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# Emission and health risk assessment of volatile organic compounds in various processes of a petroleum refinery in the Pearl River Delta, China<sup>☆</sup>

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## ABSTRACT

The process-specific emission of volatile organic compounds (VOCs) from a petroleum refinery in the Pearl River Delta, China was monitored to assess the health risk from VOCs to workers of this refinery. Over 60 VOCs were detected in the air samples collected from various sites in the refining, basic chemical, and wastewater treatment areas of the refinery using gas chromatography-mass spectrometry/flame ionization detection. The health risks of VOCs to the refinery workers were assessed using US Environmental Protection Agency (US EPA) and American Conference of Governmental Industrial Hygienists (ACGIH) methods. Monte Carlo simulation and sensitivity analysis were implemented to assess the uncertainty of the health risk estimation. The emission results showed that C5-C6 alkanes, including 2-methylpentane (17.6%), 2,3-dimethylbutane (15.4%) and 3-methylpentane (7.7%), were the major VOCs in the refining area. *p*-Diethylbenzene (9.3%), 2-methylpentane (8.1%) and *m*-diethylbenzene (6.8%) were dominant in the basic chemical area, and 2-methylpentane (20.9%), 2,3-dimethylbutane (11.4%) and 3-methylpentane (6.5%) were the most abundant in the wastewater treatment area. For the non-cancer risk estimated using the US EPA method, the total hazard ratio in the basic chemical area was the highest ( $3.1 \times 10^3$ ), owing to the highest level of total concentration of VOCs. For the cancer risk, the total cancer risks were very high, ranging from  $2.93 \times 10^{-3}$  (in the wastewater treatment area) to  $1.1 \times 10^{-2}$  (in the basic chemical area), suggesting a definite risk. Using the ACGIH method, the total occupational exposure cancer risks of VOCs in the basic chemical area were the highest, being much higher than those of refining and wastewater treatment areas. Among the areas, the total occupational exposure risks in the basic chemical and refining areas were  $>1$ , which suggested a cancer threat to workers in these areas. Sensitivity analysis suggested that improving the accuracy of VOC concentrations themselves in future research would advance the health risk assessment.

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## 1. Introduction

VOC emissions from anthropogenic sources have been of great concern in China, where VOCs contribute to the high level of surface O<sub>3</sub> pollution and production of secondary organic aerosols (SOAs) (Ramírez et al., 2012). In addition to contributing to the high levels of O<sub>3</sub> and particulate matter (PM) in the air, many VOCs are hazardous air pollutants (HAPs) that pose direct risks to human

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health, ranging from irritants to carcinogenic substances (Axelsson et al., 2010; Colman Lerner et al., 2012). For instance, exposure to BTEX (i.e. benzene, toluene, ethylbenzene, and xylene), which is always found in emissions from petroleum products, has been associated with toxicological effects on human health such as central nervous system depression, respiratory diseases and damage to circulatory systems (Alghamdi et al., 2014; Chen et al., 2016; Durmusoglu et al., 2010; Kyle et al., 2001). As a result, the recognition of potential health risks associated with exposure to some VOCs is urgently needed, and resultant action to determine and regulate exposure to these chemical is required internationally.

In a recent study, Wu and Xie (2017) identified petroleum and related industries as the top emission source of VOCs in China, accounting for 25.1% and 21.6% of total VOC emissions in the nation, respectively, which are greater than the contribution from on-road vehicles. Because petroleum and related industries emit a large amount of VOCs, it is reasonable that refinery workers and people living around refineries should pay close attention to the potential health risks from direct exposure to the VOCs emitted (Axelsson et al., 2010; Cirera et al., 2013; Edokpolo et al., 2015; Glass et al., 2000, 2010; Tsai et al., 2004; Tsai and Wendt, 2001; Wong and Raabe, 2000). However, in developing countries such as China, the underlying health impacts of VOCs emitted from petroleum refineries have not been paid enough attention because of the insufficiency of observational data.

The potential health risks of VOCs, such as cancer and non-cancer risks, can be evaluated using the standard method from the US Environmental Protection Agency (EPA), and the occupational exposure cancer risk can be evaluated using the method from the American Conference of Governmental Industrial Hygienists (ACGIH) (An et al., 2014; Ramirez et al., 2012). Nevertheless, to our knowledge, no study exists in the literature on the evaluation of the health risks from exposure to VOCs in petroleum refineries using both the US EPA and ACGIH methods.

The accuracy and reliability of VOC emission data are essential for health risk evaluation. Previously, little effort has been devoted to the measurement of VOC compositions of different processing units (including fugitive facility leaks, basic chemical units, and wastewater treatment units) in a refinery. In China, several studies have reported the VOC speciation profiles of petroleum refineries (Liu et al., 2008; Mo et al., 2015; Wei et al., 2014). However, the emission characteristics of VOCs from various pieces of equipment and units are dependent on processes of the equipment, and are also region-specific. Therefore, the measurement of VOCs for various facilities inside petroleum refineries is important for formulating effective VOC control strategies on local and regional scales.

In this study, we carried out field VOC measurement close to the source areas in a petroleum refinery in the Pearl River Delta (PRD) region, China, in order to understand the VOCs emission data from different specific processes in the petroleum refinery and to investigate the process-specific characteristics of VOC pollution and their consequent health risks. The health risks for the workers in the petroleum refinery exposed to the emitted VOCs were assessed in two ways: health risk evaluation including non-cancer and cancer risks (US EPA method) and occupational exposure risk assessment (ACGIH method) for workers in the petroleum refinery. To determine the overall uncertainty during the risks assessment, Monte Carlo simulation was used in combination with a detailed sensitivity analysis. Results and findings from this study should be valuable to China's petroleum refinery industry for better understanding of the characteristics of VOC emissions and for supporting policy-making with respect to emission control and protecting the public health.

## 2. Materials and methods

### 2.1. Location of the petroleum refinery and VOCs sampling

The petroleum refinery selected for this study is located in the PRD region in South China (Fig. 1), has an annual processing capacity of 13 million tons of crude oil, and produces 0.22 million tons of ethylene. To get the fugitive emissions characteristics of VOCs within the refinery, process-specific VOC sampling was conducted close to the major processing equipment/units during August 4–15, 2014 and covered most of the key processes of the refinery. Air sampling was carried out at 20 sites distributed across the refining, basic chemical and wastewater treatment areas within the refinery. In the refining area, major oil refining equipment exists, including a catalytic cracking unit (CCU-wax oil), an atmospheric and vacuum distillation unit (AVDU), a desulfurizer unit (DU), and a hydrogenation plant unit (HPU). In the basic chemical area, the major chemical installations include a cracking of quenching zone (CQZ), a separation cooling zone (SCZ), a compression alkali washing area (CAW), a gasoline hydrogenation unit (GH), a hot zone (HZ), a butadiene unit (BU), an aromatics extraction unit (AEU), and an aromatics distillation unit (ADU). In the wastewater treatment area, sampling was carried out next to the regulation tank (RT), oil separation tank (OST), flotation tank (FT), odor treatment unit (OTU), biological treatment unit (BTU), flocculation and sedimentation unit (FSU), adsorption and sedimentation unit (ASU), and biological aerated filter unit (BAF). A simplified flow chart showing key processes in the three sampling areas is given in Fig. 2.

To reflect the actual exposure level of workers in the operation areas, sampling was carried out close to the separate facilities of the refinery. Air samples were collected using pre-evacuated SUMMA canisters by holding the canisters about 1.5 m above the ground for 10–15 min. For each facility, two samples were collected in each observation day during 12:00–13:00 and 17:00–18:00, respectively. The whole sampling process was carried out on days when the wind speed was lower than  $0.5 \text{ m s}^{-1}$  to minimize the impact of the background and other facilities. In total, 17, 29, and 27 air samples were collected in the refining, basic chemical, and wastewater treatment areas, respectively.

### 2.2. VOC analytical methods

The collected samples were analyzed to determine the VOC concentrations using a gas chromatography-mass spectrometry/flame ionization detection system (GC, HP-7820A; MSD, HP-5977E; Agilent Technologies Inc., USA) with a DB-624 chromatography column ( $60 \text{ m} \times 250 \mu\text{m} \times 1.4 \mu\text{m}$ ; Agilent Technologies Inc., USA) based on the EPA TO-15 method (EPA, 2009). The initial temperature of the GC oven was  $38 \text{ }^\circ\text{C}$  which maintained for 3.5 min, and then increased to  $180 \text{ }^\circ\text{C}$  at  $6 \text{ }^\circ\text{C}/\text{min}$ , which was held for 15 min. The entire process took about 43 min. The purity of the carrier gas helium was higher than 99.999%. Before injection, samples were pretreated to remove  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$  and concentrated with a double-channel cryogenic pre-concentrator (Model TH-PKU 300B; Tianhong Co., China).

### 2.3. Quality assurance and quality control (QA/QC)

To minimize contamination, the cryogenic pre-concentrator was baked after the analysis of each sample, and the GC column was baked after 20 samples analyzed. The C2–C11 VOCs were quantified through external standard calibration which was determined via standard gases, including Photochemical Assessment Monitoring Stations (PAMS) and TO-15 standard mixture (65 compounds). Calibration curves were established using the certified

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