

## Article

# Volatile Organic Compound Emission Status and Control Perspectives in the Petroleum Refining Industry in China

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**Abstract:** Given the increasingly serious ozone pollution, petroleum refining has received more attention, since it is one of the dominant volatile organic compound-emitting industries in China. Volatile organic compound emission source identification, control efficiency classification, emissions calculation, emission factor generation and uncertainty analysis were performed in this study. According to the VOC emission control level, petroleum refining enterprises were divided into three levels, accounting for 10.6%, 54.4% and 35% of the total refining capacity, and 0.6%, 1.2%, and 3% were generated as the emission factor for each designed level, respectively. The total volatile organic compound emissions of the China petroleum refining industry in 2020 are estimated to be 1150 Kt by applying the hierarchical accounting method. Furthermore, the spatial distribution of volatile organic compound emissions was analyzed. The emission intensity of 15 cities is greater than the national average value of 0.12 tons/km<sup>2</sup>, where the highest level is approximately 2.7 tons/km<sup>2</sup>. To reduce the volatile organic compound emissions of PR enterprises, the collection efficiency and operation effect of treatment facilities are the most important points based on the analysis of the current situation of volatile organic compound emissions in the PR industry in China.

**Keywords:** petroleum refining industry; VOCs; emission; control



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## 1. Introduction

Volatile organic compounds (VOCs) are one of the most important precursors of ground-level ozone formation and fine particulate matter (PM<sub>2.5</sub>) generated through atmospheric photochemical reactions [1–4]. It is well-known that most organics associated with VOCs, including nonmethane hydrocarbons (alkanes, olefins, alkynes, aromatic hydrocarbons, etc.), oxygenated organics (aldehydes ketones, alcohols, ethers, etc.), chlorinated organics, nitrogen-containing organics and sulfur-containing organics, are toxic and have a strong and adverse influence on human health [3,5,6].

Although atmospheric environment quality in China showed continuous improvement from 2015 to 2020, there is still a large gap between the current conditions and the standards required for protecting human health. By 2020, the PM<sub>2.5</sub> concentration in China was still 3.3 times the WHO standard value (10 µG/m<sup>3</sup>). Meanwhile, ozone was the primary pollutant in 37.1% of the total number of excessive emission days [7,8]. The atmospheric environment still faces two arduous challenges, including the complex mechanism of pollution formation and long-term pollution treatment. The Ministry of Ecology and Environment of the People's Republic of China proposed that by 2025, the total VOC emissions need to fall by over 10% compared to those in 2020. The growth trend of ozone concentration should be effectively curbed, while fine particulate matter and ozone should

be jointly controlled [9], implying that the control of VOC emissions is one of the major tasks of air quality improvement in China.

VOCs originate from a wide variety of sources that are classified into natural and anthropogenic sources [10]. Anthropogenic VOCs usually come from industrial processes, solvent utilization, mobile sources, living sources and combustion sources. The contributions of various emission sources were found to differ greatly from 2010 to 2020. VOC emissions from industrial processes and solvent utilization rose from 39% to 61% [11]. The crude oil industry is recognized as one of the major sources of VOC emissions, as VOCs can escape during various stages of crude oil processing, from raw material input to product output.

The control and treatment of VOC pollution depend on the accurate estimation of VOC emissions. The emission inventory is usually applied in VOC estimation at the regional or industrial level. The spatial differentiation of industrial emissions has a severe impact on effective control policies and VOC emission reduction measures, which is estimated based on the correlation between the industry activity level or economic development level [12,13]. A global VOC emission inventory of anthropogenic sources was established in 1990, where the organic chemical industry was found to be one of the main emission sources [14]. Moreover, Bo et al. indicated that the petroleum industry was the largest source of VOCs in ambient air [15]. Rajabi et al. provided global-scale insight into VOC emissions in oil processing, showing that the crude oil industry was one of the major sources of VOCs released into the environment during various stages of crude oil processing [16]. Yang described the Chinese industrial VOC emission characteristics and their emission trends, claiming that 2.13 million tons of VOCs were emitted from the PR industry in 2010, which covered several emission sources, including equipment leaks, storage tanks, loading operations and wastewater treatment [17]. Dai et al. investigated the national emission inventory of VOC emissions from five petro-chemical subindustries [18]. The crude oil production and refining VOC emissions continuously increased from 810 Kt to 950 Kt during the past ten years. Liang et al. analyzed the total industrial VOC emissions in 2018 and found that the oil refinery industry was the second largest emission source [19]. VOC emissions from the PR industry were further studied by considering factors from process vents, cooling towers, equipment leaks and wastewater treatment system emission sources, leading to a more accurate evaluation than its predecessors [20,21]. For these VOC emission inventories, however, only one emission factor was usually employed to calculate the petroleum refining (PR) industry emissions. This means that uncertainty existed in the emission calculations caused by the lack of different control levels of different PR industries. Most previous studies calculated the emissions of the PR industry by using 1.82 g/kg product as an emission factor [22,23].

VOC control methods are broadly classified into recovery methods, destruction techniques, photocatalytic oxidation and plasma technology. Recovery procedures, such as membrane separation, condensation, adsorption and absorption, aim to collect, store and reuse VOCs. The adsorption method achieves high removal efficiency and automatic control for VOCs at low and medium concentrations. However, it is not suitable for high concentrations and high-temperature organic waste gas. Moreover, the adsorption materials need to be replaced regularly [11]. The absorption method is a mature technology that can efficiently treat waste gas with a large capacity. The high-temperature waste gas needs to be cooled beforehand, and the consumed absorbent needs to be recycled; otherwise, secondary pollution is formed [24]. The condensation method is mostly used for the treatment of VOCs with a single component, high concentration and high recovery value. The drawbacks of condensation include the high treatment cost and high VOC concentration limitation, which usually need to be greater than 5000 ppm [25]. Membrane separation has a high recovery rate, low energy consumption and convenient operation. The disadvantages include high equipment costs and poor membrane stability [26]. The destruction method aims to convert VOCs into CO<sub>2</sub> and H<sub>2</sub>O, where combustion and catalytic combustion are usually applied. Combustion technology has the highest removal rate and mature heat

recovery process. However, its investment and operation costs are both high. Meanwhile, large fuel consumption could result in high NO<sub>x</sub> emissions [27]. The useful VOC control technologies in the PR industry are summarized in Table 1. Photo-catalytic oxidation and plasma technology are generally recognized as inefficient treatment technologies and are rarely used in the PR industry. Accurate emission accounting is an essential precondition for developing effective control policies and VOC emission reduction measures.

**Table 1.** Summary of VOC control technologies.

| Category           | VOC Control Methods Used in the PR Industry | Strong Points                                                                                       | Weak Points                                                                       | Ref. |
|--------------------|---------------------------------------------|-----------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|------|
| Recovery procedure | Adsorption                                  | High removal efficiency; easy to automatically control VOCs at low and medium concentrations        | Adsorption materials need to be replaced regularly                                | [11] |
|                    | Absorption                                  | Efficiently treats a large capacity                                                                 | Not suitable for high-temperature waste gas; causes secondary pollution           | [24] |
|                    | Condensation                                | Recover valuable materials with a high concentration                                                | High treatment cost; high VOC concentration limitation                            | [25] |
|                    | Membrane separation                         | High recovery rate; low energy consumption; convenient operation                                    | High equipment costs; poor membrane stability                                     | [26] |
| Destruction method | Combustion                                  | Highest removal rate; heat can be recovered                                                         | Large fuel consumption; NO <sub>x</sub> emissions;                                | [27] |
|                    | Catalytic combustion                        | High removal rate; lower operation cost than a directly fired furnace; no NO <sub>x</sub> emissions | Pretreatment system is usually needed; catalyst is prone to poisoning and failure |      |

In this study, 12 emissions sources from 21 oil refining enterprises were estimated by means of theoretical formulas, actual measurements, material balances and emission coefficients. In addition, more than 200 measured data and 700 operation data were collected. The emission factors of the three levels were generated by the investigated enterprises to estimate the total VOC emissions of the PR industry in China. The investigated enterprises covered different scales and different control levels. The characteristics of VOC emissions from the PR industry based on enterprises' spatial distribution are discussed in this paper. The current situation and existing problems of VOC emission controls in the PR industry in China were analyzed based on emission predictions.

## 2. Materials and Methods

### 2.1. Study Case

The PR industry in China was taken as the study case. China's PR industry accounted for 17.44% of the global refining capacity and ranked second in the world between 2015 and 2020. The primary processing capacity of crude oil reached 890 million tons by 2020. The capacity and processing volume of the domestic PR industry are shown in Table 2. The refining capacity and refinery processing volume in China steadily increased from 2015 to 2022, which led to an increase in VOC emissions.

**Table 2.** The capacity and processing volume of the domestic PR industry from 2015 to 2020 [28].

| Year                                                   | 2015 | 2016 | 2017 | 2018 | 2019 | 2020 |
|--------------------------------------------------------|------|------|------|------|------|------|
| Oil refinery capacity (100 million tons/year)          | 7.9  | 7.9  | 8.1  | 8.3  | 8.6  | 8.9  |
| Oil refinery processing volume (100 million tons/year) | 5.22 | 5.41 | 5.68 | 6.04 | 6.52 | 6.74 |

The PR industry is developing in the direction of large-scale units, refining and chemical integration and industrial clusters. Petrochemical production capacity is mainly distributed in the eastern coastal areas, including the Yangtze River Delta, Pearl River Delta and Bohai Bay. The total refining capacity of eastern coastal areas has reached 633 million tons/year, accounting for 71.5% of the total capacity. These three refining and chemical industry clusters are also the key control areas of VOC emissions. According to the data from the national pollutant discharge permit management information platform, the Yangtze and Yellow River basins account for 32.3% of the total number of PR enterprises in China. As shown in Figure 1, there were 32 refineries with a capacity over 10 million tons per year, accounting for 50.6% of the total national refining capacity.

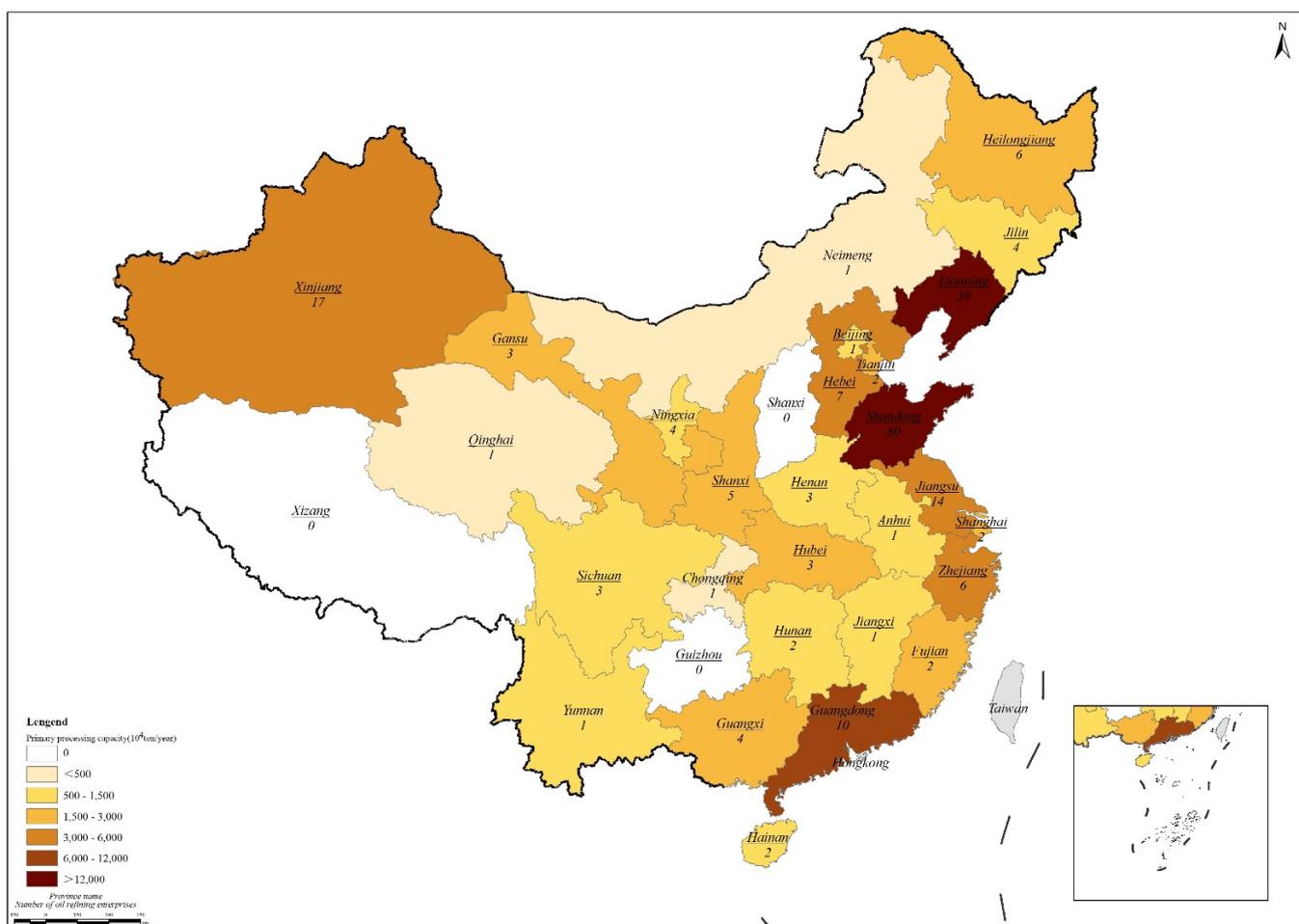


Figure 1. Number of petrochemical enterprises and distribution of refining capacity in China [29].

### 2.2. Methodology

Guidelines for the investigation of VOC pollution sources in the petrochemical industry, issued in November 2015, were employed in this study [30]. This methodology included four steps: the classification of VOC emission sources, activity and control efficiency data collection, the formula or emission coefficient analysis, and the method of emission accounting and evaluation.

In this study, the VOC emission sources of the petrochemical industry were grouped into 12 categories, including equipment leaks, storage tanks, loading operations, stationary combustion sources, process vents, flares, wastewater collection and treatment systems, cooling towers, startups and shutdowns, malfunctions, the use of organic solvents and mobile sources in plants. The accounting method was chosen according to the availability of emission data from different sources. For emission data that are collected and investi-

gated directly, actual measurement methods and theoretical formula method are preferred. The material balance and the emission coefficient method are used when operating and monitoring data are scarce.

In actual measurement methods, the removal efficiency and emissions are directly calculated by monitoring the gas volume and concentration at the inlet and outlet of exhaust gas emissions. The theoretical formula method calculates the amounts of VOCs produced according to the ideal gaseous equation and empirical coefficient. Meanwhile, the removal efficiency obtained by the measured method is also considered. The paint used in industrial anticorrosion and other operations in the refinery can be estimated by the material balance, where the amount produced and the amount discharged are equal because there is no control measure. In the emission coefficient method, VOC emissions are calculated according to the production parameters and emission coefficients.

The Emissions Estimation Protocol for Petroleum Refineries was employed to calculate the total VOC emissions in one petrochemical plant [31]. The VOC emission rate is calculated by the following equation if there are monitoring data at the organized discharge outlet, such as stationary combustion sources, process vents and treatment facilities:

$$E_j = \sum_j (Q_j \times C_j \times h_j) \quad (1)$$

where  $j$  represents the organized discharge outlet,  $E_j$  represents the annual total VOC emissions of the organized discharge outlet,  $Q_j$  is the hourly exhaust volume of organized discharge outlet  $j$ ,  $C_j$  is the VOC emission concentration of organized discharge outlet  $j$ , and  $h_j$  is the annual emission hours of organized discharge outlet  $j$ .

VOC emissions from equipment leaks, storage tanks, the use of organic solvents and loading operations are estimated by model formulas or correlation equations [31]. In this study, these emissions were calculated by Equation (2):

$$E_i = \sum_i F_i \times (1 - \eta_{c,i} \eta_{r,i} \eta_{o,i}) \quad (2)$$

where  $i$  represents the type of emission source,  $F_i$  and  $E_i$  represent the generation and emission, respectively,  $\eta_{c,i}$  is the collection efficiency,  $\eta_{r,i}$  is the treatment efficiency and  $\eta_{o,i}$  is the operation efficiency. Meanwhile, the collection efficiency, treatment efficiency and operation efficiency were used as the indices to evaluate the result of emission reduction.

The emission coefficient and operation data were adopted to estimate other emission sources, such as flares and cooling towers. The calculation formula is shown in Equation (3):

$$E_o = \sum_o EF_o \times O_o \quad (3)$$

where  $o$  represents the emission source, which is calculated by emission coefficients,  $E_o$  is the total VOC emissions,  $EF_o$  is the VOC emission coefficient and  $O_o$  is the operation data of the investigated enterprises.

The annual VOC emissions of an investigated petroleum refinery ( $E$ ) were calculated by summing the previous emissions:

$$E = E_j + E_i + E_o \quad (4)$$

### 2.3. VOCs Sampling and Analysis

The critical information affecting regional VOC emissions, such as PR enterprises' scale, distribution and control level, is necessary to associate industry activity levels with the relevant information of the enterprise for a refined emission inventory. The approach used for the collection of operation data, monitoring data, and control measures was determined specifically for each investigated plant. Site investigations were performed at 21 PR industries in 12 cities located in all provinces with concentrated production capacity as well as 15 other enterprises. The investigated content mainly included the generation and emission of VOC waste gas and the operation of treatment facilities.

The number and refining capacity of oil refining enterprises were gathered from the Refining Capacity Economic Operation Report of Petroleum and Chemical Industry issued by the China Petroleum and Chemical Industry Federation [28]. Despite this, a large proportion of the plant emission data are still difficult to acquire because the annual production statistics can only be obtained from each plant. In this situation, the emission levels of different plants were obtained by collecting statistical overviews from the China Petrochemical Corporation, China National Petroleum Corporation and China National Offshore Oil Corporation. The VOC emission data from 12 different sources for the calculation of the annual VOC emissions of one PR enterprise are summarized in Table 3.

**Table 3.** Emission source classification and collected information for one PR enterprise [32,33].

| Emission Source Type                            | Information Requirements                                                                                                                           | Calculation Method                                                                                             |
|-------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|
| Equipment leaks (i)                             | The latest leak detection and repair (LDAR) programs result                                                                                        | Correlation equation                                                                                           |
| Storage tanks (j)                               | Tank type, tank dimensions, stored liquid properties and constituent concentrations, tank condition, fitting information, throughput, etc.         | Tank-specific modeling equation                                                                                |
| Loading operations (j)                          | Pressure, temperature, service-specific liquid properties, both flow rate and gas composition of the import and export of the treatment facilities | Loading-specific equation                                                                                      |
| Stationary combustion sources (i)               | Direct measurement for both flow rate and gas composition                                                                                          | The product of flow rate and gas composition                                                                   |
| Process vents (i)                               | Direct measurement for both flow rate and gas composition                                                                                          | The product of flow rate and gas composition                                                                   |
| Flares (o)                                      | Assumed combustion efficiency and annual flare gas volume                                                                                          | Emission factors based on energy consumption                                                                   |
| Wastewater collection and treatment systems (i) | Covered situation, direct measurement for both flow rate and gas composition of the import and export of the treatment facilities                  | The product of flow rate, gas composition and collection efficiency                                            |
| Cooling towers (o)                              | Annual water recirculation rate, and concentration, based on measurement data                                                                      | Direct water measurement before and after exposure to the atmosphere                                           |
| Startups and shutdowns (o)                      | The exposure volume and gas composition of abnormal situation, flare combustion efficiency                                                         | The product of flow rate, gas composition and combustion efficiency                                            |
| Malfunctions (o)                                | Number of malfunctions in a year                                                                                                                   | Emission coefficient                                                                                           |
| Use of organic solvent (j)                      | Annual usage of organic solvents and VOC content                                                                                                   | Material balance without control                                                                               |
| Mobile sources in plant (o)                     | Fuel consumption                                                                                                                                   | Technical guidelines for the preparation of emission inventories of air pollutants from nonroad mobile sources |

### 2.4. Classification of VOC Emission Control Levels

Reliable emission inventories are essential to effectively control measures for VOCs pollution. As a key indicator relating to the estimation of pollutant emissions, emission factor analysis of three levels is defined according to the investigated plants and the crude oil processing capacity, as shown in Equation (5):

$$EF_i = E \div C \tag{5}$$

where  $EF_i$  is the emission factor of level  $i$ .  $C$  is the crude oil processing capacity of the investigated enterprises.

All domestic PR plants were grouped into 3 levels according to the statistical overview. The emission inventory method was used to estimate emissions based on emission factors and industry activity level statistics. The calculation formula is shown in Equation (6):

$$A = \sum EF_i \times Q_i \tag{6}$$

where  $A$  is the total VOC emissions of the PR industry in China,  $EF_i$  is the VOC emissions per unit of  $Q$  of level  $i$ , and  $Q$  is the crude oil processing capacity of level  $i$ .

## 3. Results and Discussion

### 3.1. Analysis of VOC Emission Calculation Method

The contributions of VOC emissions from various sources to the total emissions of the 21 investigated enterprises with six processing capacities are illustrated in Figure 2. Equipment leaks, storage tanks, loading operations, process vents, and wastewater systems cover more than 90% of the total enterprise VOC emissions. Several previous studies have shown that more than 80–90% of the VOC emissions of different PR industries in China were concentrated in equipment leaks, storage tanks, wastewater treatment systems and loading transport [34–37]. Among these 12 sources, storage tanks, loading operations and wastewater collection and treatment systems are dominant. Based on the information collected from 21 enterprises, this paper calculates emissions from 12 sources by applying the model formula method, measured method, and the material balance and emission coefficient method.

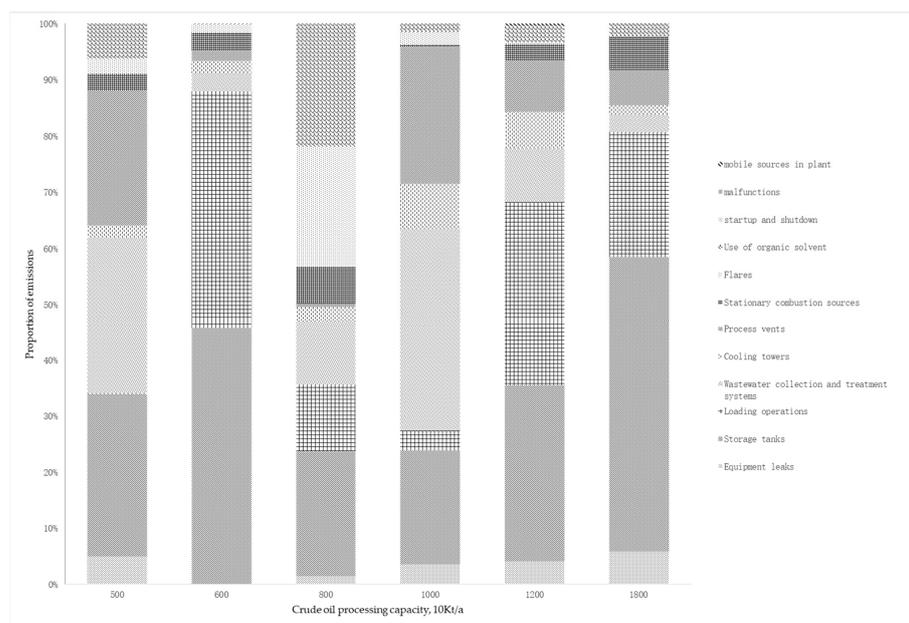


Figure 2. The proportion of emission source items of five investigated enterprises.

The VOC emissions of the storage tank and loading operation were calculated by the model formula method under the condition of complete operation data and equipment information. It is concluded that the storage tank and loading operation account for 64%, 75%, and 87% of the total VOC emissions in enterprises 12 Mt/a, 18 Mt/a and 6 Mt/a crude oil processing capacity enterprises, respectively, because the comprehensive treatment efficiency of oil and gas recovery facilities is very low. After more than 60 years of research on organic liquid storage loss and loading operations, one estimation method has been established by the American Petroleum Association (API) and the American Environmental Protection Agency (EPA). Taking organic liquid storage as an example, an emissions evaluation of standing storage and working loss for a fixed-roof tank, external floating roof tank and internal floating roof tank is compiled into a series of theoretical formulas. The key operating and equipment parameters include tank type, tank dimensions, stored liquid properties, constituent concentrations, tank condition, fitting information and throughput. The standing loss in the floating roof tank can be further decomposed into rim-seal loss, withdrawal loss, deck fitting loss and deck seam loss. The evaluation system is established based on theoretical and experimental investigations by considering several dominating factors, including loss coefficients, total deck fitting loss factor, zero wind speed rim seal loss factor, wind speed-dependent rim seal loss factor, and shell clingage factor. These parameters are correlated by considering the accessory structure, wind speed, diameter, and functional relationship between steam pressure and local atmospheric pressure.

When the monitoring data of the organized emission outlets are available, the actual measurement method is adopted to calculate the source terms such as stationary combustion, process vent, sources and discharge outlets of terminal treatment facilities. The main emission sectors from the process vents include delayed coking process exhaust, catalytic cracking flue gas and reforming regeneration flue gas, which are all discharged from the organized outlet. VOC emissions are directly obtained from the measurement of the gas flow rate and corresponding composition, since the process vents of the enterprises are constrained by emission standards. Although the monitoring data are collected based on national monitoring standard methods, certain uncertainty and errors caused by measurement and analysis still exist. On the one hand, most VOCs monitoring data are determined by gas chromatography and characterized by nonmethane total hydrocarbons. However, nonmethane total hydrocarbons only calculate the C atom in VOCs, where functional groups cannot be presented in the result. On the other hand, different organic components have different response values in the hydrogen flame ionization detector. The responses of all volatile organic compounds are different when all instruments are calibrated with methane, resulting in measurement errors.

The VOC emissions of flares and mobile sources are estimated by the emission coefficient method, while the organic solvent source is calculated by material balance. Flare emission has a linear relationship with waste gas discharged into the flare with a combustion efficiency of 95%. The assumption of organic solvents mainly comes from the equipment or pipeline of the anti-corrosion coating process. VOCs in organic solvents are assumed to be completely discharged into the atmosphere annually. In terms of mobile sources, startups, shutdowns and malfunctions present the lowest emission sources, accounting for less than 1% of all emissions, since abnormal situations and accident conditions have not been taken into account. The accuracy of the accounting method is relatively low for the source term with small emissions.

In this study, over 90% of VOC emission data from 21 enterprises are calculated with reliable methods, such as direct measurements and theoretical formulas, while the rest are estimated by empirical values or based on some assumptions.

### *3.2. Estimation of PR Industry VOC Emissions by the Emission Factor*

Three emission factors proposed for the designed levels and the corresponding crude oil processing capacity are shown in Table 4. The emission factors are divided into three levels according to the selection of the VOC treatment technology and the operation and

maintenance performance. Five enterprises were grouped into the upstream level. They applied pretreatment followed by destruction methods, achieving the minimum total emissions that account for 10.6% of the total refining capacity. For midstream, most of the enterprises, owned by Sinopec and PetroChina (54.5%), employ refrigeration, pressurization condensation and absorption methods to reuse the fuel. The emission factor was higher since the discharged VOC concentration from recycling treatment facilities was higher than that from the incineration facilities. Some small-scale private enterprises possessed the maximum emission factor due to the inadequate maintenance of governance facilities, overdue replacement of materials or low collection efficiency. Therefore, these enterprises should be grouped at the downstream level.

**Table 4.** The emission factors and crude oil processing capacity of the PR industry in China.

| Levels     | Emission Factor (Crude Oil Processing Capacity per Ton) | Crude Oil Processing Capacity in 2020 (Percentage) |
|------------|---------------------------------------------------------|----------------------------------------------------|
| Upstream   | 0.6%                                                    | 10.6%                                              |
| Midstream  | 1.2%                                                    | 54.4%                                              |
| Downstream | 3%                                                      | 35%                                                |

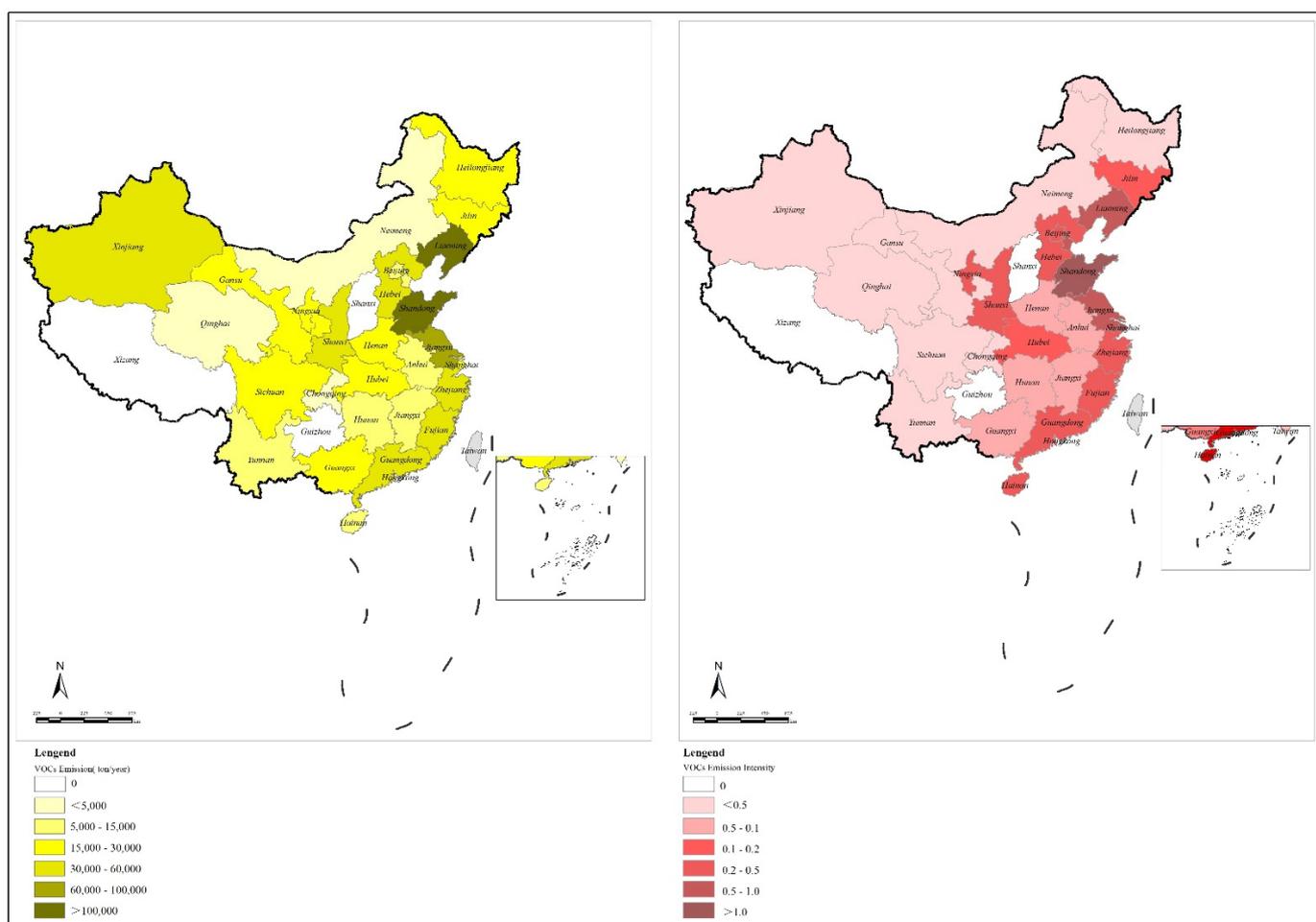
The 2017 air emission inventory of the United States released by the EPA showed that the average emission factor of 26 petroleum refineries was approximately 0.4%. This value was much lower than the average emission factor of China, since the United States has continuously tightened and refined the standard requirements of VOC emission control for more than 50 years. For example, for storage tanks, detailed sealing requirements were proposed not only for standing storage and working loss of storage tanks, but also for all the openings in the storage tanks except the automatic vent hole and edge space hole. Operating the exhaust under abnormal operating conditions was strictly forbidden. The plant operator must introduce the exhaust into the pollution control equipment to meet the requirements of 98% emission reduction efficiency or emission concentration less than 20 ppmv at a dry basis concentration.

The VOC emissions of China's PR industry in 2020 were estimated by applying the methods described in Section 2. The total VOC emissions of crude oil processing with a capacity of 674 million tons in 2020 were approximately 1150 Kt according to the level designed and the emission factors. According to the study by Dai et al., the VOC emissions of the PR industry in China were 1158 kt in 2019, with an average annual growth rate of 5.54% from 2008 to 2019 [18]. Wei et al. (2011) and Liang (2020) estimated that the VOC emissions of the PR industry were 612 Kt in 2018 and 950 Kt in 2020 [11,19]. The estimated total PR industrial VOC emissions in this study are approximately 21–50% higher than those predicted by Wei and Liang and 0.7% lower than the estimation by Dai et al. [11,18,19]. These differences may have been caused by the application of different estimation methods, the selection of activity data, emission factors and the operation data of the investigated enterprises. Previous studies mainly estimated the VOC emissions of the PR industry by multiplying emission factors and activity levels. In this work, the measured data and actual operation information are combined to estimate the VOC emissions from investigated enterprises with emission factors of different levels. The national oil refining capacity is also divided into three corresponding levels according to the VOC emission control level. Finally, the emission level of the national PR industry is estimated. Nevertheless, the overall emission situation estimated by previous data cannot clarify the key control areas of the PR industry in China. Therefore, this work further carries out data analysis on the spatial distribution of VOC emissions.

### 3.3. Analysis of Total VOC Emissions of the PR Industry and Spatial Distribution

To better identify the spatial characteristics of VOC emissions, discharge amounts and intensities in different regions of China (tons/km<sup>2</sup>) are illustrated in Figure 3. The PR industry VOC emissions of the top five provinces of Shandong, Liaoning, Jiangsu,

Guangdong, and Hebei are estimated to be 723 Kt, accounting for 62.7% of the total emissions. These provinces represent developed industrial areas where total industrial output value also holds the leading position in China. [28] The crude oil processing capacity is not directly proportional to emissions but is related to local management requirements, management level and emission control level of enterprises. For example, compared with Beijing, Anhui Province has high VOC emissions but low crude oil processing capacity. The same trend was also shown between Guangzhou Province and Jiangsu Province.



**Figure 3.** Distribution of VOC emissions and emission intensity per unit land area in the PR industry in China.

Previous work only focused on the emissions amount. The concept of emission intensity is introduced in this work because it directly affects the speed of deterioration of regional atmospheric quality. The VOC emissions of the PR industry present remarkable spatial characteristics. VOC emissions in the eastern coastal region are much greater than those in the western inland region in China [13]. Figure 3 also shows that the national average emission intensity of the PR industry is approximately 0.12 tons/km<sup>2</sup>. In order from high to low, Shandong, Shanghai, Tianjin, Liaoning and Jiangsu are the top five cities by emission intensity per unit area, where the highest emission intensity is approximately 2.7 tons/km<sup>2</sup> and the lowest is approximately 0.64 tons/km<sup>2</sup>. Therefore, the eastern coastal area and Hubei and Shanxi Provinces are the key control areas of the PR industry’s VOC emissions.

### 3.4. Control Analysis of VOC Emissions

VOC emissions are also affected by the selection of control technology. The national crude oil processing capacity is classified into three levels according to the actual collection efficiency and treatment level of each enterprise. The parameter  $\eta$  in Equation (2) is mainly affected by different capture methods and treatment technologies. The collection efficiency in Table 5 was estimated by the ratio of the amount of waste gas entering the terminal treatment facilities to the amount of waste gas generated from emission sources. The actual removal efficiency illustrated in Table 6 was sampled before and after treatment at the same time, and the facility removal rate was calculated according to the quantitative total nonmethane hydrocarbon concentration. According to the analysis results from more than 200 units of measured data and 700 units of collected data, the actual removal efficiency is generally lower than the theoretical removal efficiency. In this study, a summary of the capture and treatment situation in the domestic PR industry is provided in Tables 5 and 6, respectively. The refinement of management and control needs to be improved due to a large gap in VOC treatment levels of different enterprises in China.

**Table 5.** Summary of capture efficiency in the PR industry in China.

| Emission Sources                                                        | Capture Method                                                                         | Actual Capture Efficiency                                                                                                                                                                 |
|-------------------------------------------------------------------------|----------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Fixed-roof tanks                                                        | Pipeline connection                                                                    | Approximately 40–90%                                                                                                                                                                      |
| Submerged loading the rail cars and tank trucks with the oil from above | Press the rubber stopper or the cylinder lock tongue structure firmly down on the vent | Rubber stopper: 20–50%<br>Cylinder lock tongue structure: 80–90%                                                                                                                          |
| Submerged loading the tank trucks with the oil from the bottom          | Pipeline connection                                                                    | The collection efficiency is approximately 50% when the induced draft fan is not installed.<br>The collection efficiency can reach more than 90% when the induced draft fan is installed. |
| Wastewater system                                                       | Seal with membrane, steel structure or cement                                          | More than 90%                                                                                                                                                                             |

**Table 6.** Summary of the actual removal efficiency of treatment processes in the PR industry in China.

| Emission Sources                                              | Common End Treatment Processes                                                                                                               | Actual Removal Efficiency |
|---------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|---------------------------|
| Process vent                                                  | Heating furnace                                                                                                                              | 95–99%                    |
| Storage tanks fill with product oil                           | Low-temperature diesel/gasoline absorption + activated carbon adsorption, some enterprises connect regenerative thermal oxidizer in the end. | 95–99%                    |
| Storage tanks fill with dirty oil                             | Desulfurization connect with catalytic oxidation                                                                                             | 50–95%                    |
| Storage tanks fill with intermediate material                 | Directly fired furnace                                                                                                                       | 98–99%                    |
| Storage tanks fill with reforming raw material                | Low-temperature diesel absorption + alkaline desulfurization + desulfurization homogenization + catalytic oxidation                          | 90–97%                    |
| High-concentration waste gas from wastewater treatment system | Regenerative catalytic oxidizer, regenerative thermal oxidizer or directly fired thermal oxidizer                                            | 50–99%                    |
| Low-concentration waste gas from wastewater treatment system  | Biofilter connect with activated carbon adsorption                                                                                           | 70–90%                    |
| Loading operations                                            | Low-temperature diesel/gasoline absorption or tertiary condensation connect with activated carbon adsorption                                 | 50–99%                    |

VOC waste gas leakage and serious unorganized escape from the PR industry are mainly caused by a low capture efficiency or even uncollected situations. The capture efficiency, namely, the percentage of VOCs collected and transported to the treatment device in total VOC emissions, is one of the prominent drawbacks in VOC governance at present. For a long time, all documents related to the prevention and control of VOC emissions have proposed clear requirements for capture efficiency. In the PR industry, the VOC waste gas that needs to be collected mainly includes the gas expelled by the breathing valve on a fixed roof tank and the waste gas discharged from transport loading and sewage treatment systems. The pressure control of the storage tank and loading collection system will lead to a great difference in the actual capture efficiency, ranging from 40% to 90%. Moreover, the sealing type of submerged loading is also a decisive factor in the capture efficiency, and the rubber stopper is far inferior to the cylinder lock tongue structure. The sealing effect of the sewage treatment system is relatively good. In addition, the quality of the breathing valve, manhole and foam generator on the top of the fixed roof tank are ungraded or even damaged. The VOC emissions from the storage tank cannot be sent to the oil and gas recovery device, resulting in poor capture efficiency. Therefore, upgrading equipment and finely controlling pressure operation systems are necessary and urgent.

Waste gas from the PR industry is basically treated by introducing a nearby heating furnace. The waste gas sources mainly include the gas emitted by the breathing valve on the storage tank, the waste gas of loading and the sewage treatment system. The actual situation of enterprises needs to be taken into account during the selection of waste gas treatment technology, where the amount of waste gas, VOC concentration and composition, production requirements and investment and operation costs are the key parameters. The selected treatment technology should not only meet the requirements of emission standards but also improve pollutant removal, reduce treatment costs and avoid secondary pollution. The combination of absorption, adsorption and combustion technologies has gradually become an integrated technology for VOC treatment in the PR industry due to its high treatment efficiency, which can meet emission standards. However, the operation effect of final treatment facilities and the management of the enterprises are sometimes poor. The large deviation between the design and operation of VOCs treatment is caused by ignoring key parameters, including VOC concentration, temperature, and humidity. At the same time, enterprises lack professional technicians for VOC pollution control, leading to incomplete or nonstandard enterprise environmental management.

VOC pollution treatment is transitioning from “yes or no” to “good or bad”. The coverage rate of end treatment facilities in the PR industry is more than 90%, with the actual treatment efficiency between 50% and 95%. More than 85% of the treatment facilities were covered by the absorption, adsorption and incineration processes. The actual treatment efficiency of absorption and adsorption treatment facilities is approximately 30–90%. Approximately 10–20% of PR enterprises adopt low-efficiency treatments such as UV photooxidation, low-temperature plasma, biofilters or activated carbon adsorption in the treatment of waste gas. The actual efficiency of these treatments is lower than 20%. It appears that the VOC emissions from private enterprises are less controlled than those from Sinopec and PetroChina.

#### 4. Conclusions

This study performed emission source identification, control level classification, a compilation of monitoring and operation data, emissions calculation, and uncertainty analysis to estimate the total VOC emissions from the PR industry in China. By combining actual measurements, theoretical formulas, material balance and emission coefficient methods, 21 PR enterprises were grouped into three levels according to VOC emissions and treatment ability, and emission factors were generated. The total PR industrial VOC emissions were estimated to be 1150 Kt in 2020 by combining the emission factors and actual capacity of crude oil processing in the PR industry. The national average emission intensity of the PR industry was proposed to be 0.12 tons/km<sup>2</sup>. Meanwhile, more than 90% of VOC

emissions originate from equipment leaks, storage tanks, loading operations, process vents and wastewater systems. The capacity of enterprises midstream and downstream occupies the majority of the total domestic production capacity. Analysis of the spatial characteristics of VOC emissions shows that the eastern coastal area, including Shandong, Liaoning, Jiangsu, Guangdong, and Hebei provinces, possesses the largest VOC emissions of the PR industry in China, accounting for 62.7% of total emissions. The influence of capture and treatment technologies on VOC emissions was also investigated. The capture efficiency of pipeline connection and sealing technologies ranges from 20–90%, depending on the device's performance and fine management control. Destruction and recovery methods were found to be the most effective treatment of VOC emissions. The issues of deviation between design efficiency and operation efficiency of treatment processes are addressed by comprehensively considering key parameters of VOC emissions, such as volume concentration, temperature, and humidity. It is important to state that the method used in this paper is a general methodology that can be employed by similar cases in the PR industry of other nations.

In view of the complex emission characteristics of VOCs in the PR industry and the characteristics of VOCs unorganized emission, it is necessary to continue to carry out research on optimizing statistical investigation and accounting methods to reflect the different emission and management levels of enterprises in the accounting method, and establish an accounting method system as close as possible to the actual emissions. On the one hand, it can continuously refine VOC emission sources and emission accounting methods, and on the other hand, it can dynamically update emission factors. It is necessary for national and local government policymakers to focus on strengthening the governance of PR industries during the specific formulation of industrial VOC emission reduction policies.

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