

Source Apportionment Analysis of Volatile Organic Compounds Using Positive Matrix Factorization Coupled with Conditional Bivariate Probability Function in the Industrial Areas

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Abstract

Ambient volatile organic compounds (VOCs) concentration data from January 2013 – December 2018 were analyzed by using the US EPA PMF (positive matrix factorization) (v5.0) to identify airborne benzene source. We further analyzed for the potential emission source of benzene by analyzed of the extent and magnitude of measured ambient benzene concentrations following the New Zealand's air quality categories by using Conditional Bivariate Probability Function (CBPF). Results from the analysis revealed that the major contributors were mobile sources (62.80 – 44.58%), petroleum industry (15.74 - 43.56%) and refinery (11.86 – 21.46%). Results of CBPF analysis were agreed well with the locations of major point sources. The probability of the extent and magnitude of high level of benzene concentrations of greater than the Thailand annual ambient air quality standard (1.7 μ g/m³) at the receptor sites with respect to wind speed and wind directions were illustrated. It was found that these high concentrations were most likely occurred when the wind blew from South (S) to West (W), Northwest (NW) and Northeast (NE). These results confirmed that mobile source and petrochemical industry contributed as dominant sources of benzene concentrations in the communities were those located in the S-W direction from the benzene monitoring sites.

Keywords: Benzene; Conditional bivariate probability function (CBPF); Positive matrix factorization (PMF); Source apportionment

1. Introduction

Volatile organic compounds (VOCs) are compounds that can evaporate at normal temperature and pressure (US EPA, 2017). They are important precursors to ozone (Carter, 1994; Chameides *et al.*, 1992), can form secondary organic aerosol (Ng *et al.*, 2007), and are among the most important ambient carcinogens (McCarthy *et al.*, 2009; US EPA, 2016). Some examples of sources of personal exposure to toxic VOCs include household cleaners, vehicle exhaust, gasoline vapors, dry-cleaned clothes, and environmental tobacco smoke (ETS) (Anderson *et al.*, 2001). The majority of toxic VOCs in ambient air originate from sources that emit to the outdoors, such as dry cleaners, power plants, and vehicle emissions (UATW, 2000). Understanding the spatial characteristics of VOCs will be able to clearly know to emission source, which identification of VOCs source is essential to develop air quality management strategies to control and reduce ambient VOCs (Paatero and Tapper, 1994).

Benzene is one of the volatile organic compounds that can be found in the environment. In addition, there are important sources from industrial processes, especially coal and oil fuel combustion. Including evaporation from gas stations and from vehicle exhaust (US EPA, 2012). In terms of toxicity, benzene can accumulate in the body by accumulating in the bones and adipose tissue. When benzene enters the body, it results in both acute and chronic cases. In addition, benzene is also classified as a carcinogen (ATSDR, 1997). In Thailand, benzene ambient air concentration standard has been regulated as 1.7 μ g/m³ (annual concentration). Monitoring data of benzene during the year 2013-2018 in the vicinity of several industrial areas were found higher than recommended standard.

The IRPC industrial land is a petrochemical business operator. Refineries and petrochemical plants of the company are located in Rayong province, the company is a manufacturer of primary petrochemical products, including olefins (propylene, ethylene, acetylene and butadiene) and aromatics (toluene, xylene and benzene) and styrene monomer (IRPC, 2015).

In order to manage and control this environmental problem, identification of emission sources of pollutants is necessity. Receptor modeling is one of the most sought-after approach for identification of sources and their respective contribution to airborne VOCs. Positive Matrix Factorization (PMF) is one of receptor model which utilized multivariate method among several source apportionment methods that can satisfactorily resolve the dominant source without any prior knowledge of individual source profiles (Callen et al., 2009; Rai et al., 2016). Therefore, in this study, Positive matrix factorization (PMF) (US EPA Ver. 5.0) was used to identify sources of benzene. The Conditional bivariate probability function (CBPF) was also used in this study to analyze benzene source contributions in relation to winds at the site and has been applied to find source directions. CBPF has been widely used in conjunction with PMF to identify source directions. The IRPC industrial zone; located at Rayong province, Thailand was selected as the study area.

2. Material and method

2.1 Information about the monitoring sites

There were two VOCs monitoring stations in the vicinity of the IRPC industrial land. Monitoring stations were located at Pluagket temple (PKT), and Nongjok school (NJS) respectively. They were located near community and sensitive areas. Characteristics and spatial distribution of VOCs monitoring sites were as presented in Table 1 and Figure 1, respectively.

This industrial land is influenced by two major prevailing wind directions. The south west wind direction is dominant wind. The monitoring station was located downwind from the industrial land. In addition, the opposite wind direction is blown from northeast direction which monitoring station was also located downwind from the industrial land. Wind rose diagram during 2013-2018 is presented in Figure 2.

2.2 Data collection

VOCs ambient concentrations data used in this study were measured by the Pollution Control Department (PCD). Measured data from January 2013 to December 2018 were used for the analysis. VOCs samples were collected by 6 liters evacuated canisters (0.05 mmHg) and were analyzed using gas chromatography/mass spectrophotometer (GC/MS).

The analyze method was based on US.EPA TO15 (U.S. EPA, 1999). As for the sampling, the VOCs sample was drawn into the canisters by the differential pressure between vacuum and atmospheric pressure inside each canister. The sub-atmospheric sampling system maintained a constant flow rate from full vacuum to within about 7 kPa (1.0 psi) or less below ambient pressure by the flow controller which was adjusted to 3.3 ml/ minute for 24-h sampling. Collected sample was pressurized by humidified nitrogen about 20 psia in order to prevent the contamination entering the sample canister. Samples were transferred to the thermal desorption unit, working as a pre-concentrator prior to being sent to GC/MS (Thepanondh et al., 2011).

Monitoring	Direction	Distance	Distance	Distance	Coordinates
site	from	from	to the	to the	(UTM)
	IRPC	IRPC	nearest	main	
	Industrial	Industrial	road	road (m)	
	land	land (m)	(m)		
Pluagket	North	490.27	6.5	106.85	X: 751374
Temple (PKT)				(No.3)	Y: 1400701
Nongjok	Northwest	1650	13.76	1100	X: 750160
School (NJS)				(No.3)	Y: 1402184

Table 1. Characteristics of VOCs monitoring sites in the vicinity of the IRPC industrial land.



Figure 1. Location of the study area and sampling sites.



Figure 2. Wind rose diagram in the study area.

2.3 PMF model

Positive matrix factorization (PMF) is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices factor contributions and factor profiles which then need to be interpreted by an analyst as to what source types are represented using measured source profile information, wind direction analysis, and emission inventories. Details of the method are described in greater detail elsewhere (Paatero and Tapper, 1994; Paatero, 1997). The model is developed by the US.EPA. In this study the PMF version 5.0 is used to identify source profiles and source contributions of measured ambient VOCs.

2.4 Conditional bivariate probability function (CBPF)

Bivariate polar plots show how a concentration of a species varies jointly with wind speed and wind direction in polar

coordinates. The plots have proved to be useful in a range of settings e.g. to characterize airport sources and dispersion characteristics street canyons (Carslaw *et al.*, 2006; Carslaw and Ropkins, 2012; Tomlin *et al.*, 2009). Wind direction together with wind speed can be highly effective at discriminating different emission sources. By using polar coordinates, the plots provide a useful graphical technique which can provide directional information on sources as well as the wind speed dependence of concentrations.

In this study VOCs concentrations were calculated for each wind speed and wind direction. Statistical analysis was carried out using the sector program Statistical Package for the Social Science (SPSS) Version 21. Mean concentration was used to represent concentration of benzene in each wind speed and wind sector when the data had normal distribution. On the other hand, median value represents the benzene concentration when data had skewed distribution.

Category	Measured data	Comment
Action	Exceeds the guideline value	Exceedances of the guideline are a cause for concern and warrant action, particularly if they occur on a regular basis.
Alert	66%-100% of the guideline value	This warning level, which can lead to exceedances if trends are not curbed.
Acceptable	33% - 66% of the guide value	This a broad category, where maximum values might be of concern is some sensitive locations but are generally at a level that doesn't warrant urgent action.
Good	10% - 33% of the guideline value	Peak measurements in the range are unlikely to affect air quality.
Excellent	< 10% of the guideline value	Of little concern: if maximum values are less than a 10 th of the guideline, average values are likely to be much less.

 Table 2. Air Quality Categories (MfE of New Zealand, 2002)

Remark: benzene annual air quality standard = 1.7µg/m³

VOCs concentrations were compared with annual VOCs standard of Thailand. For better evaluation of the result, these concentrations were calculated as percentage of the guideline value (benzene annual concentration standard = $1.7 \ \mu g/m^3$) by adapting the air quality categories regulated by New Zealand. Details are as presented in Table 2. Finally, color will be plotted for each wind speed and wind direction in bivariate poplar plot.

3. Results and discussion

3.1 PMF analysis

In this study, the PMF method was performed to identify the ambient Benzene source contributions during the sampling period. In total, 69 major VOCs species were selected to use as input data for the model. Results of PMF analysis from seven factors were grouped according to presence of signature compounds of each emission category. Possible emission sources of each factor were determined by using relationship among VOCs and their percentage of contribution in the same group.

3.1.1 PMF result for PKT monitoring station

At the PKT VOCs monitoring site, the emission groups were identified as mobile sources, petrochemical industrial process and refinery. Figure 3 shows the source profiles of the seven resolved factors and percentage contributions of the identified sources. Details of each factor is presented in supplementary material Figure S1

Factor 1 was characterized by high percentages of toluene and other aromatics such as ethylbenzene, m,p-xylene, o-xylene, benzene, and 1,2,4- trimethylbenzene. These VOCs species were signature of vehicle exhaust (Muezzinoglu, 2001). Likewise, factor 2 was mainly contributed by 2-propanol, propene, 1,3 butadiene and 1,2,4 trimethylbenzene which are also mainly emitted from the combustion of gasoline and diesel vehicles (Xue *et al.*, 2017). Therefore, factor 1 and 2 were primarily attributed to vehicular exhaust. Total contribution to benzene concentration of factor 1 and 2 were estimated as 44.58 %

Factor 3 was characterized by high percentages of halogenated hydrocarbons includin 1,1-dichloroethane, 1,1,1-trichloroehtane, bromodichloromethane, chlorobenzene, trichloroethylene and 1,2-dichloroethane. Other chemicals such as bromoform, and chlorobenzene mainly used in industrial processes were also found in this factor. 1,2-dichloroethane is widely used as a composition of lubricants, industrial solvents, a gasoline explosion-proof agent is an important symbol of the petrochemical industry (Dumanoglu et al., 2014; Zhou et al., 2011). Factor 4 was characterized by high percentages of cyclohexane, acetone, acetaldehyde, acetonitrile and hexanal. Cyclohexane and acetone were reported as VOCs signature of a petrochemical complex in a study by Sanders and Hers, (2006). Factor 5 was characterized by high percentages of hexane, vinyl acetate, pentane, acrylonitrile, propene, 1,3-butadiene and styrene. Vinyl acetate and propene were shown as tracer of petrochemical plant in previous study (Ziwei *et al.*, 2015). Primary petrochemical including olefins is also manufactured in this industrial complex. This olefins plant is potentially emitted 1,3 butadiene and styrene. Therefore, factor 3, 4 and 5 were identified as Petrochemical industrial process. Total contributions to benzene concentration attributed from factor 3, 4 and 5 were 43.56 %.

Factor 6 and 7 were identified as refinery emission. Factor 6 was characterized by high percentages of 1-propanol, methyl tertbutyl ether (MTBE) and propene. Factor 7 was characterized by high percentages of isobutene, isopropyl alcohol, pentane, acetaldehyde and acetone. 1-propanol is a major constituent of oil. Methyl tert-butyl ether (MTBE) is a gasoline additive as an oxygenate to reduce carbon monoxide and soot that is created during the burning of the fuel and to increase the octane number which is typical tracer of emission of fuel evaporation from gasoline (NCBI, 2020). Isobutene and Isopropyl alcohol are also a gasoline additive. Moreover, propene, acetaldehyde and acetone are signature of fossil fuel combustion potentially released from the catalytic cracking unit (CCU) of the refinery (Wei et al., 2014). Total contribution to benzene concentration of factor 6 and 7 was 11.86 %.



Figure 3. Source profiles derived from the PMF model and source contributions to benzene concentration of PKT monitoring station.

3.1.2 PMF result for NJS monitoring station

Analytical results from the PMF model indicated that there was no contribution of emission sources in factor 1 to ambient benzene concentrations. Therefore, factor 1 was excluded from evaluation of benzene's source contribution at this receptor. Source profiles of the six resolved factors and percentage contributions of the identified sources is presented in Figure 4. Details of each factor is presented in supplementary material (Figure S2).

Factor 2 was characterized by high percentages of 1,2,4-trimethylbenzene, 1,2-dichloroethane toluene, m,p-xylene, o-xylene and ethylbenzene. 1,2,4-trimethylbenzene is signature VOCs tracer of diesel exhaust (Liu et al., 2008). 1,2-dichloroethane is gasoline additive to leaded gasoline as a lead scavenger (US EPA, 2000). Toluene, m,p-xylene, o-xylene and ethylbenzene species are signature VOCs of vehicle exhaust. Factor 3 was characterized by high percentages of propene, 1,3-butadiene, 1,2-dichloroethane and 2-butanone (MEK). Propene, 1,3-butadiene and 2-butanone (MEK) could be produced by burning fossil fuel and is present in vehicle exhaust (Hwa et al., 2002; Geng et al., 2010; NCBI, 2019). Factor 4 was characterized by high percentages of dichloromethane, toluene, benzene, ethylbenzene and cyclohexane which obviously these tracers

as vehicle exhaust. In addition, an average T/B (toluene/benzene) ratio measured at this monitoring site was less than 2 (Figure 5) which indicated that the pollutants in the area were significantly affected by vehicle exhaust (Chen *et al.*, 2012; Li *et al.*, 2013; Nelson and Quigley, 1984). Therefore, factor 2, 3 and 4 were merged into one common source as mobile source. Total contributions to benzene concentration attributed from factor 2, 3 and 4 were 62.80 %.

Factor 5 was characterized by high percentages of vinyl acetate, 1-propanol, hexanal, and cyclohexane. Vinyl acetate and cyclohexane is a tracer of petrochemical plant (Ziwei et al., 2015, Sanders and Hers, 2006). Hexanal is used to make chemical used for production of plastics in this petrochemical plant. Factor 6 1,1,2,2-tetrachloroethane, bromoform, 1,2-dibromoethane, cis-1,3-dichloropropene, trans-1,3-dichloropropene. These VOCs species are tracers of petrochemical industrial (Dumanoglu et al., 2014; Zhou et al., 2019). Therefore, factor 5 and 6 were identified as petrochemical industrial process. Total contributions to benzene concentration attributed from factor 5 and 6 were 15.74 %.

Factor 7 was characterized by high percentages of isobutene, pentane, benzene, hexane and cyclohexane. These VOCs species were tracer as refinery in previous study (Wei *et al.*, 2014). The contribution of this factor was 21.46 %.



Mobile source
 Petrochemical
 Refinery

Figure 4. Source profiles derived from the PMF model and source contributions to benzene concentration of NJS monitoring station.





Figure 5. T/B ratio of each monitoring station (a) PKT monitoring station (b) NJS monitoring station.

3.2 Bivariate polar plot results

In this study, measured ambient benzene concentrations were calculated as percentage of the annual ambient benzene standard value $(1.7 \ \mu g/m^3)$ by adapting the air quality guideline regulated by New Zealand (Table 2). Each air quality categories represented by different color were plotted for each wind speed and direction cells in the bivariate polar plot. This type of polar plot analysis has, in part, become wide-spread due to the open-source polar Plot function available in the *openair* R package (Carslaw and Ropkins, 2012; R Core Team, 2016; Grange 2016).

Measured benzene concentrations are compared with its ambient air quality standard $(1.7 \,\mu g/m^3)$. Bivariate polar plot of the percentage of measured concentrations from the standard for each wind speed and wind direction are illustrated in Figure 6. As for PKT monitoring station, the diagram illustrates that high concentrations of benzene which their values exceed ambient benzene standard were predominantly dispersed from northwest-southwest directions. These directions are situated by the petrochemical industrial facilities (about 800 meters away from southwest direction of PKT monitoring station). High concentrations of benzene traveled from northwest direction may be affected by petrol distribution activities located about 500 km away in this direction from PKT monitoring station. Moreover, in the calm wind condition (wind speed < 0.5 m/s), concentrations of benzene were within alert category (66% - 100% from the

ambient air quality standard). Considering that this monitoring site is located at the curbside of the road, the result reveals the influence of traffic emission to measured benzene concentrations at this site.

Result of the bivariate polar plot for NJS monitoring station is shown in Figure 6b. The bivariate polar plot reveal that high concentrations of benzene was dominated by S direction at wind speed 3-5 m/s. There are main roads and tank farms (petroleum and petrochemical products) located in the upwind direction from this receptor. This result was coincided with the PMF analysis which indicated that mobile sources were the major contributor to benzene ambient concentrations followed by petrochemical industrial activities. The source region in northeast direction led to high concentrations of benzene at the receptor were evaluated as a contribution from traffic emissions do lie in this wind direction.

Results from this study demonstrated that using PMF coupled with CBPF is success in identification of the potential benzene emission sources. PMF results showed that mainly petrochemical plants and vehicle exhaust were the major emission sources contributed to ambient benzene concentrations at the interested receptor point. Taking into consideration that there are petrochemical industries located in both southwest and northeast directions from PKT monitoring station, results from the bivariate polar plot clearly indicated that those emissions from southwest directions were greatly affected to high ambient concentrations measured at the receptor point.



Figure 6. Bivariate polar plot (percentage of concentrations as compare with annual standard value $(1.7 \ \mu/m^3)$ (a) PKT monitoring station (b) NSJ monitoring station.

4. Conclusion

Positive Matrix Factorization (PMF) were used to identify the emission source of airborne benzene and to evaluate contribution of each emission source to total benzene concentrations. Furthermore, Conditional Bivariate Probability Function (CBPF) were analyzed to evaluate the extent and magnitude of ambient benzene concentration towards wind sectors from each receptor sites. VOCs monitoring data from January 2013 - December 2018 were analyzed in this study. Source apportionment results identified that there were 3 major sources which mostly contributed to measured benzene concentrations at the receptors. At PKT, the source contribution to ambient benzene concentrations from mobile source, petrochemical industrial process and refinery were 44.58%, 43.56% and 21.46%, respectively. Percentage of source contribution at NJS receptor from mobile source, petrochemical industrial process and refinery were 62.80%, 15.74% and 11.86%, respectively. In term of measured benzene concentrations. measured concentrations at PKT monitoring station were higher than those at NJS monitoring station. Higher contribution of mobile source at NJS when comparing with PKT can be explained by the finding in this study which reveal that the major emission source contributed to benzene concentrations measured is the industrial source. On the other hand, the major contributed source of this compound at NJS is vehicle emission. PKT site are located closer to petroleum industrial land than NJS site. It is also located in downwind direction from the industrial source when considering the patterns of prevailing winds in Thailand. These results were consistent with diagnostic ratios which is mean value

of T/B ratios. Mean T/B ratios of NJS was 1.9 which indicated that mobile source as most significant source in PKT monitoring station. Furthermore, Results of T/B ratios for PKT was 3.1 which indicated that there are other sources besides vehicle exhaust emissions which showed benzene contributions of both monitoring site from PMF results coincided with measured T/B ratios value in each monitoring station. Bivariate polar plot of PKT monitoring station was found that these high concentrations were most likely occurred when the wind blew from South (S) to West (W) and Northwest (NW) while for NJS monitoring station, South (S) to West (W) and Northeast (NE) was prominent directions. These results confirmed that mobile source and petrochemical industrial play as dominant source of benzene concentration in the communities were those located in the S-W direction from the benzene monitoring sites.

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Author Contributions

Kanisorn Jindamanee (Postgraduate student) conducted data analysis and wrote up the manuscript. Sarawut Thepanondh (Professor) designed research methodology and proved check of the manuscript. Natchanon Aggapongpisit (Researcher) collected VOCs data and Sirapong Sooktawee (Environmental expert) assisted in CBPF analysis.

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Figure S1(Cont.) Source profiles to benzene concentration of PKT monitoring station.

