Source Identification of VOCs and their Environmental Health Risk in a Petrochemical Industrial Area

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ABSTRACT

Ambient VOCs in the vicinity of a petrochemical industrial area were analyzed for their health impact and potential emission sources. Comprehensive measurements of VOCs were conducted based on U.S. EPA TO-15. Potential carcinogenic and non-carcinogenic inhalation risks were evaluated by comparing the measured concentrations with the inhalation unit risk (IUR) and reference concentration (RfC). The results indicated that a high carcinogenic risk occurred from 1,2 dibromoethane and benzene, while non-carcinogenic risks were attributed to 1,3 butadiene, 1,1,2 trichloroethane, and 3-chloropropene. The Positive Matrix Factorization (PMF) Version 5.0 was further utilized to estimate the contribution of specific sources to the VOC mixing ratio. The results revealed that the average VOC concentration in the community area was dominated by aromatic hydrocarbons, with toluene having the highest concentration. Vehicle exhaust was evaluated as the most contributing emission source of the VOC mixing ratio, followed by industrial processes. Specific VOC ratios were also applied to identify VOC sources. The T/B ratio was within the range 3.54–5.15, confirming that vehicle emissions were the main source of pollutants during the entire investigated period in the community area. As for the industrial area, the average VOC concentration was dominated by alkenes. Industrial processes and the petrochemical industry were the major sources of VOCs. The health risk assessment in the industrial area indicated that acrolein had the highest risk for non-carcinogens. 1,2-dichloroethane and 1,3-butadiene showed high potential as carcinogens.

Keywords: Diagnostic ratio, Health risk assessment, Map Ta Phut, Source apportionment, Volatile organic compound (VOCs)

OPEN ACCESS

Received: March 24, 2021

Revised: December 17, 2021

Accepted: January 6, 2022

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Publisher:

Taiwan Association for Aerosol
Research

ISSN: 1680-8584 print

ISSN: 2071-1409 online

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1 INTRODUCTION

It is well recognized that rapid urban and industrial development are major factors leading to an increase in air pollution. The detrimental impacts of air pollution can occur in both human health and the environment (Dumanoglu *et al.*, 2014; Zhang *et al.*, 2014; Dorter *et al.*, 2020). Volatile organic compounds (VOCs) have been widely considered as one of the major air pollutants owing to their direct and indirect impacts. VOCs were defined by the World Health Organization (WHO) as organic compounds, having a boiling point within the range 50°C–260°C and vapor pressure > 10 Pa at ambient temperature (WHO, 1989; Dorter *et al.*, 2020). The photochemical interactions among VOCs and nitrogen oxide (NO_x) lead to the formation of tropospheric ozone (O₃) and other secondary pollutants, including peroxyacetyl nitrate (PAN) and secondary organic aerosol (SOA) (Carter, 1994; Leuchner and Rappengluck, 2010; Wu *et al.*, 2016). These secondary air pollutants receive a great deal of attention because of their potential environmental and health impacts (Hui *et al.*, 2019; Li *et al.*, 2020; Mozaffar *et al.*, 2020).

Emission sources of VOCs include both anthropogenic and biogenic sources (Huang *et al.*, 2015). Generally, vehicular exhaust and industrial sources are the major anthropogenic sources (Caselli *et al.*, 2010; Ling and Guo, 2014; Zhang *et al.*, 2017). Moreover, VOCs can be released from household products and pesticides (U.S. EPA, 2017b).

Identification of the sources of VOCs can be undertaken by the application of receptor-oriented models (Duodu *et al.*, 2017; Song *et al.*, 2019; Jain *et al.*, 2018; Li *et al.*, 2018). The positive matrix factorization (PMF) model was developed by Paatero (Paatero and Tapper, 1993; 1994) and has become one of the most widely used for source apportionment, following its recommendation by the U.S. EPA (Hopke, 2016). PMF is a tool of multivariate factor analysis that decomposes a matrix of specified sample data into two matrices, namely factor contributions (G) and factor profiles (F). This technique is used to derive a set of source composition profiles, each of which identifies a mixture of compounds associated with a particular emission category. Several studies have applied PMF to determine the potential emission sources of VOCs (Bari *et al.*, 2018; Li *et al.*, 2018; Liu *et al.*, 2020; Li *et al.*, 2021; Xuan *et al.*, 2021).

Health risk assessment is one of the tools for estimating the nature and probability of adverse health effects on people exposed now or in the future to chemicals in contaminated environmental media and for determining the level of treatment needed to address a particular problem. The health risks of VOCs have been reported in epidemiological studies (Jiang *et al.*, 2016; Zhao *et al.*, 2019; Yang *et al.*, 2019; Xiong *et al.*, 2020; Liu *et al.*, 2021). Some VOCs, including benzene, vinyl chloride, 1,3-butadiene, trichloroethylene, and 1,2-dichloropropane, have been classified as carcinogens by the International Agency for Research on Cancer (IARC, 2020).

Previous studies have applied the PMF model and health risk assessment method to evaluate the potential sources and health risk of VOC pollutants. For example, Zheng *et al.* (2020) reported that the main sources of VOCs are fuel evaporation, industrial sources, ethylene industry, and regional background. Acrolein and 1,3-butadiene had the highest non-carcinogenic risk and the highest carcinogenic risk in the petrochemical industry in Wuhan, China. Li *et al.* (2020) identified the major sources of VOCs and evaluated their health risk in Zhengzhou, China. The result revealed that the main source of VOCs was solvent utilization, followed by industrial production, long-lived and secondary species, vehicle emissions, and biogenic emission. None of the VOC species posed a non-carcinogenic risk, but five of them had a carcinogenic risk to the exposed population.

Since VOCs are emitted from a variety of sources and can affect human health. The rapid development of industry causes many environmental and health problems in the area. The results of previous studies indicate that VOC monitoring stations do not fully represent the impact of industrial emissions and the health risk assessment of VOCs in the environment is limited. VOC source identification and health risk assessment would facilitate the development of appropriate and effective control strategies. Findings in other studies are integrated together in this research to be the first attempt in Thailand to evaluate the source and health risk of ambient VOC in the petroleum and petrochemical estate. Comprehensive analysis of the entire potential VOCs emitting activities are intensively analyzed which make it differs from other studies when only single source/factory is considered. To support and advocate the policy in managing industrial air pollution, The Map Ta Phut industrial complex, which is the largest petroleum and petrochemical industrial complex in Thailand, was selected as the study area. This area has suffered from concentrations of ambient VOCs, including 1,2-dichloroethane, benzene, and 1,3-butadiene, that exceed the Thai annual standard (PCD, 2018). The results obtained from this comprehensive study will be very useful for managing and controlling area-based air pollution. The findings and methodology demonstrated in this study can be used to elucidate the source and effect of air pollution in other environmental studies.

2 METHODOLOGY

2.1 Study Area

The Map Ta Phut industrial complex is in Rayong Province, East Thailand (approximately 130 km east of Bangkok). In 1990, the Thai government officially opened the Map Ta Phut industrial estate, the largest industrial park of the country focused on the petrochemical industry and related sectors. The area would rapidly grow and today it houses five industrial estates, one deep-sea port,

Fig. 1. Location of the study area, and VOCs sampling sites (IE = Industrial estate).

and 151 major factories, including petrochemical plants, petroleum refineries, coal-fired power stations, and iron and steel facilities (Thepanondh *et al.*, 2011). Concern on industrial pollution has been raised by the public, particularly with the issue related to air pollution (Hanma *et al.*, 2021). High concentrations of carcinogenic VOCs (benzene, 1,2-dichloroethane, and 1,3-butadiene) were occasionally detected in the community areas.

In this study, comprehensive monitoring of VOCs was conducted within industrial and community zones. The seven monitoring stations in the industrial area were MIEO, I-4, I-3, E-IE, I-2, I-7, and I-1. Twenty VOC compounds were measured at these sites.

Monitoring sites of VOCs in the community areas were HMTP, BTKH, WNFS, MMTP, MCLT, BPLC, and NPKV. There were located covering all direction from industrial complex. Distance to the main road of HMTP, BTKH, WNFS, MMTP, MCLT, BPLC, and NPKV are 0.64, 3.23, 0.02, 0.29, 1.55, 0.63, and 0.62 km, respectively, and distance from Map Ta Phut Complex are 0.62, 0.98, 1.50, 0.32, 1.68, 0.08, and 0.22 km, respectively. Forty-three VOCs were identified and reported monthly for these stations. The spatial distribution of the monitoring sites is shown in Fig. 1.

2.2 Data Collection

Comprehensive measurements were conducted monthly from January 2012 to December 2016. Sampling of ambient VOC concentrations was carried out using 6-liter evacuated canisters (0.05 mm Hg) for 24 h. Samples were analysed in the laboratory using a gas chromatography/mass spectrophotometer (GC/MS) based on the U.S. EPA TO-15. Details of the sampling and analytical procedures are presented elsewhere (Jindamanee *et al.*, 2020; Saikomol *et al.*, 2019; Thepanondh *et al.*, 2011).

Quality assurance and quality control (QA/QC) procedures was implemented to ensure the quality of data. Before sampling, all canisters were cleaned by pressurizing with nitrogen, adding pure water to prevent VOCs adsorption to the inside wall and tested the samples as blank samples to confirm their cleanliness. Samples were transferred from canister to the preconcentration unit which concentrating and minimizing sample volume to be injected into the Chromatograph Mass Spectrophotometer (GC/MS). The air samples were drawn through the heated sampling line to remove moisture and control of the flow rate of the sampling (Saikomol *et al.*, 2019). The duplicate precision was estimated by calculating the percentage difference of sample concentration

and duplicate sample concentration, with less than 25%. For the compounds detected in blanks, the detection limit (MDL) and the method limit of quantitation (MQL) were defined as the results of the calculation by multiplying the standard deviation of field blank values with three and ten, respectively. Quality of the measured data were assured through the QA/QC criteria strictly conducted under this study. The acceptance criteria of the correlation coefficients from the calibration curves were above 0.99. The relative standard deviation values were below 20% and were used in the judgment of the calibration. Method determination (MDL) was determined for each compound and ranged from 0.002 to 0.05 ($\mu\text{g m}^{-3}$). Totally, there were 22,880 measured VOCs concentrations passed these criteria and be used in this study.

2.3 VOCs Diagnostic Ratio

The diagnostic ratio of BTEX (benzene, toluene, ethylbenzene, and xylene) has been used in several studies to identify the emission sources and the age of the air mass of pollution (Masih *et al.*, 2016; Miri *et al.*, 2016; Phuc and Kim Oanh, 2018). The toluene-to-benzene (T/B) concentration ratio is typically used as a tracer to evaluate traffic emissions. T/B in the range 1.5–4.3 represents a traffic-originated emission source (Alfoldy *et al.*, 2019; Golkhorshidi *et al.*, 2019; Kumar *et al.*, 2018; Miller *et al.*, 2012), while a ratio exceeding 10 indicates the influence of industrial sources (Kumar *et al.*, 2018; Tohid *et al.*, 2019; Xiong *et al.*, 2020). Tohid *et al.* (2019) reported that the T/B ratio of 0.13–0.71 and 0.23–0.68 were representative of the contribution from coal combustion and biomass burning, respectively. In addition, the ratios of xylene/benzene (X/B), xylene/ethylbenzene (X/EB), and ethylbenzene/benzene (EB/B) can be used to indicate the age of an air mass and photochemical reactivity in ambient air. A ratio of X/B and EB/B exceeding 1.1, indicates a fresh air mass due to a lack of hydroxyl radicals ($\cdot\text{OH}$) reacting with isomers of ethylbenzene and xylene during daytime (Golkhorshidi *et al.*, 2019; Liu *et al.*, 2008). However, m,p-X/B values lower than 1.8, and o-X/B values lower than 0.9, are also considered as indicative of vehicular emission sources (Cruz *et al.*, 2020).

In this study, the Statistical Package for the Social Sciences (SPSS) analytical software version 21 was used for statistical analysis. The relationship between the BTEX compound at each monitoring station was assessed using Spearman's rank correlation coefficient. The correlation was significant at the 0.01 level (2-tailed). The ratios of T/B, X/B, X/EB, and EB/B were analyzed to identify the emission source of the target compound, as well as their photochemical aging.

2.4 VOCs Source Identification

Several methods have been applied to identify the emission sources of VOCs, including emission inventory (Fu *et al.*, 2020), dispersion models (Song *et al.*, 2019), ratios between specific VOCs (Tan *et al.*, 2020), and receptor models (Ling *et al.*, 2011). Establishing the emission inventory for pollutants in specific area is often time and resource consuming. Uncertainty of the emission inventory is greatly influenced to the performance of the dispersion model. In addition, meteorological data is a required input, the terrains and atmospheric conditions can affect to the modelling results. Unfortunately, in many areas these local data are not available. To overcome this limitation, measured ambient air concentrations at the receptors have been used to identify for their potential emission sources through the application of the receptor-oriented models. Receptor models such as positive matrix factorization (PMF) model, principal component analysis (PCA), chemical mass balance (CMB) model, and UNMIX model have been extensively used to identify sources of VOCs. Among them, PMF has some advantage over other models. The main advantage is that it can individually weight each data point. PMF does not requires comprehensive advance information on source compositions to be able to interpret the results and the non-negativity constraint in PMF is advantage. Ratios between specific VOCs can be initially seek pollutant sources to confirm the results from receptor models.

PMF is a receptor model used to indicate the source profile and source contribution of pollutants through multivariate factor analysis (Shao *et al.*, 2016). Two input files (concentration and uncertainty files) are required to run the model. Details of the PMF model have been described elsewhere (Paatero and Tapper, 1993, 1994; U.S. EPA, 2014). In this study, the PMF model (v.5) was used to quantify the contribution of potential emission sources of VOCs. The mass balance equation of PMF can be expressed as follows:

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (1)$$

where, x_{ij} is the j_{th} species concentration measured in the i_{th} sample, g_{ik} is the species contribution of the k_{th} source to the i_{th} sample, f_{kj} is the j_{th} species fraction from the k_{th} source, e_{ij} is the residual matrix information of the j_{th} species for the i_{th} sample and p is the total number of independent sources (Paatero, 1993).

Factor contributions and profiles are derived by the PMF model minimizing the objective function Q as follows:

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right]^2 \quad (2)$$

where, u_{ij} is the uncertainty information of the j_{th} species from the i_{th} sample.

The missing concentration data were replaced by the geometric mean of the detected concentration while the uncertainty file was prepared following the recommendation from U.S EPA (U.S. EPA, 2014). Additionally, where more than 25% of missing data occurred, or data values were lower than the method detection limit, (MDL), these compounds were rejected from the PMF analysis in this study.

For model input, the uncertainty data was calculated based on USEPA PMF user guide. The concentration sample data uncertainty is calculated using the following equation.

$$Unc = \sqrt{(Error\ Fraction \times concentration)^2 + (0.5 \times MDL)^2} \quad (conc > MDL) \quad (3)$$

Otherwise, the data concentration is below or equal to MDL provided, Eq. (4) is adopted.

$$Unc = \frac{5}{6} \times MDL \quad (conc \leq MDL) \quad (4)$$

where, MDL represents the method detection limit, error fraction. The error fraction in this study was 10%.

The model was run 20 times with a random seed to determine the stability of Q values and the source profile result can be interpreted. To determine the optimal number of sources, the $Q(\text{robust})/Q(\text{true})$ ratio must be less than 1.5 for the result to be accepted (Chen *et al.*, 2019) and results are the most physically reasonable explanations. VOC species were divided into three categories according to signal-to-noise ratios (S/N) and BDL (Below Detection Limit) percentages that were calculated to evaluate the quality of species data. According to the U.S. EPA user guide, the species were divided as “strong” if the S/N ratio is > 2 , “weak” if the S/N ratio is > 0.2 but < 2 or the BDL percentage is $> 50\%$ and “bad” if the S/N ratio is < 0.2 or the BDL percentage is $> 60\%$. According to these rules, all VOC species grouped into strong category.

2.5 Risk Assessment

A standard health risk assessment method recommended by the United States Environmental Protection Agency (U.S. EPA) was applied to estimate the potential harmful health risks (carcinogenic and non-carcinogenic risks) of VOCs. The concentrations of each compound were re-calculated to generate exposure concentrations prior to use for further assessment of health risk following the equation recommended by the U.S. EPA (2009) as follows.

$$EC_i = (CA_i \times ET \times EF \times ED)/AT \quad (5)$$

where, EC is the exposure concentration ($\mu\text{g m}^{-3}$) of chemical i ; CA_i is the contaminant

Table 1. Parameters used in calculation of exposure concentration.

Variable	Description	value		Units
		Community area	Industrial area	
ET	Daily exposure time	24	8	hour day ⁻¹
EF	Exposure frequency	365	250	day year ⁻¹
ED	exposure duration	70	25	year
AT	averaging time	613200 ^a	219000 ^b	hour

^a 70 years × 365 day year⁻¹ × 24 hour day⁻¹.

^b 25 years × 250 day year⁻¹ × 24 hour day⁻¹.

concentration ($\mu\text{g m}^{-3}$) of chemical i in ambient air; ET is the daily exposure time (hours per day); EF is the exposure frequency (days per year); ED is the exposure duration during a lifetime (years); and AT is the averaging time ($ED \times 365 \text{ d y}^{-1} \times 24 \text{ h d}^{-1}$, hours). The variables are presented in Table 1.

Non-carcinogenic risk was estimated by the hazard quotient (HQ) and hazard index (HI) of the same target organ system according to the dose-response relationship. Therefore, the HQ of each compound (i) was estimated as the ratio of exposure concentration (ECi) to the reference concentration ($RfCi$). The hazard quotient (HQ) for non-carcinogenic risk was calculated as follows:

$$HQ = ECi/RfCi \times 1000 \quad (6)$$

HI is the sum of the hazard quotients of toxic air pollutants that can affect humans on the same target organ system. In this study, HI of respiratory, hematologic, nervous, cardiovascular, reproductive, developmental, alimentary, kidney, urinary, and eye systems at each monitoring station were calculated for chronic health effects in non-cancer patients. HI is calculated as the sum of the HQs of the target organ. For non-carcinogenic compounds, it is common to consider the risk to be negligible if the HI is less than or equal to 1.0, while an HI exceeding 1.0 signifies an appreciable risk of human health effects (U.S. EPA, 2009).

For the carcinogenic risk, the risk value for a single carcinogenic compound via inhalation exposure was calculated by multiplying the exposure concentration (ECi) by the inhalation unit risk ($IURi$). The risk characterization for a single carcinogenic compound is expressed as follows:

$$Risk = ECi \times IURi, \quad (7)$$

where $IURi$ is the inhalation unit risk ($\text{m}^3 \mu\text{g}^{-1}$) of chemical i , which is the upper-bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of $1 \mu\text{g m}^{-3}$ in air. The risk predicted to be less than or equal to 1×10^{-6} is usually considered negligible, whereas the risk predicted to exceed or equal 1×10^{-3} was defined as a significant risk (Rodricks *et al.*, 1987). The RfC and IUR values of each VOC were obtained from the Integrated Risk Information System (IRIS). In cases where there is no available information on the IRIS database, the values offered by the Provisional Peer Reviewed Toxicity Values (PPRTV), California Environmental Protection Agency (CALEPA), Health Effects Assessment Summary Tables (HEAST), and Agency for Toxic Substances and Disease Registry (ATSDR), were used in this study.

3 RESULTS AND DISCUSSION

3.1 Characteristics of Airborne VOCs

In the community area, 40 VOC species were analyzed at each monitoring station. Total VOC concentrations were in the range $23.07\text{--}50.31 \mu\text{g m}^{-3}$. Aromatic hydrocarbons was the dominant group ($13.26\text{--}39.79 \mu\text{g m}^{-3}$), followed by halogenated hydrocarbons ($9.65\text{--}14.0 \mu\text{g m}^{-3}$) and alkenes ($0.13\text{--}0.92 \mu\text{g m}^{-3}$). Toluene had the highest concentration ($5.53\text{--}24.61 \mu\text{g m}^{-3}$) at every monitoring stations. High concentrations of toluene, m-,p-xylene, benzene, and ethylbenzene were detected as the top ten VOCs in this area. These VOCs are typically emitted from traffic and industrial processes (Dumanoglu *et al.*, 2014; Hui *et al.*, 2018; Xie and Berkowitz, 2006; McCarthy, 2013).

The average concentrations of 20 VOCs in the industrial area ranged within 17.21–81.80 $\mu\text{g m}^{-3}$, with alkene accounting for 4.0–60.69% of the VOC mixing ratios (0.69–40.53 $\mu\text{g m}^{-3}$). The second dominant group was aromatic hydrocarbons, which ranged between 2.01–12.00 $\mu\text{g m}^{-3}$ (11.68–27.99%) follow by halogenated hydrocarbons (5.21–33.33 $\mu\text{g m}^{-3}$; 26.84–74.78%), aldehydes (5.45–11.34 $\mu\text{g m}^{-3}$; 31.67–26.45%), and others (1.07–1.75 $\mu\text{g m}^{-3}$; 2.50–2.62%). High concentrations of 1,3-butadiene and acetaldehyde were detected within the industrial area. High concentrations of 1,3-butadiene can be found in highly industrialized cities or near oil refineries, chemical manufacturing plants, and plastic and rubber factories, while acetaldehyde is used as an intermediate in the synthesis of other chemicals and used in the production of polyester resins (ATSDR, 2020; U.S. EPA, 2017a).

In community area seasonal variations showed that VOC concentration was higher in the dry (November–April) season than in the wet (May–October) season at all stations which may be due to increasing of evaporated VOCs from potential source at higher air temperatures in dry season and their ability to disperse in a longer distance from their emission sources in the dry season. This is confirmed by the finding within the overall industrial area where VOCs concentrations were higher in the wet season than in the dry season except at the I-7 station. Seasonal variation of VOCs concentrations at each monitoring station in community area and within industrial area are shown in Figs. S1 and S2, respectively. There is no temporal difference of VOC concentrations in different years. Inter-annual variation of total VOCs concentration in different monitoring station in 2012–2016 in community area and within industrial area are shown Figs. S4 and S5, respectively.

3.2 Identification of Potential VOCs Emission Sources

3.2.1 In the community area

In the community area, 40 VOC species were applied in the PMF model, and the results of 11 factors were grouped according to the percentage of tracer species in each emission source. The factors associated with a high percentage of benzene, total xylene, and ethylbenzene, which are the key tracers of gasoline combustion in mobile motors, were identified as vehicle source emissions (Bozkurt *et al.*, 2018; Dumanoglu *et al.*, 2014; Guo *et al.*, 2011; Ling *et al.*, 2014). 1,3,5-trimethylbenzene, and 1,2,4-trimethylbenzene have been demonstrated to be good tracers for diesel vehicle emissions (Bozkurt *et al.*, 2018; Huang *et al.*, 2017). In the PVC industry, vinyl chloride and 1,2-dichloroethane are used as raw materials. Therefore, these VOCs are the major signature of this industrial group. Industrial origins probably emitted toluene, styrene, and 1,3-butadiene. Accordingly, these VOCs are a signature of industrial emissions (Dorter, 2020; Lyu *et al.*, 2016). VOCs from chemicals used in households are generally associated with 1,2-dichloropropene, 1,1-dichloroethylene, acrylonitrile, 1,2-dibromoethane, 1,1,1-Trichloroethane, and benzyl chloride (Saeaw and Thepanondh, 2015). In addition, Freon 11, Freon 12, Freon 113, Freon 114, and carbon tetrachloride were the key tracers of ambient background concentrations (Li *et al.*, 2016; Saeaw and Thepanondh, 2015; Li *et al.*, 2016). The VOCs source profiles from the seven monitoring sites are presented in Figs. S5–S11. The potential emission sources of VOCs in the community area resolved by PMF were vehicle exhaust, non-PVC industrial processes, industrial processes (PVC), chemicals used in households, and background tracers. The possible emission sources at each location were also evaluated separately. For example, the possible emission sources at the HMTP can be explained as follows. There were five possible emission sources in the HMTP. Factor 1 was identified as vehicle emissions, and its contribution to the VOC mixing ratio was 36.91%. Factor 2 was an industrial process source, and the contribution to the total VOC concentration of this source was 34.65%. Factor 3 was identified as arising from industrial process (PVC) emissions, with a percentage contribution to the VOC mixing ratio of approximately 9.5. Factor 4 was the background concentration in ambient air, with a contribution to the total VOCs estimated to be 10.4%. Factor 5 showed that emissions from chemicals used in households contributing approximately 8.5% to total VOCs. The overall results from the PMF analysis indicated that the VOC concentrations in ambient air in the community areas were mainly contributed by vehicle exhaust, accounting for 36.91–48.96% of the VOC mixing ratio followed by industrial processes (15.9–37.9%). This could be explained by the fact that the monitoring stations were located near roads. This result was similar to the result of source analysis using the PMF model in other studies, which reported that vehicle emissions were the main source of VOCs in community areas (Hui *et al.*, 2018; Shao *et al.*, 2016;

Zhang *et al.*, 2017). In addition to the mobile source, emissions from industrial processes were also identified as the second largest contributor to VOC concentrations in the community area in this study.

3.2.2 Within industrial area

Within the industrial area, the PMF model calculated that there were eight factors grouped according to high correlation among compounds. However, these factors were categorized into three VOC emission sources. Sources of VOCs in the industrial area were identified using the marker VOCs of each source that had a high percent contribution to the same factors. In this study, the factors associated with a high percentage of 1,3-butadiene and benzene are markers of the petrochemical industry (Dumanoglu *et al.*, 2014; Hui *et al.*, 2018; Kalabokas *et al.*, 2001). The results from the PMF analysis revealed a similar pattern of source contribution to the VOC mixing ratio as they were in the community area. Vehicle emissions were the major source of ambient VOCs, followed by industrial emissions. However, in the industrial area, the patterns of source contributions at each monitoring station differed. Because ambient VOCs were mainly emitted from non-stack sources, high VOCs could be observed in the vicinity of their sources (Saeaw and Thepanondh, 2015) and it was observed that a high concentration of tracer VOCs could be measured near their specific emission sources. For example, at stations I-4 and I-2, the concentrations of tracer VOCs representing the petrochemical industry were higher than at other stations because these stations were located close to the butadiene manufacturing factory. The possible contribution of each source to the measured VOC concentrations at each monitoring station in this study is summarized in Table 2.

Percentage of source contribution to measured VOCs concentration at each monitoring station under different seasons is summarized in Table S3. In the community area, the patterns of source contributions at each monitoring station in different temporal period (dry, wet season and annual) were not difference. VOC concentrations were mainly contributed by vehicle exhaust followed by industrial processes. However, within industrial area during the wet season PVC source is the dominant emission source for the station No. I-3 which results from high concentration of 1,2-dichloroethane (major raw material use in the PVC manufacturing) detected there. At I-2 station, during the wet season, petrochemical industry is identified as the largest emitter contributed to VOCs concentration due to high concentration of 1,3-butadiene which is a key signature of this source detected there. Percentage of source contribution to measured VOCs concentration at each monitoring station under different seasons is presented in supporting Information (Table S3).

Table 2. Percentage of source contribution to measured VOCs concentration at each monitoring station (%).

Station	Mobile source	Industrial process	Industrial process (PVC)	Background concentration	Chemical used in households	Petrochemical industry
In the community area						
HMTF	36.9	34.6	9.5	10.4	8.5	-
BTKH	41.5	29.6	3.6	20.2	5.1	-
WNFS	48.9	21.9	8.6	13.1	7.4	-
MMTP	47.8	16.3	14.7	14.4	6.8	-
MCLT	45.4	15.9	10.7	19.9	7.9	-
BPLC	38.7	37.9	13.7	5.3	4.5	-
NPKV	43.3	33.5	5.6	12	5.6	-
Within industrial area						
MIEO	-	27.1	60.1	-	-	12.8
I-4	-	38.5	6.0	-	-	55.5
I-3	-	43.3	41.6	-	-	15.1
E-IE	-	61.3	7.3	-	-	31.5
I-2	-	28.8	7.5	-	-	63.7
I-7	-	58.1	13.2	-	-	28.7
I-1	-	43.8	21.2	-	-	35

3.3 Interspecies Ratio Analysis

In this study, the diagnostic ratios of benzene (B), toluene (T), ethylbenzene (Ebz), and xylene (X) were used as indicators to investigate and estimate the relative contributions of vehicle and non-vehicle sources and the age of air mass of pollution in the atmosphere. BTEX was used because it is a major component of vehicle fuel. Therefore, using the BTEX ratio can better identify the source of VOCs, particularly when compared with analytical data from roadside areas.

The average T/B diagnostic ratios at the seven stations in the community area are shown in Fig. 2(a). These ratios were approximately 5.15, 4.38, 3.54, 4.37, 4.71, 4.76 and 3.59 at HMTP, BTKH, WNFS, MMTP, MCLT, BPLC and NPKV stations, respectively. The results suggest that vehicular emissions are an important source of VOCs in this study area. In addition, T/B values ranged from 3.54 to 5.15, indicative of fresh air mass at every station except at the HMTP station, revealing that the monitoring sites were affected by nearby emission sources (Kumar *et al.*, 2018). This result was similar to that of a study in Orleans city, France ($T/B = 2.63\text{--}2.88$) (Jiang *et al.*, 2017), in Doha, Qatar, with T/B in the range of 2.41–3.55 (Alfoidy *et al.*, 2019), in Delhi (3.8–5.3) (Kumar *et al.*, 2018), Doha (2.41–3.55) (Alfoidy *et al.*, 2019), and Tehran (4.566) (Miri *et al.* 2016), which reported that mobile sources were the largest potential source of VOCs.

The average X/B diagnostic ratios at the seven stations in the community area are presented in Fig. 2(b). The height ratio of X/B describes the fresh air mass, indicating that the sources of pollutants were close to the sampling station and the concentration was subject to a low impact from photochemical reactions (Niu *et al.*, 2012; Singh *et al.*, 2016). In this study, the average

Fig. 2. (a) T/B and (b) X/B diagnostic ratios variability at seven stations in community area. The upper and lower bars show the max and min values. The upper and lower horizontal lines of the box indicate third and first quartile values. Horizontal lines inside the boxes show median value.

values of m,p-X/B, o-X/B, Ebz/B, and m,p-X/Ebz were between 0.66–1.55, 0.21–0.52, 0.50–0.98, and 1.33–2.27, respectively. These results confirmed that traffic emissions were the major contributor to VOC in the community area. A comparison of the calculated diagnostic ratios with other studies is summarized in Table 3.

Spearman's correlation coefficient analysis (two-tailed), was used to assess the correlation between the concentration of BTEX species at each monitoring location, as presented in Table 4. A moderate and strong correlation between ethylbenzene and xylene indicated that these VOCs might have been released from mobile emission sources. However, the low correlation between benzene and other BTEX compounds at BPLC and NPKV stations revealed contributions from other sources. However, BTEX compounds can be distributed in the industrial sector, especially in the petrochemical industry (Heibati *et al.*, 2017). A weak correlation coefficient ($r < 0.5$) was found between some BTEX species in MMTP, BPLC, and NPKV stations, and a negative correlation between benzene and ethylbenzene was observed at BPLC station.

3.4 Health Risk Assessment

Arithmetic mean concentrations of VOCs measured in the community and industrial areas were used to evaluate the exposure and health risks to general populations and industrial

Table 3. The specific VOCs ratio (community area).

Location	T/B	X/B	m.p-X/B	m.p-X/EB	o-X/B	EB/B	Sampling location	Reference
HMTP	5.15	-	1.25	2.18	0.36	0.57	urban area	This study,
BTKH	4.38	-	1.10	1.99	0.40	0.55	urban area	Map Ta Phut,
WNFS	3.54	-	1.55	1.66	0.51	0.94	urban area	Rayong,
MMTP	4.37	-	0.95	1.79	0.25	0.53	urban area	Thailand
MCLT	4.71	-	1.46	1.49	0.52	0.98	urban area	
BPLC	4.76	-	0.66	1.33	0.21	0.50	urban area	
NPKV	3.59	-	1.40	2.27	0.32	0.62	urban area	
Tehran, Iran	1.69–2.04	1.77–3.91	-	-	-	0.15–1.21	residential areas	Baghani <i>et al.</i> , 2019
Shiraz, Iran	2.02–3.07	-	0.49–0.74	-	0.62–0.89	0.19–0.28	urban area	Dehghani <i>et al.</i> , 2018
Tehran, Iran	2.63–2.88	3.33–4.40	-	-	-	2.13–2.80	residential areas	Golkhorshidi <i>et al.</i> , 2019
Orleans, France	1.1–3.84	-	-	1.9–2.5	-	-	semi-urban area	Jiang <i>et al.</i> , 2017
Gorakhpur, India	1.8	0.2	-	0.7	-	-	urban area	Masih <i>et al.</i> , 2016
Wuhan, China	1.4	-	-	-	-	-	urban area	Hui <i>et al.</i> , 2018
Algiers, Algeria	2.2–2.9	-	-	2.4–5.3	-	-	road traffic sites	Kerchich and Kerbachi, 2012
Hanoi, Vietnam	1.1–1.4	-	-	1.4–3.2	-	-	heavy traffic urban area	Phuc and Oanh, 2018
Northeastern Brazil	< 2.7	-	< 1.8	-	< 0.9	-	urban area	Cruz <i>et al.</i> , 2020
Ontario, Canada	2.0–6.9	-	-	2.6–3.7	-	-	urban industrial city	Miller <i>et al.</i> , 2012
Tehran, Iran	2.307– 8.922	-	0.887– 7.649	0.63– 36.196	-	-	urban area	Miri <i>et al.</i> , 2019
NCT, India	3.8–5.3	0.7–2.8	-	-	-	-	urban and rural	Kumar <i>et al.</i> , 2018
Doha, Qatar	2.41–3.55	0.84–5.03	-	1.62–4.04	-	-	urban, suburban and rural	Alfoldy <i>et al.</i> , 2019

Table 4. Spearman's correlation coefficient (*r*) between BTEX species at different sampling locations.

Station	Pollutant	benzene	toluene	ethylbenzene	m,p-xylene	o-xylene
HMTP	benzene	1.000				
	toluene	.600	1.000			
	ethylbenzene	.530	.686	1.000		
	m,p-xylene	.752	.562	.546	1.000	
	o-xylene	.706	.817	.752	.764	1.000
BTKH	benzene	1.000				
	toluene	.701	1.000			
	ethylbenzene	.524	.803	1.000		
	m,p-xylene	.580	.732	.780	1.000	
	o-xylene	.598	.808	.827	.904	1.000
WNFS	benzene	1.000				
	toluene	.815	1.000			
	ethylbenzene	.775	.845	1.000		
	m,p-xylene	.866	.883	.909	1.000	
	o-xylene	.774	.828	.852	.913	1.000
MMTP	benzene	1.000				
	toluene	.815	1.000			
	ethylbenzene	.492	.351	1.000		
	m,p-xylene	.189	.183	.593	1.000	
	o-xylene	.457	.409	.741	.723	1.000
MCLT	benzene	1.000				
	toluene	.813	1.000			
	ethylbenzene	.685	.774	1.000		
	m,p-xylene	.737	.866	.819	1.000	
	o-xylene	.759	.861	.818	.928	1.000
BPLC	benzene	1.000				
	toluene	.117	1.000			
	ethylbenzene	-.037	.774	1.000		
	m,p-xylene	.084	.734	.735	1.000	
	o-xylene	.124	.842	.817	.834	1.000
NPKV	benzene	1.000				
	toluene	.361	1.000			
	ethylbenzene	.269	.779	1.000		
	m,p-xylene	.585	.613	.574	1.000	
	o-xylene	.399	.847	.829	.574	1.000

correlation is significant at the 0.01 level (2-tailed).

Correlations ($r > 0.7$) are presented in bold letters.

workers. The risk level was classified into four groups. High carcinogenic risk was defined as risk $> 1 \times 10^{-4}$, probable risk = 1×10^{-5} – 10^{-4} , possible risk = 1×10^{-6} – 1×10^{-5} , and risk less than 1×10^{-6} as negligible risk (Kumar *et al.*, 2018; Tohid *et al.*, 2019).

3.4.1 Non-carcinogenic risk

Table 5 presents the cumulative non-cancer risk obtained from the calculation of the hazard quotient (HQ) of VOCs affecting each target organ system at each receptor station. Overall results in the community area indicated that the highest HQ was obtained from 1,3 butadiene, 1,1,2 trichloroethane and 3-chloropropene. Summation of HQ for the same target organ (HI) was within the safety level ($HI < 1$), indicating low non-carcinogenic risk from VOCs in the general population living in the community area.

For the industrial area, the highest HQ was computed from acrolein (in the range 1.13×10^0 – 5.75×10^0). The hazard index (HI) for the respiratory, reproductive, and nervous systems exceeded 1.0, indicating a high non-carcinogenic risk to workers. These results clearly indicate the necessity

Table 5. Cumulative hazard index (HI) of non-carcinogen chronic health impact on each target organ system.

Monitoring stations	Target organ systems										
	Respiratory System	Hematologic System	Nervous System	Cardiovascular System	Reproductive System	Development	Alimentary System	Kidney	Endocrine System	Urinary	Eye
Community area											
HMTF	5.68E-01	1.14E-01	4.41E-01	2.75E-02	3.99E-01	7.04E-02	4.78E-02	3.45E-02	2.74E-02	1.59E-01	1.39E-01
BTKH	7.23E-01	1.06E-01	2.93E-01	2.91E-02	3.71E-01	4.81E-02	4.30E-02	3.70E-02	2.89E-02	1.43E-01	1.45E-01
WNFS	5.74E-01	7.88E-02	6.50E-01	2.79E-02	1.58E-01	5.14E-02	4.12E-02	3.65E-02	2.83E-02	1.40E-01	1.14E-01
MMTP	5.73E-01	1.23E-01	5.58E-01	3.34E-02	4.95E-01	8.57E-02	5.96E-02	4.15E-02	3.30E-02	1.45E-01	1.48E-01
MCLT	6.35E-01	7.06E-02	3.04E-01	2.78E-02	1.08E-01	4.58E-02	4.12E-02	3.51E-02	2.75E-02	1.39E-01	1.50E-01
BPLC	5.78E-01	1.99E-01	3.78E-01	2.88E-02	1.76E-01	5.46E-02	4.62E-02	3.63E-02	2.95E-02	1.47E-01	1.53E-01
NPKV	5.07E-01	1.20E-01	4.29E-01	3.71E-02	9.27E-02	4.89E-02	5.04E-02	3.68E-02	2.99E-02	1.41E-01	2.68E-01
Industrial area											
MIEO	3.13E+00	1.72E-02	1.02E+00	3.06E-03	2.00E-01	1.07E-02	1.76E-02	7.03E-03	-	-	2.57E-02
I-4	3.68E+00	7.60E-02	8.20E-02	2.92E-03	1.08E+00	9.10E-03	9.28E-03	5.26E-03	-	-	3.08E-02
I-3	3.80E+00	2.87E-02	5.94E-01	2.98E-03	2.38E-01	1.08E-02	4.28E-02	6.89E-03	-	-	1.01E-01
E-IE	3.00E+00	2.25E-02	4.60E-02	2.89E-03	1.83E-01	1.03E-02	8.02E-03	6.53E-03	-	-	2.57E-02
I-2	6.29E+00	3.93E-02	6.73E-02	2.89E-03	2.52E+00	3.29E-02	2.67E-02	2.33E-02	-	-	2.57E-02
I-7	1.18E+01	2.25E-02	6.82E-02	2.98E-03	3.56E-01	9.48E-03	7.16E-03	5.13E-03	-	-	4.84E-02
I-1	3.01E+00	1.55E-02	6.55E-02	3.53E-03	4.86E-02	9.00E-03	8.73E-03	5.36E-03	-	-	2.57E-02

of industrial employees to use personal protective equipment during their work in industrial process areas.

3.4.2 Carcinogenic risk

The carcinogenic risk was analyzed for 20 and 16 carcinogens found in the community and industrial areas, respectively. In this study, the acceptable level for carcinogenic chronic risk was set at 1×10^{-6} .

1,2 dibromoethane had the highest cancer risk in the community. Other compounds were also associated with carcinogenic risks higher than the acceptable level (1,2-dichloroethane, benzene, 1,3-butadiene, acrylonitrile, hexachloro-1,3-butadiene, 1,1,2,2-tetrachloroethane, ethylbenzene, chloromethane, chloroform, carbon tetrachloride, benzyl chloride, and 1,4-dichlorobenzene) at every monitoring station. Vinyl chlorides were greater than 1×10^{-6} at MMTP and BPLC stations, while 3-chloropropene and trichloroethylene exceeded the threshold of 1×10^{-6} at WNFS and NPKV stations. This result revealed the threat to human health from inhalation of carcinogens to people living in the vicinity of this industrial complex.

Data within the industrial area indicated carcinogenic risk at every station arising from inhalation of 1,2-dichloroethane, 1,2-dibromoethane, 1,3-butadiene, benzene, benzyl chloride, 1,1,2,2-tetrachloroethane, acrylonitrile, acetaldehyde, chloroform, and 1,4-dichlorobenzene ($> 1 \times 10^{-6}$). The carcinogenic risks of hazardous VOCs in the community and industrial areas are presented in Figs. 3(a) and 3(b).

4 CONCLUSIONS

Intensive measurements of airborne VOCs were conducted in the largest petroleum/petrochemical industrial complex in Thailand. The contribution and potential health impact of VOCs monitored at 14 monitoring stations located within and outside of the industrial estate were evaluated, and likely sources investigated. In the community area, aromatic hydrocarbons contributed the most to the total concentration of VOCs, followed by halogenated hydrocarbons and alkenes, respectively. Toluene, which was mainly emitted from mobile sources, was the most abundant VOC. As for the industrial area, alkene was the largest contributor to the total VOC concentration measured within the industrial complex, followed by aromatic and halogenated hydrocarbons. PMF results showed that the signature of the vehicle emissions, industrial processes, and petrochemical profile mostly contributed to VOC concentrations. The calculation of HQ and HI indicated the probability of potential non-carcinogenic risk from inhalation in both the industrial area and its nearby community. The inhalation unit risk was also applied to evaluate potential cancer risk. Analytical results in community and industrial areas revealed that there were some VOCs with

Fig. 3. Percentile distribution (25th–75th) of individual VOCs in (a) community and (b) industrial area. The upper and lower bars show the max and min values. The lower and upper horizontal lines of the box indicate first and third quartile values. Horizontal lines inside the boxes show median values.

values exceeding the acceptable risk level of 1×10^{-6} . The findings of this research clearly indicate the potential health impact of inhalation to VOCs in this study area. The methodology presented in this study demonstrates the necessity of identifying the actual emission sources and their contributions to ambient air pollution to set up appropriate emission controls and mitigation measures for the effective management of industrial air pollution.

ACKNOWLEDGMENTS

The authors would like to thank the Pollution Control Department (PCD) and the Industrial Estate Authority of Thailand (IEAT) in providing VOCs monitoring data for this work. Financial support from the Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program (Grant No. PHD/0066/2558) to Nattaporn Pinthong and Sarawut Thepanondh is acknowledged. This study was supported for publication by Faculty of Public Health, Mahidol University, Thailand.

SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version at <https://doi.org/10.4209/aaqr.210064>

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