ORIGINAL ARTICLE

Monitoring of BTX by passive sampling in Hat Yai

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Abstract

Thammakhet, C., Villeneuve, T., Munisawang, V., Thavarungkul, P. and Kanatharana, P.
Monitoring of BTX by passive sampling in Hat Yai
Songklanakarin J. Sci. Technol., 2004, 26(Suppl. 1) : 151-160

Laboratory-built passive samplers were used for monitoring of trace benzene, toluene and xylene (BTX) in Hat Yai from 28 July to 12 August, 2003. Sampler bottles contained activated Tenax TA 60/80 mesh and a lab-built thermal well were developed and evaluated for the sampling and analysis of BTX. The sampling was carried out for two weeks before the passive samplers were thermally desorbed, trapped in a sampling loop by a laboratory built purge and trap system and analysed by gas chromatography (GC) equipped with a flame ionization detector. After optimization and calibration, the developed method showed high selectivity, a good sensitivity with detection limits for BTX of 0.8, 1.1 and 13.0 μg/m^3 respectively and an acceptable precision.

Ambient BTX measurements were conducted at many monitoring site *i.e.* hot spots (high exposure), residential areas/work places (common exposure) and park (low exposure). The concentration at hot spots range from 3.2 to 5.4 μg/m^3 for benzene, 38.0 to 80.3 μg/m^3 for toluene and 29.7 to 66.7 μg/m^3 for xylene. The low BTX were found at the city periphery (Tesco-Lotus billboard sampling stations, roof level) and in Hat Yai Municipal Park but no absolute background concentration could be defined. The monitoring results showed that at higher level from the street surface, the level of BTX tended to decrease and the BTX pollution

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Received, 1 March 2004 Accepted, 10 May 2004

built up along a street canyon (Sanehanuson Road) according to the wind direction. The highest BTX were found at the underground parking, 23.5 725.1 and 267.9 μg/m^3 respectively where both WHO guideline for Benzene (16.3 μg/m^3) and Toluene (260 μg/m^3) were exceeded.

Key words : passive sampling, BTX, Hat Yai, air monitoring

บทคัดย่อ

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การติดตามตรวจสอบปริมาณเบนซีน โทลูอีน และไซลีนในเขตเมืองหาดใหญ่ จังหวัดสงขลา โดยใช้เทคนิคพาสซีพแซมปลิง

ว.สงขลานครินทร์ วทท. 2547 26(ฉบับพิเศษ 1) : 151-160

ชุดเก็บตัวอย่างอากาศแบบพาสซีพแซมปลิงและอุปกรณ์คายการดูดซับโดยใช้ความร้อนที่ทำขึ้นเองในห้องปฏิบัติการ (lab-built passive sampler) ถูกนำมาใช้เพื่อเก็บและวิเคราะห์อากาศในเขตเมืองหาดใหญ่ จ.สงขลา ที่ปนเปื้อนด้วยสารในกลุ่มเบนซีน โทลูอีนและไซลีน ในช่วงระหว่างวันที่ 28 กรกฎาคมถึง 12 สิงหาคม 2546 โดยขวดเก็บตัวอย่างบรรจุสารดูดซับชนิด Tenax TA ขนาด 60/80 mesh ถูกนำมาใช้ในการเก็บตัวอย่างอากาศเป็นระยะเวลาสองสัปดาห์ จากนั้นจึงนำขวดเก็บตัวอย่างดังกล่าวมาต่อเข้ากับระบบที่ใช้คายการดูดซับที่ต่อเข้ากับระบบเพิร์จและแทรป (purge and trap) ที่มีแซมปลิง ลูป (sampling loop) เป็นอุปกรณ์ฉีดสารเข้าสู่เครื่องแก๊สโครมาโตกราฟที่มีตัวตรวจวัดชนิดเฟลมไอออไนเซชัน เพื่อทำการวิเคราะห์ปริมาณต่อไป จากการทดลองพบว่าขีดจำกัดการตรวจวัดของเทคนิคที่ได้รับการหาสภาวะที่เหมาะสมแล้วสำหรับเบนซีน โทลูอีนและไซลีน เป็น 0.8 1.1 และ13.0 ไมโครกรัม/ลบ.ม. ตามลำดับ โดยมีความถูกต้องอยู่ในระดับที่ยอมรับได้

จุดเก็บตัวอย่างอากาศถูกจำแนกออกตามพื้นที่ที่มีโอกาสปนเปื้อนด้วยเบนซีน โทลูอีน และไซลีน โดยความเข้มข้นที่ตรวจวัดได้อยู่ในช่วง 3.2 ถึง 5.4 ไมโครกรัม/ลบ.ม. สำหรับเบนซีน 38.0 ถึง 80.3 ไมโครกรัม/ลบ.ม. สำหรับโทลูอีนและ 29.7 ถึง 66.7 ไมโครกรัม/ลบ.ม. สำหรับไซลีน โดยความเข้มข้นที่ตรวจพบในบริเวณนอกเมืองหาดใหญ่รวมทั้ง บริเวณสวนสาธารณะหาดใหญ่จะมีค่าต่ำ นอกจากนี้ผลการทดลองยังสามารถสรุปได้ว่าความเข้มข้นของสารทั้งสามชนิดมีแนวโน้มลดลงเมื่อระดับความสูงจากพื้นดินเพิ่มขึ้น และจะมีแนวโน้มเพิ่มขึ้นตามทิศทางลมเมื่อพื้นที่ที่เก็บตัวอย่างมีลักษณะเป็นถนนแคบที่อยู่ระหว่างตึกสูง (street canyon) เช่น ถนนสเน่หานุสรณ์ โดยบริเวณที่พบว่ามีความเข้มข้นของสารทั้งสามชนิดสูงที่สุดคือ บริเวณลานจอดรถใต้ดินของลีการ์เด้นท์ พลาซ่า พบว่ามีค่าเป็น 23.5 725.1 และ 267.9 ไมโครกรัม/ลบ.ม. สำหรับเบนซีน โทลูอีนและไซลีนตามลำดับ ซึ่งมีค่าสูงกว่ามาตรฐานที่ตั้งไว้โดยองค์การอนามัยโลก คือ 16.3 และ 260.0 ไมโครกรัม/ลบ.ม. สำหรับเบนซีนและโทลูอีน

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Volatile organic compounds (VOCs) comprise a wide range of compounds including aliphatic and aromatic hydrocarbons, alcohols, aldehydes, ketones, esters and halogenated compounds. The main focus is the role VOCs play in the formation of photochemical smog and tropospheric ozone. VOCs also contribute to stratospheric ozone depletion and enhancement of the global greenhouse effect (Dewulf and Langenhove, 1999). Moreover, the acute and chronic health effects related to VOCs

(irritation and the increased risk of cancer due to exposure to benzene) require their monitoring in risk areas. There is also a concern about the possible deleterious effects on valuable materials such as electronics components in telephone exchanges and computers, and to works of art.

Among VOCs, the simplest aromatic hydrocarbons benzene, toluene and xylene (commonly referred as BTX) are of significant concern regarding environmental health. Furthermore, BTX are a good indicator for the global VOCs level since they mainly come from the same sources such as in crude petroleum and in petroleum products *i.e*. gasoline.

Benzene is a well-known human carcinogenic for all routes of exposure. EPA has classified benzene as a Group A, human carcinogen. In addition to being carcinogenic, benzene is also known to be mutagenic while the others have effects on the central nervous system.

Hat Yai is one of the big cities in Thailand but it is a small town when compared to Bangkok (more than 6 million of inhabitants in Bangkok and only 150,000 inhabitants in Hat Yai). As the economic center of southern Thailand, Hat Yai, Songkhla Province, is a fast- growing and economically developed city. There are many industries emitting high quantities of air pollutants in the area. As a consequence of rapid development and urbanization, traffic- related air pollution is expected to be one of the major environmental problems in the area.

In 1996, the Ministry of Science, Technology and Environment (MOSTE) established an air quality monitoring station in Hat Yai. The station monitors criteria pollutants PM_{10}, SO_2, NO_2, O_3 and hydrocarbons. However, the BTX ambient concentrations are not currently monitored and BTX levels were never investigated in Hat Yai. Therefore, it is necessary to have data that provides the basic information of BTX level in the city in order to assess the air quality in the future.

There is a need for rapid, effective and low cost integrated methods that would allow direct monitoring of the fate and concentrations of VOCs in the environment as well as evaluation of their effects and assessment of the hazards these chemicals pose to the environment and to human health. Many of these requirements are fulfilled by passive sampling techniques (Zabiegata *et al*., 2002).

Passive sampling can be defined as the collection of airborne gases and vapors at a rate controlled by diffusion without the active movement of air through an air sampling pump. The term passive sampling covers any sampling technique based upon free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potential of the analyte between the two media. Therefore, this study investigated the use of a lab-built passive sampling system coupled with a lab-built purge and trap technique to provide an alternative and low cost device that can be used to sample and monitor of BTX from indoor and outdoor air in Hat Yai city.

Experiments

1. Lab-built passive sampling

Lab-built passive samplers used in this study were glass bottles (longer part is 59 mm long with an inner diameter (I.D.) of 15 mm whereas the shorter is 8 mm long with an inner diameter (I.D.) of 11 mm) that were filled with 75 mg of Tenax TA (80-100 mesh). They were used for collecting both indoor and outdoor air samples. The system was calibrated by injecting standard gases into the passive sampling bottles. The adsorbent was then desorbed using a lab-built thermal device. The lid of the bottle was adapted to insert two stainless steel tubes; one was connected to the purge system and the other to the sampling loop that connected with the switching valve that routed the carrier gas either directly to GC-FID or to pass through the sampling loop before going to the GC-FID. Nitrogen gas was purged through the adsorbent in the passive sampling bottles when they were heated and the analytes were detected by Gas Chromatograph with conventional flame ionization detector (Shimadzu 14A). The analysis system is shown in

Figure 1.

2. Calibration of the cross section area and the length of diffusion of the passive sampling bottles.

According to the bottle neck of the lab-built passive samplers, the diffusion area within the bottle was not uniform. Therefore, calibrations of cross section area (A) and the length of diffusion (L) were necessary. The calibration system was based upon gas diffusion law (Fick's first law). The stream of standard gases was generated using the diffusion cell, and then an air pump (1.0 L min^{-1}) was used for dilution of the analyte concentration in the glass tube chamber. At the end of the chamber the lab-built passive sampling bottles that were used to collect the analyte molecules that diffused into the bottles and adsorbed at the surface of Tenax TA were hung (Figure 2). The theory of the passive sampling is used to convert the amount of analyte in the tube to the average ambient concentration during the sampling time. Then, the amounts of analyte obtained from the calculation and from the experiment were compared.

3. Sampling

According to the sampling rate of VOCs and their usual environmental concentration, a two-

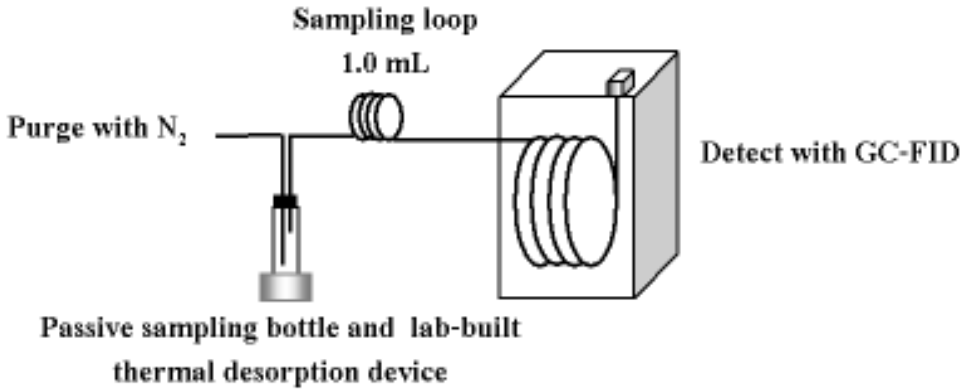

Figure 1. Schematic diagram of the system used for the analysis of BTX.

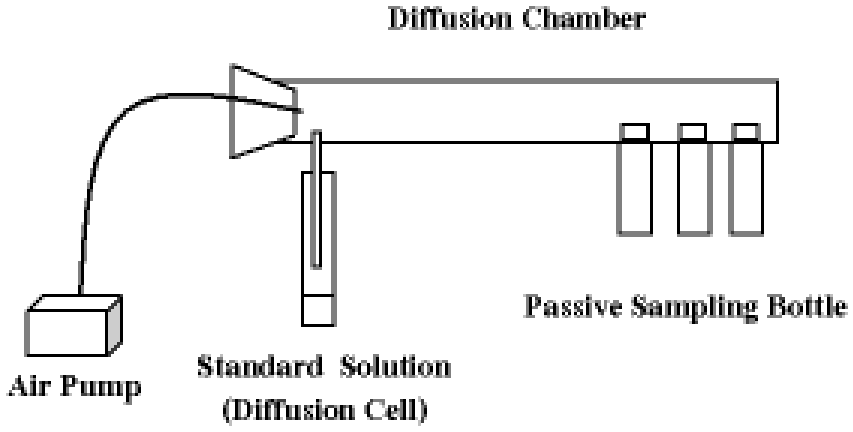

Figure 2. System used to calibrate the passive sampler.

week sampling time seems to be a good compromise between an acceptable detection limits and a not too long sampling time. In this study, field measurements of BTX were carried out during one sampling period of two weeks: from 28 July to 12 August 2003. The monitoring device is shown in Figure 3. Before choosing any monitoring site, it was important to define which strategies were suited for monitoring of BTX pollution in Hat Yai using the passive sampler. In this study, four monitoring strategies were defined. First was the common strategy, this was to monitor at sites where people spend most of their time such as apartments and offices. Second was the worst case strategy, which is high risk locations that commonly referred as "Hot Spots". For BTX, the terms "Hot Spots" include underground parking lots, petrol stations, crossroad, highways, street canyon, and areas near large point sources. Third was the background strategy, it can be defined as the level of pollution away from any potential point sources. The last one was the parameter strategy such as distance and height from point source, it can be used for investigation of the effect of parameters either on the pollution concentration or on the sampling method.

Every strategy has its advantages but none of them, alone, gives a complete view of the pollution situation. Therefore, the monitoring sites chosen for these studies are a combination of the four strategies as shown in Table 1.

Results and Discussion

The amount of BTX and the signal obtained from GC-FID showed good linear relationships of all three compounds with correlation coefficients greater than 0.99. The detection limits for BTX (IUPAC method) were 0.8, 1.1 and 13.0 μg/m^3 respectively.

The system in Figure 2 was used to calibrate the diffusion area of the lab-built passive sampling bottles. The amounts of the analytes collected in the bottles determined by the system in Figure 1 were compared to the amount of analyte calculated by Fick's first law. The result indicated that this system provided an excellent agreement between the calculated value (1.32 μg) and the value obtained from the analyses (1.34 μg). The difference between two values was only 1.49%. Therefore, these passive sampling bottles can be used for real sampling.

1. Urban Outdoor Levels

Table 1 shows the results obtained from the sampling stations. In Hat Yai outdoors area (C1, C2, C3, TIME and CLOCK), the two-weeks averaged concentration were in the range of 1.0 to 5.4 μg/m^3 for benzene, 4.3 to 80.3 μg/m^3 for toluene and n.d. to 66.7 μg/m^3 for xylene.

The benzene concentrations in Hat Yai center were lower than the WHO guideline of 16.3

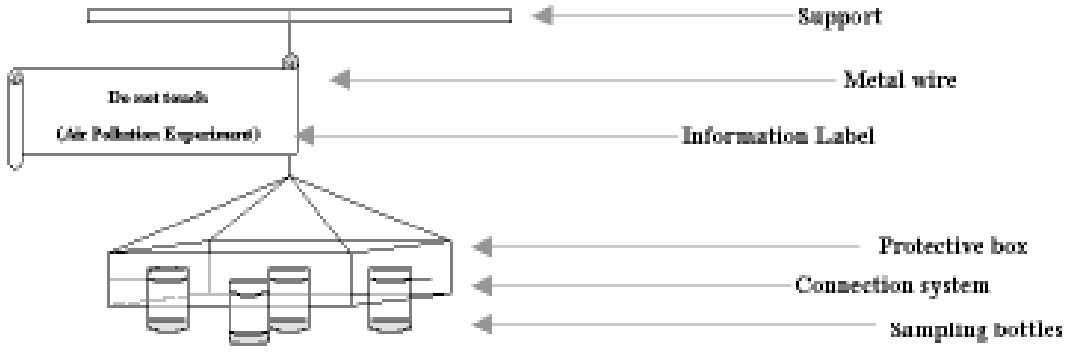

Figure 3. Monitoring device. (protective box and 4 replicate samplers)

Table 1. Results from the second sampling period.

Site Code	Location	Height (m)	Sampling strategy	Concentration (μg/m³)		
				Benzene	Toluene	Xylene
B1	Gas station (1-2)	2.5	Hot spot	4.7	43.7	29.7
B2	Gas station (3-4)	2.5	Hot spot	4.5	44.4	30.3
C1	City center (Sanehanusorn Road)	2.5	Hot spot ("canyon")	3.2	38.0	36.0
C2	City center (Sanehanusorn Road)	2.5	Hot spot ("canyon")	3.7	46.0	44.8
C3	City center (Sanehanusorn Road)	2.5	Hot spot ("canyon")	4.2	64.1	56.6
TIME	Intersection between Rajyindee Road and Tamnoonwithi Road	2.0	Hot spot	5.0	48.3	54.1
CLOCK	Clock Tower	2 .0	Hot spot	5.4	80.3	66.7
D1	Underground parking (paint side)	2.5	Hot spot+painting effect	23.5	725.4	268.3
D2	Underground parking	2.5	Hot spot+painting effect	23.2	724.8	267.4
H1	Tesco-Lotus Billboard	1.0	Height effect	1.8	6.8	18.0
H2	Tesco-Lotus Billboard	5.0	Height effect	1.3	5.6	13.0
H3	Tesco-Lotus Billboard	10.0	Height effect	1.2	5.1	n.d.
H4	Tesco-Lotus Billboard	15.0	Height effect	1.2	5.0	n.d.
Roof	Roof level	20.0	Background	1.0	4.3	n.d.
L1	Lab (book corner)	2.5	Indoor	7.8	22.8	23.1
P1	Hat Yai park	2m at 100 m above sea level	Background	n.d.	1.9	n.d.
P2	Hat Yai park	2 m at 150 m above sea level	Background	n.d.	2.0	n.d.
R1	S. Apartments	2 m	Residential area	2.5	25.6	22.2

n.d.: non detectable

μg/m³ (5 ppb) but often above the long-term target of 3.26 μg/m³ (1 ppb). Outdoor toluene and xylene concentrations were always below the WHO guideline and can be seen as acceptable.

The highest concentrations of BTX were found to be in the area near Clock Tower (CLOCK). This site has a more open topography than Sanehanuson Road (C1-C3) but much more circulation and traffic jam. Moreover, the types of vehicles are not the same in Clock Tower (truck, busses, pick-up) as in Sanehanuson Road (cars, motorcycles).

BTX level at the intersection between Rajyindee Road and Tamnoonwithi Road (TIME) are comparable to the levels found in the city center, although it is located at the center periphery.

2. Street Canyon

The positions of the sampling site and the variation of BTX concentration along Sanehanuson Road (C1-C3) are shown in Figures 4 and 5 respectively. Sanehanuson Road has canyon geometry since it is a narrow street flanked by high buildings. Moreover, both sides of the street are sandwiched by clothing stalls and Thai fried food stands. As every tourist and commercial center in Thailand, it is often crowded with cars and motorcycles. Under idling and decelerating modes, vehicles in this area will emit maximum pollutants.

Along this street, there is very little opportunity for dilution and mixing with the atmosphere. Thus, most pollutants created inside the street will stay in it and be pushed toward its Northern end (C3) because of the prevailing southern winds that usually blow along the street with a velocity from 0 to 5m/s (average ~2.5 m/s) as shown in Figure 4. Therefore, the concentration of BTX in C3 was higher than those in C1. As expected, pollutant

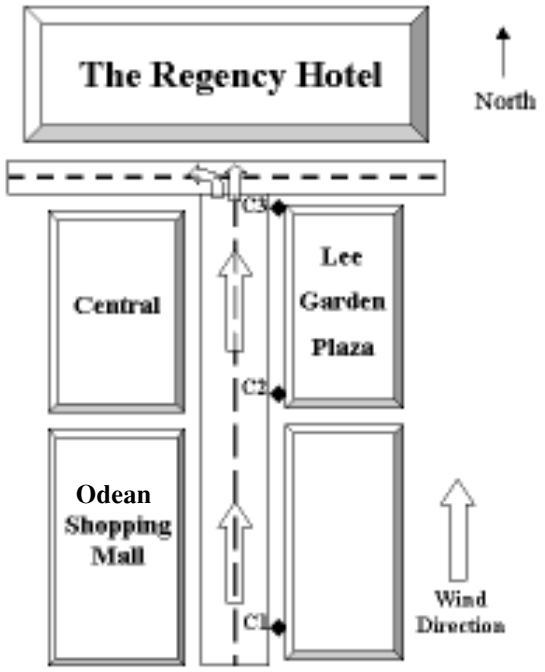

Figure 4. Sampling sites in city center. (Sanehanuson Road)

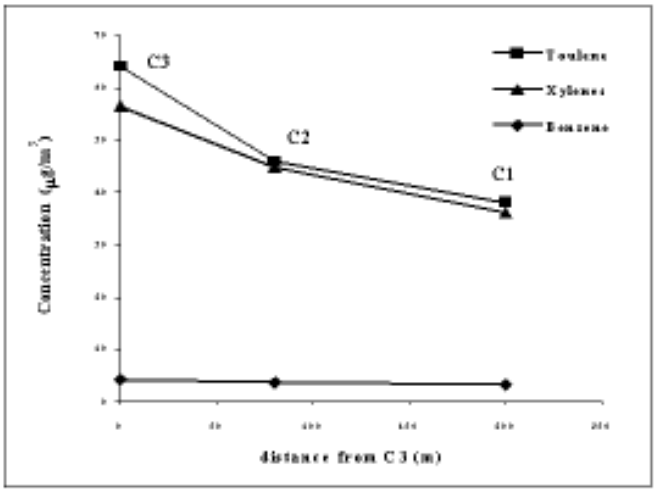

Figure 5. BTX concentration in Sanehanuson Road.

concentrations built up along the street.

Considering its geometry, location and frequentation, Sanehanuson Road (C1-C3) has the possibility to show the highest BTX levels of Hat Yai urban area. However, it was found that BTX level near Clock Tower is higher than at Sanehanusorn Road. This is certainly due to the one way-road system of the city center that included Sanehanusorn Road. Indeed this system seems really effective to avoid traffic jam and, thus, avoid the initiation of pollutant that would otherwise build up along street canyons.

3. Bangchak Gas station

The BTX levels in gas stations are the combination of exhaust emissions and evaporative emissions (from car tank or from station fuel tank). The higher benzene content of gasoline in Thailand (from 3 to 5% in Thailand) as well as a low number of cars fitted with catalytic converters may also explain the higher benzene concentration found in Thailand.

Those results could not be generalized to any other gas station in Hat Yai. Indeed, the levels are station specific and depend on many factors such as volumes of gasoline sold, wind speed, exhaust emissions and deliveries of gasoline to the station (Mukund *et al*., 1996). Therefore, the monitoring of BTX in other gas stations would have been relevant. However, the two weeks sampling time involves an attenuation of those factors and, thus, gives a good indication of the usual BTX level in Thai gas stations.

4. Underground parking lot

Very high levels of BTX (23.4, 725.1 and 267.8 $\mu g/m^3$ respectively) were found in the Underground parking lot of "Lee Garden Plaza" shopping mall. The concentration of benzene and toluene are above WHO guidelines (almost three times higher than the guideline for toluene). Those high concentrations are mainly due to the high vehicles frequentation. Furthermore, contrary to outdoor environments, neither dilution by wind nor effective ventilation system exists in this parking lot.

Toluene is used as solvent (up to 30%) in some paints. Since the same levels were found near the paint tins storage place or far away, the toluene associated with painting is more likely to come from the wall than from the tins.

5. Horizontal distribution (H1, H2, H3, H4)

Figure 6 showed the variation of benzene and toluene along the Tesco Billboard (from 1 to 15 m above the ground). According to Figure 6, both benzene and toluene concentrations seem negatively correlated with height until 5 to 10 meter. With increasing wind velocity and point source distance, the pollutants appear to be totally mixed above 10 meter. Above this height, the concentration reaches a constant value which can be defined as the background concentration for this location. However, the differences of concentration were quite small to be really significant. This area is not enough polluted to detect relevant variation. To be clearer, this kind of experience should be

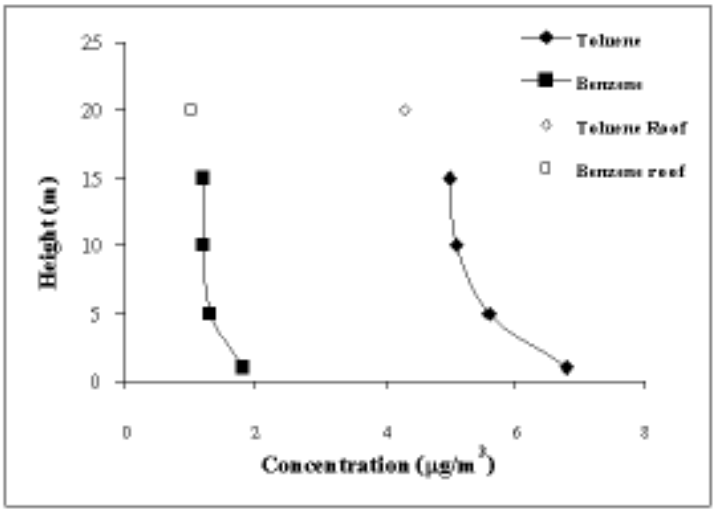

Figure 6. Effect of the height on BTX concentration.

realized in an area with higher pollution sources or in a street canyon. This study shows that this location is well ventilated thus not highly polluted.

6. Background concentrations

The results found in the roof station are also shown in Figure 6 (separated points). Those concentrations can also be assumed to be a background concentration since it is in the university area at 20 meter from the ground and 600 m from the highway (i.e. 650 m from Tesco billboard). The benzene and toluene at this location (1.0 and 4.3 $\mu g/m^3$ respectively) are consistent with those found at the Tesco billboard over 10 meters but quite low to show only the effect of the height (+5m). Accordingly, even at heights above 15 meters, BTX concentrations were still dependant on distance from point sources (no perfect mixing). The estimation of the background performed in Hat Yai municipal park (5 km from Hat Yai) give even lower concentration and only toluene was above detection limits (2.0 $\mu g/m^3$).That is, no absolute background could be defined.

7. Concentration in the laboratory room 312 at Chemistry Department, Faculty of Science, PSU

VOCs concentrations were usually higher in indoor environments. High benzene concentrations (7.8 $\mu g/m^3$: 1.5 time Clock tower concentration!) were found in the laboratory room 312. Based on the roof measurement, we can estimate the outdoor lab concentration to be around 1 $\mu g/m^3$ for benzene and 4.5 $\mu g/m^3$ for toluene. The concentration of benzene in the lab is specific to its use in this laboratory (use of benzene standards for experiments) whereas toluene concentrations could be those of any living room.

Conclusions

Monitoring information obtained in the present study found that the level of BTX in Hat Yai were below the WHO guidelines except for that in the underground parking lot.

The rapid growth of motor vehicle population in Thailand will obviously result in higher BTX emissions and concentrations in the air in the near future. Considering that there is no totally safe level of exposure for benzene, the levels of BTX should be measured to define the air quality. Therefore, BTX should be added to the species (PM_{10}, SO_2, NO_2, O_3 and methane) already monitored in Hat Yai Air Quality Monitoring station.

As preventive actions to avoid the rise of BTX pollution, the traffic should be further limited and controlled in the city center (especially for the trucks and old busses). The gasoline quality should also be improved by decreasing the legal content of benzene. More specifically, an effective ventilation system should be installed in the Lee Garden's underground parking lot. It should not be just a fan that mixes the concentration inside the parking (the results show that it is already well mixed) but a system that allows entrance of the outdoor air.

Considering the instrumentation, installation, quality control and maintenance costs, passive sampling is cheaper than any other air monitoring techniques (Hangartner, 1996). It is also cheaper than the usual commercial passive samplers. For example, the commercial passive samplers for VOCs cost between 500 and 600 Baht whereas the laboratory-built samplers used in this study costs less than 90 Baht per passive sampler (including the glass bottles, the plastic boxes, the adsorbent and metal wire).

Acknowledgements

The authors would like to thank the National Research Center for Environmental and Hazardous Waste Management (NRC-EHWM) for financial support and the Postgraduate Education and Research Program in Chemistry (PERCH). We also thank the Danish and Thai Consortium for Environment and Development Industry and Urban Area (DUCED-I&UA and TUCED-I&UA) TUCED, the Thailand Research Fund under the Royal Golden Jubilee Ph.D. Program and the Department of

Chemistry, Faculty of Science, Prince of Songkla University for partial support.

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