Process-based VOCs Source Profiles and Contributions to Ozone Formation in Typical Organic Solvent-used Industries in Hangzhou

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ABSTRACT

The solvent-used industry plays an important role in volatile organic compounds (VOCs) emission, which has caused an increasing concern. Herein, VOCs samples collected before and after treatments from the painting industry, printing industry and printing & dyeing industry in Hangzhou were measured. Then, the VOCs removal efficiencies of different treatments were detailedly investigated. Among them, high-temperature incineration technology achieved the highest VOCs removal efficiency, averaging 93.0%. Process-based source profiles suggested that aromatics and alkanes accounted for more than 76.5% of VOCs, mainly including toluene, styrene, n-decane, n-undecane and n-dodecane. Furthermore, the ozone formation potentials (OFPs) based on processes suggested that toluene, meta-xylene, n-butene, styrene and ortho-xylene should be preferentially controlled to reduce the OFPs in painting industry and printing & dyeing industry. For printing industry, the contributions of top five species to the OFPs were relatively balanced, which indicated these species should all be given more attention. Finally, the low-temperature plasma technology and the combined technology of activated carbon adsorption with condensation were found to reduce the OFPs for their ability to preferably removing aromatics or olefins. The results were beneficial to develop effective VOCs abatement strategies and complemented the VOCs source profiles in solvent-used industries.

Keywords: Solvent-used industry, Volatile organic compounds, Source profile, Chemical reactivity, Ozone formation potentials

1 INTRODUCTION

Volatile organic compounds pose an enormous threat to human health because of their toxicity. Besides, they could also lead to a series of environmental problems, such as ground-level ozone and secondary organic aerosol formation (Thepanondh et al., 2011; Huang et al., 2014; Wu et al., 2017; Maji et al., 2019). Different kinds of VOCs have different chemical reactivity to the formation of ozone and secondary organic aerosol (SOA) (Ziemann and Atkinson, 2012; Xiong et al., 2020). Therefore, studying the emission characteristics and atmospheric chemical activity of anthropogenic VOCs emission source is an important basis for understanding the formation mechanism of air pollution and devising effective control policies (Li et al., 2020). In addition, source profiles, especially the localized, are important for source apportionment, which could provide data in support of air quality model simulation and air pollution control strategies (Song et al., 2008; Fu et al., 2020).

China is suffering from VOCs pollution. Industrial emissions such as the use of solvents and industrial combustions are the largest anthropogenic sources of VOCs (Wang et al., 2011; Huang et al., 2020). The organic solvent-used industry involved many categories of complex VOCs. As a
result, most studies on the emissions and pollution characteristics of VOCs in solvent-used industry were sector-based and mainly focused on the researchers’ convenient and interested regions (Zheng et al., 2013). Yuan et al. (2010) studied the VOCs source profiles of painting applications and printing processes in Beijing, China and found aromatics and heavier alkanes were the major species. Zhong et al. (2017) compiled VOCs source profiles from the surface painting industry in the Pearl River Delta region of China and found toluene and m/p-xylene were the major species in each of these six sectors. Recently, some researchers found emission profiles of some industries were process-oriented and established the process-based VOCs source profiles (Mo et al., 2015; Cheng et al., 2021). They pointed out the refined VOCs source profiles were more conducive to identifying emission characteristics and developing effective control strategies. For the solvent-used industry in Yangtze River Delta, reports on the compositions of VOCs and the potentials of ozone formation were still lacking, let alone refined VOCs source profiles. In addition, the measured efficiency of VOCs removal technologies in the solvent-used industry were also rarely reported.

The solvent-used industry occupied an important position in Yangtze River Delta, especially for Zhejiang Province. Some studies indicated VOCs emissions from solvent-used industry accounted for more than 50% of the total emissions in Zhejiang province (Fu et al., 2013; Wu et al., 2015). Hangzhou, the capital of Zhejiang province, will be the host city of the 2022 Asian Games. Studying the emission characteristics and the VOCs removal efficiency of mainstream technologies of typical processes in solvent-used industries in Hangzhou would contribute to the air quality assurance of the Asian Games.

In this study, VOCs samples before and after different treatments in the solvent-used processes were collected and analyzed. The VOCs removal efficiencies of different treatments were evaluated. Then, process-based VOCs emission factors and source profiles were built. Furthermore, the VOCs emission characteristics of different processes were analyzed, and their OFPs based on processes were calculated. Finally, the effects on source profile and OFPs of different treatments were discussed. This study mainly concentrated on process-based VOCs characteristics in typical solvent-used industries, which helped to precisely identify the emission characterization and effectively control the VOCs emission to relieve secondary pollution.

## 2 MATERIALS AND METHODS

### 2.1 Identification of Sources of Solvent-used Industries

From the results of emissions inventories, painting industry, printing industry and printing & dyeing industry were considered to be the dominant sources of VOCs emission in solvent-used industries in Hangzhou (Lu et al., 2018). In this study, the typical companies were selected in corresponding industries. In addition, the main pollution-producing processes and the mainstream treatment measures of selected companies were comprehensively considered.

### 2.2 Sampling Information and Methods

Seven companies in Hangzhou were selected in this study, including 1 automobile spraying company and 2 metal product spraying companies representing painting industry, 2 printing companies representing printing industry and 2 printing & dyeing companies representing printing & dyeing industry. In order to study the efficiencies of VOCs treatment technologies and their influence on source profiles and OFPs, the VOCs samples before and after treatment facilities were collected in different processes strictly following the specification HJ/T 397-2007 (Technical specifications for emission monitoring of stationary source) and the standard HJ 732-2014 (Emission from stationary sources-sampling of volatile organic compounds-bags methods). A total of 19 VOCs samples emitted from the 10 processes were chosen in this study. The basic information of companies, sampling sites and the amount of samples were shown in Table S1. The sampling site was located in the center of the stack without apparent turbulence; the sampling collection time for each sample was 8 min. During the sampling process, flow-limiting valves were used to ensure that the samples were collected at a constant speed. The schematic diagram of VOCs sampling system was shown in Fig. 1. When the sampling volume reached about 80% of the maximum volume of the gas bag, the sampling ended, and then the vacuum pump was turned off. The sampling processes were done when factories were in good working conditions.
Fig. 1. Schematic diagram of VOCs sampling system.


Teflon bags (E-Switch, 1L, purchased from E-Switch official store in Shanghai) cleaned with high purity nitrogen (> 99.999%) at least three times and evacuated in the laboratory. Before sampling, the bags were rinsed thrice with the sample gases.

2.3 VOCs Analysis

VOCs samples were analyzed according to the EPA TO-15 (1999) method with gas chromatography-mass spectrometry (GC-MS; Agilent 7890A/5975C, USA) and the EPA/600-R-98/161 method with gas chromatograph which had a flame ionization detector (FID). Briefly, 300 mL diluted sample was pumped into a preconcentrator with a three-stage trapping system (Model 7100, Entech Instruments, USA). Then the concentrated sample was injected into the gas chromatograph (GC). The GC oven temperature was set initially to –10°C, held for 5 mins, and then increased to 180°C at 5°C min⁻¹ and to 200°C at 20°C min⁻¹. An DB-624 capillary column (60 m × 0.25 mm × 1.4 µm; Agilent Technologies, USA) and an HP-PLOT Q PT capillary column (30 m × 0.32 mm × 20 µm; Agilent Technologies, USA) were used to separate the mixture. The mass spectrometer was operated in scan mode and scanned 35–300 amu after 12.0 mins. The ionization method was electron impacting and the source temperature was 230°C. The Photochemical Assessment Monitoring Station (PAMS; 57 compounds) and Toxic Organic-15 (TO-15; 65 compounds) standard mixtures were used to calibrate the GC-MS/FID system that measured the C2–C12 VOCs. Calibration curves were made by the standard mixtures at five concentrations, ranging from 0.5 to 100 ppbv. The correlation coefficients of each curve were greater than 0.99, and the method detection limit (MDL) of individual species ranged from 0.09 to 0.22 ppbv. In this study, a total of 109 VOCs substances were analyzed and the TVOCs (total VOCs concentrations) was the sum of the concentrations of individual VOCs. The weighted percentage of certain VOCs in the sample was its concentration to the total VOCs concentration. For high concentration samples, the pre-detections of the total VOCs concentration were firstly made to ensure the appropriate dilution ratio. Since the concentration of different VOCs in a sample sometimes differ greatly, there were different dilution ratio for quantifying different VOCs (Cheng et al., 2021).

Three VOCs with known concentrations, including bromochloromethane, 1,4-difurobenzene and 1-bromo-3-fluorobenzene, were used as internal standards for each sample to calibrate the system. The precision of each species was within 10%. A standard gas (5 ppb) was measured each day to check the stability of the system. For quality assurance and quality control, new vacuum sampling bags were used to collect the samples. If sampling bags had to be repeatedly used, they were required to undergo a blank experiment prior to the sampling process. And no target compound (Lower than the detection limits) was detected in laboratory and transportation blank
samples during the analysis. One parallel sample was analyzed for every ten samples, and the relative deviations of the target compounds in the parallel sample were less than 30%.

2.4 Evaluation of Removal Efficiency

The measured removal efficiency of one VOCs treatment technology was calculated according to Eq. (1):

$$\eta = \frac{C_{in} - C_{out}}{C_{in}}$$

(1)

where $\eta$ was the removal efficiency, %; $C_{in}$ and $C_{out}$ respectively referred to the TVOCs of inlet and outlet of one VOCs control device, mg m$^{-3}$.

2.5 Calculation of Emission Factor

VOCs emissions of typical solvent-used industry were mainly from the use of paint, paint thinners, hardeners, adhesives and detergents etc. Based on the total annual consumption of VOCs-containing raw and auxiliary material, its percentage of VOCs, collective efficiencies and measured removal efficiencies of VOCs treatment technologies in certain process, the mass balance approach was used to estimate VOCs emission (Cheng et al., 2018). The related data were presented in SI Table S2. Accordingly, the process-based VOC emission factors could be established according to Eq. (2).

$$EF = \sum_{i=1}^{n} \frac{M_i \times C_i}{(1 - \omega \eta)}$$

(2)

where EF was the VOCs emission factor per unit of VOCs-containing raw and auxiliary material, kg kg$^{-1}$; $M_i$ was the amount of raw or auxiliary material i used, kg; $C_i$ was the VOCs content of raw or auxiliary material i, %; $\omega$ was the collective efficiencies; $\eta$ was the removal efficiencies of VOCs treatment technologies.

2.6 Estimation of the Photochemical Reactivity (PR)

The methodologies of measuring the photochemical reactions mainly include OH radical reaction rate method, equivalent-propylene concentration method and maximum incremental reaction activity method (MIR), etc. (Atkinson, 1990; Chameides et al., 1992; Derwent et al., 1996; Carter, 2010). In this study, MIR was used to calculate the OFPs of VOCs emitted from the solvent-used industries in Hangzhou (Martien et al., 2003; Liu et al., 2016). The calculation can be expressed by Eq. (3):

$$OFP_j = \sum_{i=1}^{n} X_{ij} \times MIR_i$$

(3)

where OFP$_j$ referred to the ozone formation potentials of the jth process, g O$_3$ (g VOCs)$^{-1}$. $X_{ij}$ referred to the weighted percentage of ith VOCs in the jth process. MIR referred to the MIR value of the ith VOC species, g O$_3$ (g VOCs)$^{-1}$, and these values from (Carter, 2010) were presented in Table S6 of the supplementary materials.

3 RESULTS AND DISCUSSION

3.1 The VOCs Removal Efficiencies of Treatment Technologies and Process-based VOC Emission Factors

The removal efficiencies of VOCs treatment technologies were shown in Table 1. Among them,
Table 1. The process-based VOC emission factors and the removal efficiencies of VOCs treatment technologies.

<table>
<thead>
<tr>
<th>Company code</th>
<th>Source</th>
<th>VOCs treatment technology</th>
<th>Process</th>
<th>Removal efficiency (%)</th>
<th>Emission factor (kg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Color steel spraying</td>
<td>Low-temperature plasma</td>
<td>Paint spraying</td>
<td>5.8</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Drying</td>
<td>11.9</td>
<td>0.34</td>
</tr>
<tr>
<td>B</td>
<td>Car spraying</td>
<td>High-temperature incineration</td>
<td>Electrophoresis drying</td>
<td>90.2</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Spray drying</td>
<td>95.9</td>
<td>0.11</td>
</tr>
<tr>
<td>C</td>
<td>Metal material spraying</td>
<td>Adsorption-desorption combined with catalytic combustion</td>
<td>Paint spraying and drying</td>
<td>36.8</td>
<td>0.18</td>
</tr>
<tr>
<td>D</td>
<td>Printing</td>
<td>High-temperature incineration</td>
<td>Coating</td>
<td>93.0</td>
<td>0.20</td>
</tr>
<tr>
<td>E</td>
<td>Printing</td>
<td>Activated carbon adsorption combined with condensation</td>
<td>Printing</td>
<td>-43.5</td>
<td>0.79</td>
</tr>
<tr>
<td>F</td>
<td>Post-printing coating</td>
<td>Activated carbon adsorption combined with condensation</td>
<td>Coating</td>
<td>41.3</td>
<td>0.38</td>
</tr>
<tr>
<td>G</td>
<td>Stereotype of synthetic fiber</td>
<td>Water spray combined with static fixture</td>
<td>Stereotype</td>
<td>24.1</td>
<td>0.46</td>
</tr>
</tbody>
</table>

The removal efficiency of high-temperature incineration was the highest. The VOCs removal efficiency of high-temperature incineration was mainly influenced by temperature, gas flow, and VOCs concentration etc. (Shao, 2019). In the three applications, the VOCs removal efficiencies of high-temperature incineration were greater than 90.0% since the furnace temperatures and VOCs concentrations were relatively high and the flow rates were only 5000 m³ h⁻¹. The removal efficiencies of activated carbon adsorption combined with condensation technology and adsorption-desorption combined with catalytic combustion technology were medium, 41.3% and 36.8%, respectively. In addition, the water spray combined with electrostatic technology and low-temperature plasma technology had low removal efficiencies. Removal efficiency of activated carbon adsorption technology was ~43.5%. The adsorption of activated carbon was a phase equilibrium process of adsorption and dissociation. When the adsorption was saturated without timely replacement or desorption regeneration, the desorption surpassed the adsorption, then the removal efficiency was negative (Khan and Kr. Ghoshal, 2000). Therefore, the enhanced supervision and maintenance for applying activated carbon adsorption technology were urgently needed in Hangzhou.

The measured emission factors of different processes in solvent-used industry varied greatly. As shown in Table 1, printing process had the highest emission factor of 0.79 kg kg⁻¹, which was much higher than the average of printing industry in Zhejiang province (0.48 kg kg⁻¹, calculated by mass balance approach) (Wang et al., 2018). This may be related to the extensive use of solvent-based raw and auxiliary materials and the low removal efficiency of activated carbon adsorption. The emission factors of post-printing coating, stereotype of synthetic fiber, paint spraying and drying had relatively high emission factors, with a range of 0.34 to 0.49 kg kg⁻¹. And the emission factor of electrophoresis drying was the lowest (0.06 kg kg⁻¹), far below the average level of metal painting industry in Zhejiang province (Wang et al., 2020). This may be related to low VOCs content of electrophoretic paint and high removal efficiency of high-temperature incineration. The emission factors differed by dozens of times in different processes, which also indicated the study of process-based emission characteristics was necessary.

3.2 Mass Concentration Ratio of VOCs

In this study, total 109 VOCs substances were detected, and 89 VOCs (> 99%) from collected samples were normalized by weight, including alkanes, alkenes, aromatics, chlorinated hydrocarbon, alcohols, aldehydes, ketones, etc. The top 20 VOCs (> 90%) were selected for detail analysis, which were shown in Tables S3, S4 and S5. The 20 VOCs were divided into four categories: alkanes, alkenes, aromatics and others.

As shown in Fig. 2, aromatics and alkanes accounted for more than 76.5% in all samples. In paint spraying and drying process of Company A, aromatics were the dominant VOCs, with contributions of 83.4% and 84.3%, respectively. The alkanes followed, accounting for 11.8% and 12.6%, respectively. In electrophoresis drying and spray drying process of Company B, the measured VOCs showed some difference. In electrophoresis drying process, aromatics were dominant (61.6%) and
alkanes accounted for 21.3%. In spray drying process, alkanes dominated, accounting for 85.2%, and aromatics only accounted for 6.5%. In paint spraying and drying process of Company C, the contributions of alkanes were very similar, about 50%. But the contribution of aromatics in paint spraying process was 16.0%, higher than that in drying process. Yuan et al. (2010) and Tian et al. (2017) found the VOCs emitted from the paint spraying process were mainly aromatics and alkanes, which were similar to the results in this study.

In coating process of Company D, aromatics accounted for 69.9%, and alkanes accounted for 20.2%. In printing process of Company E, alkanes (52.5%) contributed more than aromatics (33.0%). There were some differences compared with other studies. The VOCs emitted from the printing industry in Beijing were mainly alkanes and aromatics, accounted for 66.7% and 31.6%, respectively (Yuan et al., 2010). But VOCs emitted by the printing industry in Nanjing were mainly alcohols and alkanes (Xie et al., 2018). These differences may be caused by the different paint used and local standard or polies implemented in printing industry.

In printing & dyeing industry, aromatics and alkanes accounted for more than 95.4%. In the post-printing coating process of Company F, aromatics and alkanes respectively accounted for 52.5% and 42.9%. As for the fiber stereotype process of Company G, there were basically all aromatics (up to 92.1%). In Han’s research, alkanes, alcohols and benzene were the main VOCs in the exhaust gas from the setting machine (Han, 2017). Zhang et al. (2020) stated that the main components of textile printing & dyeing were alkanes (34%), OVOCs (25%) and aromatic hydrocarbons (23%) in Zhengzhou. These were quite different from our research. Nevertheless, the exhaust gas was collected from the heat setting stage of cotton in Han’s (2017) research and the exhaust gas was from the fugitive emission in Zhang et al.’s (2020) research. These differences in processed materials and sampling methods etc. made direct comparisons difficult.

3.3 Process-based VOCs Source Profiles

As a variety of VOCs were detected and the top 10 species contributed more than 90% or even 95% of the total VOCs concentration, so simplified process-based VOCs source profiles were formed to highlight the necessary pollution characteristics.

3.3.1 Painting industry

Fig. 3 showed the main VOCs compositions in different processes of painting industry, mainly including toluene, m-xylene, n-undecane, n-decane, n-butene and styrene. The details were shown in Table S3. As can be seen, the paint spraying process of Company A mainly produced toluene, accounting for 70.9%. And the TEX species (toluene, ethylbenzene and m-xylene) were the main species produced in drying process, with toluene accounting for the largest percentage (40.2%).
followed by m-xylene (20.8%) and ethylbenzene (11.4%). As for Company B, the process of electrophoresis drying mainly produced toluene, accounting for 52.0%, while the spray drying process mainly produced n-undecane and n-decane, accounting for 42.6% and 29.6%, respectively. The major species from drying process of Company C were n-undecane, styrene, butene and n-decane, accounting for 22.3%, 19.8%, 19.7% and 16.4%, respectively; and the painting process mainly produced styrene, n-undecane and n-decane, accounting for 29.9%, 21.6% and 16.0%, respectively. In total, the aromatics and the heavy hydrocarbons were the dominant VOCs produced in painting industry, which demonstrated that the solvent-based products still played an important role in the painting industry in Hangzhou (Li et al., 2018; Wu et al., 2020).

3.3.2 Printing industry
The major VOCs compositions in coating and printing process of printing industry were illustrated in Fig. 4. In coating workshop of Company D, propylbenzene and n-undecane accounted for 24.5% and 11.8%, respectively. The other VOCs contributing over 5% were m-ethyltoluene (9.4%), 1,2,4-trimethylbenzene (7.0%), and 1,2,3-trimethylbenzene (6.3%). The exhaust gas from printing workshop of Company E were mainly n-undecane, n-dodecane, styrene and n-decane, accounting for 27.7%, 16.2%, 8.9% and 8.6%, respectively. Compared with other studies, the compositions of VOCs in Hangzhou from printing industry were quite different. Isopropanol, ethanol and 1-hexene were the main VOCs emitted by the gravure process in Nanjing (Xie et al., 2018). The printing industry in the Pearl River Delta mainly emitted ethyl acetate, isopropanol, 2-butanone and toluene (Yang et al., 2013). The source profile was not only closely related to raw materials and products but also inseparable from the process technology. Thus, developing the localized process-based source profiles was imperative, which could help us identify emission characteristics and formulate better control strategies.

3.3.3 Printing & dyeing industry
As shown in Fig. 5, toluene was the most abundant species in both post-printing coating process and stereotype of synthetic fiber, accounting for 46.1% and 91.7%, respectively. In post-printing coating process of Company F, the other major VOCs were n-undecane and n-decane, accounting for 17.8% and 11.7%, respectively. Compared with the components emitted from painting industry and printing industry, the VOCs from the printing & dyeing industry were less diverse.
This was mainly related to the relatively simple types of solvent used in printing & dyeing industry.

### 3.4 Process-based Ozone Formation Potentials

As can be seen from the Fig. 6, the OFPs of VOCs emitted from different processes in different industries varied greatly. The OFPs of VOCs in drying process of coating Company A was the highest, 5.0 g g⁻¹, followed by that in coating workshop of Company D and paint spraying process.
of Company A, and their OFPs were 4.4 g g⁻¹ and 4.1 g g⁻¹, respectively. The VOCs emitted by spray drying process of company B had the lowest OFPs, which was 1.0 g g⁻¹. The OFPs of VOCs emitted by solvent-used industries in Hangzhou almost derived from aromatics, olefins and alkanes. Specifically, the contribution of aromatics to the OFPs was the highest except the spray drying process of Company B and drying process of Company C. Therefore, priority control should be given to the aromatics in solvent-used industries.

The total percentages of top 5 species based on OFPs accounted for 50.6%–99.6% in all tested samples, as shown in Fig. 7. For specific components, toluene made a great contribution to both OFPs and emissions in paint spraying process of company A, electrophoretic drying process of Company B, post-printing coating of Company F and stereotype process of Company G. In particular, the contribution of toluene to OFPs in post-print coating of Company F and stereotype of Company G even reached 75.8% and 98.3%, respectively. Thus, toluene should be controlled first in these processes. The meta-xylene and toluene in drying process of Company A and styrene in paint spraying process of Company C had higher contributions to OFPs and emission, which should be given priority to be controlled. As for the drying process of Company C, n-butene contributed 65.8% to the OFPs with only 19.8% emission, which was the key component of control. However, the n-undecane and n-decane in spray drying process of Company B had a great contribution to the OFPs, aproaching 46.7%, which was quite different from its emissions (72.2%). This was mainly due to the low reactivity of alkanes. For printing industry, 1,2,3-trimethylbenzene, m-ethyltoluene, 1,2,4-trimethylbenzene, propylbenzene and 1,3,5-trimethylbenzene were the major species contributing to OFPs in coating workshop of Company D. And 1,2,3-trimethylbenzene, m-xylene, 1,2,4-trimethylbenzene, propylene and n-undecane were the top five species in printing workshop of Company E. The top five species contributing to the OFPs in these two processes were relatively low, only about 50%, and the contributions of each species had little difference, which indicated that these species should all be given more attention without priority. Preferential species to control changed with different processes, which also demonstrated the necessity of process-based VOCs source profiles.

3.5 The Effects of VOCs Treatments on VOCs Source Profiles and Ozone Formation Potentials

The ozone formation potentials would be affected by VOCs treatment technologies through changing the VOCs source profiles. As can be seen in Table S3, the mass concentration ratios of toluene and propylene in the process of color steel spraying reduced greatly after low-temperature plasma treatment. Due to the lower ionization energy, aromatic hydrocarbons and olefins with higher MIR value were more likely to be ionized and degraded by low-temperature plasma technology compared with alkanes. From Table S5, the mass concentration ratios of most aromatics
and alkanes with higher boiling points except n-undecane in the process of post-printing coating decreased by the combined technology of activated carbon adsorption and condensation. This may be related to the better ability of the activated carbon adsorption combined with condensation technology to remove VOCs with higher boiling points. Therefore, the adoption of low-temperature plasma technology and the combined technology of activated carbon adsorption and condensation was beneficial to reduce the OFPs as shown in Fig. 8.

However, for the process of Company C, E and G (shown in Tables S3, S4 and S5), the VOCs source profiles changed little after the treatment of adsorption-desorption combined with catalytic combustion, activated carbon adsorption and water spray combined with electrostatic. These technologies had no selectivity to remove certain types of VOCs, especially highly reactive VOCs, thus had no ability to significantly reduce the OFPs for unit mass.

In addition, the pyrolysis and chemical reaction would be easy to occur at high temperature. So great differences existed in the VOCs source profiles after high-temperature incineration treatment in the process of company B and D, as shown in Tables S3 and S4. In the process of electrophoresis drying and spray drying of Company B, due to the pyrolysis of toluene, n-decane and n-undecane and subsequent recombination, the mass concentration ratios of m-xylene, styrene and 1-butene significantly increased. And in the coating process of Company D, the mass concentration ratios of m-ethyltoluene, p-diethylbenzene and n-decane etc. in VOCs source profiles improved with the propylbenzene and n-undecane degrading. The mass concentration ratios of aromatics and olefins with high MIR went up after applying high-temperature incineration technology, so the OFPs increased, as shown in Fig. 8.

4 CONCLUSIONS

The VOCs removal efficiencies of different treatments and process-based VOCs emission factors were evaluated. Then, the local process-based VOCs source profiles were built and corresponding OFPs were calculated to screen out priority control species of VOCs. In addition, the effects of VOCs removal technologies on VOCs source profiles and OFPs were discussed.
Fig. 8. Process-based OFPs profiles for unit mass before and after different treatments. (A: low-temperature plasma; B: high-temperature incineration; C: adsorption-desorption with catalytic combustion; D: high-temperature incineration; E: activated carbon adsorption; F: activated carbon adsorption with condensation; G: water spraying with static electricity treatment.)

The removal efficiency of high-temperature incineration was highest, averagely 93.0%. The emission factors of different processes varied greatly, ranging from 0.06 to 0.79 kg kg⁻¹. The process-based VOCs source profiles showed aromatics and alkanes were the main VOCs in typical solvent-used industry in Hangzhou. And the aromatics was the largest contributor to OFPs for most processes, which indicated the priority should be given to controlling the aromatics to reduce OFPs.

More specifically, toluene, meta-xylene, n-butene, styrene and ortho-xylene should be preferentially controlled in painting industry and printing & dyeing industry. For printing industry, the proportions of top five species in each process contributing to the OFPs were relatively low and balanced, which indicated that these species should be given more attention without priority.

Most technologies had no selectivity to remove certain types of VOCs. Nonetheless, the adoption of low-temperature plasma technology and activated carbon adsorption combined with condensation technology would be beneficial to remove aromatics and olefins with higher MIR, thus decreased OFPs. And the OFPs may increase due to the pyrolysis and chemical reaction after high-temperature incineration treatment.

The emission characteristics of VOCs proved the local process-based source profiles were significant and imperative. What’s more, the process-based source profiles provided evidences for the precise control of VOCs pollution, which could also serve as an important supplement to the rough source profiles of solvent-used industries in Yangtze River Delta.

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SUPPLEMENTARY MATERIAL

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