SEASONAL AND SPATIAL VARIATION OF AMBIENT AIR VOLATILE ORGANIC COMPOUNDS IN PATHUMWAN DISTRICT, BANGKOK, THAILAND

Tanasorn Tunsaringkarn¹, *, Tassanee Prueksasit², Daisy Morknoy³, Saowanee Semathong¹, Anusorn Rungsiyothin¹, Kalaya Zapaung¹

¹College of Public Health Sciences, Chulalongkorn University, Bangkok 10330, Thailand
²Department of General Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
³Environmental Research and Training Center, Ministry of Natural Resources and Environment, Pathumthani 12120, Thailand

ABSTRACT:
Ambient air pollution, mainly from motor vehicle emissions, is a serious problem in Bangkok, Thailand, and in many other cities. Ambient levels of the volatile organic compounds (VOCs) benzene, toluene, ethylbenzene and xylene (BTEX) and 12 carbonyl compounds (CCs) were evaluated at university and roadside areas in Pathumwan District, central Bangkok, Thailand, during wet and dry seasons in 2012 and 2013. Toluene was the most abundant BTEX while formaldehyde and acetaldehyde were the most abundant CCs. Benzene levels were highest in the university area in the wet season. Benzene, xylene, formaldehyde and acetaldehyde levels were significantly higher in the wet season than in the dry season (p<0.001). The ranges of toluene to benzene ratio (T/B) and formaldehyde to acetaldehyde ratio (F/A) in both seasons were 1.49-2.05 and 2.50-2.89, respectively.

The urinary trans,trans-muconic acid (t,t-MA), hippuric acid, formaldehyde and acetaldehyde of 287 outdoor workers in the study area were measured in both seasons. Urinary t,t-MA and formaldehyde at roadside areas were significantly higher in the wet season than in the dry season (p<0.001 and p<0.01). The same was true for urinary formic acid. While urinary formic acid of workers in both areas were significant higher in wet season than dry season. Overall, ambient VOC levels were higher in roadside areas than in the university area, and were higher in the wet season than in the dry season. There were associations of ambient levels of benzene, toluene, formaldehyde and acetaldehyde with urinary biomarkers of t,t-MA, hippuric acid, formaldehyde and acetaldehyde respectively.

Keywords: Volatile organic compounds, Carbonyl compounds, Urinary biomarker, Outdoorworker

INTRODUCTION

Volatile organic compounds (VOCs) of aromatic compounds as benzene, toluene, ethylbenzene and xylene (BTEX) and carbonyl compounds (CCs) of formaldehyde and acetaldehyde are abundant in atmosphere [1-3]. Most of them are mainly emitted directly from exhaust gases of motor vehicles and incomplete combustion of hydrocarbon fuels [4-5]. They have adverse health effects on human [6-8]. Bangkok, highly population city which air pollution is one of the serious problems. The population growth has led to major increasing of air pollution. There are rapidly increasing motor vehicle number a year and most them are used biofuel as gasohol and biodiesel, light petroleum gas (LPG) as government policies at present [9, 10]. Health impact of air pollution on mortality in Bangkok is fairly consistent which many effects from gaseous pollutants were attenuated in multipollutant models, while effects from particulate matter < 10 μm in aerodynamic diameter (PM₁₀) appeared to be most consistent [11]. The annual global mortality attribute to outdoor air pollution were range from 0.8 to over than 4.0 million which attributed deaths occurred in Asia [12, 13]. The epidemiological studies have been limited

* Correspondence to: Tanasorn Tunsaringkarn
E-mail: tanasorn.t@chula.ac.th

which VOCs levels continue to exceed Thailand’s standards [14, 15]. There were seasonal variations of
gaseous pollutants including PM$_{10}$ in recent studies
[16-19]. This study aimed to evaluate seasonal
variation of ambient air VOCs of BTEX and CCs in
Urban Area, Central Bangkok, Thailand.

**MATERIALS AND METHODS**

**Study sites**

The study was carried out in 16 sites particularly on 10 sites on the main roadsides of
Rama road 1, Phayathai road, Henrydunant road and
6 sites in Chulalongkorn University which all sites
are in Pathumwan area, central Bangkok, Thailand. Main study sites of roadsides were located at
Community Pharmacy Clerkship (CPC), Bangkok
Bank Public Company Limited (BBL), Krung Thai
Bank Public Company Limited (KTB), Siam
Commercial Bank Public Company Limited (SCB),
Faculty of Science (FS) and study sites in
university were located at Satit Chula (SC),
University Entrance-Exit Gate 1-4 and checkpoint
behind Faculty of Science as shown in Figure 1.

**Population study**

Total 287 outdoor workers were included by
random in this study who were 76 security
guardsmen of university, 76 motorcycle drivers and
135 street All inclusion criteria of workers were
healthy, age over 18 years old, work period more
than 3 months and signed consent from and
interviewed the characteristics of age, weight,
height, period of employment, working hour a day
and working day a week. This study was approved
by the Ethical Review Committee for Research
Involving Human Research Subjects, Health
Science Group, Chulalongkorn University (COA
No. 089/2012).

**Ambient air sample collections and analyses**

Total thirty two ambient air monitoring study
sites were collected for 8 hours working time (8.00
A.M – 15.00 P.M) of workers during wet season
(September to October 2012) and dry season
(February to March 2013). Ambient air samples
were collected by active charcoal tube with flow rate
100 mL/min for benzene, toluene, ethylbenzene,
xylene (BTEX) analyses by GC/FID [20] and
collected by 2,4-dinitrophenylhydrazine (DNPH)
cartridge for formaldehyde and acetaldehyde
analyses by HPLC/UV-VIS according to Method
TO-11A [21] and Method 150 [22]. Both cartridge
and charcoal tube were kept at 4°C during
transportation to the laboratory and were stored in a
refrigerator until further analysis. Quantification was
performed using the external calibration method.
The coefficients of BTEX and CCs determination
(R$^2$) ranges were 0.991–0.999 and 0.999–1.000. All
sample analyses were done by triplicate.

**Urinary sample collections and analyses**

The cross-sectional study of 287 urine samples
of all workers were collected by glass bottle after 8
hours working time (8.00 A.M.–15.00 P.M) of outdoor workers. All urine samples were kept at
4°C during transportation to laboratory, stored at -20°C and later analyzed for creatinine (Cr) [23],
trans, trans-muconic acid (tt-MA) [24], hippuric
acid [25], formaldehyde, acetaldehyde and formic

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**Figure 1:** Study site map - Roadside University
Table 1 The characteristics of outdoor workers

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Wet season (Mean±SE)</th>
<th>Dry season (Mean±SE)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>University sites (n=38)</td>
<td>Roadside sites (n=105)</td>
<td>University sites (n=38)</td>
</tr>
<tr>
<td>Age (years)</td>
<td>43.8±7.3</td>
<td>38.7±1.9</td>
<td>43.2±1.8</td>
</tr>
<tr>
<td>BMI (Kg/m²)</td>
<td>24.7±4.0</td>
<td>24.6±0.5</td>
<td>24.2±4.3</td>
</tr>
<tr>
<td>Period of working time (years)</td>
<td>12.9±1.1*</td>
<td>6.3±0.7*</td>
<td>12.7±1.2†</td>
</tr>
<tr>
<td>Working time a day (hours)</td>
<td>10.0±2.0</td>
<td>11.05±1.5</td>
<td>10.9±1.8</td>
</tr>
<tr>
<td>Working time a week (days)</td>
<td>6.6±0.7</td>
<td>6.4±0.3</td>
<td>6.2±0.8</td>
</tr>
</tbody>
</table>

* † significant different between different worker groups at p<0.05

Table 2 Ambient VOCs concentration (µg/m³) in Pathumwan area

<table>
<thead>
<tr>
<th>VOCs</th>
<th>Wet season (Mean ± SE)</th>
<th>Dry season (Mean ± SE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>University (n=6)</td>
<td>Roadside (n=10)</td>
</tr>
<tr>
<td>Benzene</td>
<td>72.44±6.39***</td>
<td>32.98±3.83†††</td>
</tr>
<tr>
<td>Toluene</td>
<td>28.72±2.80</td>
<td>122.29±28.12†††</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>2.05±0.24</td>
<td>5.81±0.15</td>
</tr>
<tr>
<td>Xylene</td>
<td>61.08±9.59***</td>
<td>51.43±14.9†††</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>9.67±0.48***</td>
<td>53.13±13.00†††</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>3.48±0.17***</td>
<td>16.02±0.07†††</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>0.78±0.54</td>
<td>1.13±0.40</td>
</tr>
<tr>
<td>Crotonaldehyde</td>
<td>0.23±0.46</td>
<td>0.53±0.67</td>
</tr>
<tr>
<td>Butyaldehyde</td>
<td>0.35±0.46</td>
<td>0.36±0.13</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>0.25±0.22</td>
<td>0.47±0.16</td>
</tr>
<tr>
<td>Isovaleraldehyde</td>
<td>0.07±0.17</td>
<td>0.22±0.22</td>
</tr>
<tr>
<td>Valeraldehyde</td>
<td>0.84±0.94</td>
<td>0.79±0.57</td>
</tr>
<tr>
<td>o-Tolualdehyde</td>
<td>1.27±2.08</td>
<td>0.99±1.03</td>
</tr>
<tr>
<td>m,p-Tolualdehyde</td>
<td>0.20±0.50</td>
<td>0.01±0.01</td>
</tr>
<tr>
<td>Hexaldehyde</td>
<td>1.00±1.32</td>
<td>1.14±1.22</td>
</tr>
<tr>
<td>2,5Dimethyl benzaldehyde</td>
<td>0.82±1.21</td>
<td>0.67±0.54</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>183.25±22.28</td>
<td>287.97±3.32</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Wet season (Mean ± SE)</th>
<th>Dry season (Mean ± SE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>28.8±0.71</td>
<td>30.5±0.71</td>
</tr>
<tr>
<td>Wind speed (Knots)</td>
<td>29.5±0.99</td>
<td>30.7±0.21</td>
</tr>
</tbody>
</table>

***, ††† significant different of ambient air in university and roadside areas between different seasons at p<0.001

acid analyses [26]. Acceptable limit on urinary creatinine concentrations were between 0.3 and 3.0 g/L [27] as the World Health Organization (WHO) has adopted guideline. All measured values were corrected by urinary Cr concentrations for clinical chemistry analysis [28].

RESULTS AND DISCUSSION
Characteristics of outdoor workers

The characteristics of 287 outdoor workers showed that mean age, BMI, period of employment, working days a week and working hours a day of workers were 41.1 years, 24.5 Kg/m², 9.6 years, 10.7 hours/year and 6.4 days/week respectively. They were not significantly different between wet and dry seasons but the outdoor workers in university had higher the period of employment in university than workers at roadside areas. (Independent t-test, p<0.05) (Table1).

Ambient air VOCs level between wet and dry season

Total ambient air VOCs (TVOCs=BTEX+CCs) levels at university and roadside areas were 183.25 and 287.97 µg/m³ in wet season but they were 87.12 and 121.33 µg/m³ in dry season (Table 2). TVOCs were trended higher in wet season which supported other study in Hong Kong [29] but they were not significant different of each worker groups between wet and dry seasons. There were significant higher levels of benzene, xylene, formaldehyde and acetaldehyde at university area of wet season than the same area of dry season (p<0.001). As well as there were significant higher levels of benzene, xylene, formaldehyde and acetaldehyde at roadside areas of wet season than dry season (p<0.001). The average temperature of wet and dry seasons were 28.8 and 30.5°C while wind speeds were 29.5 and 30.7 knots respectively.

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It showed that higher temperature and sunlight condition, VOCs can transfer by photo-oxidation and higher wind speed can support VOCs spread wide. The ambient air TVOCs levels of university were lower levels than roadside areas in both seasons. In addition, most of each the pollutants levels were higher at the roadside than university areas. Air pollution is as traffic-related air pollution near busy roads [30]. There were a lot of researches presented that exhaust formaldehyde and acetaldehyde were produced from bio-fuel [31, 32], but also by the decrease of fuel aromatics [33]. Seasonal variation effects on gaseous pollutants are of great significance to the life span and cycle of any pollutant in the lower atmosphere in previous study [34].

**Ambient VOCs ratios**

The toluene to benzene ratios (T/B) of university and roadside of wet season were 0.39 and 3.71 while of dry season were 1.29 and 1.68 (Table 2). T/B is as a tool for characterizing the distance from vehicle emission sources [35]. This study showed higher T/B at roadside area than university areas because most motor vehicles in university were the cars and lower number of motorcycles. This study showed the highest ambient air benzene level in wet season but low in dry season cause of recessed university. So, T/B ratio was lower in university and the lowest in university of wet season. T/B in another studies showed about 2.0 with near roads and heavy traffic flow, and range 1.0-6.0 in suburban area [36]. The average T/B was 2.51 in this study was in good agreement with previous reported values and supported this ratio higher in wet season [29, 37].

The xylene to benzene ratio (X/B) is indicated a possibility of air mass transported as well as the xylene to ethylbenzene ratio (X/EB) used to identify degree of evolution of photo-oxidation reaction. The X/B of university and roadside areas were 0.84 and 1.56 in wet season while were 0.20 of both areas in dry season. The X/EB of those areas was 29.80, 8.85 and 0.96, 1.21 respectively in wet and dry season. It indicated that there was higher air mass transportation with higher photochemical activity to ozone formation in dry season especially at roadside area. For residence area was the highest ratio of X/B and X/EB which indicated that there were lowest air mass transportation and photo-oxidation in this area because a distance was longer from a lot number of motor vehicles from nearby main roads and highways [38, 39].

The formaldehyde to acetaldehyde ratio (F/A) of university and roadside areas in wet and dry season were 2.45 and 3.32 µg/m³ and 2.43 and 2.57 µg/m³ respectively with the average ratio 2.69 while the acetaldehyde to propionaldehyde ratio (A/P) were 4.45 and 14.18 µg/m³ and 4.46 and 3.01 µg/m³ respectively with the average ratio 6.53 (Table 3). Formaldehyde and acetaldehyde are emitted by vehicles that use the oxygenated fuels methanol and ethanol [40]. F/A ratio was highest at roadside areas, it referred to there were a lot of formaldehyde emission from bio-automotive fuel which supported data from Brazil where high levels of acetaldehyde in urban air reflect the nationwide use of ethanol fuel [41]. The average F/A of this study was 2.69 which in ranged from one to two in an urban area to about ten in a rural area as other studies [42, 43].

The A/P ratio should be used as indicators of the anthropogenic origin of ambient carbonyls, since propionaldehyde is believed to be associated only with anthropogenic emissions [44]. Thus, this ratio is typically found to be high in rural air, but low in urban air [45]. A/P ratios in the study were highest at roadside area in wet season which showed that the lifetime of acetaldehyde exceeds that of propionaldehyde with respect to photolysis reactions [46]. The large photochemical production of acetaldehyde at high temperatures and strong solar radiation may be counterbalanced rapid loss by photolysis [47]. In this study propionaldehyde levels in each site were not changed but acetaldehyde levels at road sides were higher than university. It should indicate that increased acetaldehyde level was mostly emitted from motor vehicle of bio-fuel. Average A/P ratio was 6.53 which at roadside was higher in wet season (14.18)

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Wet season</th>
<th>Dry season</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>University (n=6)</td>
<td>Roadside (n=10)</td>
<td>University (n=6)</td>
</tr>
<tr>
<td>T/B</td>
<td>0.39</td>
<td>3.71</td>
<td>1.29</td>
</tr>
<tr>
<td>X/B</td>
<td>0.84</td>
<td>1.56</td>
<td>0.20</td>
</tr>
<tr>
<td>X/EB</td>
<td>29.80</td>
<td>8.85</td>
<td>0.96</td>
</tr>
<tr>
<td>F/A</td>
<td>2.45</td>
<td>3.32</td>
<td>2.43</td>
</tr>
<tr>
<td>A/P</td>
<td>4.45</td>
<td>14.18</td>
<td>4.46</td>
</tr>
</tbody>
</table>

*Table 3 Ambient VOCs ratio in Pathumwan area*
Table 4 Average urinary biomarkers of outdoor workers

<table>
<thead>
<tr>
<th>Urinary biomarkers</th>
<th>Concentration (Mean±SE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wet season</td>
</tr>
<tr>
<td></td>
<td>University (n=38)</td>
</tr>
<tr>
<td>Creatinine (g/L)</td>
<td>1.47±1.02</td>
</tr>
<tr>
<td>tt-MA (mg/gCr)</td>
<td>2.67±0.55</td>
</tr>
<tr>
<td>Hippuric acid (g/gCr)</td>
<td>0.49±0.06</td>
</tr>
<tr>
<td>Formaldehyde (mg/gCr)</td>
<td>0.11±0.02</td>
</tr>
<tr>
<td>Acetaldehyde (mg/gCr)</td>
<td>0.49±0.07</td>
</tr>
<tr>
<td>Formic acid (mg/gCr)</td>
<td>25.62±4.27*</td>
</tr>
</tbody>
</table>

* † significant different between different season at p<0.05
** †† significant different between different season at p<0.01
*** ††† significant different between different season at p<0.001

Table 5 Association between urinary biomarkers of outdoor workers and ambient air VOCs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Linear regression analysis</th>
<th>95% CI</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Standardized Coeff.</td>
<td>B</td>
<td>Std. Error</td>
</tr>
<tr>
<td>tt-MA</td>
<td>Benzene</td>
<td>0.028</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>-0.004</td>
<td>0.002</td>
</tr>
<tr>
<td>Hippuric acid</td>
<td>Toluene</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>Urinary formaldehyde</td>
<td>Toluene</td>
<td>0.019</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>Formaldehyde</td>
<td>-0.027</td>
<td>0.011</td>
</tr>
<tr>
<td>Urinary acetaldehyde</td>
<td>Formaldehyde</td>
<td>-0.004</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>Acetaldehyde</td>
<td>0.014</td>
<td>0.008</td>
</tr>
<tr>
<td>Formic acid</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Dependence variable: tt-MA, Hippuric acid, Urinary Formaldehyde, Urinary Acetaldehyde and Formic acid; Adjust by age, period of work, period of working time a day and working time a week

than in dry season (3.01). However, F/A ratio also were higher levels at roadsides than university in both seasons. It can support that formaldehyde and acetaldehyde were increased in heavy traffic and were higher in wet season.

Overall, the temperature and wind speed should be the major factors to affect to ambient VOCs levels in this study which were higher in dry season than wet season (Table 3). These results supported the previous studies [48, 49]. There was also more sunlight in dry season, so, it should be more photo-oxidation reaction of gas-phase hydrocarbons to aldehydes and ketones than wet season [50]. In addition, ambient VOCs concentrations should affected by the fuels used, type and age of vehicles, flow rates and speeds of traffic as well as environmental conditions in the city [51]. The levels of VOCs presented lower in dry season with lower ratios of both F/A and A/P in dry season.

Urinary biomarkers of outdoor workers

The urinary biomarkers of outdoor workers were presented in Table 4. At roadside area, urinary biomarkers of outdoor workers were tt-MA, hippuric acid, formaldehyde, acetaldehyde and formic acid at 1.29 mg/g Cr, 0.57 g/g Cr, 1.11 mg/g Cr, 0.52 mg/g Cr and 18.78 mg/g Cr respectively in university while they were at 0.62 mg/g Cr, 0.45 g/g Cr, 0.31 mg/g Cr, 0.31 mg/g Cr and 20.57 mg/g Cr respectively in dry season. The urinary formic acid of outdoor workers of both sites was significantly higher than security guardsman (p<0.05) and street vendor (p<0.01). The urinary tt-MA, formaldehyde and formic acid of workers were significantly higher in dry season than wet season (p<0.05). The higher atmospheric VOCs exposures as well as the higher urinary biomarkers found in outdoor workers. All workers had higher tt-MA levels than standard limited [27].
Association between VOCs exposures and urinary biomarkers of outdoor workers

Using linear regression model, the association between ambient air VOCs and urinary biomarkers of outdoor workers showed that benzene was strongly associated with t-t-MA (p < 0.001) (Table 5). Moreover, t-t-MA was associated with toluene (p < 0.05). Toluene was associated with hippuric acid (p < 0.01) as well as ambient air formaldehyde was associated with urinary formaldehyde and acetaldehyde (p < 0.05 and p < 0.01). In addition, ambient air VOCs was not associated with formic acid. These results supported the recent studies [52-54].

CONCLUSION

There was seasonal variation of ambient air VOCs in urban area which most of them were higher levels in wet season than dry season. Total VOCs level at roadside area was higher than university area. The main factors affected to atmospheric levels should be sunlight, dense and types of traffic motor vehicles, temperature and wind speed. The outdoor workers were exposed these pollutants with higher limited benzene exposure. There were the significant association of these exposures and urinary biomarkers of outdoor workers in urban area.

ACKNOWLEDGEMENTS

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