Journal of Environmental Sciences 104 (2021) 296–306

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES
Journal of Environmental Sciences
www.jesc.ac.cn

Volatile organic compounds concentration profiles and control strategy in container manufacturing industry: Case studies in China

Yunting Ke[1], *Ruiyuan Liu*[1], *Xiaofang Chen*[1], *Yang Feng*[1], *Ping Gao*[1], *Haomin Huang*[1,2,3], *Liya Fan*[1,2,3,4], *Daiqi Ye*[1,2,3,4,*]

[1] *School of Environment and Energy, South China University of Technology, Guangzhou 510006, China*
[2] *Guangdong Provincial Key Laboratory of Atmospheric Environment and Pollution Control (SCUT), Guangzhou 510006, China*
[3] *National Engineering Laboratory for VOCs Pollution Control Technology and Equipment (SCUT), Guangzhou 510006, China*
[4] *Guangdong Provincial Engineering and Technology Research Centre for Environmental Risk Prevention and Emergency Disposal (SCUT), Guangzhou 510006, China*

ARTICLE INFO

Article history:
Received 31 December 2019
Revised 24 November 2020
Accepted 24 November 2020
Available online 24 December 2020

Keywords:
Container manufacturing
Volatile organic compounds (VOCs)
Emission characteristics
Control strategy

ABSTRACT

Volatile organic compounds (VOCs), important precursors of ozone (O_3) and fine particulate matter ($PM_{2.5}$), are the key to curb the momentum of O_3 growth and further reducing $PM_{2.5}$ in China. Container manufacturing industry is one of the major VOC emitters, and more than 96% containers of the world are produced in China, with the annual usage of coatings of over 200,000 tons in recent years. This is the first research on the emission characteristics of VOCs in Chinese container manufacturing industry, including concentration and ozone formation potential (OFP) of each species. The result shows that the largest amounts of VOCs are emitted during the pretreatment process, followed by the paint mixing process and primer painting process, and finally other sprays process. The average VOC concentrations in the workshops, the exhausts before treatment and the exhausts after treatment are ranging from 82.67–797.46 , 170–1,812.65 , 66.20–349.63 mg/m^3, respectively. Benzenes, alcohols and ethers are main species, which contribute more than 90% OFP together. Based on the emission characteristics of VOCs and the technical feasibility, it is recommended to set the emission limit in standard of benzene to 1.0 mg/m^3, toluene to 10 mg/m^3, xylene to 20 mg/m^3, benzenes to 40 mg/m^3, alcohols and ethers to 50 mg/m^3, and VOCs to 100 mg/m^3. The study reports the industry emission characteristics and discusses the standard limits, which is a powerful support to promote VOCs emission reduction, and to promote the co-ordinated control of $PM_{2.5}$ and O_3 pollution.

* Corresponding author.
E-mail: cedqye@scut.edu.cn (D. Ye).

https://doi.org/10.1016/j.jes.2020.11.028

Introduction

In recent decade, China has confronted with extreme atmospheric pollution events such as smog caused by fine particulate matter ($PM_{2.5}$) and photochemical smog pollution characterized by ozone (O_3) (Guo et al., 2014; Shao et al., 2009; Xue et al., 2014), and great efforts have been made to alleviate the pollution. From 2015 to 2018, the 95th percentile concentrations of sulfur dioxide (SO_2), inhalable particles (PM_{10}), $PM_{2.5}$ and carbon monoxide (CO) in prefecture-level cities have significantly declined year by year, while O_3–8h-90per in 2018 rose by 12.7% compared with that of 2015. O_3 has become the only pollutant that has deteriorated in recent years (CNEMC (China National Environmental Monitoring Centre) 2019). The key to curb the momentum of O_3 growth and further to reduce $PM_{2.5}$ is to strengthen emissions reductions for its important precursor volatile organic compounds (VOCs) (Atkinson, 2000; Liu et al., 2010; Tang et al., 2012; Zhang et al., 2014; Zhao et al., 2013).

In human gathering areas, the emissions of anthropogenic VOCs are larger than that of natural sources, although the latter far exceed the former on a global scale (Guenther et al., 1995; Steinfeld and Pandis, 1998). In China, the emissions of anthropogenic VOCs are growing rapidly, with industrial sources contributing the most (Cai and Xie, 2007; Klimont et al., 2002; Niu et al., 2016; Wei et al., 2008; Zheng et al., 2017). In recent years, numerous researches have been carried out on VOCs emission inventory and it did help people understand the general trend of VOCs emissions (Bo et al., 2008; Fu et al., 2013; Zhou et al., 2017). However, the inventory is generally calculated by emission factors, some of which are derived from foreign studies. The emission factors may cause significant errors even if they have been localized, because complex process makes emissions vary widely. Further, the studies of emission inventory can only explore the overall situation but not the details of VOC emissions. Focusing on the VOC emission characteristics, including composition and concentration, is the best way to reveal the details of their emissions. Several studies have worked on the industries with large VOC emissions to investigate the concentration and distribution of VOCs from various sources, such as petroleum refining, automobile manufacturing, shipbuilding, furniture manufacturing, electronics manufacturing, automobile manufacturing, footwear, pharmaceuticals, packaging and printing industries (Celebi and Vardar, 2008; Fan et al., 2019; He et al., 2016; Liu et al., 2019; Mo et al., 2015a, 2015b; Wang et al., 2019, 2013; Xia et al., 2017; Zhang et al., 2019, 2017). Besides, ozone formation potential of different VOCs species and their effects on the atmospheric environment were also studied by the maximum incremental reactivity (MIR) values (Liang et al., 2017; Ou et al., 2015; Wu and Xie, 2017; Yue et al., 2017; Zhang et al., 2014).

In addition to the above industries, the container manufacturing industry also uses large quantities of organic solvents, but it is rarely noticed by researchers. China is the largest container manufacturer, accounting for more than 96% of global container production. It is necessary to conduct research in the emission characteristics and the ozone formation potential for the reduction of VOCs and O_3 pollution in China.

To the best of our knowledge, this is the first effort in characteristics of VOC emissions in the container manufacturing industry. We conducted on-site monitoring of eight container manufacturing companies, and analyzed the concentration of VOCs from the workshop, exhaust before and after treatment. Then we calculated the species ozone formation potential (OFP) according to MIR value, and identified the key VOCs species in the container manufacturing industry. Finally, we made recommendations on national emission standards of VOCs for the container manufacturing industry based on the above results. This study would be valuable for better understanding the key VOCs species in container manufacturing industry contributing to O_3 pollution and for supporting national emission standards.

1. Methodology

1.1. *Description of the study area and sampling*

In this study, we selected eight most representative companies from CIMC, Shengshi Group, Xinhuachang Group and Shanghai Haoyu Group. The target of monitoring was VOCs during the production of standard containers after water-based reformation. The study was conducted in the summer of 2017 and 2018. Each site was composed of about 20 monitoring points, including unorganized emission sampling points and organized emission sampling points. Unorganized emission sampling points included the workshops of pretreatment, primer painting, intermediate paint spraying, inner paint spraying, exterior paint spraying, drying, asphalt paint spraying and paint mixing. Organized emission sampling points included inlets and outlets of exhaust funnel. The above composed 158 sampling points (**Table S1**).

The samples were taken by three types of sorbent tube according to Chinese standard HJ 734–2014. The sorbent tubes were aged by aging device or thermal desorber with aging function before use. After aging, the sorbent tubes were sealed with a sealing cap immediately and placed in a sealed bag. The sorbent tubes were stored in the dark below 4 °C and used within one week. And 20% adsorption sampling tubes were required for blank inspection before use. The sampling flow of sampling pump (EM-300, Shenzhen Guoji, China) is in range of 20–200 mL/min and the error of ±5%. When sampling, the sampling pump flow rate was 50–100 ml/min, the sampling time was 6–10 min. Two parallel samples were set for each sampling point. Then the samples were sealed and stored in a refrigerator at −20 °C and analyzed within one week.

1.2. *VOC analysis*

The sorbent tube samples were analyzed by an automated thermal desorption-gas chromatography mass spectrometry analysis system (Turbo Matrix TD, Perkin Elmer, America and GCMS-QP2010 Ultra, Shimadzu, Japan) with a thermal desorption autosampler. The initial temperature of the thermal desorber was set to room temperature. The adsorption tubes were desorbed at 270 °C for 3 min and the desorption flow rate was 30 mL/min. The desorbed gas entered the focused cold trap at −3 °C for re-adsorption, and then the focused cold trap was

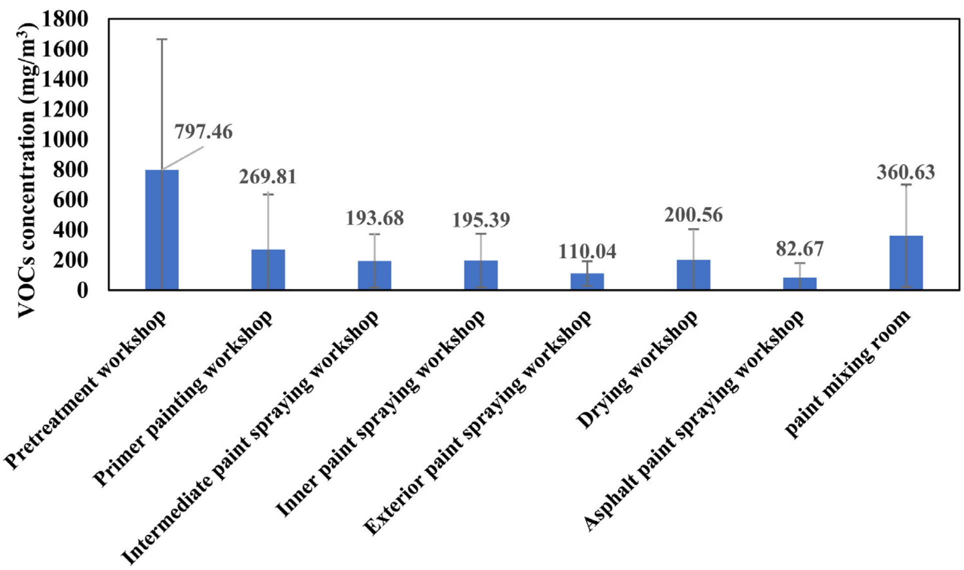

Fig. 1 – Average concentration and standard deviation of various workshops.

rapidly heated to 300 °C for secondary desorption of 3 min. Finally, the desorbed gas entered the GCMS for detection.

The initial temperature of carrier gas in GCMS was 35 °C, and the temperature was raised to 140 °C at a rate of 6 °C/min, then raised to 220 °C at a rate of 15 °C/min for 3 min. The column flow rate was 1.5 mL/min. Mass spectrometry was performed in full scan mode with a scan range of 33–180 amu (0–6 min) and 33–270 amu (6 min˜fin). The species of VOCs were identified by relative retention times and mass spectra of compounds, and the concentrations were calculated by external standard method, according to the Chinese standard HJ 734–2014 and HJ 644–2013. The calibration curves were built using standard solution (24 compounds and 35 compounds, from ANPEL Laboratory Technologies Inc.) with 10 different weights (10 levels: 400, 800, 1200, 1600, 2000, 4000, 8000, 12,000, 16,000 and 20,000 ng). The calibration curves were justified with R over 0.995.

1.3. *Estimation of ozone formation potential (OFP)*

The OFP is calculated by MIR value (Carter, 1996), and the formula is as follows:

$$OFP_i = VOC_i \times MIR_i$$

where, OFP_i (mg/m^3) is the ozone formation potential of species *i*, VOC_i (mg/m^3) is the emission of the species *i*, MIR_i is the maximum increment reactivity of species *i*. The MIR values are taken from the research of Venecek et al. (2018), which are shown in **Table S2**.

2. Results and discussion

2.1. *VOC emission characteristics*

2.1.1. *VOC concentrations of indoor air in workshops*

Container manufacturing industry has a high degree of industrial concentration in China. In this study, eight companies are selected from four group, which have occupied about 90% of the market share of global container manufacturing industry. And the companies we selected are distributed in the "Bohai Rim", "Yangtze River Delta" and "Pearl River Delta" regions with the highest concentration ration of industry. Therefore, the companies monitored in this study are well representative in the industry and geography. Besides, the container manufacturing industry has unified the implementation of water-based coatings in the form of industry self-discipline conventions since 2016. At present, the production of standard container has completed the water-based reformation basically, so this study mainly focused on the production waste gas of water-based containers.

The average VOC concentrations of indoor air in various workshops of eight container manufacturing companies were analyzed and summarized (Fig. 1), ranging from 82.67 to 797.46 mg/m^3. The VOC concentration of pretreatment workshops was the highest due to using solvent-based coatings. The diluents for solvent-based coatings are usually organic solvents such as toluene, xylene, and isopropanol, while the diluent for water-based coatings is water. Therefore, the concentrations of emitted VOCs when using solvent-based coatings are much higher than that using water-based coatings. Although the container manufacturing industry has undergone water-based reformation, it is still impossible to replace the solvent-based coating with water-based paint in the pretreatment section, for the container has high requirements for anti-corrosion and anti-rust.

The indoor VOC concentration of the paint mixing room for all coatings was also high (360.63 mg/m^3, Fig. 1). Because the ready-to-use paint is only used within a week, the paint maxing room is generally small and has no exhaust gas collection device. The air in paint mixing room can only exchanges at a low rate through the doors and windows, which may make VOCs gathering in the room.

The VOC concentrations of each full container load (FCL) spraying workshops, including primer painting workshop, intermediate paint spraying workshop, inner paint spraying

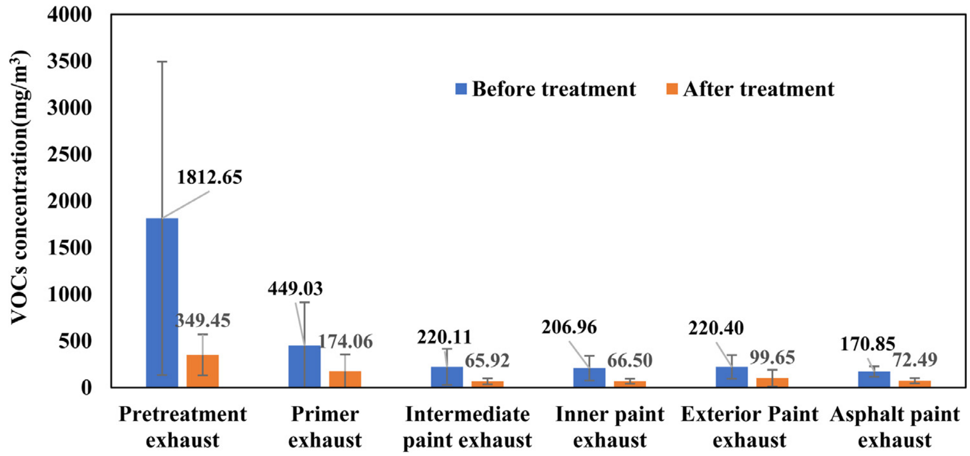

Fig. 2 – Average concentration and standard deviation of various exhaust.

workshop and exterior paint spraying workshop, were similar (Fig. 1), because water-based paint with the same magnitude of VOCs content are used in each FCL spraying process. And the air in these workshops can circulate naturally, for there is no obvious separation in the FCL spraying workshops. Besides, it is found that the VOC concentration of the primer painting workshop is slightly higher, which might be due to the high VOC content of the primer and the large amount of use. The amount of the primer is about twice that of the inner paint, intermediate paint and exterior paint.

Compared with the process at normal temperature, the VOCs remaining in the inside of the container and the coating on the surface of the steel in FCL spraying process are released in a larger amount when heated, which lead to an increase in the VOC concentration of drying workshop. The asphalt paint spraying workshop had a low VOC concentration of 82.95 mg/m^3. Only the underframe needs to be coating by asphalt paint, and the amount of asphalt paint is small, resulting in a lower VOC concentration of this workshop.

Compared to electronics manufacturing (43.01–322.34 mg/m^3) (He et al., 2016), furniture manufacturing (9.18–181.58 mg/m^3) (Zhang et al., 2019), automobile manufacturing (11.20-317.51 mg/m^3) (Wang et al., 2019; Xia et al., 2017) and printing (19.1–958.4 mg/m^3) (Liu et al., 2019), the concentrations of workshop in the container manufacturing ranged from 82.67 to 797.46 mg/m^3 with a mean of 276.3 mg/m^3, which indicates that container manufacturing is an industry of high VOCs emission. Further comparison of similar workshops in different industries was conducted. As for the primer painting workshop, the concentration of furniture manufacturing (37.15 mg/m^3) (Zhang et al., 2019) after process improvement is much lower than that of container manufacturing (269.81 mg/m^3). As for the asphalt paint spraying workshop, the concentration of automobile manufacturing (249.07 mg/m^3) (Wang et al., 2019) is higher than that of furniture manufacturing (145.54 mg/m^3) (Zhang et al., 2019) and container manufacturing (110.04 mg/m^3). In terms of drying, the concentrations of automobile manufacturing (186.43–317.51 mg/m^3) (Wang et al., 2019), furniture manufacturing (181.58 mg/m^3) (Wang et al., 2019) and container manufacturing (200.56 mg/m^3) are within a certain range.

The standard deviation of VOC concentration of workshop is large, the possible reasons are as follows. First, the companies we monitored belong to different groups around the country, and each company use diverse brands of various types of coatings because of the diversified orders of customers. There are big differences in the VOC content of each coating, even for the same brand of coatings. Second, the size of the workshops in each company and the amount of single spraying of the same process are diverse. Third, the production lines of the companies are unique. Some companies use one coating and one baking technology, while some use two coatings and one baking technology.

2.1.2. *VOCs concentration of exhaust*

The average VOC concentrations of exhaust from each workshop are demonstrated in Fig. 2. The VOC concentrations of exhaust before treatment varied significantly, ranging from 170.85 to 1812.65 mg/m^3, while the VOC concentrations of exhaust after treatment were in the range of 65.92 to 349.45 mg/m^3. The VOC concentrations of exhaust from each workshop corresponded to the VOCs concentrations of each workshop. The pretreatment exhaust had the highest concentration, followed by the primer exhaust. The VOC concentrations of the intermediate paint exhaust, the inner paint exhaust, the exterior paint exhaust and the asphalt paint exhaust were similar, including before and after treatment. There was no separate data of drying exhaust and paint mixing exhaust in this study, for drying workshop exhaust in some companies are incorporated into the exhaust of other workshops. The eight companies monitored in this study have different treatment technologies, mainly including activated carbon adsorption, catalytic combustion, adsorption + catalytic combustion and activated carbon adsorption + photocatalytic. According to the VOC concentrations of exhaust from the beginning to the end of treatment, it is found that the treatment efficiency ranged from 54% to 70%, except for the treatment efficiency of the pretreatment exhaust of 80%. In Gao's research (Gao et al., 2015), the treatment efficiency of water spray-solution absorption, water spray-activated carbon adsorption, activated carbon adsorption-catalytic combustion separately ranged from 2.7% to 19.6%, from −167.4% to 57.5%,

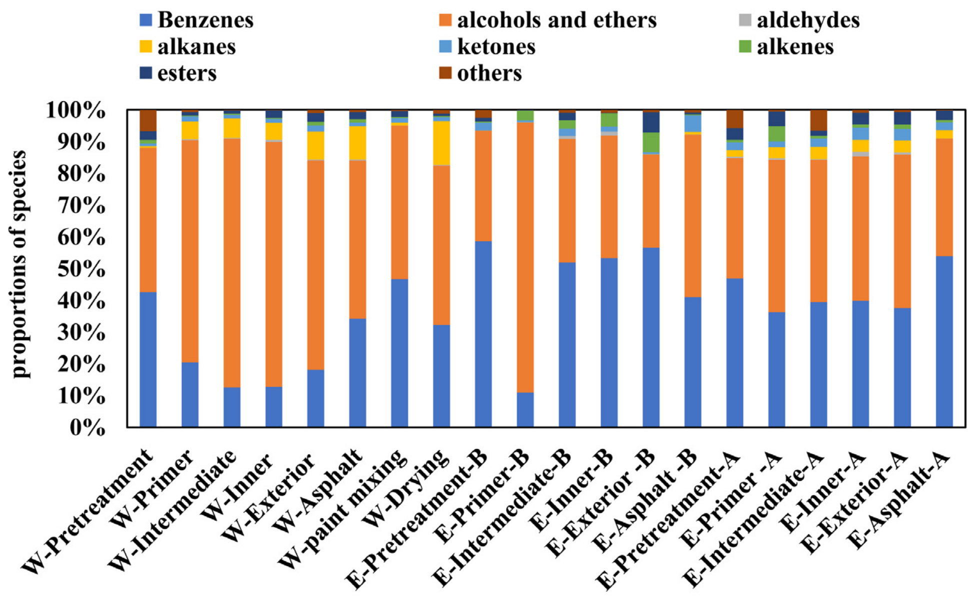

Fig. 3 – Proportions of species from various workshops, exhaust before treatment, and exhaust after treatment. W means workshop, E means exhaust, B means before treatment, A means after treatment.

and from −3.8% to 66.5%. Comparing with Gao's study, it was found that the overall average treatment efficiency (65.4%) in this study is higher, but there is still great potential for emission reduction.

The standard deviation of VOC concentrations of the exhaust is also large, and the possible reasons are similar with those of the workshop. And there are three additional possible reasons. First, the setting of exhaust pipes is different in each company. some companies set separate exhaust pipes for different painting links and drying links, and some discharge painting exhaust and drying exhaust through the common exhaust pipe. Second, the companies use various treatments with different treatment efficiency, which make a difference to VOC concentration. Third, the size of the exhaust pipes and the air volume of the fan are different. Under the same conditions, the greater the air volume, the lower the concentration of VOCs in the pipeline.

2.2. *Composition of VOC emission*

A total of 278 VOCs species were detected and classified into alkanes, alkenes, benzenes, alcohols and ethers, aldehydes, ketones, esters, and others for general analysis. The proportions of species from various workshops, exhaust inlets, and exhaust outlets are shown in Fig. 3. The average concentrations and standard deviation of five most abundant species of workshops in each category were shown in **Table S3**, and a part of them are shown in Table 1. As shown in Fig. 3, benzenes, alcohols and ethers were the main species, and the proportion of the sum of them exceeded 80% in all kinds of sources. Among them, the proportion of benzenes was between 11% and 63%, and the proportion of alcohols and ethers was between 29% and 85%. Five most abundant species in benzenes include toluene, ethylbenzene, p-xylene, o-xylene, m-xylene, m-ethylbenzene, p-ethylbenzene, o-ethylbenzene, and the benzene species were basically identical in different sources. However, little benzene was detected in the monitoring of this study, because it has been banned from being used in coating products internationally for its carcinogenic. Toluene, xylene, etc. are used in large quantities to replace pure benzene as diluent and additive in coatings. Five most abundant species of alcohols and ethers were concentrated in 1-methoxy-2-propanol, dimethoxymethane, 1-butoxy-2-propanol, 1-ethoxy-2-propanol, ethanol, isopropanol, 2-butoxyethanol, 2-propoxyethanol, 1-butanol. Five most abundant species of esters were concentrated in 1-methoxy-2-propyl acetate, butyl acetate, ethyl acetate, methyl acetate, isopropyl S-(-)-lactate, 2-ethylhexyl acetate, methyl formate, 2-methoxyethyl acetate. Taken as a whole, five most abundant species in each source were similar.

Comparing the VOC species from the workshop, it can be found that the concentration and proportion of benzenes in the pretreatment workshop and the paint mixing room were larger than those in other workshops. This is because solvent-based coatings and their associated diluent, whose main components are benzenes and alcohols, are still used in the pretreatment section. The concentration of benzenes in the paint mixing room was lower than that in the pretreatment workshop, and higher than other workshops. It is presumed that both the solvent-based paint and the water-based paint are mixed in the paint mixing room. In the workshops such as primer spraying, intermediate paint spraying, etc., alcohols and ethers account for a relatively high proportion, mostly between 65% and 78%, for the main components of the water-based paint were alcohols and ethers. This is consistent with the conclusions of many studies (Fan et al., 2019; Wang et al., 2019; Zhang et al., 2019). When using solvent-based solvents, the VOC emissions of the solvent-use industry show the characteristics of benzenes as the primary species. After the realization of water-based solvent substitution, the species com-

Table 1 – Five most abundant species of workshops in each category and their average concentration and standard deviation (unit: mg/m^3).

Pretreatment workshop		Primer painting workshop		Intermediate paint spraying workshop		Inner paint spraying workshop	
Species	Mean±sd	Species	Mean±sd	Species	Mean±sd	Species	Mean±sd
Benzenes (42.62%) [a]		Benzenes (20.51%)		Benzenes (12.56%)		Benzenes (12.77%)	
p-Xylene	104.56±120.11	p-Xylene	19.31±38.17	p-Xylene	8.57±13.07	p-Xylene	8.64±12.99
Ethylbenzene	47.79±50.12	o-Xylene	10.94±21.78	o-Xylene	5.01±8.78	o-Xylene	5 ± 8.78
Toluene	46.97±68.16	Ethylbenzene	7.61±12.42	Toluene	3.47±1.88	Toluene	4.46±2.71
o-Xylene	42.65±51.66	Toluene	4.76±8.13	Ethylbenzene	2.8 ± 2.94	Ethylbenzene	2.88±2.84
3-Ethyltoluene	12.22±24.86	m-Xylene	4.23±10.04	3-Ethyltoluene	1.38±2.46	3-Ethyltoluene	0.93±2.21
Alcohols and ethers (45.48%)		Alcohols and ethers (69.97%)		Alcohols and ethers (78.42%)		Alcohols and ethers (77.16%)	
Dimethoxymethane	278.16±486.02	Isopropyl alcohol	116.11±252.58	1-Methoxy-2-propanol	101.53±132.41	1-Methoxy-2-propanol	101.25±134.72
1-Methoxy-2-propanol	11.28±12.71	1-Methoxy-2-propanol	50.64±32.95	1-Butoxy-2-propanol	12.66±18.95	Isopropyl alcohol	11.54±25.98
bis(2-Chloroisopropyl) ether	3.39±6.42	Dimethoxymethane	13.33±22.4	Isopropyl alcohol	11.24±26.1	1-Ethoxy-2-propanol	10.93±28.92
Isopropyl alcohol	2.51±4.98	1-Butoxy-2-propanol	2.29±2.69	2-Propoxyethanol	9.35±23.01	1-Butoxy-2-propanol	8.21±20.36
1-Butanol	1.79±4.11	2-Propoxyethanol	2.13±3.81	1-Ethoxy-2-propanol	8.76±23.18	Dimethoxymethane	6.05±9.71
Exterior paint spraying workshop		Asphalt paint spraying workshop		paint mixing room		Drying workshop	
Species	Mean±sd	Species	Mean±sd	Species	Mean±sd	Species	Mean±sd
Benzenes (18.16%)		Benzenes (34.2%)		Benzenes (46.76%)		Benzenes (32.27%)	
p-Xylene	6.09±4.78	p-Xylene	10.99±16.75	p-Xylene	60.01±72.78	p-Xylene	28.01±49.86
Ethylbenzene	3.3 ± 1.51	Toluene	5.31±6.98	Toluene	34.62±47.32	o-Xylene	14.73±29.69
o-Xylene	2.3 ± 1.62	o-Xylene	5.01±7.45	Ethylbenzene	26.46±32.13	Toluene	8.92±15.65
3-Ethyltoluene	1.05±1.96	Ethylbenzene	4.44±4.37	o-Xylene	25.38±32.79	Ethylbenzene	8.73±13.41
Toluene	5.05±8.02	m-Xylene	1.18±1.97	3-Ethyltoluene	5.03±5.66	3-Ethyltoluene	3.5 ± 6.94
Alcohols and ethers (65.95%)		Alcohols and ethers (49.88%)		Alcohols and ethers (30.15%)		Alcohols and ethers (50.17%)	
1-Methoxy-2-propanol	47.57±61.87	Dimethoxymethane	26.87±56.41	Dimethoxymethane	148.8 ± 177.52	1-Methoxy-2-propanol	45.29±65.8
Dimethoxymethane	9.38±13.98	1-Methoxy-2-propanol	9.26±15.35	1-Methoxy-2-propanol	12.49±11.3	Isopropyl alcohol	16.21±35.05
Isopropyl alcohol	6.22±12.65	1-Butoxy-2-propanol	1.05±1.26	Isopropyl alcohol	5.73±8.29	Dimethoxymethane	11.25±24.77
1-Butoxy-2-propanol	2.38±5.06	2-Propoxyethanol	0.94±1.92	1-Butanol	3.24±6.43	1-Butoxy-2-propanol	10.32±21.86

[a] "Benzenes (42.62%)" mean benzenes accounted for 42.62% of Volatile Organic Compounds (VOCs) in the corresponding pollution source, and same for others.

Table 2 – Concentrations of volatile organic compounds (VOCs) species from low and high temperature drying of primers in a container manufacturing company.

Species	Concentration of low temperature drying (mg/m^{3})	Concentration of high temperature drying (mg/m^{3})
1-Butanol	——	0.50
1-Methoxy-2-propanol	10.05	16.09
Propanedial	2.64	8.32
2,3-Dimethylpentanal	0.77	4.15
2-Propoxyethanol	58.72	104.16
Ethylbenzene	1.75	2.50
p-Xylene	6.41	6.90
m-Xylene	——	1.80
2-Butoxyethanol	3.22	7.72
1-Butoxy-2-propanol	34.78	94.66
Sec–butyl ether	0.67	2.86
2,2,4,6,6-Pentamethylheptane	76.13	161.09
2,2,4,4,6,8,8-Heptamethylnonane	10.13	24.58
bis(2-Chloroisopropyl) ether	2.59	6.83
2-(2-Hydroxypropoxy)−1-propanol	——	102.91
t-Butylacetic acid	——	3.08
VOCs	207.85	548.15

position characteristics are changed to alcohols and esters as the dominant species.

In addition, we found that the VOCs species emitted during low-temperature drying and high-temperature drying are basically coincident. As shown in Table 2, high-temperature drying cause more VOCs to emit than low-temperature drying, and the concentration of VOCs during high-temperature drying will be higher, which is in line with common sense that high temperature can promote volatilization of VOCs.

The treatment efficiency of different types of species from the exhaust were calculated. (Species with a concentration below 3 mg/m^3 before treatment are not involved in the calculation of the treatment efficiency, because the values are average values and it will cause great deviations after calculate if values are too small.) The results showed that the treatment efficiency of each species was mainly between 50% and 85%. The concentrations of benzenes before treatment ranged from 66.18 to 1127.24 mg/m^3 with a mean of 286.43 mg/m^3, while the concentrations ranged from 25.37 to 177.35 mg/m^3 with a mean of 60.43 mg/m^3 after treatment. The concentrations of alcohols and ethers before treatment ranged from 86.43 to 688.94 mg/m^3 with a mean of 260.93 mg/m^3, while the concentrations ranged from 22.86 to 143.69 mg/m^3 with a mean of 59.45 mg/m^3 after treatment. Five most abundant species from different types of exhausts before and after treatment and their average concentrations and standard deviation are shown in **Table S4**. All species from different types of exhausts after treatment in the three main regions and their average concentrations and standard deviation are shown in **Table S5**. The main species changed little before and after treatment, and the main species of various types of exhaust gas were similar.

2.3. *Ozone formation potential (OFP) contribution*

The calculation result of OFP is shown in Fig. 4. On the whole, OFP values of VOCs from three sources were in the following order: exhaust before treatment > workshops > exhaust after treatment. It can be found that the sources related to pretreatment show the highest OFP values, which may due to its highest VOCs concentration and the high MIR values that its species own. And the OFP values of the sources related to the primer painting, the intermediate paint spraying, the inner paint spraying, the exterior paint spraying workshop and the asphalt paint, fluctuate within a certain range. There won't be much difference related to different paints for roughly similar amounts and components.

In three-quarters of the sources, benzenes were the largest contributor of OFP, which accounted for 50%–88%. Alcohols and ethers gave the second largest OFP contribution, ranging from 10% to 75%. The sum of the contribution of other categories, such as aldehydes, ketones, alkanes, was less than 10%.

In Fig. 5 and **Table S6**, we summarize the top 10 most abundant OFP species and its concentration and proportion for each source in the container manufacturing companies. The top 10 most abundant OFP species are mainly benzenes, alcohols and ethers, in addition to a small amount of olefins, aldehydes, esters and ketones. The species with high incidence are mainly toluene, m-ethylbenzene, o-xylene, m-xylene, p-xylene, ethylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, 1-methoxy-2-propanol, 1-butoxy-2-propanol, dimethanol formal and 2-propoxyethanol. The top 10 most abundant OFP species contribute an average of 89.14% of OFP, while contribute an average of 80.85% of VOCs. It can be found that in the container manufacturing industry, the contribution of species to concentration does not differ much from the contribution to OFP. In some studies (Jing et al., 2018; Liu et al., 2019), they found that aromatic hydrocarbons and oxygen-containing VOCs are the most important emission species and the most important contributors to OFP, which is consistent with this study. The reason may be that the concentrations of benzenes, alcohols and ethers is much higher than others in the monitoring results. At the same time, their MIR values are high, especially for benzenes. Their average MIR are

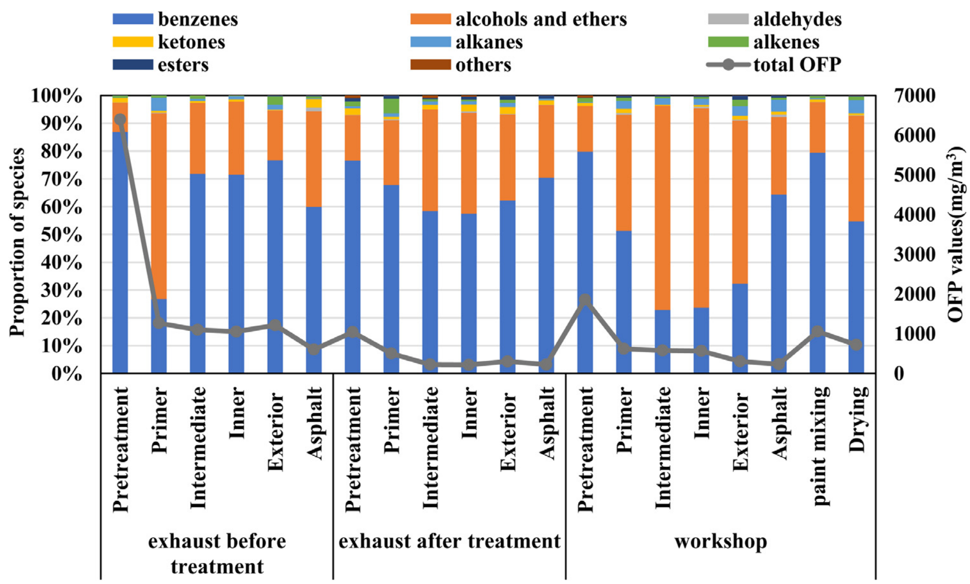

Fig. 4 – Calculation result of ozone formation potential (OFP).

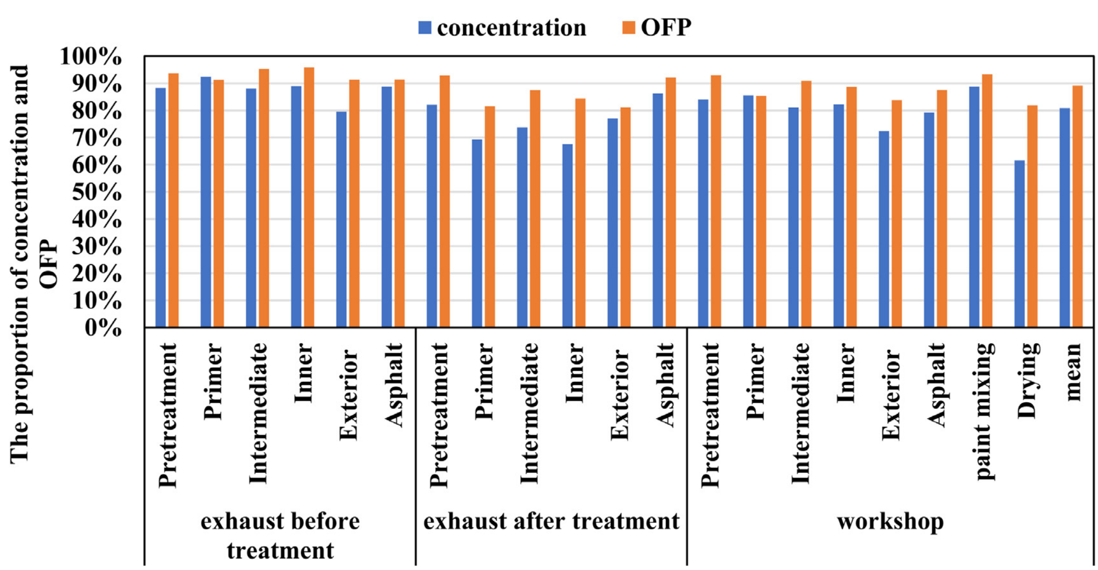

Fig. 5 – Proportion of concentration and OFP of top 10 most abundant OFP species emitted for the container manufacturing companies.

5.64 and 2.80, respectively. The high MIR value of the benzenes makes the contribution to OFP greater than the contribution to concentration after calculation.

2.4. Advice on emission standards

Based on the study, several recommendations are made for national emission standards and control strategies of VOCs for the container manufacturing industry. According to the monitoring results, benzenes, alcohols and ethers are the main VOCs species in the container manufacturing industry with large emissions and OFP, and should be included in the key control targets. China has clearly stipulated that benzene-containing solvents cannot be used due to toxic and carcinogenic of benzene. But a small amount of benzene was detected in this study, and it is recommended to set benzene indicators separately and set limits by reference to other emission standards. Toluene, xylene and other benzenes are toxic (Chang et al., 2007; Chen and Mei, 2010; Janasik et al., 2008), while their emissions are large and MIR values are high. It is recommended to establish toluene, xylene and benzenes indicators. The alcohols and ethers are less toxic, but they also need to be controlled separately for their large emissions and OFP. Their concentration distribution interval table is shown in **Table S7**, and the concentration distribution map is shown in Fig. 6 (rank the concentration from high to low). The monitoring results show that the average concentrations of benzene, toluene, xylene, benzenes, alcohols and ethers, VOCs are

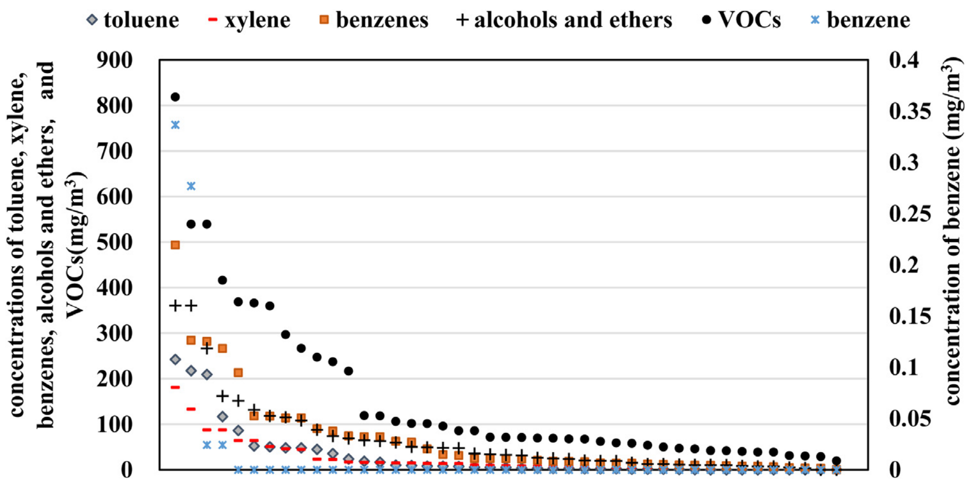

Fig. 6 – Concentrations of benzene, toluene, xylene, benzenes, alcohols and ethers and VOCs in each company (sort by concentration from left to right).

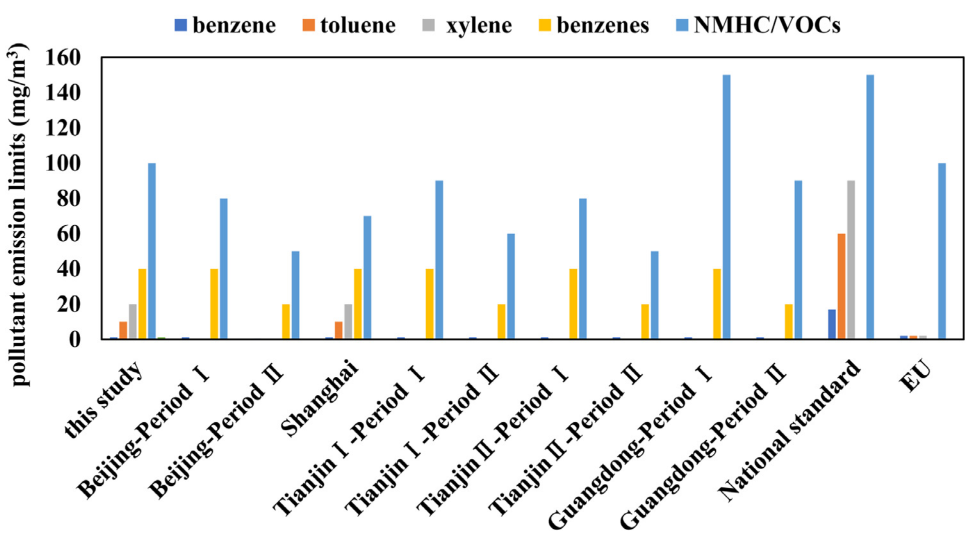

Fig. 7 – Comparison of pollutant emission limits of exhaust in various standards. a. "Beijing" means emission standards of air pollutants for industrial surface coating (DB11/1226–2015). "Period I" and "period II" mean emission limits for different periods, and same for below. b. "Shanghai" means emission limits in integrate emission standards of air pollutants (DB31/933–2015). c. "Tianjin" means emission control standard for industrial enterprises volatile organic compounds (DB12/524–2014). "Tianjin I" refers to paint mixing and spraying process. "Tianjin II" refers to drying process. d. "Guangdong" means emission standard of volatile organic compounds for container manufacturing (DB44/1837–2016). e. "National standard" means integrated emission standard of air pollutants (GB16297–1996). f. "EU" means council directive on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations (1999/13/EC).

0.015 , 30.04 , 24.26 , 68.42 , 64.44 , 154.88 mg/m^3, respectively. We compared the limits in the relevant standards at home and abroad, and the results are shown in Fig. 7. Suggestions for setting the standard limit are proposed from the following two aspects. First, considering the technical feasibility and the effectiveness of the standard, at least 60% of the organized emission sources should reach the limit. Second, reference should be made to the relevant standards at home and abroad. The setting process of limit are shown in supplement information I. It is recommended to set the emission limit of benzene to 1.0 mg/m^3, toluene to 10 mg/m^3, xylene to 20 mg/m^3, benzenes to 40 mg/m^3, alcohols and ethers to 50 mg/m^3, and VOCs to 100 mg/m^3.

In addition, it was found that the concentration of VOCs emitted after the water-based reform was reduced. However, it still did not reach the ideal state, compared with the current national emission standards. The reason may be that the water-based paint of domestic container manufacturing industry reduces the use of benzenes while increases the use of alcohols and ethers due to technology limitations. It has reduced the toxicity, but actually it is closer to solvent-based paints for high VOC contents. Therefore, VOCs concentrations that we detected were not as low as expected, and the proportions of alcohols and ethers are large.

3. Conclusions

This study focused on the characteristics of VOCs emitted from container manufacturing industry in China. It showed that VOCs concentrations of workshop ranged from 82.67 to 797.46 mg/m³ with a mean of 276.28 mg/m³. The VOCs concentrations of exhaust before treatment varied a lot, ranging from 159.15 to 1812.65 mg/m³ with a mean of 513.33 mg/m³. The VOCs concentrations of exhaust after treatment ranged from 66.20 to 349.63 mg/m³ with a mean of 138.01 mg/m³. The sources related to pretreatment emit VOCs with the highest concentration, followed by the paint mixing and primer painting. The overall average treatment efficiency was 63.8%. Benzenes, alcohols and ethers were the main emitting species and OFP contributors, accounting for more than 80% in all kinds of sources. For the exhaust after treatment, the OFP contribution of benzenes was especially prominent, ranging from 55% to 80%. The top 10 most abundant OFP species with high incidence were mainly toluene, m-ethylbenzene, o-xylene, m-xylene, p-xylene, ethylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, 1–methoxy–2-propanol, 1-butoxy-2-propanol, dimethanol formal and 2-propoxyethanol. Overall, the VOCs emissions from the container manufacturing industry should not be underestimated and the government need to strengthen supervision.

Based on the relevant standards and monitoring results, recommendations are made for emissions limits for standard container production. It is recommended to set the emission limit of benzene to 1.0 mg/m^3, toluene to 10 mg/m^3, xylene to 20 mg/m^3, benzenes to 40 mg/m^3, alcohols and ethers to 50 mg/m^3, and VOCs to 100 mg/m^3. It is recommended to implement comprehensive control of VOCs and independent control of some species with great harm. In this study, the concentrations of VOCs emitted after the water-based reform were not as low as expected, and there will be great emission reduction of VOCs in the container manufacturing industry if the above recommendations are implemented.

Acknowledgments

This work was supported by the National Key Research and Development Project of Research (No. 2017YFC0212805); the Natural Science Foundation of Guangdong Province, China (NO. 2015B020236002); the Project of Emission Standard of Air Pollutants for Freight Container Manufacturing (No. 2017.413); the National Natural Science Foundation of China (No. 41605092); Project of the establishment of the VOCs organic solvent database in industrial use for the second national survey of pollution sources (No. 20182061).

Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.11.028.

REFERENCES

Atkinson, R., 2000. Atmospheric chemistry of VOCs and NO_x. Atmos. Environ. 34, 2063–2101.
Bo, Y., Cai, H., Xie, S.D., 2008. Spatial and temporal variation of historical anthropogenic NMVOCs emission inventories in China. Atmos. Chem. Phys. 8, 7297–7316.
Cai, H., Xie, S.D., 2007. Estimation of vehicular emission inventories in China from 1980 to 2005. Atmos. Environ. 41, 8963–8979.
Carter, W., 1996. Development of ozone reactivity scales for volatile organic compounds. J. Air Waste Manag. Assoc. 44, 881–899.
Celebi, U.B., Vardar, N., 2008. Investigation of VOC emissions from indoor and outdoor painting processes in shipyards. Atmos. Environ. 42, 5685–5695.
CNEMC (China National Environmental Monitoring Centre), 2015-2018. Report on air quality in China in 2015-2018. Available: http://www.cnemc.cn/jcbg/kqzlzkbg/ Accessed December 28, 2019
Chang, F.K., Chen, M.L., Cheng, S.F., Shih, T.S., Mao, I.F., 2007. Evaluation of dermal absorption and protective effectiveness of respirators for xylene in spray painters. Int. Arch. Occup. Environ. Health 81, 145–150.
Chen, H.X., Mei, Y., 2010. Progress in research on biological monitoring indicators of occupational xylene exposure. Chin. J. Ind. Hyg. Occup. Dis. 28, 397–399.
Fan, L., Liu, W.W., Chen, D.N., Li, G.H., Wang, D., Shao, X., et al., 2019. Source profiles of volatile organic compounds (VOCs) from typical solvent-based industries in Beijing. Environ. Sci. 40, 4395–4403.
Fu, X., Wang, S.X., Zhao, B., Xing, J., Cheng, Z., Liu, H., et al., 2013. Emission inventory of primary pollutants and chemical speciation in 2010 for the Yangtze River Delta region, China. Atmos. Environ. 70, 39–50.
Gao, Z.J., Li, C., Zheng, J.Y., Guo, H.X., 2015. Evaluation of industrial VOCs treatment techniques by field measurement. Res. Environ. Sci. 28, 994–1000.
Guenther, A., Hewitt, N.C., Erickson, D., Fall, R., Geron, C., Graedel, T., et al., 1995. A global model of natural volatile organic compound emissions. J. Geophys. Res. 100, 8873–8892.
Guo, S., Hu, M., Zamora, M.L., Peng, J.F., Shang, D.J., Zheng, J., 2014. Elucidating severe urban haze formation in China. Proc. Natl. Acad. Sci. U. S. A. 111 (49), 17373.
He, M.L., Wang, N., Chen, Y.D., Wu, Z., Chen, J.D., Fan, L.Y., et al., 2016. . Emission characteristics of volatile organic compounds (VOCs) from electronic manufacturing factory of Guangdong Province. Acta Sci. Circum. 36, 1581–1588.
Janasik, B., Jakubowski, M., Jałowiecki, P., 2008. Excretion of unchanged volatile organic compounds (toluene, ethylbenzene, xylene and mesitylene) in urine as result of experimental human volunteer exposure. Int. Arch. Occup. Environ. Health 81, 443–449.
Jing, S.G., Wang, H.L., Zhu, H.L., Yang, Q., Lu, B., Xia, Y., et al., 2018. Treatment status and emission characteristics of volatile organic compounds from typical industrial sources. Environ. Sci. 39, 3090–3095.
Klimont, Z., Streets, D.G., Gupta, S., Cofala, J., Fu, L.X., Ichikawa, Y., 2002. Anthropogenic emissions of non-methane volatile

organic compounds in China. Atmos. Environ. 36, 1309–1322.
Liang, X.M., Chen, X.F., Zhang, J.N., Shi, T.L., Sun, X.B., Fan, L.Y., et al., 2017. Reactivity-based industrial volatile organic compounds emission inventory and its implications for ozone control strategies in China. Atmos. Environ. 162, 115–126.
Liu, W.W., Fan, L., Guo, X.R., Nie, L., Wang, M.Y., 2019. Emission characteristics and ozone formation potential of VOCs in printing enterprises in Beijing-Tianjin-Hebei. Environ. Sci. 40, 3942–3948.
Liu, X.H., Zhang, Y., Xing, J., Zhang, Q., Wang, K., Streets, D.G., et al., 2010. Understanding of regional air pollution over China using CMAQ, part II. Process analysis and sensitivity of ozone and particulate matter to precursor emissions. Atmos. Environ. 44, 3719–3727.
Mo, Z.W., Niu, H., Lu, S.H., Shao, M., Gou, B., 2015a. Process-based emission characteristics of volatile organic compounds (VOCs) from paint industry in the Yangtze River Delta. China. Environ. Sci. 36, 1944–1951.
Mo, Z.W., Shao, M., Lu, S.H., Qu, H., Zhou, M.Y., Sun, J., et al., 2015b. Process-specific emission characteristics of volatile organic compounds (VOCs) from petrochemical facilities in the Yangtze River Delta, China. Sci. Total Environ. 533, 422–431.
Niu, H., Mo, Z.W., Shao, M., Lu, S.H., Xie, S.D., 2016. Screening the emission sources of volatile organic compounds (VOCs) in China by multi-effects evaluation. Front. Environ. Sci. Eng. 10, 1–11.
Ou, J.M., Zheng, J.Y., Li, R.R., Huang, X.B., Zhong, Z.M., Zhong, L.J., et al., 2015. Speciated OVOC and VOC emission inventories and their implications for reactivity-based ozone control strategy in the Pearl River Delta region, China. Sci. Total Environ. 530, 393–402.
Steinfeld, J.H., Pandis, S.N., 1998. Atmospheric chemistry and physics: from air pollution to climate change. Environ. Sci. Policy Sustain. Dev. 40, 26 -26.
Shao, M., Zhang, Y.H., Zeng, L.M., Tang, X.Y., Zhang, J., Zhong, L.J., et al., 2009. Ground-level ozone in the Pearl river delta and the roles of VOC and NO_x in its production. J. Environ. Manag. 90, 512–518.
Tang, G.Q., Wang, Y.S., Li, X.Q., Ji, D.S., Hsu, S., Gao, L., 2012. Spatial-temporal variations in surface ozone in Northern China as observed during 2009-2010 and possible implications for future air quality control strategies. Atmos. Chem. Phys. 12, 2757–2776.
Venecek, M.A., Carter, W.P.L., Kleeman, M.J., 2018. Updating the SAPRC Maximum Incremental Reactivity (MIR) scale for the United States from 1988 to 2010. J. Air Waste Manag. Assoc. 68, 1301–1316.
Wang, D., Zhao, W.J., Zhang, W.Q., Dang, H.Y., Zhang, X.M., 2019. Emission profile and control countermeasures of Volatile Organic Compounds in solvent-using source. Res. Environ. Sci. 32, 1687–1695.
Wang, H.L., Nie, L., Li, J., Wang, Y.F., Wang, G., Wang, J.H., Hao, Z.P., 2013. Characterization and assessment of volatile organic compounds (VOCs) emissions from typical industries. Chin. Sci. Bull. 58, 724–730.
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.
Wu, R.R., Xie, S.D., 2017. Spatial distribution of ozone formation in china derived from emissions of speciated volatile organic compounds. Environ. Sci. Technol. 51, 2574–2583.
Xia, S.J., Qiao, Y.Z., Mu, S., Zhao, Q.Y., 2017. Emission characteristics and control of VOCs for typical automotive coating enterprise in Jiangsu. Environ. Monit. Forewarning 9, 19–23.
Xue, L.K., Wang, T., Gao, J., Ding, A.J., Zhou, X.H., Blake, D.R., et al., 2014. Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes. Atmos. Chem. Phys. 14, 13175–13188.
Yue, T.T., Yue, X., Chai, F.H., Hu, J.N., Lai, Y.T., He, L.Q., et al., 2017. Characteristics of volatile organic compounds (VOCs) from the evaporative emissions of modern passenger cars. Atmos. Environ. 151, 62–69.
Zhang, J.N., Zeng, C.L., Liu, R.Y., Yao, Y.J., Ke, Y.T., Fan, L.Y., et al., 2019. Volatile organic compound emission characteristics of furniture manufacturing enterprises and the influence on atmospheric environmental. Environ. Sci. 40, 5240–5249.
Zhang, Q., Yuan, B., Shao, M., Wang, X., Lu, S., Lu, K.D., et al., 2014. Variations of ground-level O_3 and its precursors in Beijing in summertime between 2005 and 2011. Atmos. Chem. Phys. 14, 6089–6101.
Zhang, Z.J., Wang, H., Chen, D., Li, Q.Q., Thai, P., Gong, D.C., et al., 2017. Emission characteristics of volatile organic compounds and their secondary organic aerosol formation potentials from a petroleum refinery in Pearl River Delta, China. Sci. Total Environ. 584, 1162–1174.
Zhao, P.S., Dong, F., Yang, Y.D., He, D., Zhao, X.J., Zhang, W.Z., et al., 2013. Characteristics of carbonaceous aerosol in the region of Beijing, Tianjin, and Hebei, China. Atmos. Environ. 71, 389–398.
Zheng, C.H., Shen, J.L., Zhang, Y.X., Huang, W.W., Zhu, X.B., Wu, X.C., et al., 2017. Quantitative assessment of industrial VOC emissions in China: historical trend, spatial distribution, uncertainties, and projection. Atmos. Environ. 150, 116–125.
Zhou, Y.D., Zhao, Y., Mao, P., Zhang, Q., Zhang, J., Qiu, L.P., et al., 2017. Development of a high-resolution emission inventory and its evaluation and application through air quality modeling for Jiangsu Province, China. Atmos. Chem. Phys. 17, 211–233.