

Segment-based Volatile Organic Compound Emission Characteristics from Different Types of Coking Plants in China

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ABSTRACT

The source profiles, emission factors, and chemical reactivity of volatile organic compounds (VOCs) generated by two typical coking plants, one employing a non-recovery process and the other, a mechanical process, in Shanxi Province, a major coking hub in China, were determined for different segments of coke production during normal operations. The primary components in the stack flue gas were ethylene, 1-butene, benzene, acetylene, and 2,2-dimethylbutane for the non-recovery plant and styrene, benzene, and ethylene for the mechanical plant. The fugitive emissions were also monitored at the mechanical plant, and the most abundant species leaking from the oven were benzene, toluene, ethane, *m*-xylene, and ethylene, whereas those leaking from byproducts were benzene, propane, ethane, ethylene, *n*-pentane, *n*-butane, isobutene, 1-butene, toluene, and propylene. The stack flue gas at the non-recovery and mechanical coking plants exhibited VOC emission factors of 96 g Mg⁻¹-coke and 0.4 g Mg⁻¹-coke, respectively; thus, VOCs released by the former merit greater concern. Since the highest ozone formation potential (OFP) was observed for the stack flue gas at the non-recovery plant (80.26 mg m⁻³), followed by fugitive oven emissions at the mechanical plant (7.22 mg m⁻³), controlling these VOCs will significantly reduce their conversion into ozone. Overall, replacing non-recovery coking plants with mechanical coking plants will decrease VOC emissions and improve the ambient air quality in China.

Keywords: Volatile organic compounds, Source profiles, Emission factors, Coking plant, Coking segments

1 INTRODUCTION

Coking, which involves heating coal to approximately 1000°C in the absence of oxygen, is a manufacturing process that converts coal into coke, coke oven gas, and byproducts. China is the largest coke producer in the world, with a yield of 431 million tons in 2017, accounting for approximately 68% of global coke production (CCIA, 2019). Additionally, China is one of the largest global exporters of coke, with exports of approximately 8 million tons in 2017, accounting for 28% of global coke exports (United Nations, 2019).

Mechanical coking is a major coking technology in China, yielding 386 million tons in 2017 (CCIA, 2019). Although coke yields of non-recovery coking process declined sharply due to strict policies

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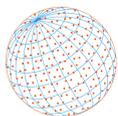
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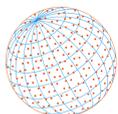


implemented from 2008–2014, it still accounted for 8 million tons of coke in 2017 (CCIA, 2019). Mechanical coking plants produce coke in a carbonization chamber, then recover the byproducts from the coke oven gas, including tar, benzene, and ammonia. Differently, in non-recovery coking plants, the byproducts are burned and the heat is recovered during the coal conversion process (He, 2006). The emission pathways of pollutants vary with different coking process. Pollutants can be discharged into atmosphere from stack, coke oven leaks, or the byproduct production area in a mechanical coking plant. However, for non-recovery coking plants, pollutants are predominantly emitted from the stack; coke oven leaks can be neglected under the negative pressure conditions of the coke oven. Previous studies have found that pollutants such as particulate matter, nitrogen oxide, sulfur dioxide, toxic metals, polycyclic aromatic hydrocarbons (PAHs), and volatile organic compounds (VOCs) are released into the environment during coke production (Mu *et al.*, 2012; Liu *et al.*, 2014; Mu *et al.*, 2014). VOCs emitted from the coking process account for the largest proportion (12.8%) of all VOCs emitted from industrial processes (Wu *et al.*, 2017). Long-term exposure to these pollutants, especially PAHs and VOCs, can lead to adverse health effects in coke plant workers (He *et al.*, 2015).

The source profiles and emission factors of VOCs are key information for establishing VOCs emission inventories, source apportionment, environmental management, etc. VOCs source profiles and emission factors have been widely researched in the USA, and the results have been integrated into the SPECIATE 4.5 database (U.S. EPA, 2016) and EPA AP-42 (U.S. EPA, 2008), respectively. The emission factors of various sources have also been identified in other countries, such as Denmark (EMEP, 2016) and UK (NAEI, 2018). Considering the large uncertainty inherent in referencing the results from other countries, scientists in China have recently obtained some VOCs' domestic source profiles and emission factors (Shi *et al.*, 2015; Yan *et al.*, 2016; Zhong *et al.*, 2017; Shen *et al.*, 2018; Yang *et al.*, 2018; Zhang *et al.*, 2018; Zhong *et al.*, 2018). For example, for the coking industry, He (2006) reported that C4 and C6 hydrocarbons are the most abundant VOCs in the coking oven stack flue gas from a coke plant, whereas C6 and C8 hydrocarbons are dominant in coal charging and coke discharging. By comprehensively evaluating the coking process and VOCs from the top of the coke oven, Li (2009) revealed that the major VOCs emissions from coke production are benzene, ethane, ethylene, propylene, toluene, propane, and 1-butene. Jia *et al.* (2009) identified the major VOCs species of coke oven gas as ethylene, ethane, propene, propane, benzene, toluene, and xylene, and showed that the concentration of VOCs from the coal charging process is significantly higher than that from coking. Moreover, Shi *et al.* (2015) showed that toluene and *n*-hexane are the most abundant species in coke production, whereas Li *et al.* (2018) found that the five most abundant species emitted from the coking process are acetylene, benzene, ethane, toluene, and propene, accounting for > 86% of total VOCs. The source profiles of VOCs for the coking process differ between different studies. This suggests that VOCs from different emission segments or processes may affect the overall source profile for coke production.

In terms of VOCs emission factors from Chinese coke production, He (2006) calculated a VOCs emission factor via stack flue gas of 487.16 g Mg⁻¹-coke. Emission factors of VOCs from coal charging (56.84 g Mg⁻¹-coke) and coke discharging (1.26 g Mg⁻¹-coke) have also been reported by Li (2009). In the emission factor guidebooks of U.S. EPA (2008), NAEI (2018), and EMEP (2016), the emission factors of VOCs were given as 68 g Mg⁻¹-coke, 41 g Mg⁻¹-coke, and 47 g Mg⁻¹ coal, respectively. This difference between VOC emission factors from different studies could lead to uncertainty in emission estimates. Moreover, previous source profiles only consider the coking process of mechanical coking plants, neglecting coke oven leaks and byproduct production as well as the coking process in non-recovery coking plants; therefore, the existing source profiles may not accurately reflect VOCs emissions from different coking segments. As such, it is crucial to determine localized VOCs source profiles and emission factors based on different emission segments within different types of coking plants in China, specifically, mechanical and non-recovery coking plants.

Shanxi is the largest coke production province in China (Fig. S1) (National Bureau of Statistics of China, 2018; MIIT, 2019), which produced approximately 84 million tons of coke in 2017, accounting for 19% of total coke production in China (National Bureau of Statistics of China, 2018). Statistics data also showed that Chinese coking plants are predominantly concentrated in Shanxi Province, which boasts approximately 67% of domestic mechanical coking plants and 34%



of domestic non-recovery coking plants (MIIT, 2019). A typical non-recovery coking plant and mechanical coking plant in Shanxi are investigated in this study. To evaluate the emission segments from two types of coking plant, samples are collected directly from the stack (non-recovery coking plant and mechanical coking plant) and from emission leaks from the coke oven and byproducts in the mechanical coking plant. The primary objectives of this study are to: (1) establish and compare the VOCs source profiles based on emission segments; (2) calculate the emission factors of VOCs emitted from the stack in different types of coking plants; and (3) investigate the source chemical reactivity of VOCs to access the potential effects of different emission segments on ozone generation.

2 MATERIALS AND METHODS

2.1 Description of Sampling Coking Plant

Two typical coking plants, a non-recovery coking plant and a mechanical coking plant, were selected to obtain the source profiles of VOCs from different emission segments. The coking plants locate in Shanxi Province, a centralized coking plant area in China. Designed annual yield of coke of non-recovery and mechanical coking plant is 0.5 million tons and 1.6 million tons with the operating load is 75% and 75% during the sampling time, respectively. The height of the coke oven in the non-recovery and mechanical coking plant is 2.1 m and 4.3 m, respectively. Detailed information of the coking plants is listed in Table 1. It is important to note the cleaned coal for coking is put into the furnace directly through a closed cleaned coal conveyance corridor in non-recovery coking plant. As the predominantly emitted pathway of pollutants in non-recovery coking plant, stack flue gas is the target in this study. While coke oven leakage is ignored due to the negative pressure conditions of the coke oven during the normal operation. Like most mechanical coking plants, metallurgical coke is produced in coke oven under the positive pressure condition and chemical products, including tar, benzene, and ammonium sulfate, come from coal gas recovery in this studied mechanical coking plant. VOCs can leak from coke oven and pipeline in these processes. Thus, the stack flue gas, oven leaks, and byproduct plant leaks are all investigated in the mechanical coking plant in this study. Samples were collected from the stacks after desulfurization and dedusting.

2.2 Sample Collection

A flow chart of coke production and the VOC sampling sites (A–D) are shown in Fig. 1. The sites included stack flue gas from the non-recovery coking plant (SFN; Site A) and stack flue gas (SFM; Site B), oven leaks (OLM; Site C), and byproduct plant leaks (BLM; Site D) from mechanical coking plant. The sampling sites of stack flue gas (Sites A–B) were monitoring holes installed on the chimney at approximately 10–22 m above the ground. The stack flue gas

Table 1. Characteristics of the two coking plants.

	Non-recovery coking plant	Mechanical coking plant
Long × wide × height of coke oven (m)	20 × 3 × 2.1	14.08 × 0.5 × 4.3
Oven battery	4	2
Campaign age of oven (a)	~15	~15
Designed annual yield (t)	500,000	1,600,000
Operating load (%)	75	75
Coking time (h)	72	21
Stack height (m)	38	100
Terminal control facilities (efficiency)	Electrostatic-fabric integrated dedusting (99%) Wet limestone-gypsum desulfurization (96%)	Bag filter dedusting (99%) Wet oxidative desulfurization (99%)
Byproducts	Non-recovery	Crude benzene, ammonium sulfate, coal tar

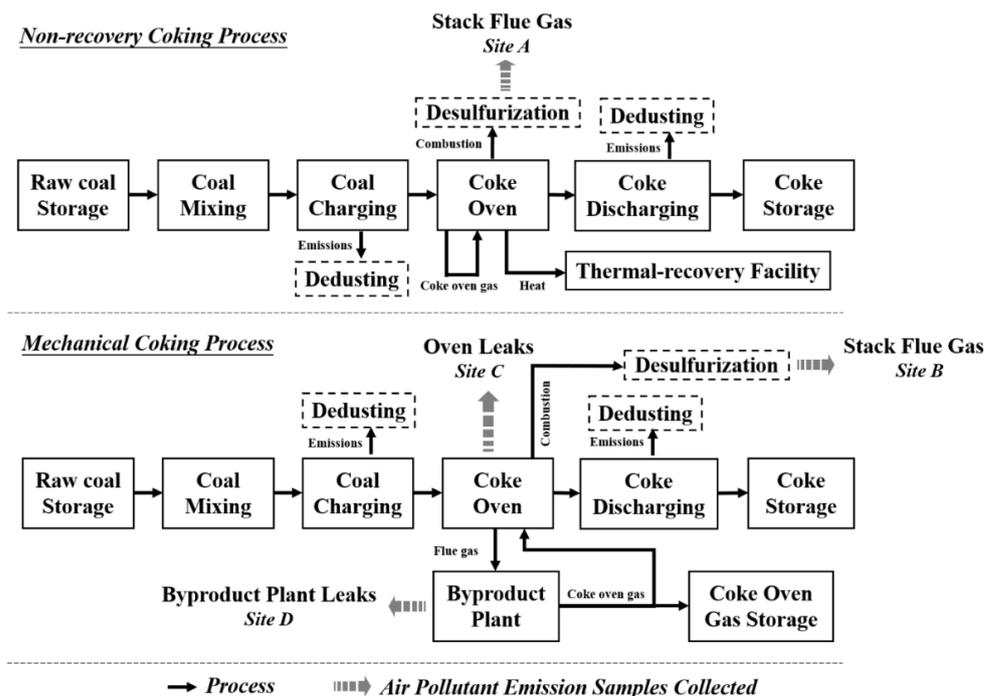
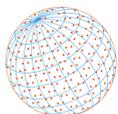


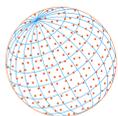
Fig. 1. Flow chart of coke production and VOCs emission sampling sites.

was collected after the byproducts burning and heat recovering in non-recovery coking plant, while different, it was gathered after byproducts recovery in mechanical coking plant. The samples were collected in Tedlar bags (with a volume of 2 L), which are made of Teflon and covered in black plastic. During sampling, the sampling bags were connected to a stainless-steel tube, whose length was enough sufficient to reach into the stack through the sampling holes, and a sampling pump (LP-4™; A.P. Buck Inc., USA), in which all interfaces were sealed. Samples were pumped into the sampling bags at the flow rate of 1.0 L·min⁻¹ for a sampling duration of 2 min. To sample fugitive emissions, i.e., leaks, stainless-steel SUMMA canisters (1.0 L Silonite® Canisters; Entech Instruments Inc., CA, USA), pre-cleaned with high-purity nitrogen and evacuated to vacuum then equipped with a restricted sampler (39-RS-0; Entech Instruments Inc., CA, USA) were used to collect the instantaneous samples for a sampling duration of 5 min. The sampling sites (Sites C–D) were located at the top of the coke oven according to the State Standard of the People’s Republic of China (GB 16171-2012) and approximately 20 m downwind of the byproduct production workshop area, respectively. Parallel experiments were conducted whereby samples were collected from the same sampling point at least three times to ensure that the results were representative.

2.3 Chemical Analysis

The Model 7100 Preconcentrator (Entech Instruments Inc., USA) coupled with a gas chromatography-mass selective detector/flame ionization detector (7890A/5975C GC-MSD/FID; Agilent, USA) was used to detect the compounds in each sample. A detailed description of the analytical method can be found in previous studies (Wang *et al.*, 2010; Yan *et al.*, 2015; Yan *et al.*, 2017; Li *et al.*, 2018). Briefly, the samples were first pumped into the Preconcentrator to enrich the VOCs with tertiary cold hydrazine and remove H₂O and CO₂. Then, the trapped VOCs were rapidly vaporized and transferred to the GC-MSD system for analysis. The methods, materials, and parameters of the analysis system are shown in Table S1.

The retention times and mass spectra were selected to identify the target compounds, and the multi-point external calibration method was used for quantitative analysis. 100 ppbv of standard Photochemical Assessment Monitoring Stations (PAMS) gas (Spectra, USA) was dynamically diluted to 0.5, 1, 5, 15, 50, and 100 ppbv. Then, the calibration curve was drawn based on the response signal for each of the five concentration levels. A total of 47 VOCs were detected in this study (Table S2), the sum of which was defined as *total VOCs*.



2.4 Quality Control and Quality Assurance

As described by Yan *et al.* (2015), humidified zero air was used to clean all sampling bags (or canisters) repeatedly to guarantee vacuum conditions before sampling. One or two of the cleaned sampling bags (or canisters) were randomly selected for blank tests. The blank sampling bags (or canisters) were filled with high-purity nitrogen and analyzed using the same procedure as for the field samples. When no target VOCs were detected or the concentration was lower than the method detection limits (MDLs; approximately 11–72 pptv of various target VOCs species), the sampling bags (or canisters) was perceived as clean and free from contamination. A reference standard (typically 1 ppbv) was selected for detection every day before sample analysis, and the concentration was obtained from the calibration curve. Recalibration was performed if the deviation between the detected concentration and the theoretical concentration was beyond $\pm 15\%$. The relative standard deviation (RSD) of the target VOCs obtained by repeated experiments should be within 10%.

2.5 Data Analysis

The coefficient of divergence (COD) calculated using Formula (1) (Massoud *et al.*, 2011) was usually used to estimate the comparability between two different source profiles. The COD value ranges from 0 to 1, where a value closer to 0 indicates that the source profiles are more similar:

$$COD_{ij} = \sqrt{\frac{1}{p} \sum_{k=1}^p \left(\frac{x_{ki} - x_{kj}}{x_{ki} + x_{kj}} \right)^2} \quad (1)$$

where, COD_{ij} is the COD value between source profile i and source profile j , p is the number of the species, and x_{ki} and x_{kj} are the proportion of the k^{th} species in source profile i and source profile j , respectively.

The emission factors (EFs) were expressed in grams of pollutants per megagram of coke yield (g Mg^{-1}), which partly reflects the intensity of the emission sources. It was calculated using Formula (2):

$$EF(\text{g Mg}^{-1}) = \frac{C \times F}{M} \times 10^3 \quad (2)$$

where C is the mass concentration of total VOCs (mg m^{-3}), F is the flow rate of flue gas in the stack ($\text{m}^3 \text{h}^{-1}$), and M is the weight of the coke yield per hour (kg h^{-1}).

The ozone formation potential (OFP) is typically used to assess the reactivity of VOCs' transformation to ozone under optimal photochemical conditions. It was calculated by multiplying the mass concentration of individual VOCs by the corresponding maximum incremental reactivity according to Formula (3):

$$OFP_i = [VOCs_i] \times MIR_i \quad (3)$$

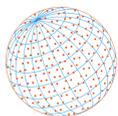
where OFP_i is the ozone formation potential of the i^{th} species (mg m^{-3}), $[VOCs_i]$ is the mass concentration of i^{th} species (mg m^{-3}), and MIR_i is the maximum incremental reactivity for the i^{th} species ($\text{g-O}_3 \text{ g-VOCs}^{-1}$) (Carter, 2010).

3 RESULTS AND DISCUSSION

3.1 Source Profile Characteristics

3.1.1 Segment-based VOC emissions and source profiles

The overall source profiles were established using the average weight fraction for different coking plant emission segments (SFN, SFM, OLM, and BLM) to illustrate the emission characteristics of VOCs in different types of coking plant. A total of 47 VOC species developed by the U.S. EPA PAMS program, which exhibit high reactivity in photochemical reactions, were quantified in this study. The average mass concentration of total VOCs from SFN, SFM, OLM, and



BLM were 11.65 mg m^{-3} , 0.63 mg m^{-3} , 2.32 mg m^{-3} and 0.27 mg m^{-3} , respectively (Fig. 2). The high emission levels of SFN and OLM imply that the non-recovery coking plant and coke oven of the mechanical coking plant pose more serious risks to humans and the ecological environment.

All monitored VOCs species were categorized into four groups, i.e., alkanes, alkenes, alkynes and aromatics (Table S2). As shown in Fig. 2, aromatics were the most abundant compounds of SFM, OLM, and BLM, accounting for 69.17%, 72.57%, and 45.97% of the total VOCs, respectively. The VOC patterns which is mainly characterized by aromatics from different emission segments are similar in the same coking plant and that fugitive leakage should not be ignored during the manufacturing process. On the contrary, the proportion of alkenes to total VOCs was 70.13% for SFN, implying that the overall source profile varies significantly in different plants with different production engineering.

The concentration of aromatics increases during the process of coal gasification due to the cracking of polycyclic aromatic hydrocarbons contained in the coal (Dong *et al.*, 2012). Moreover, some small molecules, such as alkanes, alkenes, alkynes, and other active reactants for aromatic formation derived from the breakdown of coal, were formed in relatively large concentrations of aromatics via some relevant byproduct reactions of the mechanical coking process, including cyclization, recombination, and dehydrogenation (Richter and Howard, 2000). Conversely, in the non-recovery coking plant, all coke oven gas and byproducts were sufficiently burned and converted to heat. Numerous small molecules were simultaneously released through the chimney throughout the coking process as a result of the high concentration of low carbon alkenes emitted from the stack flue gas in the non-recovery coking plant.

3.1.2 Segment-based individual VOC species profiles

The source profiles of individual VOC species were also established using the average weight fraction of the four emission segments determined during field sampling, and the results are shown in Fig. 3. As shown in Fig. 3(a), the most abundant components of the stack flue gas in the non-recovery coking plant were ethylene (42.51%), 1-butene (26.27%), benzene (12.11%), acetylene (10.3%), and 2,2-dimethylbutane (2.06%). The sum of C2–C4 alkene hydrocarbons accounted for approximately 69.96% of total VOCs, indicating that the major components released by the non-recovery coking plant were alkene hydrocarbons of low molecular weight (C2–C4). It should be noted that 1-butene and 2,2-dimethylbutane were not appropriate as source indicator species of the stack flue gas in the non-recovery coking plant because of their multiple sources. For example, 1-butene is a major emission species of power plants (Yan *et al.*, 2016), solvent use/print ink (Wang *et al.*, 2014), LPG-related sources (Wang *et al.*, 2014; Zhang *et al.*, 2015), and iron and steel facilities (Tsai *et al.*, 2008), whereas 2,2-dimethylbutane is a potential indicator of vehicular exhaust in many regions of the world (Chang *et al.*, 2006). In contrast to stack flue gas in the non-recovery coking plant, styrene and benzene were the most abundant components of stack flue gas in the mechanical coking plant, accounting for 32.28% and 25.95% of total VOCs, respectively. The next most dominant species with an average weight fraction of 2–15% were ethylene, propane, ethane, *m*-xylene, toluene, and ethylbenzene. Moreover, high-weight-fraction benzene series were detected in the stack flue gas of the mechanical coking plant. This result was predominantly attributed to the different coking

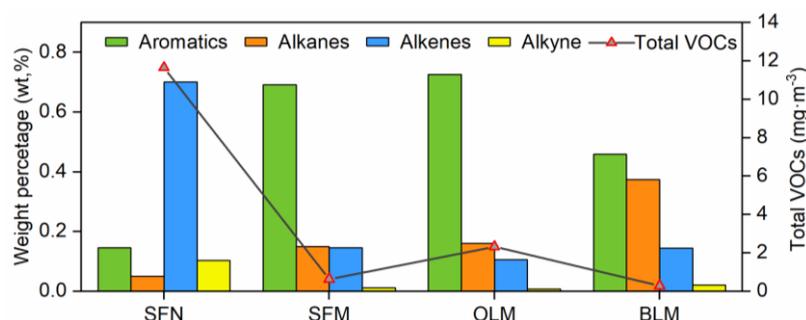


Fig. 2. Overall VOCs characteristics for different emission segments in the two coking plants.

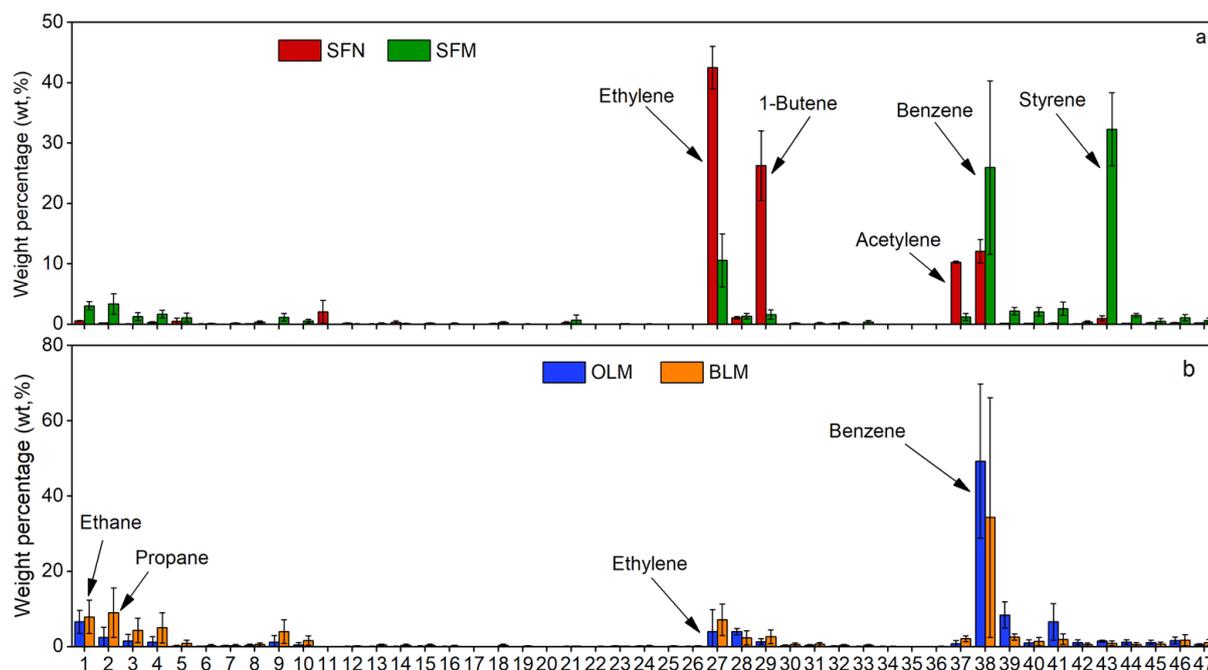
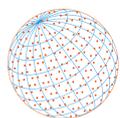


Fig. 3. VOC profiles of (a) stack flue gas (SFN and SFM) and (b) fugitive emissions (OLM and BLM). The ID number of each VOCs species is listed in Table S2.

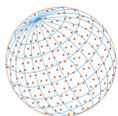
process and provides key data for source apportionment. During the mechanical coking process, the cracking of polycyclic aromatic hydrocarbons and the cyclization reaction or recombination of small molecules can generate more aromatics, as mentioned previously.

Regarding fugitive emissions, the top five species from oven leaks in the mechanical coking plant were benzene, toluene, ethane, *m*-xylene, and ethylene, accounting for 49.3%, 8.43%, 6.64%, 6.60%, and 4.06% of the total VOCs, respectively. These results agree with those of previous studies (Li *et al.*, 2018). As presented in Fig. 3(b), the major species of byproduct plant leaks from the mechanical coking plant were benzene, propane, ethane, ethylene, *n*-pentane, *n*-butane, isobutene, 1-butene, toluene, and propylene, accounting for 34.34%, 9.03%, 7.95%, 7.15%, 5.04%, 4.35%, 4.04%, 2.67%, 2.58%, and 2.38% of the total VOCs, respectively. The sum of C₂–C₄ hydrocarbons accounted for 32.04% of the total VOCs, revealing that C₂–C₄ hydrocarbons were also the main VOC components emitted from leakage from the byproduct production area in the mechanical coking plant. The VOC characteristic of byproduct plant leaks was different from stack flue gas and oven leaks in the mechanical coking plant because the crude material originates from different coking segments. Stack flue gas and oven leaks in a mechanical coking plant have a similar source for coal gasification process and combustion of coke oven gas, whereas byproduct plant leaks in a mechanical coking plant come from the byproduct recovery process of the coal gas.

3.1.3 Coefficient of divergence

As listed in Table S3, COD values between the VOCs profile in SFN and those in previous reported of coking plant (He, 2006; Jia *et al.*, 2009; Shi *et al.*, 2015; U.S. EPA, 2016) analyzed in this study were mostly in the range of 0.5–1, revealing that the profile of SFN differed substantially from the other profiles. However, the VOCs profile of non-recovery coking has either rarely been studied or the few studies have reported very small VOCs emissions from non-recovery coking (U.S. EPA, 2008). The VOCs profile of non-recovery coking plant in this study may be served as a start point for future VOCs emission research in this type coking technology. The COD value was 0.68 between SFN and SFM, which also suggests clear differences in the stack flue gas characteristics of coking plants with different technologies.

The COD values between SFM and OLM, and SFM and BLM were 0.17 and 0.51, respectively; thus, the profile of the stack flue gas was similar to that of oven leaks from the same mechanical



coking plant, but very different from that of byproduct plant leaks. This phenomenon probably reflects a change in the pattern of emission sources during the production and processing of coke as discussed previously. Note that the proportion of styrene from SFM is much higher than that from OLM; it therefore can be considered as indicator species of SFM to distinguish the profile of OLM.

3.2 Emission Factors of VOCs

Emission factors are used as essential data for building the emission inventories and for environmental management. Production engineering, equipment, fuel sources, combustion conditions, treatments, etc. are all factors influencing VOCs source emissions. The VOCs EFs for SFN and SFM were $96 \text{ g Mg}^{-1}\text{-coke}$ and $0.4 \text{ g Mg}^{-1}\text{-coke}$, respectively (Fig. 4), indicating that the emission intensity from the stack in a non-recovery coking plant is far greater than that in a mechanical coking plant. As the coke oven gas produced by the coking procedure in a non-recovery coking plant operates under negative pressure, the atmospheric pollutants are predominantly discharged through the stack to the atmosphere. However, the EFs of coke production from the mechanical coking plant only involved estimation of the VOCs emissions from the stack flue gas and neglected fugitive emissions such as coke oven and byproduct plant leaks, which partly explains the small EFs from the stack in the mechanical coking plant. As shown in Fig. 4, the EFs of alkenes and aromatics in SFN and SFM were 67.15 g Mg^{-1} and 0.29 g Mg^{-1} , respectively, representing the groups with highest emission intensity. The major species with high emission intensity in SFN were ethylene, 1-butene, benzene, and acetylene, with EFs of 40.58 g Mg^{-1} , 25.26 g Mg^{-1} , 11.71 g Mg^{-1} , and 9.89 g Mg^{-1} , respectively. For SFM, the major species were styrene, benzene, and ethylene, with EFs of 0.16 g Mg^{-1} , 0.08 g Mg^{-1} , and 0.04 g Mg^{-1} , respectively. The results of this study indicate that phasing out non-recovery coking plants in China and strongly promoting mechanical coking plants instead would help reduce VOCs emissions, especially alkene emissions, which is significant for improving the ambient air quality.

A significant difference was observed in the EFs of the mechanical coking plant analyzed in this study and those reported in previous studies around the world, such as $68 \text{ g Mg}^{-1}\text{-coke}$ in USA (U.S. EPA, 2008), $41 \text{ g Mg}^{-1}\text{-coke}$ in UK (NAEI, 2018), and $47 \text{ g Mg}^{-1}\text{ coal}$ in Denmark (EMEP, 2016). Although the EFs in this study might be lower than the actual emissions because of the limited sampling set, VOCs emissions from the stack in a mechanical coking plant may be overestimated using previous emission factors. Many factors can contribute to this discrepancy, including coal quality, coking process, flue gas treatments, etc. The conversion efficiency from coal to coke varies with the coal quality in different countries, which would lead to the change of VOCs emissions from coking production in different countries. In addition, the emissions of VOCs decreased with the upgrading of coking process and the terminal control measures of flue gas implementing. That may also be the reasons of VOCs emission factors from stack in the studied mechanical coking plant is lower than that in the others results. In terms of the EFs from

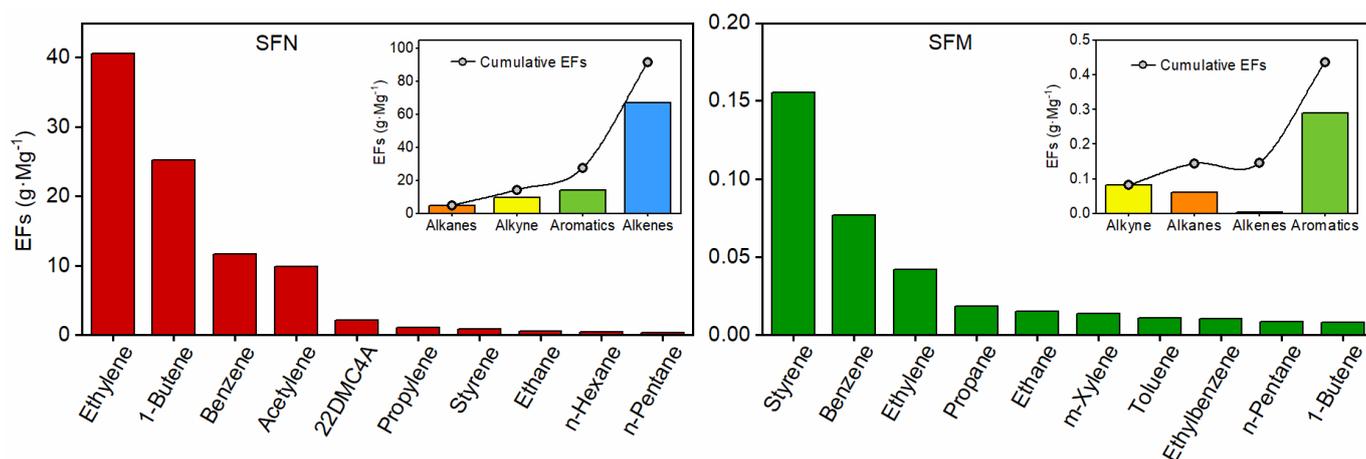
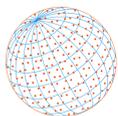


Fig. 4. EFs of major VOCs species and the four major groups emitted from SFN and SFM (22DMC4A: 2,2-dimethylbutane).



the stack in a non-recovery coking plant, there are no available EFs for VOCs emission evaluation due to previous studies reporting no significant levels of VOCs (U.S. EPA, 2008). The VOCs EFs determined for the stack in the non-recovery coking plant analyzed in this study therefore provides an important reference.

Due to the limited number and coverage of samples in this study, the segment-based VOCs source profile and emission factors will have contained large uncertainties. However, these data are relatively scarce for the coking process in China, especially for the non-recovery coking process. These results will support the existing source profile library and provide insights for assessing domestic VOCs emissions from the coking process, as well as VOCs source apportionment. Future research is required to collect more detailed samples from different segments within the coking process and expand the number of sampled coking plants.

3.3 Ozone Formation Potential

The OFP was used to assess the chemical reactivity of VOCs from different emission segments, which revealed the priority control emission source according to ozone formation. In this study, the OFP values of SFN, SFM, OLM, and BLM were 80.26 mg m^{-3} , 1.91 mg m^{-3} , 7.22 mg m^{-3} , and 0.21 mg m^{-3} , respectively. SFN with the higher emission intensity of VOCs (11.65 mg m^{-3}) and consequently to higher ozone formation on the atmosphere should be regarded as a priority emission source. However, the OFP of OLM was considerably greater than that of other sources in the mechanical coking plant, suggesting that control of leakage from the coke oven would substantially reduce the formation of ozone.

The contribution of alkanes, alkenes, alkynes and aromatics to OFP from the different segments within coking plants are shown in Fig. 5. Alkenes were the largest contributor to OFP in SFN and aromatics were the largest contributor to OFP in OLM, accounting for 94.51% and 70.18% of the total OFP, respectively. These findings are consistent with the concentration characteristics of VOCs. Then, alkenes and aromatics in SFM and BLM exhibited the most abundant contribution to OFP, accounting for 49.94% and 45.92%, and 43.33% and 40.29% of the total OFP, respectively. A difference was observed between the characteristic contribution to OFP and the concentration characteristics, suggesting that both the concentration and reactivity of VOCs should be considered in order to reduce the ozone formation of VOCs emitted from coking processes.

For single VOCs species, the top ten largest contributors to OFP from the different emission segments in the coking plants are shown in Fig. S2. Ethylene, propylene, 1-butene, benzene, toluene, xylene, and trimethylbenzene were the largest contributors to the OFP from the four emission segments, indicating that these VOCs are the major pollutants that should be controlled in coking plants.

4 CONCLUSIONS

We measured the VOCs emitted from various segments of coke production at a non-recovery plant and a mechanical coking plant in China and then analyzed the source profiles, emission factors, and chemical reactivity. The VOCs were monitored in the stack flue gas of both the non-recovery (SFN) and the mechanical (SFM) plant as well as in fugitive emissions due to leakage

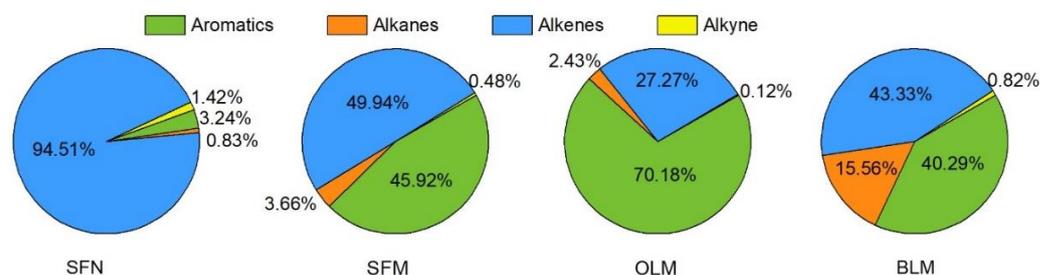
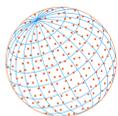


Fig. 5. Contributions of VOC groups emitted from SFN, SFM, OLM, and BLM to OFP.



from the oven (OLM) and from byproducts (BLM) at the mechanical plant. The primary components in the SFN were ethylene, 1-butene, benzene, acetylene, and 2,2-dimethylbutane, whereas those in the SFM were styrene, benzene, and ethylene. The OLM was dominated by benzene, toluene, ethane, *m*-xylene, and ethylene, and the BLM, by benzene, propane, ethane, ethylene, *n*-pentane, *n*-butane, isobutene, 1-butene, toluene, and propylene. These results imply that acetylene and styrene can serve as indicators of non-recovery and mechanical coking processes, respectively. Furthermore, low-molecular-weight hydrocarbons (C₂–C₄) are synergetic indicators of byproduct emissions at coking plants. The VOCs emission factors for the SFN and SFM were 96 g Mg⁻¹-coke and 0.4 g Mg⁻¹-coke, respectively, demonstrating that VOCs in the stack flue gas of non-recovery coking plants should be controlled due to their high emission intensity. By determining the VOC source profile and emission factor for the SFN, this study provides crucial reference data for the existing source profile library and enables us to assess domestic VOC emissions generated by the coking process. The highest source reactivity was exhibited by the SFN (80.26 mg m⁻³), followed by the OLM (7.22 mg m⁻³), which suggests that controlling VOCs in the stack flue gas at non-recovery plants and in the fugitive oven emissions at mechanical plants will greatly reduce the conversion of these pollutants into ozone. Finally, replacing non-recovery coking plants with mechanical ones in China will decrease VOC emissions and significantly improve the ambient air quality.

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DISCLAIMER

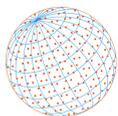
The authors declare no competing financial interests.

SUPPLEMENTARY MATERIAL

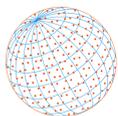
Supplementary data associated with this article can be found in the online version at <https://doi.org/10.4209/aaqr.2020.04.0145>

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