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PRIORITIZATION AND COMPLEXITY EVALUATION OF AIRBORNE VOLATILE ORGANIC COMPOUNDS CHARACTERISTICS

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ABSTRACT

In this study, VOCs ambient concentrations measured in Bangkok, Thailand from January 2008 to January 2012 were analyzed. Data from VOCs monitoring stations represented roadside, general, and suburban areas of Bangkok were interpreted. Each VOCs sample was speciated for 44 compounds and was reported on a monthly basis. Data analysis was carried out for the concentration and the hazard quotient (HQ) of each compound to evaluate the potential hazards to human health. Prioritization of VOCs was carried out by numerical analysis using a Pareto distribution and Power Zipf law principle of the concentration and the hazard quotient data. Results indicated that toluene had the highest concentration, while trichloroethylene and 1,3 butadiene were found mostly in Bangkok Metropolitan Area. Furthermore the results also showed that these compounds were dominant chemical species which resulted in small complexity of VOCs in the study area.

Keywords: Volatile organic compounds, Hazard quotient (HQ), Pareto distribution, Power zipf law

1. INTRODUCTION

Increasing economic activities in the Bangkok Metropolitan Region (BMR) has been a predominant force in Thailand's growth over the past 30 years.The rise in population and transportation sectors resulting from rapid economic growth has raised concerns for acute air pollution in Bangkok. Traffic congestions and associated poor air quality have traditionally been majorproblems in Bangkok (Energy Sector Management Assistance Programme, 2003).Emissions from motor vehicles are the dominant source of VOCs and NO_2 in the urban area (Srivastava *et al.*, 2004; Srivatava *et al.*, 2006; Parra *et al.*, 2009).

VOCs (Volatile Organic Compounds: VOCs) are defined by WHO (World Health Organization) as organic compounds having boiling point below 240 – 260 degree Celsius; under this definition, numerous organic compounds fall into this category. VOCs are released easily from a source to the ambient air and cause air pollution.

Health impacts of VOCs are well recognized (Elbir *et al.*, 2007; Yang *et al.*, 2012). The main non-carcinogenic chronic effects of VOCs are irritative, sensory effects, damage to the liver, kidneys and central nervous system, asthma and other respiratory problems. The main carcinogenic effects are lung, blood, liver, kidney and biliary tract cancer (WHO, 2000). There are 3 pathways of VOCs exposure routes to human: inhalation, oral, and dermal exposure.The main exposure route to most VOCs is through inhalation (Ramirez *et al.*, 2012). Although the evidence as to whether VOCs cause health problems remains equivocal, it generally is widely accepted that it has potential negative effects on health (Atari and Luginaah, 2013). However, while low levels of VOCs may have no significant health impacts, the interaction between VOCs species and other criteria pollutants can cause adverse health outcomes (Leikauf, 2002).

As for Bangkok, routine monitoring of airborne VOCs has been carried out since August 2006. Samples were collected once a month. Samples were taken for 24±1 hours from the start of sampling until the end of sampling on the following day. Twelve dataset were collected and were utilized for calculations of moving annual average concentrations. At present, the Thai government designate ambient air quality standard for nine VOCs compounds namely benzene, 1,3 butadiene, chloroform, dichloromethane, 1,2 dichloroethane, 1,2 dichloropropane, tetrachloroethylene, trichloroethylene and vinyl chloride. It was discovered that an annual concentration of benzene and 1,3 butadiene exceeded ambient air quality standard in some areas in Bangkok (Thepanondh *et al.*, 2011). High concentrations of these compounds were expected to be mainly emitted from mobile sources.

2. METHODOLOGY

In this study, VOCs ambient concentrations measured in Bangkok, Thailand from January 2008 to January 2012 were analyzed. Data from VOCs monitoring stations namely ERTC, Chulalongkorn hospital, Chokchai4, Bansomdej and Dindaeng were used in this analysis. These data were obtained from the Pollution Control Department. VOCs were sampled and analyzed using US.EPA TO 15 method. Each sample was speciated for 44 compounds and reported on a monthly basis.

Data analysis was divided into concentrations and hazard quotients (HQ) in order to evaluate the potential of the hazards on human health. HQ isa ratio of estimated exposure to reference level at which no adverse health effects are expected. The HQ was calculated from Equation (1)as shown below (Zhang *et al.*, 2012).

$$\boxed{HQ = LEC/RfC} \qquad (1)$$

Where:

HQ = Hazard quotient

LEC = Average daily received concentration ($\mu g/m^3$) at 95 %

RfC = Reference concentration ($\mu g/m^3$)

HQs >1 indicated that the VOC concentrations exceed the benchmark concentration and could be of public health concerns. If the HQ was < 1, no harm was expected because the exposure was below the threshold (the RfC) for an adverse effect (Lerner *et al.*, 2012).

3. RESULTS AND DISCUSSIONS

Prioritization of VOCs compounds was carried out by using Pareto distribution analysis and power Zipf law equation. Spatial evaluation from prioritization analysis was carried out by comparing these results at each station. Results from analysis of VOCs concentration, as indicated in the top tenth compounds having contribution more than 80% of total VOCs concentration, were as presented in Figure 1-5.

Figure-1. Prioritized VOCs of ERTC (using VOCs concentrations)

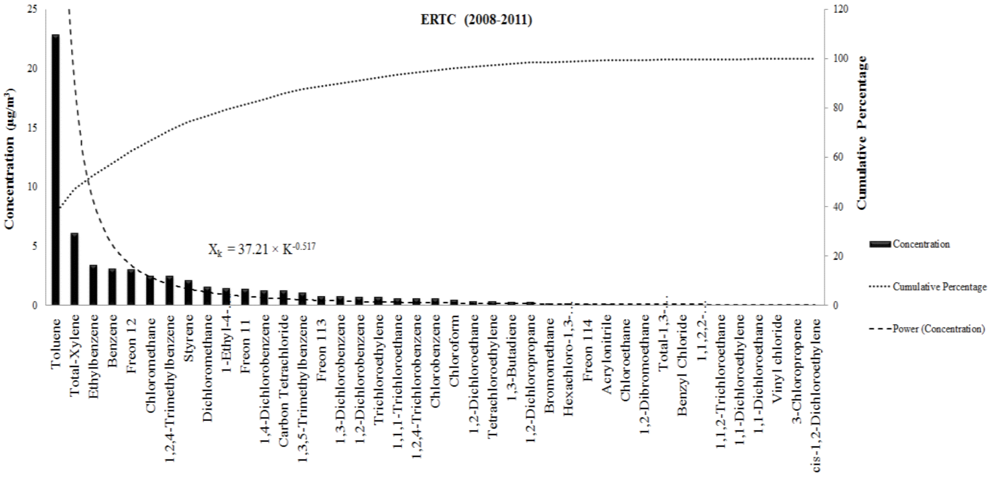


Figure-2. Prioritized VOCs of Chulalongkorn hospital (using VOCs concentrations)

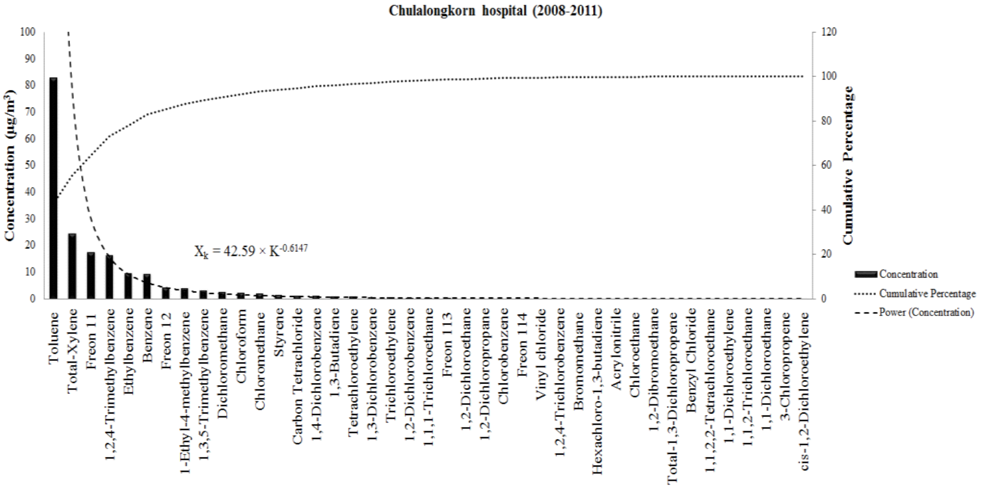


Figure-3. Prioritized VOCs of Chokchai4 (using VOCs concentrations)

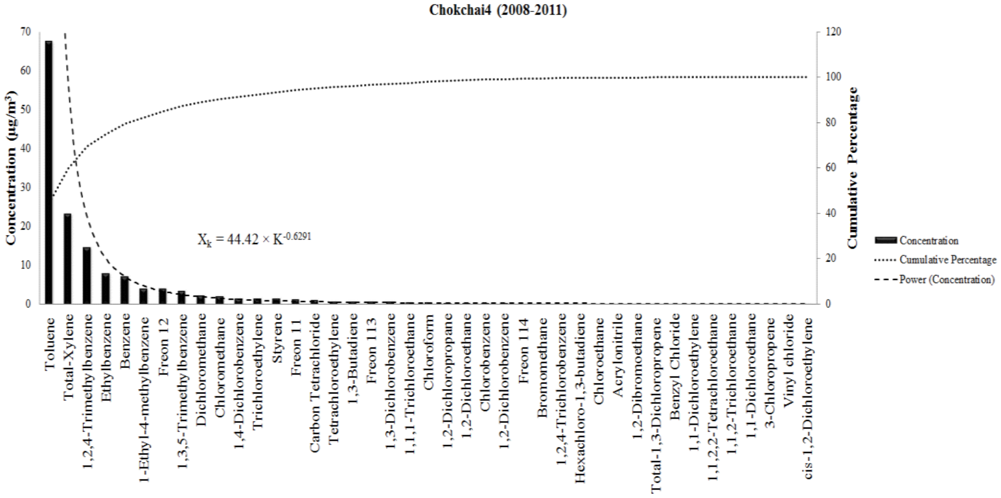


Figure-4. Prioritized VOCs of Bansomdej (using VOCs concentrations)

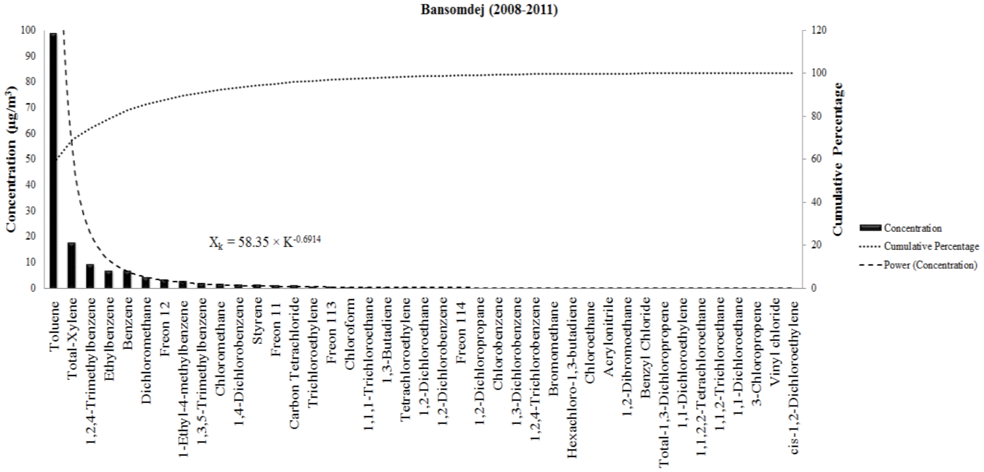
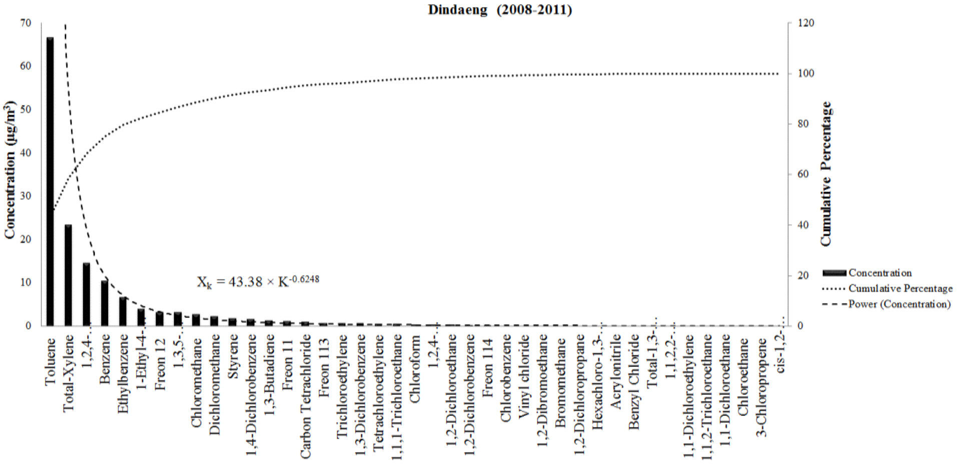


Figure-5. Prioritized VOCs of Dindaeng (using VOCs concentrations)



While toluene had the highest concentration, a Pareto distribution analysis of HQ indicated that trichloroethylene and 1,3 butadiene were the most hazardous VOCs found in the Bangkok Metropolitan Area as shown in Figure 6 - 10.

Figure-6. Prioritized VOCs of ERTC (using the Hazard Quotients)

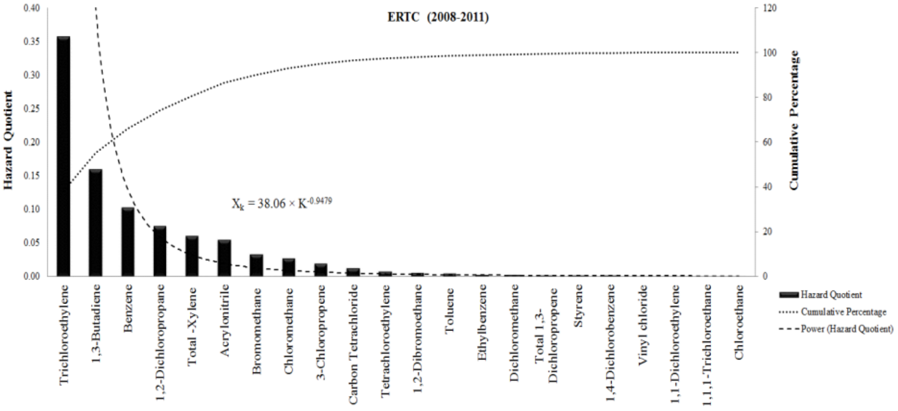


Figure-7. Prioritized VOCs of Chulalongkorn hospital (using the Hazard Quotients)

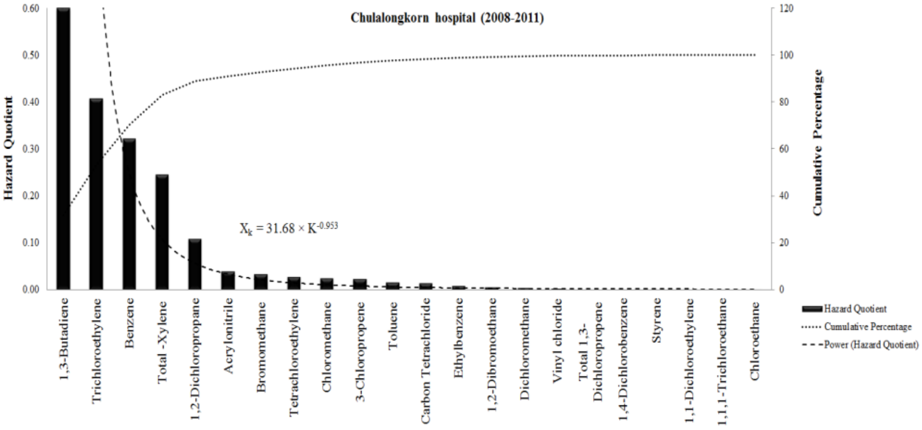


Figure-8. Prioritized VOCs of Chokchai4 (using the Hazard Quotients)

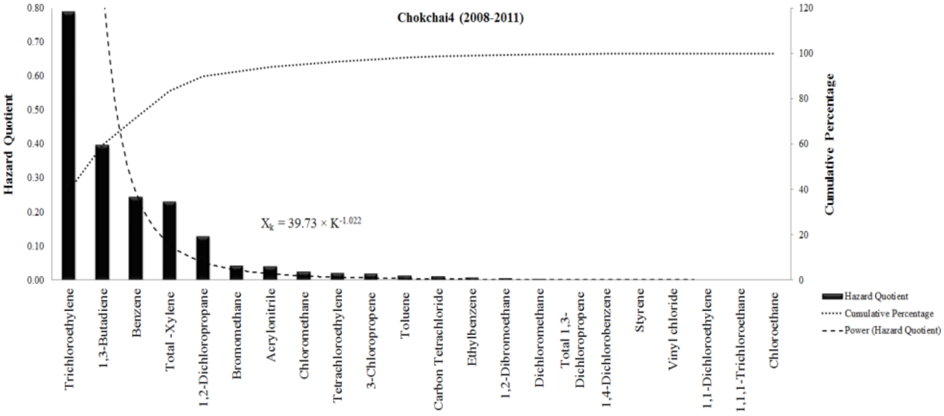


Figure-9. Prioritized VOCs of Bansomdej (using the Hazard Quotients)

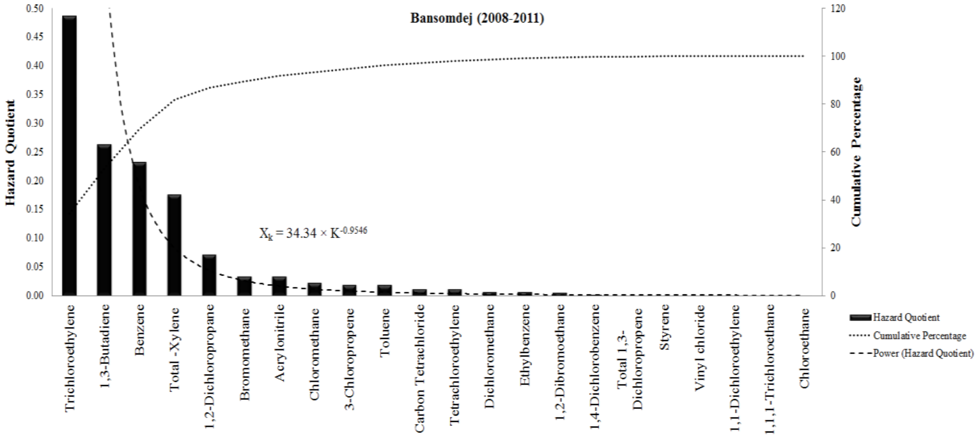
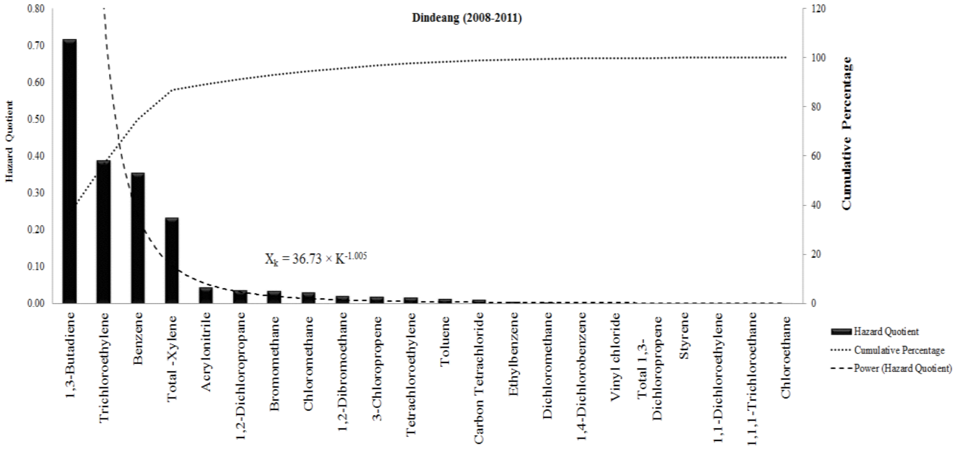


Figure-10. Prioritized VOCs of Dindaeng (using the Hazard Quotients)



VOCs monitoring stations in this study were grouped and classified to represent roadside/traffic area and general area of Bangkok. We further examined the common species of VOCs found in traffic and general areas in Bangkok using intersect analysis. Firstly, prioritized VOCs obtained from analysis of concentration and Hazard Quotient (HQ) data from roadside monitoring stations (Dindaeng, Chokchai 4, Chulalongkorn hospital) were grouped and were analyzed. By intersect analysis, common species of VOCs which were normally found in traffic areas in Bangkok were revealed. Results from this analysis were used to intersect with those prioritized VOCs at Bansomdej station (representing the general area of Bangkok). Results revealed common VOCs species which should be given priority for management in Bangkok areas. It was found that the prioritized VOCs at these represented areas were similar. These compounds were 1,3-Butadiene, Trichloroethylene, Benzene and Total-Xylene, respectively.

Evaluation of complexity of VOCs in the study area was carried out by analysis of α value in a power zipf law equation. Power law relates the frequency or probability of occurrence of an item or event and its rank -- "k" through an inverse dependence relationship (Ginebreda *et al.*, 2012). This relationship can be expressed as the following equation:

$$X_k = X_1 \times (\frac{1}{k})^{\alpha} = X_1 \times k^{-\propto}$$

Where X_k is the frequency (or probability) of occurrence of k element, k is the rank and α a power parameter. In our case, X_k is identified either with the percent of concentration or the normalized hazard quotient.

Since α exponent actually governs the shape of the curve (i.e., how steep or flat it is), it can be also interpreted as an alternative measure of "complexity". In the context of Equations and taking into consideration that α is comprised between 0 and ∞, the term complexity must be understood in the following sense: minimum complexity (maximum simplicity) corresponds to a "mixture" of only one compound which occurs when $\alpha = \infty$ (from Equations, it is straightforward to see that $X_k$vanishes for all k> 1, since $k^{-\infty} = 0$; only if $k = 1$ then $k^{-\infty} = 1^{-\infty} = 1$); by contrast, the opposite situation ($\alpha = 0$) can be thus qualified as "maximum complexity". In that case, $X_1 = X_2 = \ldots = X_k$, since $k^{-0} = 1$ for all k. Lowering a more even distribution of compounds, or in other words, they would denote more complex mixture in the above sense (Ginebreda *et al.*, 2012).

A place having the highest complexity of VOCs was ERTC as shown by the lowest value of α (α = 0.517). It was found from the analysis that the complexity of VOCs, measured at roadside and general areas in Bangkok, were quite similar (α = 0.691-0.615) as shown in Table 1. This finding indicates that there were some VOCs in these areas having dominant concentration over other compounds. These compounds were Toluene, Total-Xylene, 1,2,4-Trimethylbenzene, Ethylbenzene and Benzene.

Table-1. Summary of complexity analysis for spatial evaluation (Concentration)

Station Name	**α**	**Prioritized VOCs**		**Complexity**
		Pareto distribution	**Zipf law**	
Bansomdej	0.691	5	2	Lowest
Chokchai 4	0.629	6	3	
Dindaeng	0.625	6	3	↓
Chulalongkorn hospital	0.615	6	3	
ERTC	0.517	11	3	Highest

Results of the complexity analysis by using hazard quotient data indicated that there were no spatial differences in complexity of VOCs compound. The lowest value of α was calculated at ERTC (α = 0.948) while the highest α was predicted at Chokchai4 (α = 1.022). These results indicated that there were only some VOCs compounds having their concentrations in the level that might cause a health impact in the study area. Beyond 44 VOCs, measured in the monitoring program; there were only 4 compounds that could be considered as prioritized VOCs taking into consideration their level of hazard quotient. These compounds were Trichloroethylene, 1,3-Butadiene, Benzene and Total-Xylene. Summary of the analysis was as shown in Table 2.

Table-2. Summary of complexity analysis for spatial evaluation (Hazard Quotient)

Station Name	α	Prioritized VOCs		Complexity
		Pareto distribution	Zipf law	
Chokchai 4	1.022	4	4	Lowest
Dindaeng	1.005	4	5	
Bansomdej	0.955	4	5	↓
Chulalongkorn hospital	0.953	4	6	
ERTC	0.948	5	4	Highest

4. CONCLUSION

Results from analysis of the complexity of VOCs characteristic in Bangkok indicate that the sub-urban area has the highest complexity of VOCs. At roadside station complexity of VOCs is smaller than the general area and sub-urban area. These results indicate that there are some dominant VOCs species that should be given priority in VOCs management in the study area. By considering concentration of the compounds, toluene should be given a priority in pollution management since it accounts for more than 50% of total VOCs concentration in Bangkok. However, by considering the health impact of VOCs substances; trichloroethylene and 1,3 butadiene should be given priority for the management. The results clearly indicate differences of prioritized VOCs at each monitoring sites. It also should be noted that using only measured concentrations without considering the impact on human health might mislead the management of these air toxics. Prioritization method can reveal the common VOCs species which are required for further management.

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