



Improved speciation profiles and estimation methodology for VOCs emissions: A case study in two chemical plants in eastern China[☆]

Lei Zhang^{a,b,*}, Xinzhi Zhu^a, Zeren Wang^a, Jie Zhang^{c,d}, Xia Liu^e, Yu Zhao^{a,b}

^a School of the Environment and State Key Laboratory of Pollution Control and Resource Reuse, Nanjing University, 163 Xianlin Avenue, Nanjing, Jiangsu, 210023, China

^b Jiangsu Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (CICAET), Nanjing University of Information Science and Technology, Jiangsu, 210044, China

^c Jiangsu Key Laboratory of Environmental Engineering, Jiangsu Provincial Academy of Environmental Sciences, Nanjing, Jiangsu, 210036, China

^d Jiangsu Environmental Engineering Technology Co., Ltd, Nanjing, Jiangsu, 210000, China

^e Ocean University of China, College of Chemistry and Chemical Engineering, 238 Songling Road, Qingdao, Shandong, 266100, China

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ABSTRACT

Volatile organic compounds (VOCs) poses a serious health risk through not only their own toxicity but also their role as precursors of ozone and secondary organic aerosols. The chemical industry, as one of the pillar industries in eastern China, is a key source of VOCs emissions. In this study, speciated VOCs emissions were measured in two chemical plants in eastern China. Oxygenated VOCs and aromatics were found to be the dominant species categories in both plants. The ozone formation potential (OFP) and secondary organic aerosol formation potential (SOAFP) of VOCs from dedicated resin production were both higher than general resin production. Three process-based models were used for the estimation of VOCs emissions from the two tested plants as a case study. The comparison between the emission factor model and the model with best available estimation methods (e.g., the measurement-based method, the mass balance method, the empirical formula method, and the correlation equation method) implied possible overestimation of the widely used emission factor model for the chemical industry. The probabilistic model developed in this study incorporated probability distribution of key parameters and proved to be a promising tool for emission inventory development and uncertainty analysis. The overall uncertainties of VOCs emissions based on the model were (−48%, +147%) and (−48%, +139%) for the two tested plants. In this study, the speciation profiles and estimation methodology for VOCs emissions from the chemical industry in China were both improved, which could benefit the accurate evaluation of the impacts of VOCs emissions.

1. Introduction

Volatile organic compounds (VOCs) play an important role in the formation of both tropospheric ozone (O₃) and secondary organic aerosols (SOA), and have an adverse impact on human health (Geng et al., 2007; Li et al., 2011; Wang et al., 2017). In recent years, VOCs have been of great concern in China with total anthropogenic emissions reaching 25–30 Tg (Li et al., 2019a; Sun et al., 2018; Wu and Xie, 2017). Petroleum-related industries are one of the main VOCs emission sources in China, responsible for 16%–27% of the total emissions (Li et al., 2019a; Sun et al., 2018; Wu and Xie, 2017). The Yangtze River Delta

(YRD) region in eastern China is a hotspot region for VOCs emissions, due to its relatively developed economy and high levels of industrialization (Fu et al., 2013; Simayi et al., 2019; Wei et al., 2008; Wu et al., 2016). Petroleum-related industries were estimated to account for 25%–36% of the total anthropogenic VOCs emissions in the YRD region (An et al., 2021; Huang et al., 2011; Simayi et al., 2019; Wu et al., 2016).

Efforts have been made to obtain accurate anthropogenic VOCs emission inventories. Studies on the national emission inventories (Li et al., 2019a; Simayi et al., 2019; Wu et al., 2016; Wu and Xie, 2017) have refined the VOCs emission source categorization and taken into consideration the VOCs removal efficiencies of air pollution control

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* Corresponding author. School of the Environment and State Key Laboratory of Pollution Control and Resource Reuse, Nanjing University, 163 Xianlin Avenue, Nanjing, Jiangsu, 210023, China.

E-mail address: lzhang12@nju.edu.cn (L. Zhang).

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devices (APCDs). Regional inventories have gained access to activity level data at the city- (Liu et al., 2018; Wang et al., 2018), county- (Simayi et al., 2019), and even enterprise-level (Zhao et al., 2017a; Zheng et al., 2019; Zhong et al., 2018), and used refined emission factors with APCDs considered. However, VOCs emission inventories still have much higher uncertainties than criteria air pollutants. The overall uncertainty range of the national VOCs emission inventories for China with a 95% confidence level was estimated to be (−51%, +133%) by Wei et al. (2011) and (−40%, +107%) by Wu et al. (2016). The uncertainties of the emission inventories for the industrial sector, with petroleum-related industries dominating, were estimated to be around (−60%, +150%) on a regional scale (Fu et al., 2013; Huang et al., 2011; Zhao et al., 2017a) and as large as (−88%, +283%) on a national scale (Wei, 2009). The uncertainties of the emission inventories for petroleum-related industries originate mainly from the complexity of manufacturing and ancillary processes (Zhao et al., 2017a).

To reduce the uncertainties in the VOCs emission estimation for petroleum-related industries, a process-based method adapted from the *Emissions Estimation Protocol for Petroleum Refineries* released by the United States Environmental Protection Agency (US EPA, 2015) was recommended by the Ministry of Environmental Protection (MEP) of China for the petrochemical industry in China (MEP, 2015), and applied in limited studies (Liu et al., 2020; Yen and Horng, 2009). The emission processes in petroleum-related chemical industries include the manufacturing lines, storage tanks, equipment leaks, loading operations, the wastewater collection and treatment system, the circulating water system, flares, stationary combustion sources, sampling operation, abnormal operational conditions (including startup, shutdown and maintenance), and malfunctions (US EPA, 2015).

Among all emission processes, equipment leaks, storage tanks, and manufacturing lines are usually considered to be the main contributors to the VOCs emissions in petrochemical industries and responsible for over 90% of the total (Ke et al., 2020; Liu et al., 2020; Yen and Horng, 2009). Leaks of equipment components are a major fugitive emission process throughout the entire manufacturing area. More than 90% of the total equipment leak emissions come from 0.1% to 0.4% of highly leaky components (Epperson et al., 2007; Ke et al., 2020), and consequently the probability distribution of the leak emission rate greatly affects the overall VOCs emissions from equipment leaks. Moreover, the application of the leak detection and repair (LDAR) program has changed the leak emission rate distribution, resulting in high uncertainties in emission estimation (Ke et al., 2020). For the emission process of storage tanks, breathing losses and operational losses are the two sources of VOCs emissions (Chen and Carter, 2020). The differences in tank types, physiochemical properties of storage materials, storage temperature, liquid storage height, turnover, etc. could lead to large variation in VOCs emissions (Chen and Carter, 2020; Jovanovic et al., 2010; Liu et al., 2015; Lu et al., 2013; Lu, 2017). Manufacturing line VOCs emission sources include the stack emission process and the fugitive emission process. The manufacturing stack emissions can be calculated based on the measured VOCs concentration and the flue gas flowrate at the stack, while the manufacturing fugitive emissions is difficult to estimate due to the lack of detailed manufacturing information (Lu et al., 2020).

The process-based methodology has revealed better performance in VOCs emission estimation for the petroleum-related industries than the commonly used emission factor approach. However, large uncertainties still exist in the estimation for key processes in these industries. In this study, speciated VOCs concentrations in flue gas were measured and detailed information was collected in two chemical plants in China. Ozone formation potential (OFP) and secondary organic aerosol formation potential (SOAFP) were calculated based on the derived VOCs speciation profiles. A probabilistic process-based method was developed to estimate VOCs emissions from the petroleum-related industries. More accurate emission estimation and more reasonable uncertainty evaluation were benefited from this method, which could contribute to the improvement of the accuracy of VOCs emission inventories.

2. Methodology

2.1. Description of tested chemical plants

The synthetic chemical industry and the fine chemical industry are two dominant petroleum-related industries for VOCs emissions in the YRD region in eastern China, accounting for 22%–44% and 18%–29% of the total, respectively (Liang et al., 2020; Simayi et al., 2019; Wu et al., 2016; Zheng et al., 2017). Synthetic resin production and paint production are two important subsectors in these two chemical industries, respectively, with multiple product types and diverse manufacturing techniques. The total outputs of synthetic resin production and paint production in China in 2017 were 83.78 and 20.41 Mt, respectively (CPCIF, 2018). Synthetic resins can be divided into general resins and dedicated resins, accounting for 68% and 32% of the total outputs in 2017, respectively. The outputs of dedicated resins had an even higher proportion than those of general resins in eastern China (CPCIF, 2018). There is limited information on VOCs emissions from the production of dedicated resins. Therefore, one moderate-scale dedicated resin production plant (Plant 1) and one small-scale paint production plant (Plant 2) were selected for emission measurements in this study. In 2018, 36.6 kt of furan resin, 6.3 kt of phenolic resin, and 15.8 kt of sulfonic acid curing agent were produced in Plant 1, and about 8 kt of metal packaging coatings was produced in Plant 2.

In Plant 1, the stacks for the phenolic resin production workshop, the furan resin production workshop, the curing agent production workshop, the storage tank area, and the wastewater treatment area were selected for flue gas sampling, and the furan resin production workshop was selected for fugitive emission sampling during the loading operation of raw materials. It should be noted that there were fugitive gas collection systems for both storage tanks and wastewater treatment, which converted most of the fugitive emissions to stack emissions. The main workshop in Plant 2 was selected for both stack and fugitive emissions sampling. Activated carbon adsorption (ACA) based APCD combinations were adopted by both plants. To assess the impacts of APCD combinations on VOCs emissions, stack emissions were tested at both inlets and outlets of APCDs. The VOCs emission processes and their corresponding APCDs in the two tested plants are listed in Table S1 in the Supplementary Information (SI).

2.2. Sampling and analytical methods

VOCs emissions were measured using two methods. The non-methane hydrocarbons (NMHC) concentration was monitored using a portable flame ionization detector (FID) (PF-300, Pollution, Italy). For speciated VOCs measurements, flue gas or fugitive gas samples were collected by Summa canisters with passivation treatment on the inner wall, and analyzed using a gas chromatography-mass spectrometry/flame ionization detector (GC-MS/FID) system (Trace1300-ISQD300, Thermo Fisher, USA). The C₂–C₄ species were separated with a TG-BOND alumina column and quantified using FID. The C₄–C₁₂ species were separated with a TG-624 column and quantified using MS. To ensure the representativeness of samples, the sampling time was set to be 20 min, and three parallel samples were collected at each sampling sites for quality assurance and quality control (QA/QC). The speciated VOCs measurements were calibrated by a Photochemical Assessment Monitoring Stations (PAMS) standard mixture and a TO-15 standard mixture, and a total of 108 VOC species (Table S2 in the SI), including alkanes, alkenes, alkynes, aromatics, halohydrocarbons, oxygenated VOCs (OVOCs), and others, were measured. Details of the sampling and analytical methods can be found in Section S1 of the SI.

2.3. Estimation methods for VOCs emissions from key processes

The best available estimation methods for the four key processes in the tested plants are introduced below. Details on the calculation

methods for all processes can be found in Table S3 and Section S2 in the SI.

2.3.1. Manufacturing lines

Manufacturing line stack emissions can be calculated based on total VOC (TVOC) concentrations in the exhausted flue gases. The manufacturing line fugitive emissions are difficult to estimate. The best available estimation method is based on the TVOC concentrations before APCDs and the capture efficiencies of the fugitive flue gas collection systems. Therefore, the best available estimation method for manufacturing line emissions used in this study for both Plant 1 and Plant 2 is shown as Eq. (1).

$$E_m = E_{ms} + E_{mf} = C_{out}Q_{out}t + C_{in}Q_{in}t \left(\frac{1 - \eta_c}{\eta_c} \right) \quad (1)$$

where E_m is the total VOCs emission from a manufacturing line; E_{ms} and E_{mf} are the stack and fugitive emissions from the manufacturing line, respectively; C_{in} and C_{out} are the flue gas TVOC concentrations at the inlet and outlet of the APCD combination for the manufacturing line, respectively; Q_{in} and Q_{out} are the flow rates at the inlet and outlet of the APCD combination, respectively; η_c is the capture efficiency for fugitive VOCs emissions, which was estimated to be 90% in this study; and t is the operation time of the manufacturing line.

When applying the method described above to the two tested plants in this study, the TVOC concentrations used in Eq. (1) were not equal to the total concentrations of the 108 VOCs species measured by the GC-MS/FID system. This was because some of the characteristic VOCs species (formaldehyde, phenol and furfuryl alcohol for Plant 1, and butanol and butyl acetate for Plant 2) were unmeasurable by the analytical system. The concentrations of the missing species were estimated based on results from the mass balance method provided by the tested plants. Detailed information on the method can be found in Section S2.1 in the SI.

2.3.2. Storage tanks

The TANKS model is most widely used in the calculation of VOCs emissions from storage tanks (Chen and Carter, 2020; Howari, 2015; Jovanovic et al., 2010; Saikomol et al., 2019). However, some key parameters for the model were unavailable from the two tested plants. In this study, the VOCs emissions from storage tanks in Plant 1 were calculated based on the empirical formula method used in AP-42 (US EPA, 2006; 2015). The fugitive emissions from storage tanks were collected and converted to stack emissions mostly, with APCDs applied. Therefore, the best available estimation method for storage tanks in this study is shown as Eq. (2).

$$E_t = E_{ts} + E_{tf} = C_{out}Q_{out}t + E_{t0}(1 - \eta_c) \quad (2)$$

where E_t is the total VOCs emission from storage tanks; E_{ts} and E_{tf} are the stack and fugitive emissions from storage tanks, respectively; E_{t0} is the VOCs generated from storage tanks calculated by the AP-42 empirical formula; C_{out} and Q_{out} are the TVOC concentration (with unmeasurable species added) and the flue gas flow rate at the outlet of the APCDs for storage tanks, respectively; η_c is the capture efficiency for fugitive VOCs emissions, which was estimated to be 90%; and t is the operation time of storage tanks. Detailed information on the method can be found in Section S2.2 in the SI.

2.3.3. Equipment leaks

The estimation method for VOCs emissions from equipment leaks (US EPA, 2015) used in this study for Plant 1 and Plant 2 is shown as Eq. (3).

$$E_l = \sum_{i=1}^n \left(\left(\frac{WF_{VOCs,i}}{WF_{TOCs,i}} \right) e_{TOCs,i} t_i \right) \quad (3)$$

where E_l is the total VOCs emission from equipment leaks; e_{TOCs} is the emission rate of the total organic compounds (TOCs) for an equipment component; WF_{VOCs} and WF_{TOCs} are the average weight fractions of VOCs and TOCs in the stream of the component; t is the operation time of the component; i is the component; and n is the number of components. The ratio of WF_{VOCs} over WF_{TOCs} was considered to be 1 in this study.

The emission rate e_{TOCs} was calculated using the correlation equation method (MEP, 2015) as shown in Eq. (4).

$$e_{TOCs} = \begin{cases} e_0 & 0 \leq SV < 1 \\ a \cdot SV^b & 1 \leq SV < 50000 \\ e_p & SV \geq 50000 \end{cases} \quad (4)$$

where SV is the screening value (Lev-On et al., 2007); a and b are the two parameters in the correlation equation; and e_0 and e_p are the default zero emission rate and the pegged emission rate, respectively. The parameterization scheme of each type of components is shown in Table S4.

The distribution of leaks (Fig. S1) has significant influence on the total emission. The leak detection and repair (LDAR) program is an effective way for VOCs emission control for the process of equipment leaks in chemical plants. It uses portable VOCs monitoring instrument to detect SV at the seals, so as to repair the equipment leaks in time. The application of LDAR could change the distribution of leaks significantly. To evaluate the impacts of LDAR, three scenarios were established in this study for comparison. Scenario 1, without LDAR, adopted the distribution of leaks from an early study (Lev-On et al., 2007), while Scenarios 2 and 3 used the data from a recent LDAR report for Plant 1 before and after repairing, respectively. The distribution of emission rates from Lev-On et al. (2007) was also adopted for the probabilistic model described in Section 2.4. More detailed information can be found in Section S2.3 in the SI.

2.3.4. Wastewater collection and treatment system

The wastewater system consists of the collection unit and the treatment unit. The emission from the wastewater treatment unit was calculated based on the TVOC concentration in the exhausted flue gas. Due to the lack of information, the emission from the wastewater collection unit was estimated using the emission factor method. Therefore, the best available estimation method for the wastewater system in this study is shown as Eq. (5).

$$E_w = E_{wc} + E_{wt} = EF_{wc}A_w + C_{out}Q_{out}t \quad (5)$$

where E_w is the total VOCs emission from the wastewater system; E_{wc} and E_{wt} are the emissions from the collection unit and the treatment unit, respectively; EF_{wc} is the VOCs emission factor for the collection unit (Zhang et al., 2019); A_w is the total amount of wastewater; C_{out} and Q_{out} are the TVOC concentration and the flue gas flow rate at the outlet of the APCDs for wastewater treatment, respectively; and t is the operation time of the wastewater treatment unit. Detailed information on the method can be found in Section S2.4 in the SI.

2.4. Models for VOCs emission estimation

Three models at different accuracy level were used in this study for VOCs emission estimation. Higher level models produce more accurate estimates.

2.4.1. Process-based emission factor model (Model 1)

If basic information on VOCs emission processes is accessible, the process-based emission factor model can be adopted, shown as Eq. (6).

$$E = \sum_{j=1}^m (EF_j \cdot A_j \cdot (1 - \eta_j)) \quad (6)$$

where EF_j is the uncontrolled emission factor for process j ; A_j is the activity level of emission process j ; and η_j is the overall VOCs removal

efficiency of APCDs used for emission process j . It should be noted that the emission factors and activity levels for each process are in different forms. Details on Model 1 for each process can be found in Section S3 in the SI. All the emission factors and removal efficiencies were listed in Section S3 and Table S5–S7.

2.4.2. Deterministic process-based model with best available methods (Model 2)

All the best available estimation methods for key processes in the two tested plants have been introduced in Section 2.3. If detailed information for each process is available as it was in this study, the process-based model with best available methods can be used. In Model 2, the total VOCs emissions from the two plants were calculated as the sum of VOCs emission from each process, following Eq. (7).

$$E = \sum_{j=1}^m E_j \quad (7)$$

where E_j is the estimation of the VOCs emission from process j based on the best available method for process j .

2.4.3. Probabilistic process-based model with best available methods (Model 3)

The two models introduced above were all deterministic. However, a number of key parameters used in the best available estimation methods in Model 2 were skewedly distributed, indicating that the arithmetic mean values used for parameterization could lead to bias in VOCs emission estimation. Therefore, a probabilistic process-based model with best available estimation methods (Model 3) was developed in this study. Model 3 was based on the Monte Carlo simulation in which the probability distribution of the input parameters could be passed on to the final outputs (Romano et al., 2004). Crystal Ball™, a popular software for the Monte Carlo simulation (Liu et al., 2018; Simayi et al., 2019; Sun et al., 2018; Zhao et al., 2011; Zhao et al., 2017b), was utilized in this study. The times of simulation was set to be 10,000. The 50th percentile (P50) was considered as the best estimate, and the uncertainty range was at a confidence level of 95% (Zhao et al., 2017b).

The activity levels were assumed to be normally distributed. The standard deviations were determined by the reliability of the data source and the accuracy of the data (Wei et al., 2011). The VOCs emission concentrations at the stack for the measurement-based methods were assumed to be lognormally distributed. The distribution parameters were based on the test results. The collection efficiencies for exhaust gases were assumed to be normally distributed as well, and the distribution parameters were based on the collection method (Liang et al., 2019). The distribution parameters for VOCs removal efficiencies were based on the measurements conducted in this study and the self-monitoring data by the two chemical plants. For the empirical formula method, the distribution parameters were obtained from previous studies (Chen and Carter, 2020; Liu et al., 2015; Lu et al., 2013). Details of the probability distribution assumptions can be found in Section S4 and Table S8–S9.

2.5. Calculation method for OFP and SOAFP

OFP and SOAFP of a VOCs emission source profile were calculated to evaluate the reactivity of VOCs emitted from the manufacturing of a certain product. OFP_r denotes the weighted average maximum incremental reactivity (MIR) based on the VOCs speciation profile, as shown in Eq. (8).

$$OFP_r = \sum_{i=1}^n (p_i \cdot MIR_i) \quad (8)$$

where p_i is the proportion of VOCs species i emitted from the manufacturing of a certain product; MIR_i is the maximum incremental

reactivity of VOCs species i ; and n is the number of VOCs species. The MIR values were obtained from Carter (2010).

SOAFP_r denotes the weighted average SOA yield based on the VOCs speciation profile, as shown in Eq. (9).

$$SOAFP_r = \sum_{i=1}^n (p_i \cdot Y_{SOA,i}) \quad (9)$$

where $Y_{SOA,i}$ is the corresponding SOA yield of VOCs species i , which was obtained from previous studies (Wu and Xie, 2018; Wu et al., 2017); and n is the number of VOCs species.

MIR values and SOA yields of different VOCs species used in this study were listed in Table S10.

3. Results and discussion

3.1. Concentrations and speciation profiles of VOCs emissions

3.1.1. Plant 1 for resin production

Table 1 shows the results from VOCs emission measurements in the two tested plants. The total concentrations of the 108 VOCs species measured by the GC-MS/FID system were 1.9, 4.0, 30.8, 3.4, and 6.7 mg/m³ in the exhaust flue gases from the five stacks in Plant 1 for the furan resin workshop, the phenolic resin workshop, the curing agent workshop, storage tanks, and the wastewater treatment system, respectively. With the unmeasurable characteristic species added (as illustrated in Section 2.3.1), the TVOC concentrations in the exhaust flue gases from stacks for the furan resin workshop, the phenolic resin workshop, and storage tanks were estimated to be 10.2, 14.5, and 9.0 mg/m³, respectively. However, the corresponding NMHC concentrations (unit: mg C/m³) at these three stacks were all higher than the TVOC concentrations. The discrepancies could be caused by the high uncertainty in the estimates from the mass balance method and the different species that are detectable by the GC-MS/FID method and the portable NMHC analyzer. It should be noted that, although known as “hydrocarbons” analyzer, the NMHC analyzer is able to detect a considerable amount of OVOCs with small molecular weight (Gierczak et al., 2017; Jorgensen et al., 1990). The APCD combinations in Plant 1 were all ACA-based, with choices of alkali spray (AS), water spray (WS), gas-water separator (GWS), and photocatalytic oxidation (PCO) upstream. The TVOC removal efficiencies of APCDs for the furan resin workshop and the phenolic resin workshop were both around 87%.

Speciation profiles of VOCs emissions for tested processes were obtained from the GC-MS/FID method, as demonstrated in Fig. 1. The dominant species emitted from the furan resin workshop were furfuryl alcohol (32.5%) and formaldehyde (29.1%), which were originated from the raw materials for furan resin production. For the stack gas of the phenolic resin workshop, naphthalene, formaldehyde, and phenol contributed 41.4%, 21.4%, and 7.1% to the total emissions, respectively. Naphthalene was used as the solvent, and formaldehyde and phenol were the raw materials for production. For the curing agent workshop, n-nonane (27.3%), toluene (19.7%) and ethylbenzene (19.6%) were the dominant species. Toluene (20.0%), naphthalene (18.1%), phenol (17.9%), furfuryl alcohol (7.9%), and ethylbenzene (6.0%) dominated the profile for storage tanks, which could be due to the large turnover and high volatility of these substances. Ethylbenzene, toluene, naphthalene and m/p-xylene, accounting for 30.6%, 16.5%, 15.4%, and 9.1% of total VOCs emissions, respectively, were abundant for wastewater treatment. Overall, OVOCs, halohydrocarbons, and alkanes took the lead in the speciation profile for Plant 1.

3.1.2. Plant 2 for paint production

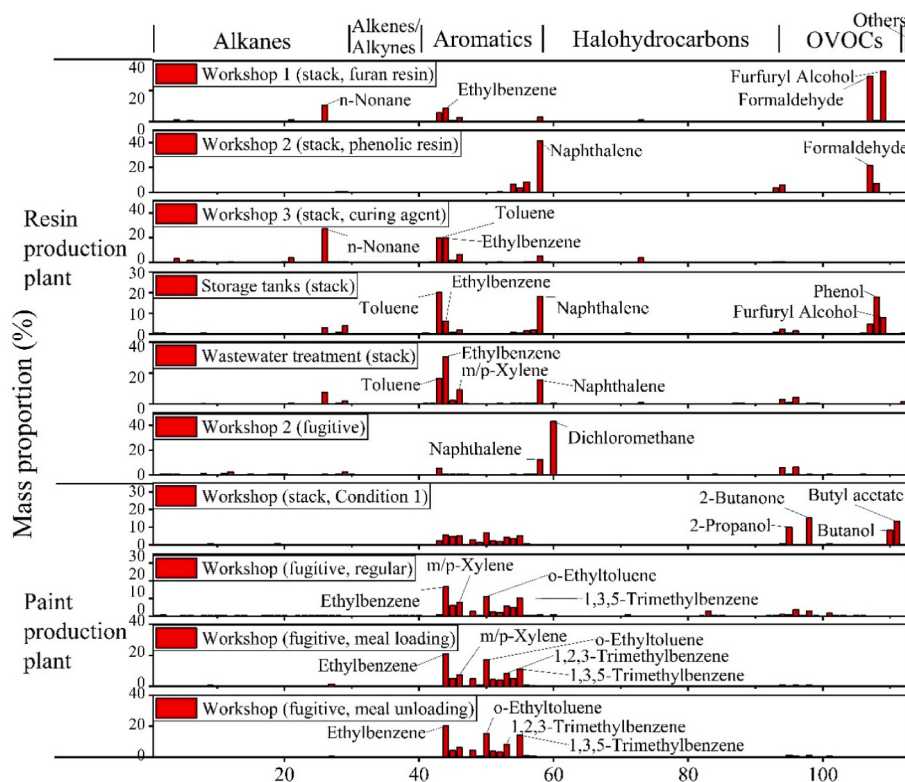
Plant 2 is a small-scale enterprise with only one main workshop. Stack and fugitive VOCs emissions were tested for the main workshop. Stack flue gases were measured under two operational conditions (Table 1). Under Condition 1 with only 2 reactors in operation, the total

Table 1

VOCs concentrations at different sampling sites and removal efficiencies of APCDs in the two tested plants.

Plant	Process	APCDs	Inlet/ outlet	VOCs ^a (mg/ m ³)	TVOC ^b (mg/ m ³)	NMHC (mg/ m ³)	Efficiency of APCDs (%)
Resin production plant	Workshop 1 (stack, furan resin)	AS + GWS + ACA	Inlet	29.7	78.5	–	87.1
			Outlet	1.9	10.2	30.5	
	Workshop 2 (stack, phenolic resin)	AS + GWS + ACA	Inlet	79.1	110.7	–	86.9
			Outlet	4.0	14.5	38.1	
	Workshop 3 (stack, curing agent)	WS + GWS + ACA (malfunction)	Inlet	–	–	–	–
			Outlet	30.8	30.8	–	–
	Storage tanks (stack)	WS + AS + GWS + ACA	Inlet	–	–	–	–
			Outlet	3.4	9.0	42.0	–
	Wastewater treatment (stack)	AS + GWS + PCO + ACA	Inlet	–	–	–	–
			Outlet	6.7	6.7	–	–
Paint production plant	Workshop 2 (fugitive)			4.6	–	–	
	Workshop (stack, Condition 1 ^c)	AS + PCO + ACA	Inlet	54.0	68.8	–	15.6
			Outlet	45.7	58.0	–	
	Workshop (stack, Condition 2 ^d)	AS + PCO + ACA	Inlet	–	–	2680.1	85.1 ^e
			Outlet	–	–	399.4	
	Workshop (fugitive, regular)			1.8	–	–	–
	Workshop (fugitive, meal loading)			5.5	–	–	–
	Workshop (fugitive, meal unloading)			6.5	–	–	–

Notes: a: “VOCs” here represents the total concentration of the 108 VOCs species; b: “TVOC” represents the total VOCs concentrations including the unmeasurable characteristic species calculated by the mass balance method; c: “Condition 1” stands for the condition when only 2 reactors were in operation; d: “Condition 2” stands for the condition when 20 reactors were in operation; e: the VOCs removal efficiency here was calculated from NMHC results. AS: alkali spray; WS: water spray; GWS: gas-water separator; PCO: photocatalytic oxidation; ACA: activated carbon adsorption.

**Fig. 1.** Speciation profiles of VOCs emissions from each process in the two tested plants.

concentration of the 108 measured VOCs species in the stack exhaust flue gas was 45.7 mg/m³. With the unmeasurable characteristic species added (as illustrated in Section 2.3.1), the TVOC concentration in the stack exhaust flue gas was estimated to be 58.0 mg/m³. Under Condition 2 with 20 reactors operating simultaneously, the NMHC concentration at the outlet of APCDs turned out to be 399.4 mg/m³ (too high for the GC-MS/FID method). The overall VOCs removal efficiency of the APCD combination of AS + PCO + ACA increased from 16% to 85% when the

VOCs concentration at the inlet increased, which was consistent with the conclusion of Su et al. (2016) that higher VOCs concentration at the inlet leads to higher removal efficiency of APCDs and more stable effectiveness as well. The fugitive VOCs emission concentrations in the main workshop during meal loading and unloading periods were 5.5 and 6.5 mg/m³, respectively, which were higher than under the regular condition (1.8 mg/m³), because the loading and unloading processes were not completely enclosed and the fugitive gases were not well collected by

the gas-collecting hoods.

As shown in Fig. 1, the dominant VOCs species in the stack flue gas from the main workshop in Plant 2 were 2-butanone (15.1%), butyl acetate (13.2%), 2-propanol (10.0%), butanol (8.2%), o-ethyltoluene (6.9%), and ethylbenzene (5.6%), which mainly came from raw materials and organic solvents. The fugitive VOCs speciation profiles during meal loading and unloading processes were similar to that under the regular condition, mainly including trimethylbenzene, ethylbenzene, o-ethyl toluene, and xylene, which were consistent with the main constituents of raw and auxiliary materials. Overall, OVOCs and halo-hydrocarbons dominated the speciation profile for Plant 2.

3.2. Comparison with existing VOCs speciation profiles

Based on the weighted-averaging approach, VOCs speciation profiles for different products from Plant 1 were established after incorporating stack emissions from storage tanks and wastewater treatment, as shown in Fig. 2. The most abundant categories of VOCs species were OVOCs (58.5%), aromatics (25.1%), and alkanes (14.3%) in furan resin production, aromatics (57.5%) and OVOCs (36.5%) in phenolic resin production, and aromatics (58.5%) and alkanes (34.5%) in sulfonic acid curing agent production. The VOCs emission profiles for different resin production processes were compared in Fig. 2. The dominant VOCs species in the emission profiles for polyethylene (PE) and polypropylene (PP) resins production are alkenes, for polystyrene (PS) resin production are aromatics, for polyvinyl chloride (PVC) resin production are halo-hydrocarbons, and for acrylonitrile butadiene styrene (ABS) resin production are aromatics and others (Chen et al., 2017; Hsu et al., 2007; Wu and Xie, 2017; Zhao et al., 2017a). For dedicated resins production, the dominant VOCs species for polyurethane (PUR) and polyacrylic acid (PAA) resins production are aromatics (Chen et al., 2017; Hsu et al., 2007), for polypropylene glycol (PPG) resin production are OVOCs (Zhao et al., 2017a), and for furan and phenolic resins production are OVOCs and aromatics based on this study.

For paint production, the VOCs species are mainly originated from raw materials and solvents used in the paint manufacturing process. Results from Plant 2 in this study exhibited consistency with most of

existing studies (Chen et al., 2017; Shao, 2019; Yu, 2012; Zhai et al., 2018; Zheng et al., 2013; Zhou et al., 2018), as shown in Fig. 2. Aromatics and OVOCs had equivalent contributions (48.0% and 48.5%, respectively) to the total VOCs emissions. Chen et al. (2017) claimed the dominance of aromatics, while Zhou et al. (2018) and Zhai et al. (2018) found the proportion of OVOCs slightly higher than aromatics. Most of the unidentified VOCs species in the profiles from the SPECIATE database were likely OVOCs which were unmeasurable with the PAMS calibration for most SPECIATE profiles. Results from the two chemical plants tested in this study have contributed updates to the VOCs emission profile database in China.

3.3. OPF_r and $SOAFP_r$ in the two tested plants

As shown in Table 2, the OPF_r for the production of furan resin, phenolic resin, sulfonic acid curing agent, and paint in this study were 5.93, 5.08, 2.80, and 4.02, respectively. Formaldehyde and furfuryl

Table 2

OPF_r and $SOAFP_r$ for the production of resins and paints in different studies.

Product		OPF_r	$SOAFP_r$	Source of VOCs profiles
General resins	PE	1.68	0.011	Li et al. (2019a, 2019b); Wu et al. (2017)
	PP	4.56	0.017	Li et al. (2019a, 2019b); Wu et al. (2017)
	PVC	1.63	–	Li et al. (2019a, 2019b)
	PS	1.86	0.041	Li et al. (2019a, 2019b); Wu et al. (2017)
	ABS	1.66	0.033	SPECIATE
Dedicated resins	Furan resin	5.93	0.068	This study
	Phenolic resin	5.08	0.167	This study
Sulfonic acid curing agent		2.80	0.165	This study
Paint		4.02	0.033	This study
Paint		3.41	0.056	Li et al. (2019a, 2019b); Wu et al. (2017)
Paint		2.69	0.051	Liang et al. (2020)

Notes: PE: polyethylene resin; PP: polypropylene resin; PVC: polyvinyl chloride resin; PS: polystyrene resin; ABS: acrylonitrile butadiene styrene resin.

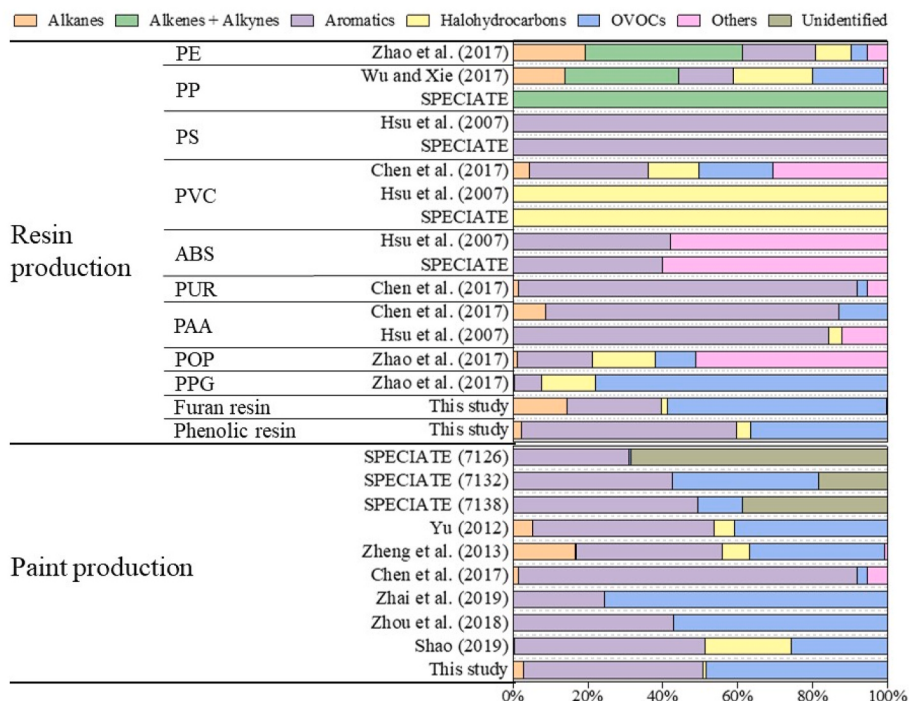


Fig. 2. Speciation profiles of VOCs emissions by category for different resins and paint manufacturing.

alcohol contributed 43.5% and 35.9% to the total OFP_r for furan resin production, respectively. Formaldehyde was also responsible for 34.0% of the total OFP_r for phenolic resin production, followed by naphthalene (26.6%), m-diethylbenzene (10.3%), and 1,2,4-trimethylbenzene (9.9%). The largest contributors to the total OFP_r for sulfonic acid curing agent production were toluene (36.3%), ethylbenzene (19.9%), and m/p-xylene (16.6%). For paint production, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, m/p-xylene, o-ethyltoluene and o-xylene contributed 15.5%, 13.4%, 9.9%, 9.5% and 9.1% to the total OFP_r, respectively.

The SOAFP_r for the production of furan resin, phenolic resin, sulfonic acid curing agent, and paint in this study were 0.068, 0.167, 0.165 and 0.033, respectively. Toluene (43.3%), n-nonane (20.5%) and naphthalene (13.3%) were the top three contributors to the total SOAFP_r for furan resin production, while Naphthalene (72.6%) and phenol (19.2%) took the lead for phenolic resin production. Toluene (53.3%) and n-nonane (19.5%) were the main contributors to the total SOAFP_r for sulfonic acid curing agent production. For paint production, toluene (24.5%), o-xylene (14.7%), o-ethyltoluene (11.8%) and m/p-xylene (11.0%) contributed the most to the total SOAFP_r.

According to the comparison in Table 2, the OFP_r values for the production of the two dedicated resins in this study were 3–4 times higher than those for most general resins (except for PP). The SOAFP_r values for the production of the two dedicated resins (especially phenolic resin) and sulfonic acid curing agent were much higher than those for general resins as well. The OFP_r value for paint production in this study was higher than those calculated from the VOCs speciation profiles from previous studies (Wu et al., 2017; Li et al., 2019b; Liang et al., 2020), while the SOAFP_r value was lower. The comparison suggests that the overall OFP and SOAFP for the resin industry in China could be underestimated if the VOCs speciation profiles for dedicated resin production are simply inherited from general resins.

3.4. Comparison of VOCs emission estimations by the three models

3.4.1. Overall emissions

Fig. 3 shows the comparison of VOCs emission estimates by the three models. The overall VOCs emission estimates by Model 2 for both tested plants were much lower than the yields from Model 1. With detailed information considered, Model 2 provided more reasonable estimates for each process. The overall VOCs removal efficiencies benefited from the fugitive gas collection systems and the APCDs applied were estimated to be 54% and 51% for Plant 1 and Plant 2, respectively. As shown in Fig. S2, for Plant 1 without APCDs, the VOCs emissions from manufacturing lines, storage tanks, and loading operations accounted for 65.1%, 12.3%, and 12.1% of the overall emission, respectively. With the applied APCDs, the contributions of manufacturing lines and storage tanks dropped to 47.9% and 5.3%, respectively, while the contribution

of loading operations rose up to 26.1%. The main workshop in Plant 2 was the dominant emission process. With the installation of APCDs, the proportion of manufacturing line fugitive emissions in the total emission decreased from 74.5% to 64.1%. The overall VOCs emissions estimated by Model 3 were 13.2 t and 12.3 t for Plant 1 and Plant 2, respectively, both of which were slightly higher than the estimates from Model 2. This indicated the positively skewed distribution of the outcome from Model 3. The dominant processes in Plant 1 and Plant 2 were both manufacturing lines, contributing 65.3% and 99.5% of the total emission, respectively.

3.4.2. Manufacturing lines

The annual VOCs emissions through manufacturing lines estimated by Model 1 were 13 and 7.8 times that estimated by Model 2 for Plant 1 and Plant 2, respectively. The large discrepancies implied that the emission factors for dedicated resin production (Bo et al., 2008; TEPA, 2009) and paint production (US EPA, 2006) were either outdated or not widely applicable. Fugitive emissions play an important role in manufacturing line emissions, especially for batch reactors in chemical plants with meal loading and unloading operations. The two tested plants both had fugitive emission collection facilities, and a large amount of the original fugitive gases were collected and treated as stack gases. Based on Model 2, the ultimate fugitive emissions accounted for 29% and 64% of the total manufacturing line emissions for Plant 1 and Plant 2, respectively (Fig. S2). The overall fugitive gas collection efficiency for the manufacturing lines in Plant 1 was higher than Plant 2, which was mainly due to the plant scale. The VOCs emission from manufacturing lines in Plant 1 estimated by Model 3 was 31% higher than by Model 2. This was mainly caused by the negatively skewed distribution of the VOCs removal efficiency of APCDs.

3.4.3. Storage tanks

The annual VOCs emission from storage tanks in Plant 1 estimated by Model 1 was 12 times the estimate from Model 2, indicating that the existing emission factors (TEPA, 2009) for the process of storage tanks (Table S6) were probably not suitable for resin production plants. These emission factors were designed only for fixed-roof tanks and obtained based on the regression formula for storage tank emissions according to AP-42 and characteristics of storage materials. However, the VOCs emission rates of fixed-roof tanks were estimated to be higher than inner and external floating-roof tanks (Lu, 2017; Liu et al., 2020; Jovanovic et al., 2010). The differences in parameters for tank structure and operation, physiochemical properties of materials, and meteorological factors lead to large discrepancies in emissions. Model 3 considered the probability distribution of these parameters and yield an estimate of 0.58 t VOCs emission from storage tanks in Plant 1, which was 8.8% lower than the estimate by Model 2.

3.4.4. Equipment leaks

The largest discrepancy between Model 1 and Model 2 occurred in the emission process of equipment leaks. The emission estimate from Model 1 was over two orders of magnitude higher than Model 2. There were two major drivers for the significant difference: one was the unsuitable emission factors (Table S7) used in Model 1 for equipment leak emission estimation (US EPA, 1995) which were mainly for the petroleum refineries, resulting in the likely overestimation of emission rates by Model 1; and the other was the application of the LDAR program, resulting in the change of the number and the distribution of leaks. To investigate the impacts of the two drivers, a case study on the VOCs emission from equipment leaks in Plant 1 was conducted. Four methods were applied to the estimation of VOCs emissions from the leaks of flanges, pumps, and valves. Fig. S3 shows the comparison of emission estimates using the emission factor method and the correlation equation method with three scenarios (as introduced in Section 2.3.3). The estimates from the emission factor method were 1–2 orders of magnitude higher than the results from the correlation equation method without

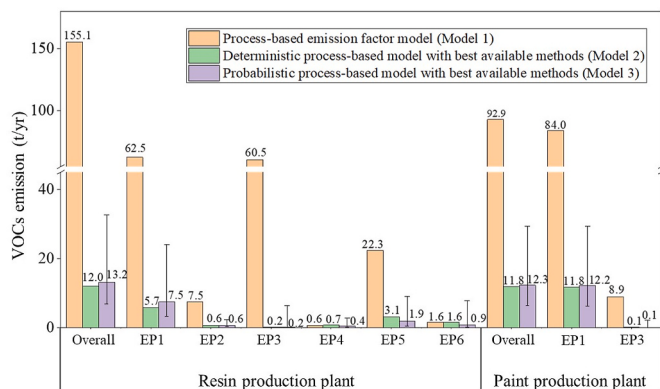


Fig. 3. Comparison of VOCs emission estimates for the two tested plants by process using the three models.

LDAR information. With LDAR data provided, the estimates from the correlation equation method got about one more order of magnitude lower for leaks of pumps and valves. In the scenario with LDAR after repairing, the emission estimate for leaks of flanges was 58% lower than the case before repairing. The comparison suggests that the VOCs emissions from equipment leaks with LDAR application in China could be largely overestimated.

The correlation equation method with the LDAR data was evaluated to be the best available estimation method for equipment leaks. However, the existing correlation equation method still has two major limitations: (1) local studies (Gao et al., 2016; Min et al., 2020) found that the emission rates measured by the bagging method for light liquid valves, connectors, and flanges were lower than the estimates by the correlation equations announced by US EPA (1995); (2) there might be non-standard operations for the LDAR system, resulting in the underestimation of VOCs emissions. Therefore, more bagging measurements and LDAR auditing are required to establish localized correlation equations and distribution of leaks.

3.4.5. Wastewater collection and treatment system

Due to the limitation of available test results, the best available estimation methods to estimate VOCs emissions from the wastewater system were the emission factor method and the measurement-based method for the collection unit and the treatment unit, respectively. The VOCs emission from the wastewater collection unit accounted for 79.6% of the total emission from the wastewater system in Plant 1. Therefore, results from Model 1 and Model 2 were close to each other. VOCs emission from the wastewater collection and treatment system is affected by wastewater temperature, meteorological condition, the type of treatment system, etc. (Zhang et al., 2019), and thus localized emission factors are required for more accurate estimation. The estimate by Model 3 was 42% lower than Model 2, which was mainly caused by the positively skewed distribution of the emission factor adopted for the wastewater collection unit.

3.5. Uncertainty analysis

Model 3 was utilized for uncertainty analysis by emission process. The uncertainty ranges with 95% confidence interval are shown in Fig. 3. The overall uncertainty range for the total emission from Plant 1 was estimated to be (−48%, +147%). The uncertainty ranges for manufacturing lines, storage tanks, equipment leaks, and the wastewater system in Plant 1 were (−57%, +221%), (−60%, +310%), (−97%, +3062%), and (−69%, +555%), respectively. In Plant 2, the overall uncertainty range was calculated to be (−48%, +139%). Existing VOCs emission inventories for the industrial sector on a regional scale (Fu et al., 2013; Huang et al., 2011; Zhao et al., 2017a) had an uncertainty range of about (−60%, +150%). These inventories were all established by the product-based emission factor model. The uncertainty ranges of these inventories were estimated based on the sources (local or exotic) and numbers of available emission factors, which was essentially semiquantitative. When the inventory scale goes down to the enterprise level, with the same model for emission estimation, the uncertainty level would be much higher according to the uncertainty propagation principle. It could be implied that the method for uncertainty analysis in this study was a quantitative attempt for the VOCs emission estimation, and the uncertainty ranges for the overall VOCs emission estimates were much lower than existing studies. Therefore, the probabilistic process-based model with best available methods developed in this study proved to be a better way for quantitative uncertainty analysis and could largely reduce the overall uncertainty if detailed information is provided. Nonetheless, the probability distributions of the key parameters used in Model 3 were based on available data. A great amount of information was based on exotic tests or estimation that could be different from the actual situation in China. More localized data should be obtained through field investigation, especially for emission

processes like equipment leaks. More localized auditing data from the LDAR program could be utilized to produce distribution of leaks and make more accurate fugitive VOCs emission estimation.

4. Conclusions

Two chemical plants in eastern China were tested in this study. OVOCs and aromatics dominated the VOCs speciation profiles for both dedicated resin production and paint production. The proportions of OVOCs in the speciation profiles for the manufacturing of the two types of dedicated resins measured in this study were much higher than the proportions for general resins. The overlook of OVOCs in the synthetic resin industry could lead to underestimation of the overall OFP and SOAFP in existing VOCs emission inventories for the chemical industries. The VOCs emissions from the two tested plants were estimated using three process-based models. With detailed information on key processes incorporated, the two models with best available estimation methods (Model 2 and Model 3) showed better performance than the emission factor model (Model 1). Based on results from Model 3, manufacturing lines were responsible for 65% of the total VOCs emissions in Plant 1. The probabilistic process-based model (Model 3) developed in this study could largely reduce the overall uncertainty of VOCs emission estimation, and proved to be a promising approach for both VOCs emission inventory development and quantitative uncertainty analysis. We suggest policy makers organize more field measurements and investigations, and adopt this methodology to develop more accurate VOCs emission inventories.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2021.118192>.

Credit author statement

Lei Zhang: Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision, Funding acquisition. Xinzhi Zhu: Formal analysis, Investigation, Writing – original draft, Visualization. Zeren Wang: Writing – original draft. Jie Zhang: Writing – review & editing, Funding acquisition. Xia Liu: Writing – original draft. Yu Zhao: Writing – review & editing, Funding acquisition.

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