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Historical emission and reduction of VOCs from the petroleum refining industry and their potential for secondary pollution formation in Guangdong, China

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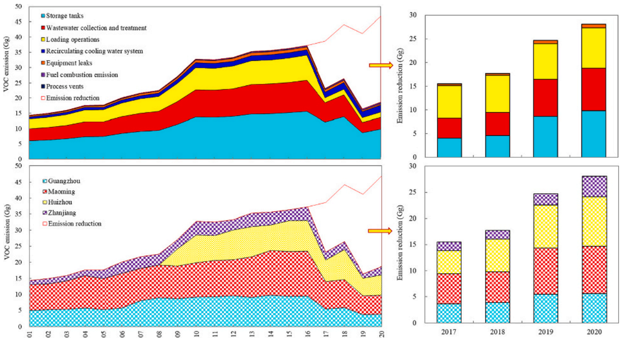
HIGHLIGHTS

- Source-specific emission factors of VOCs for different control periods was established.
- Composite source profiles considering the variation in process emission intensity was developed.
- Historical emission and reduction of VOCs from petroleum refining industry in Guangdong from 2001 to 2020 were evaluated.
- Historical emission and reduction of VOCs from petroleum refining industry for China from 2001 to 2020 were also assessed.

GRAPHICAL ABSTRACT



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ABSTRACT

China became the world leader in crude oil processing capacity in 2021. However, petroleum refining generates significant volatile organic compound (VOC) emissions, and the composite source profile, source-specific emission factors, and emission inventories of VOCs in the petroleum refining industry remain poorly understood. In this study, we focused on Guangdong, China's major province for crude oil processing, and systematically evaluated the historical emissions and reduction of VOCs in the petroleum refining industry from 2001 to 2020. We accomplished this by establishing local source-specific emission factors and composite source profiles. Finally, we quantitatively assessed the potential impact of these emissions on ozone and secondary organic aerosol formation. Our results revealed that VOC emissions from the petroleum refining industry in Guangdong followed an increasing-then-decreasing trend from 2001 to 2020, peaking at 37.3 Gg in 2016 and declining to 18.7 Gg in 2020. Storage tanks and wastewater collection and treatment remained the two largest sources, accounting for 41.9 %–53.4 % and 20.6 %–27.5 % of total emissions, respectively. Initially, Guangzhou and Maoming made the most significant contributions, with Huizhou becoming a notable contributor after 2008. Emission reduction efforts for VOCs in Guangdong's petroleum refining industry began showing results in 2017,

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with an average annual VOC emission reduction of 21.5 Gg from 2017 to 2020 compared to the unabated scenario. Storage tanks, wastewater collection and treatment, and loading operations were the primary sources of emission reduction, with significant contributions from Maoming, Huizhou, and Guangzhou. Alkanes made the largest contribution to VOC emissions, while alkenes/alkynes and aromatics comprised the most significant portions of ozone formation potential (OFP) and secondary organic aerosol formation potential (SOAP). We also estimated VOC emissions and reduction from petroleum refining for China from 2001 to 2020, and measures such as "one enterprise, one policy" and deep control strategies could reduce emissions by at least 103.9 Gg.

1. Introduction

Natural crude oil is refined into various oil products, including gasoline, diesel, heavy oil, and other products, to be used by humans. As the world's largest consumer and producer of energy, China plays a pivotal role in the petroleum products market (Masnadi Mohammad et al., 2018; Xu et al., 2018a, 2018b; BP Energy, 2020). In 2021, China surpassed the United States for the first time to become the world leader in crude oil processing capacity, accounting for 18 % of global refining capacity (Liu et al., 2022). However, the petroleum refining process generates significant VOC emissions (Wei et al., 2014; Mo et al., 2015; Zhang et al., 2017, Zhang et al., 2018a,Zhang et al., 2018b; Feng et al., 2020; Lv et al., 2021a, 2021b). In China, petroleum refining accounts for 3 % to 10 % of anthropogenic VOC emissions (Wu et al., 2016; Li et al., 2019). Therefore, controlling VOC emissions from the petroleum refining industry is crucial for alleviating O_3 and SOA pollution in China, and understanding the fine VOC emission characteristics from petroleum refining is essential for scientific and precise emission reduction.

Current research on VOC emission characteristics in petroleum refining primarily focuses on the chemical composition of VOC emissions from typical enterprises or enterprise groups. There are two main types of research. One examines petroleum refining enterprises as a consortium, emphasizing the temporal characteristics of VOCs and chemical composition near the enterprise, conducting source apportionment, and assessing environmental impacts and health risks (Chen et al., 2019; Zhou et al., 2019; Zheng et al., 2020; Pinthong et al., 2022). However, due to the large differences in VOC emissions between process units, results that do not identify key VOC emission sources or process units cannot easily be used to support precise VOC emission reduction. The other type of research focuses on specific process units, such as production devices, storage tanks, loading, and wastewater treatment, to study their VOC chemical composition characteristics, thus obtaining the VOC source profiles of the entire petroleum refining process (Wei et al., 2014; Mo et al., 2015; Zhang et al., 2017, Zhang et al., 2018a, Zhang et al., 2018b; Shen et al., 2018; Feng et al., 2020; Gao et al., 2021; Lv et al., 2021a, 2021b; Sarkar et al., 2021). However, few researchers consider the different VOC emission intensities from each emission source or process unit when establishing the composite source profiles of VOCs in petroleum refining (Mo et al., 2015; Lv et al., 2021a, 2021b).

Very few studies have explored VOC emission factors and emission inventories for petroleum refining. Lu (2017) and Lv et al. (2021b) established comprehensive and source-specific VOC emission factors for typical refining enterprises in the Yangtze River Delta (YRD) and Shandong in China, respectively. However, the source-specific emission factors only include storage tanks and loading operations, lacking other key emission sources such as wastewater collection and treatment systems and equipment leaks. Therefore, the source-specific emission factors are not systematically organized.

Simayi et al. (2021) constructed a VOC emission inventory of petroleum refining for China from 1949 to 2018 and predicted future VOC emissions before 2030 using scenario analysis. However, the source-specific VOC emission factors they used were derived from different literature sources, which introduces high uncertainty, and some were also obtained from the USA-EPA AP-42, 2009. Sha et al. (2022) established comprehensive VOC emission factors for three different control levels and estimated the VOC emission inventory of China's petroleum refining industry for 2020. However, on the one hand, applying the emission factors requires considering the contribution of crude oil processing capacity at different control levels. Currently, in the context of China's VOC emission reductions, the contribution structure is rapidly changing. Using the contribution structure given in the literature will introduce significant uncertainty to VOC emission estimates. On the other hand, although the emission factors were divided into three control levels, they were still comprehensive emission factors for the entire industry and could not provide essential support for accurate emission reduction of specific sources within petroleum refining.

Some scholars have estimated the VOC emission inventory of petroleum refining using a uniform VOC emission factor for anthropogenic or industrial sources (Liang et al., 2017, 2020; Li et al., 2019), but they have been unable to capture the specific VOC emission characteristics of individual sources or identify key VOC emission sources within petroleum refining. As a result, the composite source profile, source-specific emission factors, and emission inventories of VOCs for the petroleum refining industry remain poorly understood, making it difficult to provide technical support for VOC control. In this study, we focus on Guangdong, the major province accounting for 8 %–10 % of the crude oil processing capacity in China, and establish local VOC source profiles and source-specific emission factors for petroleum refining through measurements and estimations. We then evaluate the historical emissions and reduction of VOCs from the petroleum refining industry in Guangdong from 2001 to 2020 and quantitatively assess their potential for ozone and secondary organic aerosol formation. This research aims to provide important technical support for accurately reducing VOC emissions in the petroleum refining industry.

2. Methodology

2.1. Tested petroleum refining enterprise

2.1.1. Basic information

The tested petroleum refinery in this study is located in western Guangdong and has an annual crude oil processing capacity of 5 million tons. The enterprise operates over 20 sets of production equipment, including atmospheric and vacuum distillation, catalytic cracking, catalytic reforming, hydrocracking, polypropylene production, aromatic hydrocarbon extraction, sulfur recovery, and other facilities. It produces more than 50 types of products across nine categories, such as gasoline, diesel, polypropylene, naphtha, liquefied petroleum gas, benzene, mixed xylene, sulfur, etc.

The tested enterprise had not implemented VOC control before 2014. During 2015–2016, some rectification has been carried out, including equipment leak detection and repair (LDAR), recovery of VOCs from vaulted tanks, and recovery of VOCs from crude oil and gasoline loading, as well as collection and treatment of VOCs from wastewater collection and treatment system. However, due to the time required for the design, installation, and commissioning of these reduction efforts, no reduction benefits were generated during this stage. During 2017–2018, the above-mentioned control measures provided certain reduction benefits. The unorganized emission of VOCs from the process of equipment leaks, storage tanks, loading operations and wastewater treatment have all been alleviated. Simultaneously, the enterprise implemented oil and gas recovery treatment for internal floating-roof tanks and further improved and upgraded the existing control measures. The reduction benefits resulting from these measures were primarily generated in 2019–2020. It should be noted that the loading process of the enterprise's main petroleum products was entrusted to another port enterprise. To ensure the integrity of the entire petroleum refining process as much as possible, this study included the emissions from this loading process.

2.1.2. Estimation of VOC emissions and emission factors

Currently, VOC emissions from petroleum refining are mainly calculated using the source classification analysis method (Ministry of Ecology and Environment (MEE), P.R. of China, 2015a,Ministry of Ecology and Environment (MEE), P.R. of China, 2015b). There are four primary methods for calculating VOC emissions from each source: measurements, material balance, model/formula, and emission factors, listed in decreasing order of accuracy.

The measurement method calculates VOC emissions based on the actual measurement of the exhaust gas flow rate and the concentration of VOCs. This method can accurately reflect the emission level of the process unit and has the highest level of accuracy. However, it also requires the most significant manpower and material resources. When the measurement method is challenging to obtain, material balance and model/formula methods can be used, but these require more parameters and have specific application difficulties. The most used calculation method is the emission factor method, which is simple to apply but has higher uncertainty.

In this study, suitable calculation methods were determined for each emission source of the enterprise based on a field investigation of the enterprise's basic activity level. Measurement methods were used for organized process emissions and combustion flue gas emissions. Model/formula methods were employed for equipment leaks, storage tanks, and loading operations. Emission factors were used for emissions from the wastewater collection and treatment system and the recirculating cooling water system. The details of the method primarily refer to the guidelines provided by Ministry of Ecology and Environment (MEE), P.R. of China, 2015a,Ministry of Ecology and Environment (MEE), P.R. of China, 2015b.

$$E_{Enterprise} = \sum E_{\mathrm{unabated},i} \times (1 - \eta_i) \tag{1}$$

Where i represents the specific emission source, E is the VOC emissions, and η is the comprehensive removal efficiency.

To establish a VOC emission inventory for the entire petroleum refining industry, we combine the VOC emission inventory of the tested enterprise with the amount of crude oil processed to create comprehensive and source-specific VOC emission factors for the entire refinery. The formula is as follows:

$$EF_i = \frac{\sum E_{\mathrm{unabated},i}}{A} \tag{2}$$

where EF is the VOC emission factor, and A is the amount of crude oil processed.

2.1.3. Sampling and analysis

Sampling of the tested enterprise was conducted in May 2018. Sampling points were closely related to the VOC emission characteristics of each process unit. For production equipment units and storage tanks, such as atmospheric distillation and catalytic cracking, VOC emissions mainly come from unorganized leakage of valves, flanges, and pumps, as well as organized process emissions. In principle, samples of both stack and fugitive emissions should be collected for each process unit. Based on the calculation results of the VOC emissions from various emission sources, the contributions of stack emissions from process and combustion flue gas were found to be small—less than 3 % (Section 3.1.1). Due to sampling conditions and cost, the stack VOC emissions were not sampling in this study. Unorganized samples from each production unit were collected approximately 1.5 m above the ground and near the target equipment or component location. For loading operations, VOC emissions mainly come from unorganized evaporation during loading, so samples were collected during the loading of the major organic materials. For wastewater collection and treatment processes, both stack and fugitive samples were collected. Additionally, background monitoring points were established upwind of the production enterprise.

Samples mainly consisted of two types: stack and fugitive emission samples, both of which were collected using 3.2 L Summa canisters (with flow restrictors). Fugitive emission samples were collected by placing the Summa canisters directly in VOC emission areas, while stack emission samples were collected by connecting Teflon tubes with silanized filter heads to the Summa canisters. Prior to sample collection, the interior of the canisters was passivated to reduce the decay of reactive substances and ensure sample stability. The petroleum refining sampling points in this study mainly involved five major emission sources, with a total of 14 different process units. The wastewater collection and treatment system and storage tanks both involved VOC emissions from equipment leaks, so the study assumed that their VOC emissions characteristics from equipment leaks were consistent with their emission processes. In addition, due to the limitations of recirculating cooling water systems for VOC sample collection and analysis conditions, we assumed that the emissions from this source mainly came from the leakage points of relevant equipment's dynamic and static seals, and that the chemical composition characteristics of this source were consistent with equipment leaks. Details about sampling are shown in Table 1.

The VOC samples were analyzed based on the United States Environmental Protection Agency (USEPA) TO-15 method using gas chromatography–mass spectrometry (GC–MS; 7890A/5975C; Agilent, USA). The VOC species, including alkanes, alkynes, aromatics, halogenated compounds, and oxygenated VOCs, were identified using the Photochemical Assessment Monitoring Stations (PAMS) network and TO-15 standard mixtures. Specifically, samples were pre-concentrated and pre-treated, with water, carbon dioxide, nitrogen, and other substances removed twice by cold trapping, and then separated and analyzed through deep-cryo focusing and injection by high-purity helium into a gas chromatography column. The sample analysis process was executed with strict quality control and assurance measures. Detailed methods can be found in Liang et al. (2022).

2.1.4. Composite VOC source profiles

Considering the varying emission intensity of VOCs from each process unit, the composite source profile of petroleum refining was obtained using the weighted average method. In this process, the emissions from process and combustion flue gas were not considered for weighting

Table 1
Sampling information in each measured sample.

No. of samples	Source item	Sampling process unit	Sample type
1	Equipment leaks & Recirculating cooling water system	Atmospheric and vacuum distillation	Fugitive
2		Catalytic reforming	Fugitive
3		Catalytic cracking	Fugitive
4		Hydrocracking	Fugitive
5		Xylene production	Fugitive
6		Styrene production	Fugitive
7		MTBE production	Fugitive
8		Polypropylene production	Fugitive
9		Sulfur recovery	Fugitive
10	Storage tanks& Equipment leaks	Raw material area	Fugitive
11		Product area	Fugitive
12	Loading operations	Gasoline loading	Fugitive
13	Wastewater collection and treatment system & Equipment leaks	Wastewater treatment	Fugitive
14		Wastewater treatment	Stack
15	Boundary upwind direction		Fugitive

due to their small contribution (<3 %) (Section 3.1.1) and not being sampling in this study. The equation for the weighted average method is as follows:

$$SP_k = \sum \left(SP_{k,i} \times \frac{E_i}{\sum E_i} \right) \tag{3}$$

where k is VOC species, SP is source profile, and E is emission.

2.2. Petroleum refining industry in Guangdong

2.2.1. Estimation of VOC emission inventory from 2001 to 2020

The emission of VOCs from petroleum refining industry in Guangdong from 2001 to 2020 was estimated by emission factor method, as follows:

$$E_i = AD \times EF_{unabated,i} \times (1 - \eta_i) \tag{4}$$

where AD is the activity level, that is, the crude oil processing capacity, and η is the comprehensive removal efficiency in Guangdong.

The crude oil processing volume of various cities in Guangdong was obtained from the Statistical Yearbook of each city between 2002 and 2021. As shown in Fig. 1, from 2001 to 2020, petroleum refining in Guangdong was mainly concentrated in Guangzhou, Maoming, Huizhou, and Zhanjiang. From 2001 to 2008, crude oil processing in Guangdong was mainly distributed in Guangzhou, Maoming, and Zhanjiang, with Maoming providing the largest contribution. Starting in 2009, the petroleum refining industry in Huizhou began to develop, and from 2009 to 2017, its crude oil processing volume was comparable to that of Guangzhou. From 2018 to 2020, with further industry development, Huizhou's crude oil processing capacity continued to increase, giving it the largest crude oil processing volume in Guangdong.

The unabated VOC emission factors of specific sources are obtained from Section 2.1.2. The emission factors at different time periods are closely related to the integrated control of VOCs in petroleum refining in Guangdong. Table S1 lists the strategies and main control requirements of VOCs in petroleum refining in China and Guangdong. Based on the government requirements and governance path of the enterprise in this study, the control of VOCs for petroleum refining in Guangdong from 2001 to 2020 was divided into four stages, including 2001–2014, 2015–2016, 2017–2018 and 2019–2020 (Table 2). Control measures and emission reduction benefits in different control periods have significant characteristics were detailed in Text S1 in the Supplementary materials.

2.2.2. Speciated emission inventory

Total VOC emissions from the petroleum refining industry in Guangdong in 2020 were broken down into individual species to create a speciated VOC emissions inventory, as shown in Eq. 5:

$$E_k = \sum_k E \times SP_k \tag{5}$$

where E_k is the total VOC emissions of species k; E is the total VOC emissions of petroleum refining industry in Guangdong in 2020; and SP_k is the weight percentage of species k (Section 2.1.4).

2.2.3. Ozone formation potential (OFP)

Ozone formation potential (OFP) for the petroleum refining industry was compiled based on the speciated VOC emissions inventory and MIR values. It was calculated as follows:

$$OFP = \sum_k E_k \times MIR_k \tag{6}$$

where OFP is the total OFP emissions; E_k is the total VOC emissions of species k and MIR_k is the maximum incremental reactivity of species k. The updated MIR values reported by Venecek et al. (2018) were used in this study.

2.2.4. Secondary organic aerosol formation potential (SOAP)

Secondary organic aerosol formation potential (SOAP) for the petroleum refining industry was compiled based on the speciated VOC emissions inventory and SOA yields (Cai et al., 2019; Huang et al., 2022). It was calculated as follows:

$$SOAP = \sum_k E_k \times Y_k \tag{7}$$

where $SOAP$ is the total SOAP emissions and Y_k is the SOA yield of species k, which were obtained from McDonald et al. (2018).

3. Results and discussion

3.1. Characteristics of VOC emissions from tested petroleum refining enterprise

3.1.1. VOC emissions and emission factors

We developed a VOC emission inventory for the tested petroleum refining enterprise for three periods, which included unabated VOC emissions from 2001 to 2016, as well as emissions during 2017–2018 and 2019–2020, with amounts of 3.87 Gg, 2.32 Gg, and 1.24 Gg, respectively. As shown in Fig. 2, the contribution of each emission source varied during different periods. Storage tanks and wastewater collection and treatment remained the largest contributors, accounting for 66.2 %–80.0 % of total VOC emissions. The next two largest contributors were loading operations and recirculating cooling water systems, which together accounted for 15.0 %–26.9 % of emissions. Equipment leaks were relatively stable at around 3 %. Fuel combustion

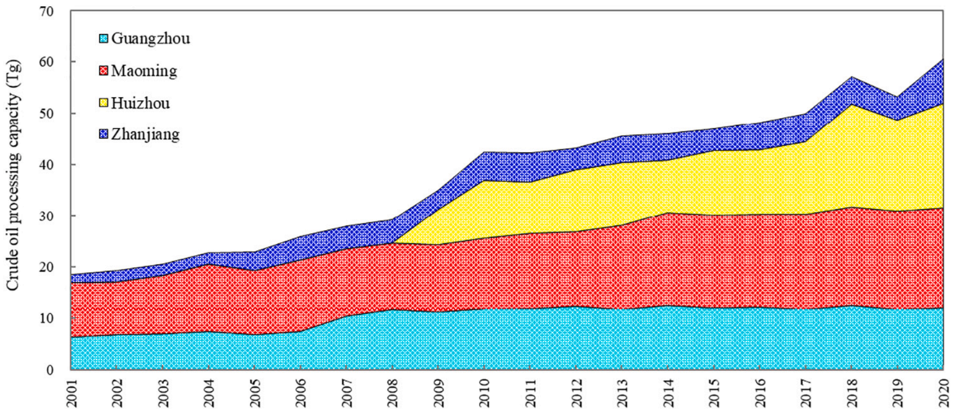

Fig. 1. Crude oil processing capacity of petroleum refining in Guangdong from 2001 to 2020.

Table 2
Control period of VOCs in Guangdong's petroleum refining industry from 2001 to 2020.

Period stage	Main characteristics	Emission reduction measures	Composite emission reduction benefits of each source
2001–2014	No requirements	/	/
2015–2016	Excessive implementation of national standards	Initial implementation of LDAR Recovery of VOCs from vaulted tanks Recovery of VOCs from crude oil and gasoline loading Collection and treatment of VOCs from wastewater collection and treatment	/
2017–2018	Special control of VOCs for "one enterprise, one policy" in Guangdong	Stable implementation of LDAR	Equipment leaks: 30 %
		Improvement of VOC recovery in vaulted tanks; About 50 % of the internal floating roof tanks completed VOC recovery	Storage tanks: 25 %(The removal efficiency refers to the national emission standard: 95 %)
		Improvement of VOC recovery in loading process of crude oil and gasoline	Loading operations: 81 % (The removal efficiency refers to the national emission standard: 95 %)
		Improvement of waste gas treatment in wastewater collection and treatment system	Wastewater collection and treatment system: 40 %
2019–2020	Generation of emission reduction benefit of "one enterprise, one policy"	All control measures were in stable and normal operation	Equipment leaks: 60 % Storage tanks: 50 % (The removal efficiency refers to the special control requirements of the national emission standards: 97 %) Loading operations: 83 % (The removal efficiency refers to the special control requirements of the national emission standards: 97 %) Wastewater collection and treatment system: 70 %

emissions and process vents each accounted for less than 3 %.

During 2017–2018, the contribution of specific sources was similar to that observed by Lu (2017) for a typical petroleum refining enterprise in the YRD. Storage tanks and wastewater collection and treatment were the two largest contributors for both our study and Lu (2017), accounting for 52.6 % and 27.4 % of emissions in this study, compared to 50.4 % and 29.0 % in Lu (2017). The proportion of VOC emissions from storage tanks during this period was also similar to that reported by Lv et al. (2021b) for typical petroleum refining in Shandong, accounting for 56.4 % of emissions. However, these characteristics were very different from the specific source reported by Lv et al. (2021a) for a typical petroleum refining enterprise in Hebei, where the wastewater collection and treatment system was the largest source of emissions, accounting for 59.6 % of total emissions. The relatively high VOC emissions from the wastewater collection and treatment system in the petroleum refinery might be due to inefficient waste gas treatment in storage tanks and poor treatment in the wastewater collection and treatment system.

According to the VOC emission data from the tested enterprise and relevant VOC control measures for petroleum refining in China and Guangdong, we calculated the comprehensive and source-specific VOC emission factors of petroleum refining based on crude oil processing capacity for Guangdong. Our emission factors included unabated emissions for the periods of 2001–2016, 2017–2018 and 2019–2020. We found the emission factors for the three periods to be 0.773 g/kg, 0.463 g/kg, and 0.309 g/kg, respectively (Fig. 3 and Table S2).

Our results indicate that the VOC emission factors for 2017–2018 and 2019–2020 were reduced by around 40 % and 60 %, respectively, compared to the unabated emission factors. VOC emission factors of key emission sources were reduced after implementing control measures, with loading operations being the emission source with the greatest reduction. Despite the reduction, storage tanks and wastewater collection and treatment remained the two largest contribution sources for VOC emissions, both before and after mitigation, and remain critical for future emissions reductions. The unabated emission factors reported in this study were similar to those reported by Lv et al. (2015) for a typical petroleum refining enterprise in northern China, which were approximately 0.73 g VOCs/kg. However, they were lower than the factors reported by Lv et al. (2021b) and Lu (2017) for Shandong and YRD, which were 1.33 g VOCs/kg and 1.00 g VOCs/kg, respectively. This was mainly due to the fact that petroleum refining enterprises in the two studies also have some petrochemical projects that contribute to VOC emissions.

3.1.2. Characteristics of measured source profiles

This study sorted the VOC species into five categories: alkanes, alkene/alkynes, aromatics, halocarbons, and oxygenated volatile organic compounds (OVOCs). The detailed chemical composition characteristics from each process unit were presented in Text S2 in the Supplementary materials. Fig. 4 depicts the VOC species of different process units in the petroleum refining industry, which are closely related to the units' main raw materials or products. In petrochemical production units, the atmospheric and vacuum distillation unit produces various oil products, such as gasoline, naphtha, diesel, and residual oil. The top five VOC species were related to the main components of the oil products, which were isopentane (20.8 %), n-pentane (17.2 %), ethane (10.7 %), propane (10.2 %), and n-butane (8.4 %). In the catalytic reforming unit, the light naphtha fraction is transformed into high octane gasoline (reforming gasoline) that is rich in aromatics, resulting in byproducts such as liquefied petroleum gas and hydrogen gas. The top five VOC species were related to both raw materials and products, which were propane (24.0 %), ethane (17.1 %), isobutane (11.7 %), n-butane (7.9 %), and benzene (6.0 %). In the catalytic cracking unit, n-butane, n-pentane, isopentane, and propylene accounted for over 10 % of total species, making them the primary contributors. In the hydrocracking unit, vacuum wax oil, vacuum residue, and atmospheric residue and catalysts to produce cracking gas, gasoline, diesel, etc. The top five VOC species were closely associated with the unit's product ingredients, namely ethane (11.9 %), propane (10.6 %), isobutane (8.7 %), isopentane (7.9 %), and n-butane (7.2 %).

In the xylene production unit, the top VOC-contributing species primarily come from the unit product m/p-xylene, accounting for 49.0 % of the total VOC emissions. The styrene production unit is a unit for dehydrogenation of ethylbenzene to produce styrene. The key VOC species were closely related to both raw materials and products, namely styrene (25.4 %), ethylene (11.5 %), ethylbenzene (11.0 %), and benzene (4.9 %). In the MTBE production unit, the main VOC species were

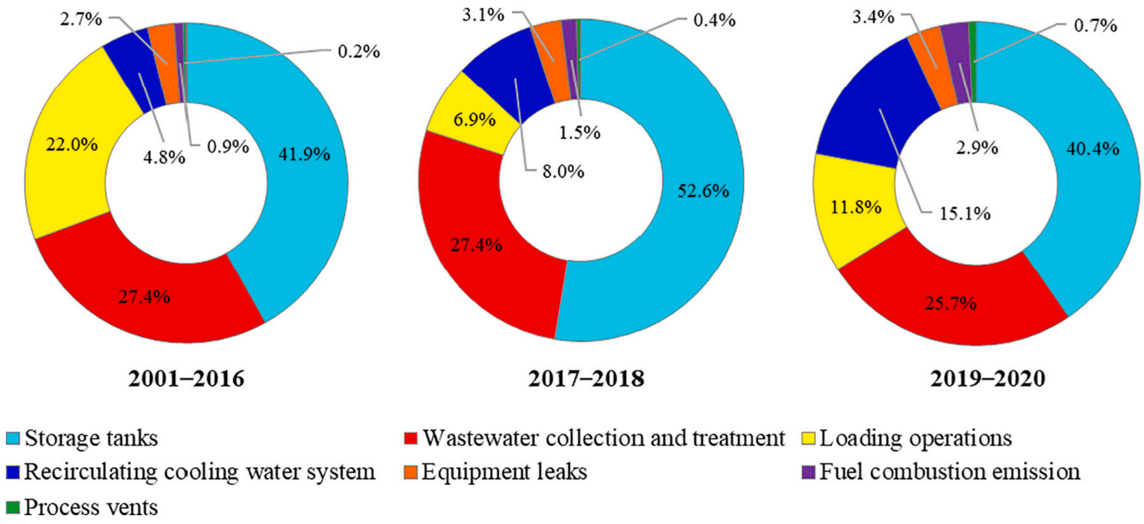

Fig. 2. Source-specific contribution of VOCs in different stages of tested petroleum refining enterprise in Guangdong.

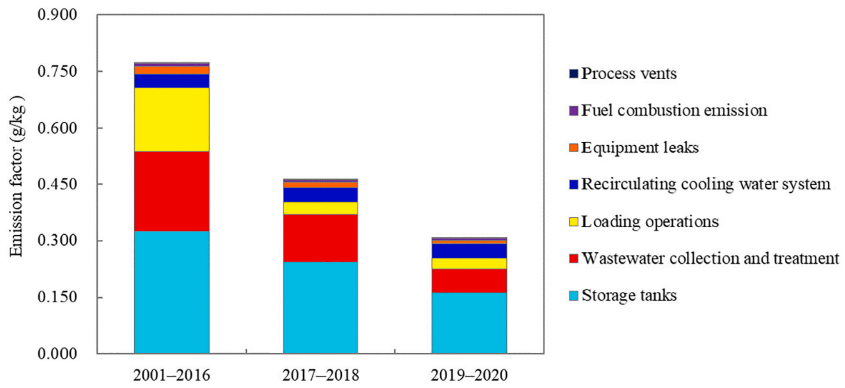

Fig. 3. Source-specific VOC emission factors in different stages of Guangdong's petroleum refining industry.

isobutane (20.8 %) and MTBE (23.4 %), with isobutane primarily sourced from the C4 feedstock of the process and MTBE as the primary product. The polypropylene unit is a unit in which propylene monomer is polymerized to produce polypropylene. The VOCs from this unit mainly come from the raw material propylene, which accounted for 66.2 %. The sulfur recovery unit transforms sulfides in sulfur-containing products, catalytic liquefaction gas, and catalytic gasoline into elemental sulfur. The top five VOC species were 1-butene (19.1 %), isopentane (18.5 %), n-butane (6.7 %), ethylbenzene (6.4 %), and ethylene (6.4 %).

The storage tank unit is responsible for both raw material and product storage of the petrochemical industry. In the raw material storage area, primarily for crude oil, the top five VOC species were n-butane (11.8 %), isopentane (7.7 %), n-pentane (5.7 %), propane (5.1 %), and ethylene (4.7 %). The product storage area, mainly for various oil products, had top VOC species of n-pentane (18.7 %), isopentane (18.3 %), n-butane (12.7 %), propane (6.1 %), and ethane (5.7 %). In the loading unit, isopentane was the primary contributor during gasoline loading, accounting for 42.1 %. For wastewater collection and treatment unit, ethylbenzene was the primary contributing species for both fugitive and stack emissions, accounting for 14.3 % and 16.2 %, respectively, likely from the styrene production unit based on process analysis.

3.1.3. *Composite source profiles*

By categorizing and weighting process-based source profiles for VOCs, this study established a composite VOC source profile for oil refining. Alkanes were the predominant chemical component, accounting for 66.9 %, followed by aromatics and alkene/alkynes at 15.5 % and 9.2 %, respectively. OVOCs and halocarbons were minor components, representing 6.4 % and 2.0 %, respectively. The top five species were isopentane (13.2 %), n-butane (10.0 %), n-pentane (9.5 %), propane (5.6 %), and ethylbenzene (5.1 %).

Comparisons of the top ten contributing species of VOC source profiles for oil refining in the YRD (Mo et al., 2015), Hubei (Shen et al., 2018) and Hebei (Lv et al., 2021a) (Fig. 5) revealed some similarities, with isopentane, n-butane, ethane, and propylene appearing among the top ten contributors in all regions. These species had a combined proportion of 30.3 %, 32.5 %, 39.7 %, and 19.9 % in Guangdong, YRD, Hebei, and Hubei, respectively. Seven key VOC species in the YRD and both five of that in Hebei, and Hubei were simultaneously identified. All these species are crucial for controlling oil refining emissions.

Although the top ten species contributing to VOC emissions were similar across various studies, their contribution proportions for each species varied significantly. Isopentane was the most significant species in this study, contributing 13.2 %, whereas in other comparative studies, its contribution ranged from 3.4 % to 8.3 % (Mo et al., 2015; Shen et al., 2018; Lv et al., 2021a). Each study also had unique key species not found in other regions. For instance, ethylbenzene was the fifth-ranked species in this study, accounting for 5.1 %, but it did not appear as a key species in the other three studies. This discrepancy was mainly due to the fact that tested enterprise in this study produces styrene, which emits ethylbenzene. The variation in the key contributing species among the studies was partly due to different production processes, with some enterprises including petrochemical production processes. The

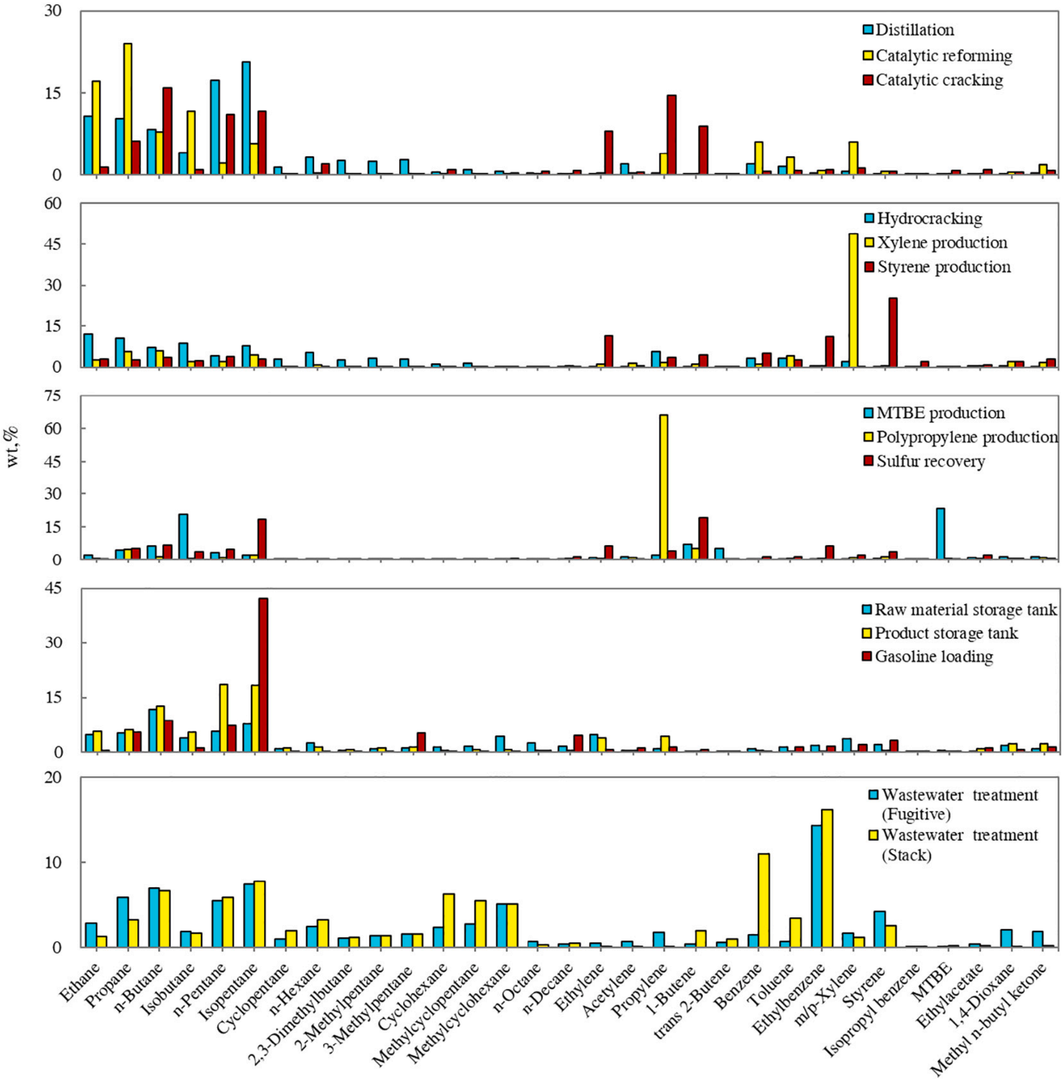

Fig. 4. Key VOC species for each process unit. (Note: the species included in the Figure exceed 2 % within at least one of the individual profiles).

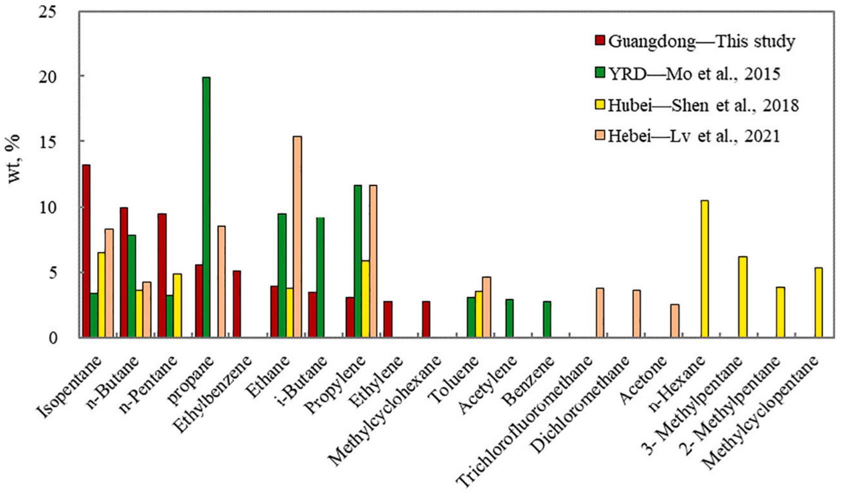

Fig. 5. Comparison of the top ten VOC species in petroleum refining.

differences were also attributed to the methods used for establishing the composition spectra in different studies. Emission intensities from different process units and sources were thoroughly considered in this study. Furthermore, factors such as actual sampling processes, sampling locations, and waste gas treatment also influenced the differences in source profiles.

3.2. Characteristics of VOC emissions from petroleum refining industry in Guangdong

3.2.1. VOC emission inventory for the period of 2001–2020

Fig. 6 and Fig. 7 depict the trends in VOC emissions from the petroleum refining industry in Guangdong between 2001 and 2020. Changes in VOC emissions were closely linked to crude oil processing volume and source reduction measures. The trend of VOC emissions during this period was characterized by an initial increase followed by a decrease. From 2001 to 2016, annual VOC emissions from petroleum refining continuously increased, with peak emissions recorded in 2016 (37.3 Gg) and an average annual growth rate of 6.8 %. However, since the implementation of VOC reduction measures in 2016, emissions have significantly declined. In 2020, the emissions of VOCs from petroleum refining fell to 18.7 Gg, with an average annual reduction rate of 11.9 %. The increase in VOC emissions in 2018 and 2020 compared to the previous year was primarily attributed to the increase in crude oil processing capacity.

Regarding the specific sources of VOC emissions (Fig. 6), storage tanks were consistently the primary source of VOC emissions from petroleum refining in Guangdong, contributing 41.9 %–53.4 % of the total emissions, followed by wastewater collection and treatment, accounting for 20.6 %–27.5 % of emissions. The implementation of effective reduction measures has resulted in the decrease of loading operations' contribution to VOC emissions from 22.0 % in 2001–2016 to 9.4 % in 2019–2020. Conversely, emissions from the recirculating cooling water system have gradually increased due to the absence of appropriate treatment technologies, rising from 4.8 % in 2001–2016 to 12.1 % in 2019–2020. Meanwhile, the contribution of other sources to VOC emissions has remained relatively consistent.

Focusing on city-specific emissions (Fig. 7), before 2008, VOC emissions from petroleum refining in Guangdong were mainly distributed in Guangzhou, Maoming, and Zhanjiang, accounting for 28.5 %–39.8 %, 44.8 %–58.0 %, and 8.7 %–17.5 %, respectively, with Maoming providing the highest contribution. With the development of the petroleum refining industry, Huizhou began to expand in 2009, and its VOC emissions became comparable to Guangzhou's emissions between 2009 and 2017. After 2017, as Huizhou's crude processing capacity expanded, its VOC emissions increased significantly and even surpassed Maoming's emissions. In 2020, the percentages of VOC emissions from Guangzhou, Maoming, Zhuhai, and Zhanjiang were 20.0 %, 32.0 %, 33.7 %, and 14.2 %, respectively, with Huizhou having the highest contribution.

3.2.2. VOC reduction for the period of 2001–2020

The reduction of VOC emissions from the petroleum refining industry in Guangdong did not begin to show benefits until 2017. If the VOC control level had remained the same as before 2016, as depicted in Fig. 6, emissions would have continued to rise until 2020, with an increase rate of 226.8 % compared to the 2001 level. From 2017 to 2020, the average annual reduction amount of VOC emissions from the petroleum refining industry in Guangdong, compared to the unabated scenario, was 21.5 Gg. As of 2020, current VOC emissions decreased by about 29.1 % compared to the level in 2015 (36.3 Gg), indicating that transitions of national standards implementation and "one enterprise, one policy" in Guangdong's petroleum refining industry has made obvious achievements in reducing VOCs emission.

Fig. 8 indicates the absolute reduction of VOC emissions in petroleum refining in Guangdong from 2017 to 2020 by specific sources and cities. Between 2017 and 2018, loading operations had the most significant contribution to the reduction of VOC emissions, accounting for around 44.5 %. Storage tanks and wastewater collection and treatment contributed equally, accounting for 26.1 % and 27.4 %, respectively. Equipment leaks contributed only 2.0 %, while other sources showed no reduction benefits. From 2019 to 2020, storage tanks, wastewater collection and treatment, and loading operations each contributed equally to the reduction of VOC emissions, accounting for 34.9 %, 32.0 %, and 30.5 %, respectively. Equipment leaks' contribution to the reduction was only 2.7 %, and other sources had not yet brought any reduction. By city, Maoming, Huizhou, and Guangzhou made the largest contributions to the reduction of VOC emissions in petroleum refining in Guangdong, accounting for 32.0–37.2 %, 28.4–35.1 %, and 20.0–23.5 %, respectively, from 2017 to 2020.

3.2.3. Speciated emission, OFP and SOAP

In 2020, a speciated VOC emission inventory of the petroleum refining industry in Guangdong was created, and OFP and SOAP were also estimated. Examining the chemical groups (Fig. 9), alkanes were found to be the most significant contributors to VOC emissions at 66.9 %, followed by aromatics at 15.5 %, while other chemical groups contributed relatively small amounts. For OFP, alkenes/alkynes made the most significant contribution, accounting for 36.7 %, while alkanes and aromatics accounted for 31.7 % and 24.8 %, respectively. In contrast, in terms of SOAP, aromatics were the largest contributor, accounting for 71.0 %, followed by alkanes at 27.4 %, with other chemical groups contributing relatively small amounts due to their relationship with SOA yields.

The top contributing species varied significantly among the three categories as well. For emissions, the top five contributing species were isopentane, n-butane, n-pentane, propane, and ethylbenzene, accounting for a total of 43.3 %. For OFP, the top five were propylene, ethylene, isopentane, ethylbenzene, and n-pentane, accounting for a total of 42.6 %. Lastly, for SOAP, the top five contributing species were ethylbenzene, toluene, m/p-xylenes, styrene, and methylcyclohexane, accounting for a total of 60.7 %. These species should be the key VOC chemical components for control in the petroleum refining industry.

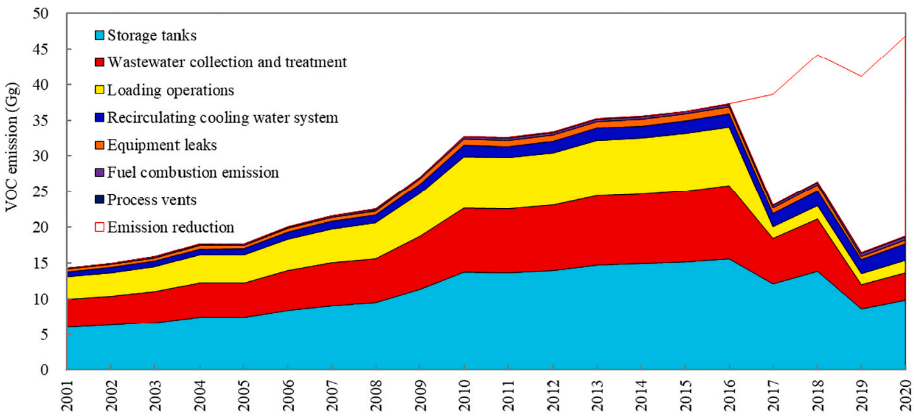

Fig. 6. Source-specific VOC emissions from petroleum refining in Guangdong from 2001 to 2020.

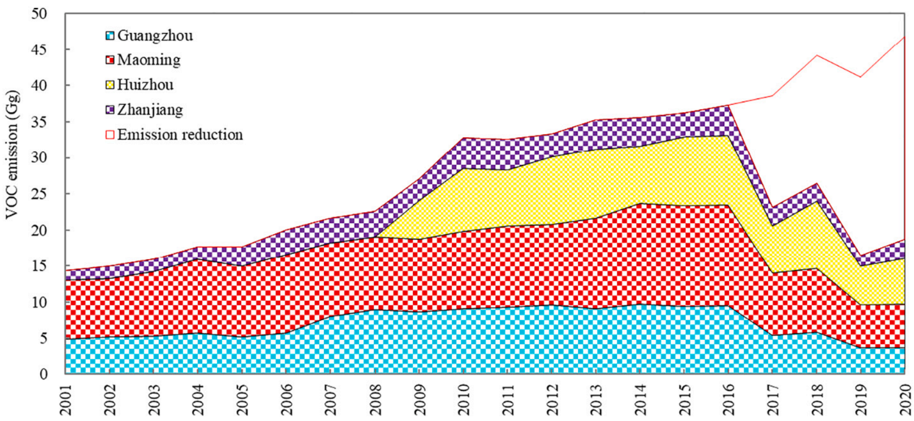

Fig. 7. City-specific VOC emissions from petroleum refining in Guangdong from 2001 to 2020.

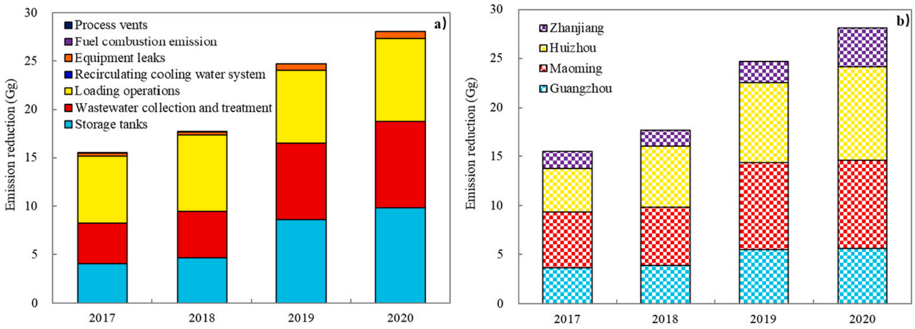

Fig. 8. VOC emission reduction from petroleum refining by source a) and city b) in Guangdong from 2017 to 2020.

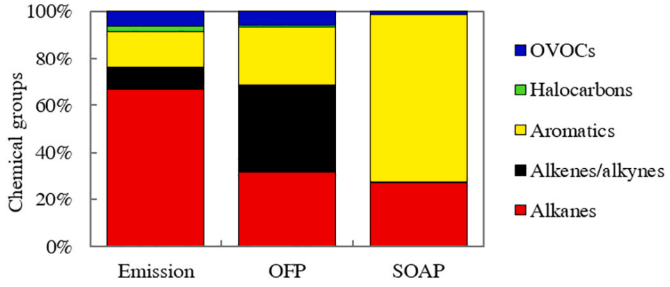

Fig. 9. Total chemical groups of VOC emissions, OFP and SOAP from the petroleum refining in Guangdong in 2020.

3.2.4. Uncertainties

The uncertainties in the emission estimates from the petroleum refining in Guangdong in 2020 were quantified using Monte Carlo simulations. The uncertainties in VOC emissions from the petroleum refining are due to that of the level of crude oil processing capacity and the source-specific emission factors. We assumed that crude oil processing capacity followed a normal distribution. The activity level was collected directly from the Statistical Yearbook of each city in Guangdong (2021). It can be classified as level I in the evaluation system for uncertainty in activity data developed by Wei et al. (2011) and had a minimum coefficient of variation of ±30 %. We assumed that the emission factors followed a lognormal distribution. Similarly, according to the evaluation system for uncertainty in emission factors established by Wei et al. (2011), the coefficient of variation of emission factors was determined. Emission factors based on field measurement could be classified as level I with a coefficient of variation of ±50 %, including fuel combustion emission and process vents. Emission factors based on model and formula method with little difference in source emissions could be classified as level II with a coefficient of variation of ±80 %, including storage tanks, loading operations and equipment leaks. Emission factors based on model and formula method with large difference in source emissions could be classified as level IV with a coefficient of variation of ±300 %, including wastewater collection and treatment and recirculating cooling water system. The Monte Carlo simulation was repeated for 10,000 times based on the probability density distribution and the results was shown in Fig. 10. The 5th, 95th percentile, and mean values of the emissions were 14.2, 26.9and 19.7 Gg, respectively. The uncertainty at a 95 % confidence interval was approximately (−28.86 %, 48.94 %).

3.3. Policy implications

Using the VOC emissions data from the petroleum refining industry in Guangdong and relevant national policies in China (shown in Table S1), we estimated the VOC emissions from petroleum refining for China from 2001 to 2020. Between 2001 and 2014, no control measures were implemented in China's petroleum refining industry. During the 2015–2016 period, national standard reform was underway, but the reduction benefits had not yet been realized. As a result, the comprehensive emission factor for the 2001–2016 period in China's petroleum refining industry was 0.773 g/kg. From 2017 to 2018, the effectiveness of the previous control measures began to show, but China as a whole still lagged behind developed provinces such as Guangdong. Therefore, we assumed that the comprehensive emission reduction benefit in this period was half of that in Guangdong, resulting in an emission factor of 0.618 g/kg. From 2017 to 2020, although China's petroleum refining industry had not fully implemented the "one enterprise, one policy" VOC control measures like Guangdong, efforts to reduce VOCs were ongoing. We assumed that the average emission factor for this period was the same as that of Guangdong during 2017–2018, at 0.463 g/kg.

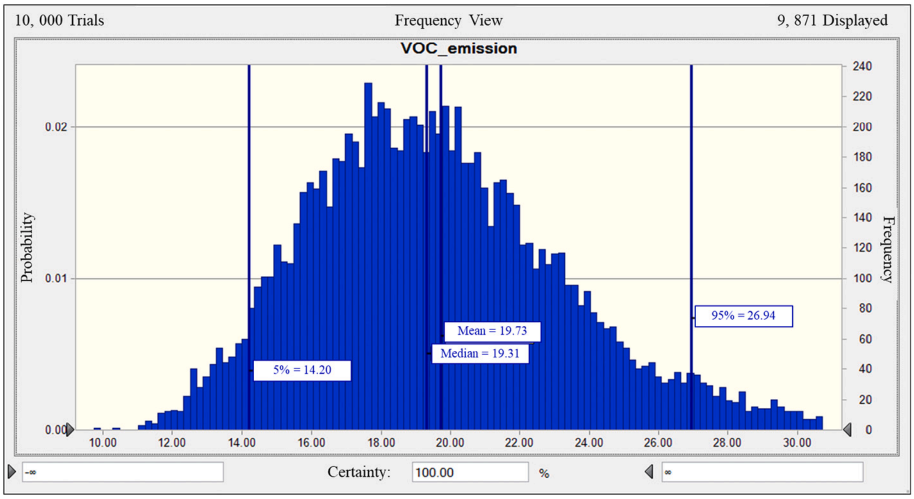

Fig. 10. Probability distribution of VOC emissions from the petroleum refining in Guangdong in 2020, on the basis of 10,000 Monte Carlo simulations.

Fig. 11 illustrates the VOC emissions from China's petroleum refining industry between 2001 and 2020, which steadily increased from 162.3 Gg in 2001 to 418.2 Gg in 2016, with an average annual growth rate of 6.6 %. However, emissions started to decrease from 2017and reduced to 312.3 Gg in 2020, which is 209.1 Gg less than the pre-control period. The study also analyzed VOC emissions from China's petroleum refining industry using VOC control measures employed in Guangdong (GD-control). VOC emissions further decreased from 2017 to 2020 in GD-control period. In 2020, VOC emissions were 208.4 Gg, representing a 103.9 Gg reduction from the existing emissions. During the 14th Five-Year Plan period (2021–2025) in China, Guangdong implemented a deep emission reduction campaign to control VOC emissions (Department of Ecology and Environment of Guangdong Province (DEEGP), 2021), with petroleum refining as one of the key industries. Therefore, without considering changes in future activity levels, phased implementation of "one enterprise, one policy" VOC control measures and deep control measures could potentially reduce Chinese petroleum refining emissions by at least 103.9 Gg. The storage tanks, loading processes, and wastewater collection and treatment are the key sources of VOC reduction in China's petroleum refining industry. It is critical to design and maintain control technology systematically and regularly operate it appropriately to ensure emissions reduction benefits. Otherwise, the control facilities would only serve as a public display for environmental inspections.

4. Summary and conclusions

Historical emissions and reductions of VOCs from the petroleum refining industry during 2010–2019 for Guangdong, China, were systematically estimated based on local investigations and measurements. Source-specific EFs, composite source profiles, mass and speciated VOC emission inventories, OFP, and SOAP were established.

Our study showed that the VOC emissions from the petroleum refining industry in Guangdong followed a trend of initially increasing and then decreasing during 2001–2020, peaking at 37.3 Gg in 2016 and declining to 18.7 Gg in 2020. Storage tanks and wastewater collection and treatment were consistently the two primary sources of VOC emissions, contributing 41.9 %–53.4 % and 20.6 %–27.5 % of total emissions, respectively. Before 2008, Guangzhou and Maoming had the highest contributions, followed by Huizhou after 2008. The benefits of VOC reduction in the petroleum refining industry in Guangdong began to manifest after 2016, with an average annual emission reduction of 21.5 Gg from 2017 to 2020, compared to the unabated scenario. Storage tanks, wastewater collection and treatment, and loading operations were the key contributors to the reduction of VOC emissions, with Maoming, Huizhou, and Guangzhou making the largest contributions, accounting for 32.0 %–37.2 %, 28.4 %–35.1 %, and 20.0 %–23.5 %, respectively. Among the chemical groups, alkanes made the largest contribution to VOC emissions, accounting for 66.9 %, while alkenes/alkynes and aromatics contributed the most to OFP and SOAP, accounting for 36.7 % and 71.0 %, respectively. The top five species contributing to VOC emissions were isopentane, n-butane, n-pentane, propane, and ethylbenzene. Propylene, ethylene, isopentane, ethylbenzene, and n-pentane were the top five contributors to OFP, while ethylbenzene, toluene, meta/para-xylenes, styrene, and methylcyclohexane were the top five contributors to SOAP. These species should be prioritized as the key VOC chemical compositions for control in the petroleum refining industry. We also estimated VOC emissions and potential reductions in petroleum refining for China from 2001 to 2020, which could be reduced by at least 103.9 Gg through the phased implementation of "one enterprise, one policy" measures for VOC control and deep control measures.

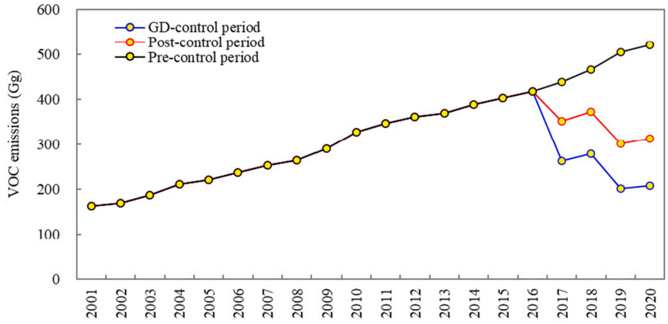

Fig. 11. VOC emissions from petroleum refining for China from 2001 to 2020.

CRediT authorship contribution statement

Xibo Sun: Investigation, Methodology, Formal analysis, Writing – original draft. **Xiaoming Liang:** Investigation, Writing – review & editing, Supervision. **Limin Chen:** Supervision. **Chenghao Liao:** Investigation. **Yongbo Zhang:** Investigation. **Daiqi Ye:** Conceptualization, Methodology, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.166416.

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