. According to the VOC source profiles [8, 9], benzene was the dominant species in vehicle emissions and toluene was the dominant species in biomass and coal burning. A B/T ratio of around 0.6 has been considered to be characteristic of traffic-originated emission sources, and values ≥1 have been considered as signal for coal and biofuel burning [34].

![Figure 3: Yearly variation of BTEX in urban atmosphere of China (average annual time-weighted concentration; Data are from [7, 71-81, 83, 85-87].](image)

![Figure 4: Ratios of B to T in atmosphere of China’s coastal cities, the atmospheric samples were collected in 2008 for Anshan, Daqing, Haerbin, Jilin, Changchun, Fushun and Huludao; in 2011 for Wenzhou, Ningde, Fuzhou, Quanzhou, Putian, Xiamen, Zhangzhou and Shantou; in 1996, 1997, 2002, 2004 and 2011 for Guangzhou; in 2001, 2006, 2007 and 2014 for Nanjing; in 2004 and 2007-2010 for Shanghai; in 2006, 2009 and 2008-2010 for Beijing; in 1997, 2001 and 2002 for Hongkong; in 2006 for Lianyungang (Data are from [7, 62, 71-80, 82-87, 114-118].)](image)
Figure 4 showed that observed higher B/T ratios in the North and lower in the South. The low B/T values in South implied that the sources other than vehicle emission (such as evaporation of solvents and paints and emissions from factories and other stationary sources) could make remarkable contribution to atmospheric BTEX concentrations. In north China, the B/T values were larger than 1 in some cities [85]. This means that coal and biofuel burning could make noticeable contribution to atmospheric BTEX concentrations in some cities in North China [32, 119].

Many studies have been conducted in Beijing urban area [62, 119], the results suggested that the vehicle exhaust was the major source of BTEX. Vehicle emissions play important roles in sustaining the atmospheric BTEX levels in cities of North China. However, other sources, such as evaporation of solvents, were more important in south China. The sources are usually irregular emissions (except vehicle emissions), their seasonally and yearly emissions must vary notably and might be also partially responsible for the source variation of atmospheric BTEX.

6. Conclusion

- A fairly comprehensive review of potential sources and fates of BTEX in the general environment and its distribution in atmosphere of China’s coastal cities was presented. Based on the discussion above, the following conclusions can be drawn:
  - BTEX concentrations in the general environment were closely related to the human activities.
  - Based on recent published results, the annual average atmospheric BTEX concentration was 20.0 μg/m³ and 46.7 μg/m³ for the cities in north and south China, respectively. Toluene was the most abundant species followed by benzene. The atmospheric BTEX concentrations were significantly reduced during the past decades.
  - The atmospheric concentrations of BTEX were higher in winter than in summer. The main factors controlling the seasonal change are meteorological conditions, including temperature, wind direction and speed, intensity of the sunlight and precipitation.

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