Component Characteristics and Emission Factors of Volatile Organic Compounds from Dyestuff Production

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ABSTRACT

Volatile organic compounds (VOCs) are critical components in the generation of secondary organic aerosol (SOA) as well as ozone. In this study, the compositions of VOC emissions from two dyestuff plants were sampled and quantitatively analyzed using SUMMA canister sampling, a pre-concentrator, and GC-MS. Based on the organized emission concentrations, the two plants generated an estimated 443.0 kg a⁻¹ and 667.8 kg a⁻¹ of VOCs, which were dominated by halogenated hydrocarbons. The differences in composition between the plants, plant workshops, and production chains were remarkable. The average removal rate of the VOCs was calculated to be 86.1%, with alkanes and alkenes exhibiting the maximum rate, followed by halogenated hydrocarbons and OVOCs. Our research establishes the characteristics of VOCs—including their EFs, which have hitherto remained unassessed—generated by dyestuff production and offers supporting air quality data for emission inventories of relevant industries as well as policy making.

Keywords: Component; Dyestuff; Emission factor; VOCs.

INTRODUCTION

Volatile organic compounds (VOCs) act as important precursors of secondary organic aerosols (SOA) (Huang *et al.*, 2014; Kelly *et al.*, 2018) and ozone (Shao *et al.*, 2009; Wang *et al.*, 2016), and can have adverse impacts on human health (Mccarthy *et al.*, 2013; Gong *et al.*, 2017). The magnitude and components of the VOCs are closely related to the generation of ozone and SOA, and VOCs contributed 35–51% of the measured SOA (Liu *et al.*, 2008; Yuan *et al.*, 2013). It has been observed that ozone concentrations exceeded the ambient air quality standard by 100–200% in China's major urban centers, such as the Beijing-Tianjin-Hebei region, the Yangtze River Delta, and the Pearl River Delta (Wang *et al.*, 2016).

Over the past four decades, China has experienced rapid economic development and accelerated industrialization, while accompanied with rising fossil fuel consumption and increased emission of air pollutants (Wang and Hao, 2012; Li *et al.*, 2016;). However, in recent years, the emissions of

SO₂, NO_x, and PM show a significant downward trend (2018 China Environmental Status Bulletin, 2019), while the VOCs emission has become more prominent and drawn more and more attention (Shen *et al.*, 2019). Previous studies on anthropogenic VOCs emission in China showed that industry is an important source (Wei *et al.*, 2008; Liang *et al.*, 2017; Wu *et al.*, 2016). The industrial VOC emissions in China increased at an annual average growth rate of 38.3% from 2011 to 2013 (Zheng *et al.*, 2017), and the VOCs emission from the industrial source “use of VOCs products” reached up to 7.56 Tg in 2015 (Liang, 2017). In order to fully address the issue of air pollution problem, China has made efforts to strengthen the prevention and control of VOCs (MEE *et al.*, 2017a; MEE *et al.*, 2017b; MIIT and MF, 2016).

Many studies on VOCs emissions have been carried out in China, as well as in certain areas, such as the Yangtze River Delta (Huang *et al.*, 2011; Fu *et al.*, 2013; Shao *et al.*, 2016), the Pearl River Delta (Ou *et al.*, 2015; Yang *et al.*, 2015; Yin *et al.*, 2015), and other cities (Jia *et al.*, 2016). As for the industrial sector, researchers have conducted in-depth research on the source profiles of VOCs, including petrochemistry (Mo *et al.*, 2015; Dong *et al.*, 2016; Wei *et al.*, 2018), solvent use (Yuan *et al.*, 2010; Wang *et al.*, 2014; Zhai *et al.*, 2018), electronic manufacturing (Cui and Ma, 2013), and pharmacy (He *et al.*, 2012; He *et al.*, 2015). However, as one of the main sources of industrial VOCs

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emission, the dyestuff production industry has been insufficiently recognized by researchers. In fact, the yield of dyes and organic pigments had been increasing from 2011 to 2015 at an annual rate of 4.0% (SDIA, 2016). However, at present, only the removal of organic dyes from wastewater, which was generated during dyestuff production, was studied (Cotillas *et al.*, 2018).

Under such circumstances, many questions need to be answered, such as *What are the component characteristics of VOCs emissions from dyestuff production?* and *What are the emission factors (EFs) of VOCs components?* Answers to these questions are fundamental for many VOCs studies on constructing emission inventories, better understanding the effects of VOCs emissions on air quality and human health, and making efficient mitigation strategies. In this study, VOCs emission samples from different parts of individual production lines of two representative dyestuff plants in an industrial park of China were collected and analyzed. The main objectives of this study are to (1) identify the differences of VOCs components among various product lines, (2) discuss the emission characteristics and connection of VOCs emissions from different parts of a production line, and (3) evaluate the effectiveness of the flue gas treatment facility and give the EFs of the components.

METHODS

Description of the Sampling Sites

Two dyestuff plants (“A” and “B”) located in an industrial park were selected to carry out the sampling and analysis. Based on the preliminary investigation, different products were produced in different workshops in both plants, and the intermediates and final products of certain product lines were also in different workshops. The main process is “diazotization + coupling + post-treatment,” and the difference lies in the variety of intermediates. Detailed product lines and sampling points are shown in Fig. 1. Plant A was divided into two parts, from which the flue gas was collected through pipelines and transported to the regenerative thermal oxidizer (RTO) device in each part, respectively. The main raw materials of Plant A included nitrosylsulfuric acid, sulfuric acid, 1,3-diethylbenzene, etc., and the product yield was 14,724 t a⁻¹. Each workshop of Plant B was equipped with an exhaust funnel separately, and the flue gas emitted from each workshop was discharged after treatment. The main raw materials of Plant B included sulfuric acid, liquid caustic soda, N-phenylglycinonitrile, etc., and the product yield was 30,000 t a⁻¹. During the production process, three samples were collected for each sampling port at the inlet and outlet of the exhaust funnels. Since some of the exhaust funnels have no sampling ports before the flue gas treatment, only the treated flue gas samples were collected.

Analytical Methods

The U.S. Environmental Protection Agency (EPA) method TO-15, which is widely used in the emission characteristics identification of VOCs from stationary pollution sources (Ma, 2012; Wang *et al.*, 2014; Wei *et al.*, 2014), was adopted in this study. The quantitative analysis of unorganized

VOCs emissions from workshops and organized emissions from exhaust funnels was conducted using SUMMA canister sampling, a pre-concentrator, and GC-MS. Before sampling, the SUMMA canisters should be checked for air tightness first, and then be cleaned with high-purity nitrogen and vacuumed by using Entech 3100D automatic summa canister cleaner.

The SUMMA canisters were brought to the plants, and the samples were collected under normal operation of the production equipment. The unorganized samples were collected near the main reaction equipment in the workshop. The organized samples were collected through a silicon tube with one end of the SUMMA canisters attached and the other end with a filter head connected with a stainless steel tube extended into the chimney. For each sample, a pressure gauge was used to ensure the completion of sample collection. When the pressure gauge showed zero, the canister valve was closed and the relevant data of sampling were recorded. The SUMMA canisters were brought back to the laboratory for storage at room temperature, and the analysis was completed in five days.

According to the U.S. EPA TO-15 mixed standard gas, the standard curves of target compounds were established based on the relationship between the integrated peak area and the corresponding concentration. During the sample analysis, the samples were automatically injected through an autosampler (7016; Entech Instruments), and were subjected to a gas chromatography (7890B; Agilent) for separation after being concentrated and decontaminated by a pre-concentrator (7200; Entech Instruments). The detection was performed by using the single-ion monitoring of the mass selective detector (5977C; Agilent). The qualitative analysis was performed by mass spectrum and retention time, and the quantitative analysis was performed according to chromatogram and standard curve by internal standard method. Bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d5 were selected as internal standard substances.

Quality Control and Assurance

Before sampling, the SUMMA canisters need to be cleaned, humidified and leakage tested. During sampling, a vacuum SUMMA canister was taken as a sample blank, which undergone the same on-site exposure, transportation, storage, laboratory analysis and other processes with other samples. Parallel sampling and analysis were also carried out, and the standard deviation of the results at the same point should be less than or equal to 5%, which indicates that the results are reliable. When the samples were transported back to the laboratory, the pressure of each SUMMA canister should be measured and recorded. When the pressure was less than 12 psig (83 kPa), it must be pressurized to 15 psig with high-purity nitrogen and the dilution factor should be calculated. Sample analysis was completed within five days after sampling.

Automatic tuning of the mass spectrum detector (MSD) was performed periodically to ensure that the parameters meet the requirements and achieve the necessary sensitivity, resolution and qualitative capabilities. For the calibration curves, the relative standard deviation was less than or equal

Fig. 1. Detailed product lines and sampling points in the dyestuff plants A and B. (The numbers marked in blue are the serial numbers of sampling point, and the bold blue arrows represent where the flue gas is going.)

to 30%. After a continuous injection every 12 hours, a point in the standard curve was taken again for analysis, and the deviation between the response factor of each compound and the initial calibration was less than or equal to 30% to confirm the validity. Laboratory blank samples should be analyzed before actual samples or after every 24 hours of continuous injection. When the concentration of the sample exceeds the detection limit by 10 times, it needed to be reanalyzed, and the relative deviation was less than or equal to 20%. In addition, the recovery rate was measured by adding substitutes in each sample. 4-bromo-1-fluorobenzene was chosen as a substitute and the recovery rate should be between 70% and 130%.

RESULTS AND DISCUSSION

VOCs Emission from Different Production Lines

The organized emission concentration basically represents the overall emission characteristics of each plant. The

composition ratios and mass percentages of the high-concentration components of the organized VOCs from Plant A and B are shown in Fig. 2. It can be seen that the dyestuff plants are mainly responsible for the emission of halogenated hydrocarbons. However, even in the same industry, the difference in VOCs components between plants is still extremely significant. The types of organized VOCs with the highest concentration emitted by Plant A (AI, AII-2 and AIII) are halogenated hydrocarbons and OVOCs, specific for chlorine toluene, methylene chloride and acetone. The components from Plant B are mainly halogenated hydrocarbons (BI, BII, and BV), which are mainly chlorobenzene, 1,2-dichlorobenzene, and dichloromethane. The components from BIII are mainly aromatic hydrocarbon (naphthalene), and from BIV are OVOCs (4-methyl-2-pentanone and 2-methoxy-2-methyl-propane).

Meanwhile, Fig. 2 shows the emission characteristics of unorganized VOCs from Plant A and B. It can be seen that the unorganized emission components are complex and the

Fig. 2. Composition ratio and mass percentage of high-concentration components of VOCs from Plant A and B. (The serial number of points in this figure refers to Fig. 1.)

difference in emission characteristics among workshops is also remarkable. The main components discharged from most workshops of Plant A are OVOCs. The most concentrated component from Workshops A1-1, A3, A4-2, and A5 is isopropyl alcohol, while from Workshops A2 and A4-1 it is acetone. Workshop A1-2 is mainly composed of halogenated hydrocarbons, and the component with the highest concentration of VOCs is chloroethane. The VOCs emitted from Workshops B1-1, B2, B3, and B5 of Plant B are OVOCs, and the dominant components are methylbenzene, acetone, isopropyl alcohol, and 4-methyl-2-pentanone, respectively. The main component emitted from Workshop B1-2 is halogenated hydrocarbons, and chlorobenzene has the highest mass concentration. In addition, the dominant component of Workshop B4 is aromatic hydrocarbons, with the highest naphthalene.

VOCs Emission from Different Production Chains of a Line

The production line of a certain product can be operated separately by a workshop, or it can be split and then produced by different workshops, which means that the raw materials are first transported to one workshop to complete part of the production process and the intermediates are obtained. The intermediates are then transported as raw materials to another workshop to complete the remaining production process and the final products are obtained. Plant A has two production lines, while Plant B has only one. Studying the emission characteristics of VOCs from different chains of production lines can help us understand the relationship between VOCs emission and raw materials as well as processes, and grasp the reasons for the formation of each component, which can provide theoretical basis for the formulation of subsequent VOCs emission standards in the industry and the control of VOCs pollutants from the sources.

Two production lines from the two plants are taken as an example to illustrate the emission concentration of VOCs components in different chains of the same production line (Fig. 3). A1-1, A1-2, and AI of Plant A are chosen, where AI deals with the flue gas of A1-1. Meanwhile, since each workshop of Plant B is equipped with separate exhaust funnels, the production line in Fig. 3 contains two organized discharge outlets. As can be seen from Fig. 3, there is a significant difference in the emission types and concentrations of VOCs from A1-1 and A1-2. The emission characteristics of B1-1 and B1-2 are similar, but both the unorganized and organized emission concentrations of VOCs in B1-1 are generally higher than those in B1-2.

Isopropyl alcohol (A1-1: 0.20 mg m^{-3} , A1-2: 0.25 mg m^{-3} , AI: 0.20 mg m^{-3}) and dichloromethane (A1-1: 0.12 mg m^{-3} , A1-2: 0.32 mg m^{-3} , AI: 0.13 mg m^{-3}) are found in all chains of Plant A. In comparison, in Plant B, dichloromethane (B1-1: 0.08 mg m^{-3} , B1: 0.07 mg m^{-3} , B1-2: 0.04 mg m^{-3} , BII: 0.06 mg m^{-3}) is found in all chains. In addition, the emission concentration of chloroethane in Workshop A1-2 is particularly high, which is 3.38 mg m^{-3} . And that of methylbenzene is also higher, reaching 0.16 mg m^{-3} in both A1-1 and A1-2. Chlorobenzene has an outstanding discharge of 1.47 mg m^{-3} in BI, while in B1-1 and B1-2 are 0.07 and 0.05 mg m^{-3} ,

respectively. Therefore, as a whole, the unorganized emission of Plant A is more serious, and in Plant B, the concentration of organized emission is slightly higher than that of unorganized emission. Comparing the technological process, it can be seen that the chemical reactions mainly occurred in the production process of the products. The VOCs emitted from different production lines of the two plants are mainly derived from the raw materials used (such as chlorobenzene), or contain the same chemical elements or functional groups as the raw materials. Therefore, the premise of effective control of the VOCs emissions is to pay attention to the management of raw materials and production processes.

Evaluation of the Effect of the Treatment Facility

Currently, RTO is a relatively efficient treatment technology for industrial VOCs reduction. Since some of the exhaust funnels have no sampling ports before the flue gas treatment, only the VOCs removal rate of Plant A within RTO technology was analyzed in this study. As can be seen from Fig. 4, the average removal rate is 86.1%, and the removal rates of different VOCs species and components are also different. RTO has the highest removal rate of alkanes and alkenes, up to 95.4%, followed by halogenated hydrocarbons (85.7%) and OVOCs (79.2%). The removal rate of aromatic hydrocarbons is the lowest. For the components, 84.4% of the alkane and alkene components are removed. Among the halogenated hydrocarbons, the removal rates of bromomethane, tribromomethane, chloroform, chloroethane, and 1,1,1-trichloroethane are higher, all higher than 97.5%, and the removal rate of 1,1,1-trichloroethane is close to 100%. However, the removal rates of dibromochloromethane, tribromomethane, and 1,2-dichlorobenzene are relatively low, only 44.1%, 39.7%, and 40.1%, respectively. Among OVOCs, 96.3% isopropyl alcohol and 97.5% ethyl acetate are removed, while only 61.2% 2-butanone is got rid of. Among the aromatic hydrocarbons with the lowest total removal rate, the removal rate of *o*-xylene is as high as 98.2%, while that of methylbenzene is only 45.6%. These VOCs components have relatively low concentrations, and may be swept out of the RTO without being incinerated due to the fast flow rate of the flue gas, resulting in a lower removal rate.

Su *et al.* (2016) measured the removal rates of ten VOCs treatment technologies in six industries, and Zhang *et al.* (2018) summarized the effects of eight VOCs treatment technologies in six industries based on investigation. They suggested that the inlet VOCs concentration has a greater impact on the removal rate of the treatment technology. The RTO treatment facility is suitable for flue gas with a VOCs concentration in the range of $500\text{--}2000 \text{ mg m}^{-3}$ (Xu, 2019), and when the concentration is less than 100 mg m^{-3} , the removal rate is in the range of 9.1–99.7% (Su *et al.*, 2016; Zhang *et al.*, 2018). The inlet VOCs concentration in Plant A is approximately 33.5 mg m^{-3} , which may be another reason for the lower removal rate.

Emission Factors of the VOCs Components

Both unorganized and organized emissions exist in the plants. At present, the estimation methods for unorganized emissions mainly include material balance method, flux

Fig. 3. Unorganized and organized emission concentration of VOC components from different workshops of the production lines of the two dyestuff plants.

concentration inverse method, chemical reaction method, and empirical formula method (Wang, 1989). However, the raw materials are complex and a wide variety of VOCs are discharged. Due to the lack of selection basis for important parameters, it is difficult to obtain accurate unorganized emissions. In addition, when the plant adopts a unified way to collect and remove the flue gas from the workshops, the inside of the pipeline is actually under negative pressure,

and it is difficult for the exhaust pollutants to diffuse to the external environment through the concentration difference. In this case, the unorganized emission can be controlled at a lower level. Compared to unorganized emission, organized emission can basically reflect the actual emission of the plants. Therefore, the annual VOCs emissions of the plants were estimated based on the organized emission concentration and associated parameters of the treatment facilities (Table 1).

Fig. 4. Concentration of VOCs components before and after treatment and removal rate.

Table 1. Treatment facility and air volume of exhaust funnels of Plant A and B.

Plant	Treatment facility	Air volume (m ³ h ⁻¹)
A	Three-stage lye absorption	4860
	1#RTO	5000
	2#RTO	12,000
B	Condensation + three-stage lye/soda absorption	8000
	Three-stage condensation + acid absorption + alkali absorption	20,450
	Condensation + two-stage acid absorption	43,177
	Two-stage lye absorption	8000
	Two-stage condensation + two-stage sodium thiosulfate absorption + alkali absorption	14,000

Table 2. Emission factors of VOCs components from Plant A and B (g t⁻¹ products).

		Alkanes, alkenes			
Components	<i>n</i> -Hexane	Cyclohexane	<i>n</i> -Heptane	Propylene	1,3-Butadiene
Plant A	2.5	0.003	0.4	0.2	-
Plant B	0.2	0.01	0.04	0.2	0.02
		Aromatic hydrocarbons			
Components	Benzene	Methylbenzene	<i>o</i> -Xylene	<i>p</i> -Xylene	Ethylbenzene
Plant A	0.2	1.3	0.1	0.1	0.3
Plant B	0.9	1.3	0.03	0.002	0.01
Components	4-Ethyltoluene	1,2,4-Trimethylbenzene	Styrene	Naphthalene	
Plant A	0.004	16	0.02	-	-
Plant B	0.004	0.1	0.03	1.7	
		Halogenated hydrocarbons			
Components	Bromomethane	Chloromethane	Dichloromethane	Tribromomethane	Dibromochloromethane
Plant A	0.2	1.6	4.7	0.02	0.004
Plant B	0.2	0.3	1.9	0.3	0.03
		Halogenated hydrocarbons			
Components	Bromodichloromethane	Chloroform	Carbon tetrachloride	Chloroethane	1,2-Dibromoethane
Plant A	0.01	0.2	0.0002	0.5	-
Plant B	0.004	0.2	-	0.004	0.001
Components	1,2-Dichloroethane	1,1,2-Trichloroethane	1,2-Dichloropropane	Vinyl chloride	1,1-Dichloroethylene
Plant A	0.1	0.1	-	-	0.5
Plant B	0.4	0.1	0.1	0.05	-
Components	<i>cis</i> -1,2-Dichloroethylene	<i>trans</i> -1,2-Dichloroethylene	Trichloroethylene	Tetrachloroethylene	Chlorobenzene
Plant A	0.1	0.02	0.002	-	0.1
Plant B	-	-	-	0.0001	3.8
Components	Benzyl chloride	1,2-Dichlorobenzene	1,3-Dichlorobenzene	1,4-Dichlorobenzene	1,2,4-Trichlorobenzene
Plant A	4.7	0.001	0.9	-	-
Plant B	0.1	3.5	0.7	2.6	0.01
		OVOCs			
Components	Isopropyl alcohol	Acetone	2-Butanone	4-Methyl-2-pentanone	2-Hexanone
Plant A	1.4	4.7	0.2	0.4	0.05
Plant B	0.1	1.9	0.2	0.5	0.1
Components	Acrolein	2-Methoxy-2-methyl-propane	Methyl methacrylate	Ethyl acetate	Vinyl acetate
Plant A	0.3	0.1	0.01	0.3	0.5
Plant B	0.02	0.3	0.001	0.3	0.1
		Others			
Components	Carbon disulfide	Tetrahydrofuran	1,4-Dioxane		
Plant A	0.3	0.7	-		
Plant B	0.04	0.03	0.1		

The results showed that the VOCs emissions from Plant A and B were 443.0 kg a⁻¹ and 667.8 kg a⁻¹, with halogenated hydrocarbons accounting for the largest proportion, which were 47.7% and 63.5% of the total emissions, respectively.

Meanwhile, EFs can correlate pollutant emissions from the environment with their source activities, representing the emission of the unit's activity intensity, which is critical to the establishment of pollutant emission inventory. Most of China's VOCs emission inventories were constructed based on the EFs with reference to that of developed countries such as the United States. Although it has been revised to some extent, there are still some deviations from actual emissions in China. In addition, due to the lack of EFs of the VOCs components, the construction of emission inventories is mostly for the total VOCs. However, the toxic and harmful levels of VOCs and their impacts on ozone generation potential are different because of the difference in components' properties. In the initial stage of prevention and control of VOCs in China, emphasis should be put on control of key VOCs components. Based on the emission of VOCs in the previous section, combined with the actual production of disperse dyes in the plants, the EFs of VOCs components are obtained (Table 2), which can provide data support for the study of emission inventory of relevant industry.

CONCLUSIONS

VOCs emitted from the workshops and exhaust funnels of two representative dyestuff plants, Plants A and B, in China were quantitatively analyzed using SUMMA canister sampling, a pre-concentrator, and GC-MS. The emission characteristics of the VOCs from various product lines and chains were identified, and the effectiveness of the flue gas treatment facilities at the plants was evaluated. We also aimed to establish, for the first time, the EFs of VOCs generated by the dyestuff industry.

Based on the organized emission concentrations, an estimated 443.0 kg a⁻¹ and 667.8 kg a⁻¹ of VOCs were emitted by Plant A and B, respectively, and halogenated hydrocarbons were the dominant component. The difference in VOC composition between the plants was significant, with Plant A emitting both more halogenated hydrocarbons and OVOCs than Plant B. The unorganized emission concentrations also revealed remarkable differences between the workshops. Whereas most of the workshops at Plant A as well as Workshops B1-1, B2, B3, and B5 at Plant B mainly discharged OVOCs, Workshops B1-2 and B4 primarily emitted halogenated and aromatic hydrocarbons, respectively. Furthermore, the removal rate of VOCs at Plant A using RTO technology averaged 86.1%, with alkanes and alkenes exhibiting the maximum rate, followed by halogenated hydrocarbons and OVOCs. Lower removal rates for VOCs at low concentrations may be attributable to these compounds exiting the treatment facility without being incinerated due to the fast flow rate of the flue gas.

Previous studies have suggested that VOCs play an important role in the generation of SOA as well as ozone via complicated non-linear interactions. Thus, the management of raw materials and production processes in the dyestuff

industry must be considered, as VOCs mainly originate from the raw materials used and contain the same chemical elements or functional groups. Continuous efforts to reduce VOC emissions are necessary, and the emphasis at this stage should be placed on controlling key components. However, large uncertainties in the estimated emissions and EFs of VOCs may still exist because of the small sample size and significant differences between processes and products. Further studies, including reliable in situ experiments, are required to improve the EFs.

ACKNOWLEDGMENTS

This work was supported by the National Key Research and Development Program of China (2016YFC0209102), and Zhejiang S&T Programs (2017C03007).

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Received for review, September 25, 2019

Revised, November 27, 2019

Accepted, November 30, 2019