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# Emission characteristics and associated health risk assessment of volatile organic compounds from a typical coking wastewater treatment plant

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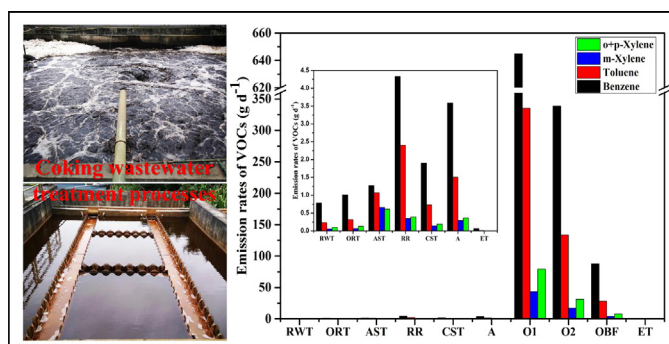
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## HIGHLIGHTS

- Emission characteristics of VOCs were investigated in a full-scale coking WWTP.
- Emission rates of VOCs were calculated, and anterior aerobic tank was the major emission contributor (about 62.2%).
- Carcinogenic risks of VOCs exposure to workers of this coking WWTP exceeded acceptable level ( $1 \times 10^{-6}$ ).
- Non-carcinogenic risk hazard ratio (HR) of benzene was higher than the acceptable limit ( $HR = 1$ ) at several sites.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Coking wastewater is a typical industrial wastewater and contains a number of toxic and harmful organic pollutants which threaten human health. However, emission of volatile organic compounds (VOCs) from coking wastewater treatment plants (WWTPs) is rarely studied. Here, the emission characteristics of VOCs were investigated in a full-scale coking WWTP composed of an anaerobic-oxic-oxic (A-O<sub>1</sub>-O<sub>2</sub>) treatment system. Furthermore, the potential health risks were assessed in this study. VOC emission rates were estimated at each unit of the coking WWTP and the influencing factors of emissions were discussed. Seventeen VOCs were identified in the air phase by gas chromatography–mass spectrometry combined with Tenax adsorption–thermal desorption method; benzene, toluene, and xylenes were predominant, and the concentration of total VOCs decreased gradually from the raw water tank ( $857.86 \pm 131.30 \mu\text{g m}^{-3}$ ) to the effluent tank ( $28.56 \pm 3.96 \mu\text{g m}^{-3}$ ). The total VOC emission rate from all units was  $1773.42 \text{ g d}^{-1}$ , corresponding to an annual emission of  $0.65 \text{ tons year}^{-1}$ . Since the treatment capacity of this coking WWTP was about  $1500 \text{ m}^3 \text{ d}^{-1}$ , it was estimated that  $1.18 \text{ g}$  of VOCs are emitted during the treatment of  $1 \text{ m}^3$  wastewater. Influencing factors of VOC emission mainly include the background concentration of VOCs in wastewater, operational parameters of the treatment processes, and physicochemical properties of VOCs. The carcinogenic risk of VOCs for workers in this coking WWTP ranged from  $3.0 \times 10^{-5}$  to  $7.8 \times 10^{-4}$ , which exceeded an acceptable level ( $1.0 \times 10^{-6}$ ). The non-carcinogenic risk hazard ratio of benzene exceeded 1, indicating that benzene has an obvious non-carcinogenic risk. Understanding VOCs emission

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characteristics and emission rates can help to identify the adverse effects of coking WWTPs on human health and provide relevant information for policy-making.

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## 1. Introduction

Wastewater, especially industrial wastewater, is an important source of volatile organic compounds (VOCs). Significant amounts of benzene, toluene, and xylenes are released during the wastewater treatment process (Fatone et al., 2011). The particularly high volatility of VOCs leads to their significant evaporation or sublimation from solid or liquid phase into the atmosphere under normal atmospheric conditions (Jiang et al., 2015; Chen et al., 2014). Once discharged to the ambient atmosphere and transported to downwind receptors, VOCs adversely impact human health due to their carcinogenic, teratogenic, and mutagenic effects (Yeh et al., 2011). VOCs also cause environmental effects such as ozone generation, secondary aerosol generation, and photochemical smog (Agarwal et al., 2016; Wu et al., 2017; Yang et al., 2012). Recently, VOCs emissions from wastewater treatment plants (WWTPs) have attracted significant attention (Escalas et al., 2003; Lebrero et al., 2011; Zhang et al., 2018). It is vital to study the occurrences and distribution characteristics of VOCs in WWTPs, because VOCs monitoring is a critical step for the development of pertinent strategies for air pollution control at WWTPs.

A number of studies have investigated VOC emissions from WWTPs. Widiana et al. (2017) identified 33 VOCs from the air of a municipal WWTP area in Taiwan. Wu et al. (2006) identified 54 VOCs at various stages of treatment processes in an industrial science park in Taiwan. The total VOC concentration at the coarse screen unit of a sewage treatment plant in southern Beijing was 120–221 mg m<sup>-3</sup>, accounting for 93% of the total VOCs concentration of all sampling points (Lin et al., 2016). The concentration of toluene reached levels as high as 460 µg m<sup>-3</sup> in several sewage treatment plants in Poland (Suschka et al., 1996). Activated sludge processes are prevalent in >80% of all WWTPs, where VOCs are removed via air stripping, surface volatilization, biodegradation, and adsorption to solids (Chen et al., 2014; Forsgren, 2015; Benintendi, 2016). Volatilization removes VOCs during wastewater treatment; thus, efficiencies of WWTPs are typically overestimated (Yang et al., 2014), while emissions are typically underestimated (Benis et al., 2016). Studies on VOC emissions mostly focus on municipal WWTPs, and VOC emissions from a coking WWTP has not been reported to date. However, a clear smell of phenol and sulfide is noticeable in the vicinity of coking WWTPs (Pal and Kumar, 2014). Coking wastewater is a typical industrial wastewater with complex composition and

high chemical oxygen demand (COD) of about 4000 mg L<sup>-1</sup>. This suggests that coking wastewater contains a large number of organic compounds (Kong et al., 2018; Wei et al., 2019). Up to 15 categories of 558 types of organic compounds were detected in coking wastewater, including phenols, organic nitriles, polycyclic aromatic hydrocarbons, heterocyclic compounds, and a small numbers of esters, alkanes and halogenated organic compounds (Zhang et al., 2012). Moreover, about 340 million tons coking wastewater is generated per year during the coke production process (Wei et al., 2012; Wei et al., 2019). Thus, VOC emissions from coking WWTPs should be studied, and public concern should be raised.

The direct measurement of VOC emissions from WWTPs is difficult and requires rigorous fieldwork (Padalkar and Kumar, 2018). Modeling methods and theoretical methods for estimating the rate and flux of VOCs emission in WWTPs were developed. Comprehensive VOC emission models include BASTE (Govind et al., 1991; Corsi and Card, 1991; Oskouie et al., 2008), TOXCHEM+ (Melcer et al., 1994; Fabiyi et al., 2012), and WATER9 (USEPA, 2004; Malakar and Saha, 2015). The emission rate and flux can be calculated by modeling based on the VOCs concentration in the water and gas phases and on system parameters (e.g. flow rate). Based on the concentration of VOCs in the water-phase and the modified surface-renewal theory, the emission rate was estimated via Equations. For instance, Atasoy et al. (2004) estimated the emission rate of non-methane VOCs (0.041 kg h<sup>-1</sup>) and concluded that the aerated biological treatment stage contributed the majority (about 83.27% w/w) of the total emissions (0.3626 tons year<sup>-1</sup>) from all units. The emission characteristics of atmospheric VOCs varied from different WWTPs due to several factors, such as the wastewater sources, the treatment technology, the nature (physical, chemical and biological properties) of VOCs, and meteorological conditions. Padalkar and Kumar (2018) investigated various effects on VOCs removal such as active biomass concentration, Henry's law constant, and the air-to-effluent ratio. They found that the dominant VOC removal mechanism at the equalization tank was stripping, while it was weir-drop at the primary clariflocculator and secondary clarifier. In the aeration tank, the main VOC removal mechanism was biodegradation which competed with stripping for VOCs. However, halogenated compounds are hydrophobic, which tend to be removed by stripping rather than biodegradation. The characteristics of wastewater such as its high temperature and high VOC concentration in the water phase of the inlet flow indicate it as

**Table 1**  
Parameters of processing units in the coking WWTP and sampling locations.

Processing units	Size (m)	Open/closed	Aeration	Aeration rate (m <sup>3</sup> h <sup>-1</sup> )	Water sampling	Air sampling
Raw water tank (RWT)	4 × 3 × 5	Open	No	0	Yes	Yes
Oil removal tank (ORT)	6 × 4 × 5	Open	No	0	Yes	No
Ammonia stripping tower (AST)	16 × 8 × 12	Closed	No	480	Yes	Yes
Regulating reservoir (RR)	16 × 12 × 4	Open	No	0	Yes	No
Coagulation sedimentation tank (CST)	10 × 6 × 10	Open	No	0	Yes	No
Anaerobic tank (A)	12 × 10 × 10	Open	No	0	Yes	Yes
Anterior aerobic tank (O1)	8 × 8 × 9	Open	Yes	1875	Yes	Yes
Posterior aerobic tank (O2)	8 × 8 × 9	Open	Yes	1250	Yes	Yes
Aerobic biofilter (OBF)	10 × 8 × 6	Open	Yes	350	Yes	No
Inclined-tube clarifier (ITC)	6 × 8 × 6	Open	No	0	No	No
Effluent tank (ET)	4 × 2 × 2	Open	No	0	Yes	Yes

Note: The size of each technology units is represented by either length (L) × width (W) × depth (D). Processing units include raw water tank (RWT), oil removal tank (ORT), ammonia stripping tower (AST), regulating reservoir (RR), coagulation sedimentation tank (CST), anaerobic tank (A), anterior aerobic tank (O1), posterior aerobic tank (O2), aerobic biofilter (OBF), inclined-tube clarifier (ITC) and effluent tank (ET).

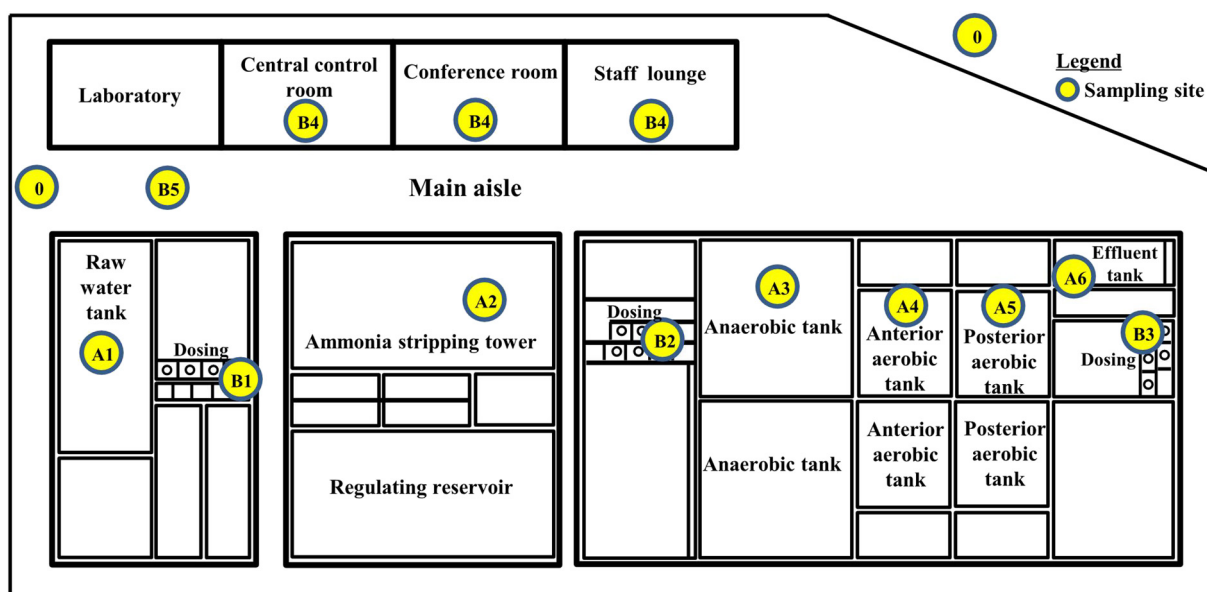


Fig. 1. Locations of air sampling in the coking WWTP.

a main source of VOC emissions (Mo et al., 2015; Wei et al., 2014; Tata et al., 2003). Therefore, both the concentration levels and temperature of the influent wastewater are influencing factors of VOC emissions.

The health risks of VOCs were assessed at various industrial processes. The total cancer risk of seven VOCs in the coke-making process was  $3.0 \times 10^{-2}$  (Chiang et al., 2010). The carcinogenic risk of five VOCs, emitted from the entire furniture manufacturing process, ranged within  $5.67 \times 10^{-7}$ – $1.87 \times 10^{-4}$ , the non-carcinogenic risk ranged within  $5.9 \times 10^{-2}$ – $8.01$ ; different positions in the workshops showed different risk levels (Tong et al., 2019). The total hazard ratio for the non-cancer risk from VOCs was as high as  $3.1 \times 10^3$  and the total cancer risks ranged from  $2.93 \times 10^{-3}$  to  $1.1 \times 10^{-2}$  in various processes of a petroleum refinery in the Pearl River Delta (Zhang et al., 2018). The carcinogenic incidences of four VOCs from municipal WWTP of Harbin City were all below  $10^{-5}$ , which indicated that the carcinogenic effects were less significant; however, the hazardous quotients of benzene above 1 indicated that benzene posed no cancer risk to workers (Yang et al., 2012). The potential cancer risks induced by hazardous air pollutants to the habitants near a WWTP in northern China were  $2.0 \times 10^{-7}$ – $4.6 \times 10^{-6}$  (Yang et al., 2014). The health risks of VOCs from a coking WWTP had not been studied to date.

This study determined the atmospheric VOCs concentrations to investigate the VOCs emission characteristics and associated health risks at different designated sites on and around the coking WWTP, and to

estimate the VOC emission rates. This study provided supporting data to understand the VOCs removal mechanisms. The emissions of VOCs from WWTPs to the atmosphere and the environment can pose health risks to the staff at the treatment site and to residents nearby; thus, VOC emissions need to be controlled especially for unorganized emissions. An improved understanding of the behaviors of VOCs emission is important for the implementation of stronger regulatory frameworks as well as safer design consideration and control initiatives (Beghi et al., 2012).

## 2. Experiments and methods

### 2.1. Location of the coking WWTP

The coking WWTP that was investigated for this study is located in the Shaoguan coking plant in Guangdong province, China. The WWTP adopts an anaerobic-oxic-oxic (A-O<sub>1</sub>-O<sub>2</sub>) biological treatment process and has been running stably for more than 10 years. Fig. S1 shows a schematic of the processes of this coking specific WWTP. The coke production capacity of this coking plant is 1 million tons year<sup>-1</sup>, and the coking wastewater treatment capacity of this WWTP is about 1500 m<sup>3</sup> d<sup>-1</sup>. Indicators of coking wastewater such as temperature, pH, COD and dissolved oxygen (DO) at various stages are shown in Table S1. Raw coking wastewater with high COD contains a large

Table 2

Parameters of carcinogenic risk assessment considered as random variables.

Parameters	Values (mean ± std)	Distribution	References
C <sub>i</sub> (mg m <sup>-3</sup> )	Fig. 2	Normal	This study
EF (d year <sup>-1</sup> )	250 ± 32	Normal	USEPA (1989)
ED (year)	25 ± 22	Lognormal	USEPA (1989)
ET (h d <sup>-1</sup> )	8 ± 6	Lognormal	USEPA (1989)
LT (year)	73	Point	USEPA (1989)
IR (m <sup>3</sup> h <sup>-1</sup> )	1.5 <sup>a</sup> ± 0.3	Normal	USEPA (1989), standard deviation (std) was taken as 20% of the mean.
BW (kg)	65 <sup>b</sup> ± 18	Lognormal	Guangdong NPHMB
PF <sub>i</sub> (kg d mg <sup>-1</sup> )	0.1 <sup>c</sup> ± 0.02 for benzene	Normal	USEPA IRIS; Yang et al., 2012

Note: Concentration of VOC in the air (C<sub>i</sub>); exposure frequency (EF); exposure duration (ED); daily average exposure time (ET); average expected lifetime (LT); inhalation rate (IR); average body weight (BW); carcinogenic risk potency factor (PF<sub>i</sub>).

<sup>a</sup> The value of IR was estimated based on the values of different places, such as 1.68 m<sup>3</sup> h<sup>-1</sup> of iron and steel workers (Chang et al., 2010), and 1.06 m<sup>3</sup> h<sup>-1</sup> of electromechanical repair and car painting center (Colman Lerner et al., 2012).

<sup>b</sup> Based on the investigation of Guangdong National Physical Health Monitoring Bulletin (NPHMB), the average weight of adult (age: 25–55) was 63 kg. Average body weight of the worker of a coking WWTP is slightly higher; therefore, 65 kg was selected.

<sup>c</sup> Adopted from USEPA Integrated Risk Information System (IRIS) Database, <http://www.epa.gov/ncea.iris/>, 2012.

amount of organic matter, part of which already consists of VOCs, and a further part may be degraded into VOCs during the treatment process. Table 1 shows the parameters of processing units and sampling locations in this coking WWTP.

## 2.2. VOC sampling

To obtain the emission characteristics of VOCs, air sampling was conducted over the main wastewater treatment units and in the specific operating areas. Sampling method followed the USEPA method (Rodríguez-Navas et al., 2012; Maceira et al., 2017). The air sampling

locations in the WWTP are illustrated in Fig. 1. Sampling sites of the wastewater treatment units include a raw water tank (site A1), an ammonia stripping tower (site A2), an anaerobic tank (site A3), an anterior aerobic tank (site A4), a posterior aerobic tank (site A5), and an effluent tank (site A6). In the operating areas, sampling sites include a dosing point of the pretreatment system (site B1), a dosing point of the anterior biological system (site B2), a dosing point of the posterior biological system (site B3), office rooms (site B4), and a main aisle (site B5). Blank samples (site 0) were also collected at the same time. Four parallel samples were collected at each sampling site. Samples were collected from August to October 2016.

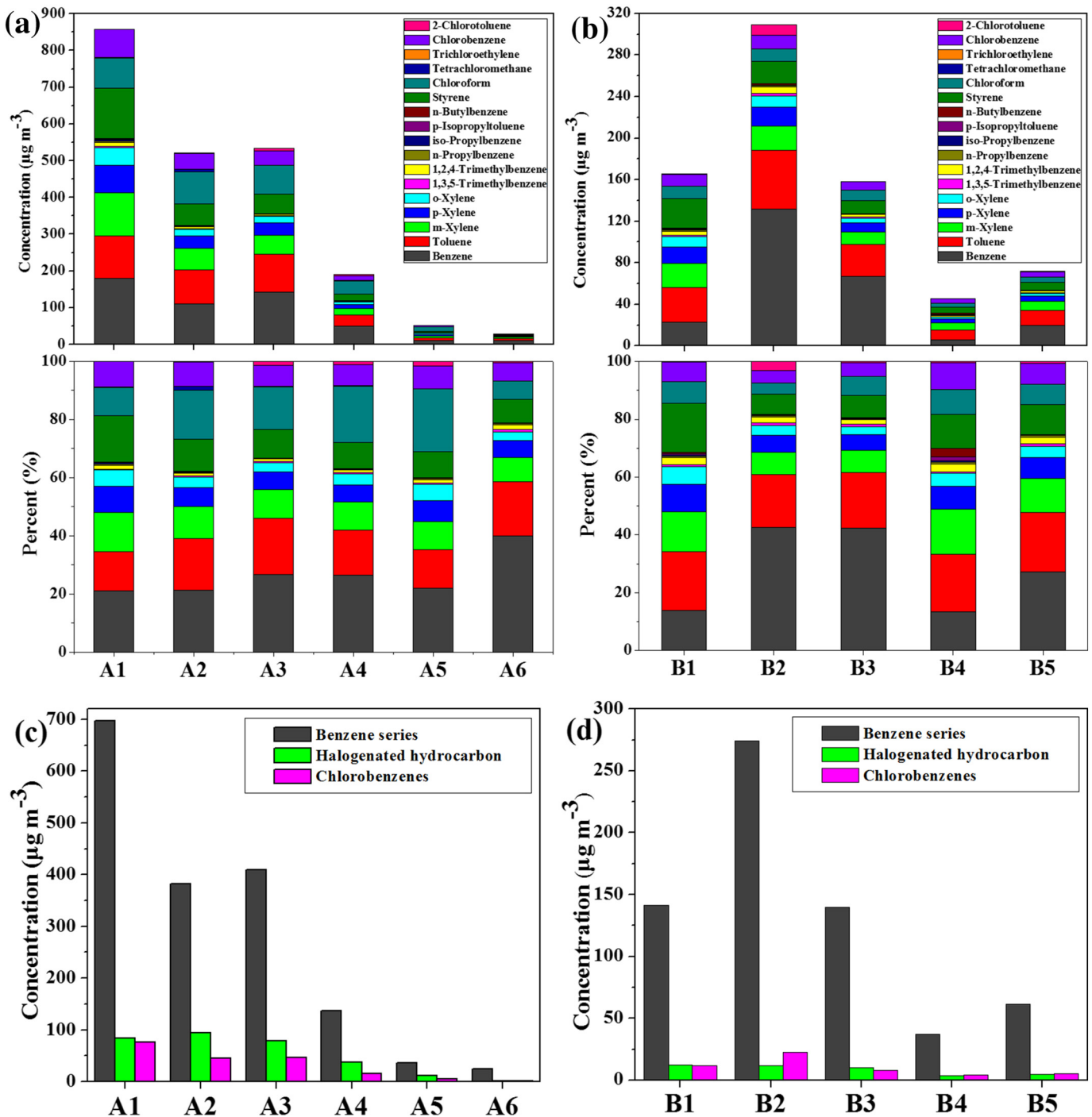


Fig. 2. Concentrations and percents of VOCs in air phase of the coking WWTP. Sampling sites include raw water tank (A1), ammonia stripping tower (A2), anaerobic tank (A3), anterior aerobic tank (A4), posterior aerobic tank (A5), effluent tank (A6), a dosing point of the pretreatment system (B1), a dosing point of the anterior biological systems (B2), a dosing point of the posterior biological systems (B3), the office rooms (B4), and main aisle (B5).

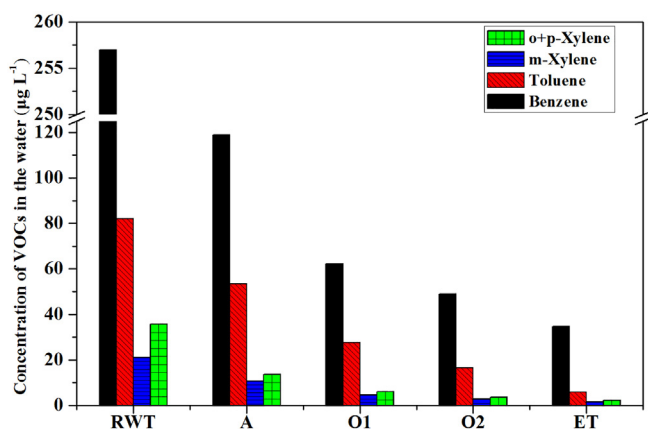


Fig. 3. Concentrations of VOCs in water phase of the coking WWTP. Treatment units include raw water tank (RWT), anaerobic tank (A), anterior aerobic tank (O1), posterior aerobic tank (O2), and effluent tank (ET).

The gas-collecting hood above the wastewater was used to collect gaseous VOCs emitted from the tanks. One end of the gas-collecting hood was connected to a pumping air sampler (TH-150, medium flow TSP sampler) and a pre-treatment Tenax-TA tube (the conditions of the pretreatment process were: a temperature of 300 °C, a nitrogen flow rate of 50 mL min<sup>-1</sup>, and a duration of 0.5 h). The other end was connected to an activated carbon adsorption tube to prevent the interference of air. Next to the Tenax-TA tube was a drying tube that was loaded with sodium sulfate to remove moisture. All connecting tubes were made of polytetrafluoroethylene. Before connecting the Tenax-TA tube, the pump was run for about 20 min to ensure that all gases in the gas-collecting hood had been discharged from the tank. During the collection process, the gas flow rate was (200–300) mL min<sup>-1</sup>, and the sampling time was (0.5–1) h. Both sampling temperature and atmospheric pressure were recorded. Immediately after sampling, both ends of the sampling tube were sealed with stainless steel end fittings and a cap. Samples were refrigerated below 4 °C and analyzed within seven days. To reduce the impact of both background and nearby

facilities, all sampling was conducted on days with calm wind conditions (wind speed < 0.5 m s<sup>-1</sup>).

### 2.3. VOCs analytical method

Based on the USEPA TO-17 method (United States Environmental Protection Agency) (USEPA, 1999; Rodriguez-Navas et al., 2012; Maceira et al., 2017), atmospheric samples were analyzed using a gas chromatography–mass spectrometry (GC–MS) joined with a thermal desorption equipment (Gerstel Varian, USA: TDS3-3800GC-4000MS) to determine the concentrations of VOCs. The temperature of the thermal desorption equipment was 280 °C. The gaseous VOCs in the Tenax-TA tube were blown off for 10 min by helium, cooled and collected by a cooling trap, and then blown into the GC. In the GC a fused silica capillary column (HP-VOC, 60 m × 0.32 mm × 1.80 µm) was used to separate gases. The following column temperature program was used: 35 °C for 5 min, ramped to 100 °C at 2 °C min<sup>-1</sup>, and then ramped to 220 °C at 5 °C min<sup>-1</sup>, which was maintained for 5 min (total time about 67 min). VOCs were quantified using standard compounds containing 54 VOCs (Table S2), each at a concentration of 200 mg mL<sup>-1</sup>. Dichloromethane, acetone, hexane and methanol were purchased from Merck (Darmstadt, Germany).

For quality assurance and control, analyses were conducted in duplicate and blank samples were analyzed. Quantitative analysis was obtained by calibration curves based on peak areas by injecting 10 µL standard samples at concentrations of 0.25, 0.50, 1.00, 2.50, 5.00, 10.00 and 40.00 µg mL<sup>-1</sup> into sampling tubes. The calibration curve was developed for each individual VOC, and the correlation coefficient of each VOC calibration curve exceeded 0.99. Method detection limits (MDLs) for each compound in the air samples were 0.077–0.48 ng mL<sup>-1</sup>.

Water samples were collected at the outlets of each process unit at intervals of 2 h and mixed six times to obtain the final water samples. Prior to analysis, the water phase was passed through a 0.45 µm filter membrane to remove particulate matter. Samples were pretreated by adding 0.02 g L<sup>-1</sup> ascorbic acid after adjusting the pH to <2 with 10% hydrochloric acid. Samples were analyzed by the method of dispersive liquid-liquid microextraction coupled with gas chromatography-flame

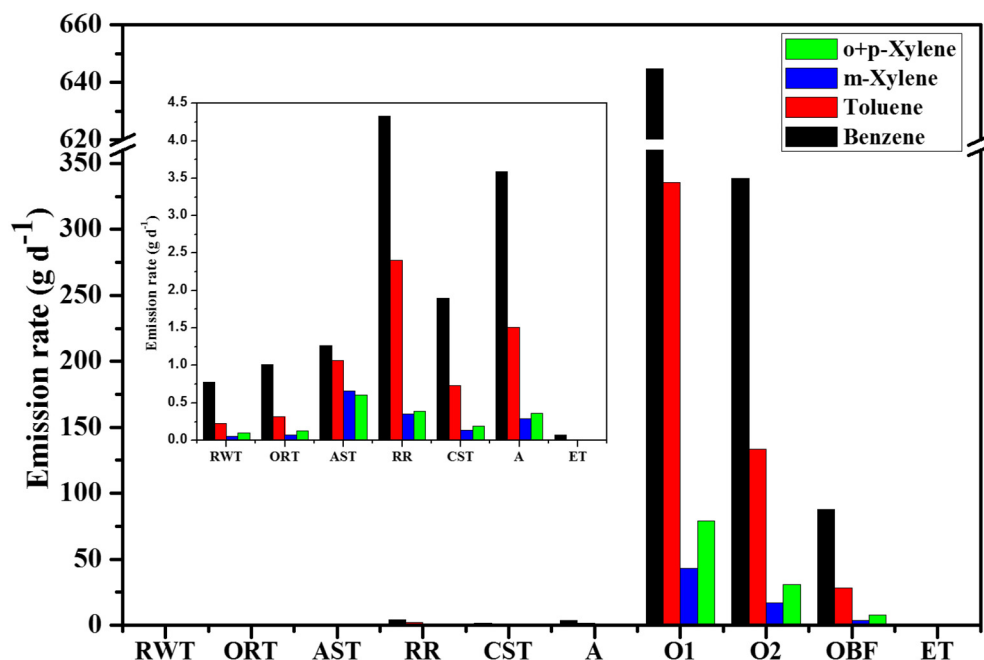


Fig. 4. The calculated emission rates of VOCs in the coking WWTP. Processing units include raw water tank (RWT), oil removal tank (ORT), ammonia stripping tower (AST), regulating reservoir (RR), coagulation sedimentation tank (CST), anaerobic tank (A), anterior aerobic tank (O1), posterior aerobic tank (O2), aerobic biofilter (OBF), and effluent tank (ET).

**Table 3**  
Relationship between VOC concentrations and physicochemical properties.

	$C_g/C_w$	$H_c$	MW	BP	$S_w$	$\text{Log}K_{ow}$	P
$C_g/C_w$	1						
$H_c$	0.6122	1					
MW	0.7626	0.1908	1				
BP	0.7902	0.2389	0.9987	1			
$S_w$	-0.6694	-0.2936	-0.9583	-0.9596	1		
$\text{Log}K_{ow}$	0.7467	0.2334	0.9960	0.9960	-0.9798	1	
P	-0.6850	-0.3075	-0.9610	-0.9631	0.9998	-0.9818	1

Note:  $C_w$  and  $C_g$  represent the concentration of each VOC in the water and in the air, respectively. MW = molecular weight; BP = boiling point; MP = melting point;  $S_w$  = water solubility; P = steam pressure;  $\text{Log}K_{ow}$  = log of octanol-water partition coefficient;  $H_c$  = Henry's law coefficient (dimensionless).

ionization detector (GC-FID). The detection limits were 0.01–0.10  $\mu\text{g L}^{-1}$  at the linear range of 0.05–10.00  $\mu\text{g L}^{-1}$ . The relative standard deviations were <12.6%, and the relative recovery rates exceeded 77.8%.

#### 2.4. Emission rates estimation

Mechanisms of VOCs removal from wastewater include volatilization induced by mechanical surface aeration, stripping by diffused aeration, biodegradation and adsorption onto solids. During the wastewater treatment processes, mass transfer of VOCs into the atmosphere involved transfer from water to the interface, followed by transfer across the interface, and finally transfer from the interface to the air phase (Montgomery, 1985; Jr et al., 2018). In an open system, the emission rate formula of a VOC from wastewater to the atmosphere across an air-wastewater interface can be expressed as shown in Eqs. (1) and (2) (adopted from Cheng and Chou, 2003). In a closed system, the emission rate can be calculated by Eq. (3):

$$E(\text{Aeration}) = Q_g C_g^* = Q_g C_L H_c \quad (1)$$

$$E(\text{No aeration}) = K_L A C_L \quad (2)$$

$$E(\text{Closed}) = Q_g C_g \quad (3)$$

where E represents the emission rate of the VOC from water to air in an open system;  $Q_g$  represents the aeration rate of an aerator or blower ( $\text{m}^3 \text{h}^{-1}$ );  $C_g^*$  represents the gaseous VOC concentration at equilibrium with aqueous VOC concentration ( $\text{mg m}^{-3}$ );  $C_L$  represents the VOC concentration in the water-phase ( $\mu\text{g L}^{-1}$ );  $C_g$  represents the VOC concentration in air ( $\text{mg m}^{-3}$ );  $K_L$  represents the overall mass transfer coefficient ( $\text{m s}^{-1}$ ); and A represents an interfacial contact area between air and wastewater ( $\text{m}^2$ );  $C_g$  represents the gaseous VOC concentration.  $K_L$  can be determined by Eq. (4):

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{H_c k_g} \quad (4)$$

where  $k_l$  represents the liquid-phase transfer coefficient ( $\text{m s}^{-1}$ );  $k_g$  represents the gas-phase transfer coefficient ( $\text{m s}^{-1}$ ); and  $H_c$  represents the dimensionless Henry's law coefficient ( $\text{m}^3 \text{liquid m}^{-3} \text{gas}$ ). Since both  $k_l$  and  $k_g$  are directly proportional to molecular diffusivities, and since molecular diffusivities of VOCs are generally much higher in gas than in liquid, the gas-phase resistance has often been assumed to be negligible for  $H_c > 0.1$ . For this condition, the liquid-phase resistance to mass transfer is limiting, and  $K_L \approx k_l$ . Samples were collected in still air, i.e., the wind speed was below  $3.3 \text{ m s}^{-1}$ . When  $0 < U < 3.25$ ,  $k_l$  can be obtained by Eq. (5):

$$k_l = 2.78 \times 10^{-6} \left( \frac{D_{i,w}}{D_{ether,w}} \right)^{2/3} \quad (5)$$

where  $D_{i,w}$  and  $D_{ether,w}$  represent the diffusion coefficient of the substance and ether ( $(\text{C}_2\text{H}_5)_2\text{O}$ ) in diluted water solution, respectively ( $\text{m}^2 \text{s}^{-1}$ ); U represents the wind speed above the water surface ( $\text{m s}^{-1}$ ). The water-phase diffusion coefficients of VOCs in diluted water solution were calculated using Eq. (6).

$$D_{i,w} = \frac{7.7 \times 10^{-15}}{\mu \left( \nu_A^{1/3} - \nu_0^{1/3} \right)} T \quad (6)$$

where  $\mu$  represents the viscosity of the solution (Pa s); T represents the temperature (K);  $\nu_A$  represents the molecular volume of the substance ( $\text{cm}^3 \text{mol}^{-1}$ ); and  $\nu_0$  is a coefficient equal to  $8 \text{ cm}^3 \text{mol}^{-1}$ .

#### 2.5. Human health risk assessment

This study also assessed the potential health risks of benzene series including both carcinogenic risks and non-carcinogenic risks. Inhalation exposure is the major route of exposure to benzene series. The carcinogenic risk associated with benzene series was assessed by Eqs. (7) and (8).

$$CR_i = LADD_i \times PF_i \quad (7)$$

$$LADD_i = \frac{C_i \times IR \times ET \times EF \times ED}{BW \times LT \times 365} \quad (8)$$

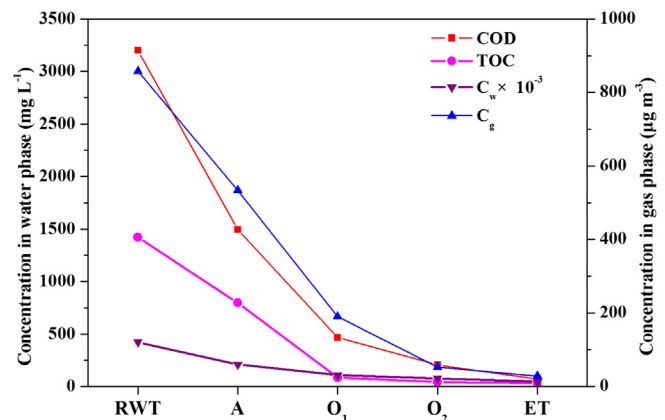
where  $CR_i$  represents the carcinogenic risk of benzene series for lifetime through respiratory exposure;  $LADD_i$  represents the lifetime average exposure dose of benzene series ( $\text{mg kg}^{-1} \text{d}^{-1}$ );  $C_i$  represents the concentration of each VOC in the air ( $\text{mg m}^{-3}$ );  $PF_i$  represents the carcinogenic risk potency factor ( $\text{kg d mg}^{-1}$ ).

The non-carcinogenic risk of benzene series was evaluated via Eq. (9):

$$HR_i = \frac{C_i}{R_f C_i} \quad (9)$$

where HR represents the hazard ratio;  $C_i$  represents the concentration of each VOC in the air ( $\mu\text{g m}^{-3}$ );  $R_f C_i$  represents the reference concentration of benzene series for non-carcinogenic risk through long-term respiratory exposure ( $\mu\text{g m}^{-3}$ ). The  $R_f C$  values of benzene series were adopted from the USEPA Integrated Risk Information System (IRIS) or the California Environmental Protection Agency (CalEPA). Parameters of carcinogenic risk assessment are list in Table 2.

USEPA considered the cancer risks of the compounds to be negligible or insignificant at a cancer risk below  $10^{-6}$ . Compounds were defined to



**Fig. 5.** COD, TOC,  $C_w$ , and  $C_g$  in different units. All the data were average values. Treatment units include raw water tank (RWT), anaerobic tank (A), anterior aerobic tank (O1), posterior aerobic tank (O2), and effluent tank (ET).  $C_w$  represents the concentration of each VOC in the water, and  $C_g$  represents the concentration of each VOC in the air.

**Table 4**  
Correlation analysis between COD, TOC,  $C_w$  and  $C_g$  of VOCs.

	COD	TOC	$C_w$	$C_g$
COD	1			
TOC	0.990	1		
$C_w$	0.999	0.982	1	
$C_g$	0.986	0.989	0.981	1

pose a possible risk at a cancer risk between  $10^{-5}$  and  $10^{-6}$ , a probable risk at a cancer risk below  $10^{-4}$  and above  $10^{-5}$ , and a definite risk at a cancer risk exceeding  $10^{-4}$  (Sexton et al., 2007; Ramírez et al., 2012; Widiana et al., 2019). The World Health Organization (WHO) suggested an acceptable CR below the range between  $1 \times 10^{-5}$  and  $1 \times 10^{-6}$  (Colman Lerner et al., 2012, 2018). HR values larger than or equal to 1 indicate that long-term exposure may pose non-carcinogenic health risks (Xing et al., 2018; Tong et al., 2019).

## 2.6. Uncertainty analysis

Uncertainty emerges in estimation of both exposure and effects. A Monte Carlo simulation is a popular method adopting the Crystal Ball software (v11.1.2.4) to quantify the uncertainty and variability in the risk assessment (Dai et al., 2017; Hu et al., 2007; Zhou et al., 2011). The distribution type was selected for both IR values and exposure concentrations. Probability distributions for random variations were shown in Table 2 (e.g. lognormal, normal, and point). The lognormal distribution fit the most measured VOC concentrations based on Anderson-Darling test (Jia et al., 2008). Therefore, exposure concentrations of VOCs were described by lognormal distribution in this study, and the IR value recommended by the USEPA was described by normal distribution.

## 3. Results and discussion

### 3.1. Atmospheric VOCs emissions in an actual coking WWTP

Understanding the distribution and contribution of VOCs emitted from the different units of coking WWTPs will help to identify the sources of VOCs pollution. However, little is known about VOC emissions from the different processes of a coking WWTP. This study investigated the distribution characteristics of VOCs that escape from different units of a coking WWTP. Fig. 2 shows the concentrations and distributions in each treatment process and working areas of the coking WWTP. Seventeen VOCs were detected including 12 species of benzene series, three species of chlorinated hydrocarbons, and two species of chlorinated benzene compounds. Benzene, toluene, xylenes, styrene, chloroform, and chlorobenzene were ubiquitous and the main pollutants, accounting for 97% of the total concentration of 17 VOCs ( $\Sigma$ VOCs). Concentrations of VOCs in different units followed this order: raw water tank > anaerobic tank > ammonia stripping tower > anterior aerobic tank > posterior aerobic tank > effluent tank. VOCs emission from each unit varied from 28.56 to 857.86  $\mu\text{g m}^{-3}$ , and had an average concentration of 266.87  $\mu\text{g m}^{-3}$ . The concentration of VOCs around working areas varied from 45.66 to 308.85  $\mu\text{g m}^{-3}$ . The concentration of benzene series was clearly higher than that of

chlorinated hydrocarbon and chlorobenzenes at all sampling sites, as shown in Fig. 2(c) and (d). Among the xylenes, o-xylene had the lowest concentration due to its low volatility (Ning et al., 2015). These results show that concentrations of VOCs emitted from the raw wastewater tank were relatively high, especially for the benzene series, since raw wastewater has a high concentration of VOCs, as shown in Fig. 3. The raw wastewater tank was a main source of VOCs exposure.

### 3.2. Emission rates of VOCs

The selected VOCs including benzene, toluene and xylenes were the most harmful detected species in the petrochemical industry (Zhang et al., 2017). These cause lung and kidney cancers and have been classified as priority pollutants by the USEPA (Yadav and Reddy, 1993). Their individual emission rate was estimated using Eqs. (1), (2) and (3) (Tables S3 and S4). The emission rates of VOCs from water to the atmosphere in coking WWTP are presented in Fig. 4. The results show that the total emissions of each VOC ranged from 65.80 to 1084.46  $\text{g d}^{-1}$  and benzene was the main VOC. The emission rates of all VOCs at each unit ranged from 0.09 to 1102.55  $\text{g d}^{-1}$ , and the anterior aerobic tank had the highest VOC emission rate. The total emission rate of VOCs was 1773.42  $\text{g d}^{-1}$ , corresponding to an annual emission of 0.65 tons  $\text{year}^{-1}$ . These results show that the aeration at the aerobic tank plays an important role for VOC emissions. It is advisable to minimize aeration while ensuring an appropriate level of dissolved oxygen.

Emission factors can be expressed as the weight of pollutants divided by a unit weight, volume, distance, or duration of the emission activity. Emission flux is best expressed as an emission potential (Cheng and Chou, 2003). This study expressed emission flux by dividing the emission rate by the wastewater flow rate. Since the treatment capacity of this coking WWTP is about 1500  $\text{m}^3 \text{d}^{-1}$  and the total emission rate of VOCs was 1773.42  $\text{g d}^{-1}$ , the emission flux in this coking WWTP was 1.18  $\text{g VOCs/m}^3$  of wastewater. The emission of the measured VOCs was 0.036  $\text{g m}^{-3}$  wastewater treated in the Skyway plant in Burlington, which received approximately 17% industrial wastewater input (Bell et al., 1993). The total VOCs emission from petroleum refinery WWTP units of India was 60.7  $\text{g m}^{-3}$  wastewater treated (Malakar and Saha, 2015). VOC emissions found in this study were higher than those reported for the Skyway plant and lower than those of the petroleum refinery WWTP. Based on the total amount of coking wastewater in China (about  $3.4 \times 10^8 \text{ m}^3$  in 2018), the total emission of VOCs was 408 tons  $\text{year}^{-1}$  during the wastewater treatment processes. The total VOC emission from the coking industry of China was about 52,584 tons; therefore, VOC emissions from the coking wastewater treatment processes accounted for 0.78%. Although VOC emissions from the wastewater treatment processes are small compared to coke production processes, long-term exposure to VOCs is harmful for worker health. Recovery and control of VOCs will not only fully use energy, but also reduce pollution emissions.

### 3.3. Influencing factors of VOC emissions

#### 3.3.1. Effect of physicochemical parameters

The biological treatment processes mainly remove VOCs via volatilization, biosorption or biodegradation, and these removal processes are related to various physicochemical properties of compounds (e.g. their

**Table 5**  
The LADD ( $\text{mg kg}^{-1} \text{d}^{-1}$ ) of carcinogenic risk for workers exposed to benzene series.

LADD ( $\text{mg kg}^{-1} \text{d}^{-1}$ )	A1	A2	A3	A4	A5	A6	B1	B2	B3	B4	B5
Benzene	0.0078	0.0048	0.0061	0.0022	0.0005	0.0005	0.0010	0.0057	0.0029	0.0003	0.0008
Toluene	0.0050	0.0040	0.0045	0.0013	0.0003	0.0002	0.0015	0.0025	0.0013	0.0004	0.0006
Xylenes	0.0104	0.0048	0.0045	0.0016	0.0005	0.0002	0.0021	0.0023	0.0011	0.0006	0.0007



**Table 6**  
Carcinogenic risk for workers exposed to benzene series.

	$PF_i$ ( $\text{kg d mg}^{-1}$ )	A1	A2	A3	A4	A5	A6	B1	B2	B3	B4	B5
Benzene	0.1 <sup>a</sup>	7.8E-04	4.8E-04	6.1E-04	2.2E-04	5.0E-05	5.0E-05	1.0E-04	5.7E-04	2.9E-04	3.0E-05	8.0E-05
Toluene	N.A. <sup>b</sup>	–	–	–	–	–	–	–	–	–	–	–
Xylenes	N.A. <sup>b</sup>	–	–	–	–	–	–	–	–	–	–	–

<sup>a</sup> Adopted from USEPA Integrated Risk Information System (IRIS) Database, <http://www.epa.gov/ncea/iris/>, 2012.

<sup>b</sup> N.A. denotes the information which is not available.

$H_c$  and  $K_{ow}$  values) and operational parameters of the system (e.g. aeration). Concentrations of atmospheric VOCs and their emission rates were different, which is likely affected by their different physicochemical properties. The physicochemical properties of the detected VOCs are listed in Table S5. Mass transfer of VOCs from water to air is driven by  $\Delta C$  forming concentration gradient.  $\Delta C$  represents the concentration difference between the determined aqueous concentration ( $C_w$ ) and the calculated concentration ( $C_g H^{-1}$ ) based on Henry's law; therefore, the  $H_c$  of each VOC plays an important role during the mass transfer. Removing the influence of VOC concentration in wastewater by the ratio of  $C_g$  and  $C_w$ , the relationship was investigated between gaseous VOC concentrations and physicochemical properties of VOCs, Table 3. In unit concentration solution, there is a certain correlation between gaseous VOC concentrations and  $H_c$ , molecular weight, boiling point, water solubility, Log of octanol-water partition coefficient, and steam pressure.

VOCs with high volatility and low solubility have higher  $H_c$  and therefore, have to overcome higher resistance for the transfer into the gaseous phase. VOCs with higher solubility tend to have a smaller  $H_c$  and have to overcome higher resistance of transfer into the liquid phase. The emission of VOCs with a higher Henry's constant by stripping is higher than that with a lower Henry's constant. However, with increasing Henry's constant, the removal rate of VOCs by biodegradation decreases. In a bioreactor, the presence of activated sludge positively affects the transfer of VOCs from air to water, and then from water to sludge, especially for VOCs with a high octanol-water partition coefficient ( $K_{ow}$ ). Differences among the VOCs species exerted different effects on VOC emissions.

### 3.3.2. Effect of organic compound concentration

The removal rates of VOCs from wastewater in a coking WWTP could be overestimated due to VOC emissions from water to air. VOC removal rates are related to the concentration of VOCs in the water. VOCs increase COD or total organic carbon (TOC) concentrations in the wastewater. COD may serve as an indicator of VOC contamination in wastewater. The relationship between COD, TOC, and VOC concentrations in both the air phase ( $C_g$ ) and the water phase ( $C_w$ ) in different units is shown in Fig. 5. In summary, the concentrations of VOCs decreased with the gradual decrease of COD. Correlation analysis (Table 4) indicates that VOC emissions from wastewater into the air are positively correlated with COD, TOC, and VOC concentrations in the wastewater. Those are the influencing factors of VOC emissions.

### 3.3.3. Effect of treatment technological parameters

In the aeration tank, the aeration rate is the main influencing factor of emissions; however, in non-aeration tanks, the major factor is the

surface area of the gas-liquid interface. Forced air enhances VOC emissions, but decreases the concentration of VOCs due to dilution. These laws are consistent with Eqs. (1) and (2). During the treatment processes, in covered tanks, VOC emissions are suppressed, and a higher proportion of VOCs remains in solution in the wastewater compared to units that are not covered. Ventilation decreases the concentration of VOCs in air, thus causing VOCs to transfer from the wastewater to the air due to the concentration gradient between both phases. In weir configuration unit, a higher drop between water surfaces leads to higher emissions. Longer weirs and shallow tail water depths also result in higher emission rates. All other conditions being equal, higher retention times and higher temperatures generally result in higher emissions. A higher air-wastewater flow ratio leads to higher VOC emissions by stripping and lower VOC biodegradation. The emission rate is highly sensitive to the air-to-water ratio.

### 3.4. Health risk assessment

Benzene, toluene, and xylenes were dominant VOCs therefore attention should be paid to their potential health risks by emissions from the different units. The lifetime average exposure doses of the benzene series through the respiratory pathway were calculated (Table 5). Exposure risks were associated with the concentrations of benzene series. A higher concentration of benzene series leads to higher related carcinogenic exposure risks. Carcinogenic risk and non-carcinogenic risk of benzene series for lifetime estimation are shown in Tables 6 and 7, respectively.

Associated carcinogenic risks of compounds above  $1 \times 10^{-4}$  were considered as "definite risk", risks between  $1 \times 10^{-5}$  and  $1 \times 10^{-4}$  were considered as "probable risk", risks between  $1 \times 10^{-6}$  and  $1 \times 10^{-5}$  were considered as "possible risk", and risks below  $1 \times 10^{-6}$  were considered as "negligible risk". The results of the carcinogenic risk show that the associated carcinogenic risks were between  $3.0 \times 10^{-5}$  and  $7.8 \times 10^{-4}$ . The total risk value was  $3.26 \times 10^{-3}$ . The risks of benzene series at each WWTP unit were all above the acceptable level of health risk for the public recommended by the USEPA ( $1 \times 10^{-6}$ ). Therefore, emission of benzene series from this coking WWTP had clear cancerogenic effects on human health. Benzene exceeded the non-carcinogenic risk hazard ratio ( $HR > 1$ ). Toluene and xylenes were of potential concern. In addition, due to the limitation of this method and undetermined VOCs such as alkanes, alkenes, and sulfur-containing VOCs, health risks were only assessed for benzene series in this study. Due to the shortage of  $PF_i$ s, risk values associated with individual VOCs have not been presented.

**Table 7**  
Hazard ratios (HR) of non-carcinogenic risk for workers exposed to benzene series.

	$R_f C_i$ ( $\mu\text{g m}^{-3}$ )	A1	A2	A3	A4	A5	A6	B1	B2	B3	B4	B5
Benzene	60 <sup>a</sup>	3.008	1.841	2.366	0.837	0.194	0.190	0.382	2.194	1.118	0.102	0.325
Toluene	300 <sup>a</sup>	0.386	0.309	0.344	0.098	0.023	0.018	0.112	0.189	0.102	0.030	0.050
Xylenes	300 <sup>b</sup>	0.800	0.368	0.343	0.123	0.040	0.016	0.163	0.174	0.084	0.043	0.055

<sup>a</sup> Adopted from USEPA IRIS.

<sup>b</sup> Adopted from CalEPA.

## 4. Conclusions

This study identified 17 VOCs, including benzene series, chlorinated hydrocarbons, and chlorobenzenes that were emitted from different treatment units of a coking WWTP. Emission profiles, emission rates, and health risks were studied. The obtained results showed that the concentrations of benzene and toluene were highest in the air phase. The highest concentration ( $857.86 \pm 131.30 \mu\text{g m}^{-3}$ ) of air VOCs was found in the raw wastewater tank. The total emission rate of VOCs was  $1773.42 \text{ g d}^{-1}$ , corresponding to an annual total emission of  $0.65 \text{ tons year}^{-1}$  in this coking WWTP. The treatment capacity of this coking WWTP was about  $1500 \text{ m}^3 \text{ d}^{-1}$ ; therefore, the total VOC emission flux was  $1.18 \text{ g VOCs/m}^3$  of treated wastewater. The non-cancer risk assessment ( $\text{HR} > 1$ ) suggests that the workers suffered an occupational exposure risk from benzene emission from the coking WWTP. The definite carcinogenic risk of VOCs for workers in this coking WWTP above an acceptable level ( $1 \times 10^{-6}$ ) should be noticed. Thus, VOC emissions from coking WWTPs should not be ignored and should be controlled to reduce occupational VOCs exposure.

To reduce unorganized emissions, an imperative control measure should be provided. Special control measures for VOC emission are proposed as follows: Based on the process principle, anaerobic technology is preferred to be selected and used; a pure oxygen or oxygen-enriched reactor is used in an aeration process; powdered activated carbon is added to sludge to increase VOC adsorption. Based on control of VOC emission, the tank should be covered and sealed; therefore, VOCs in exhaust gas are collected for reuse as carbon sources entering the aeration system, or for combustion treatment. Control of VOC emissions from WWTPs is an important work and needs further study.

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## Appendix A. Supplementary data

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