นิพนธ์ต้นฉบับ

Assessment of urine tertiary butyl alcohol levels as biological exposure marker for methyl tertiary butyl ether of road toll station workers in Bangkok

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Abstract

The aim of this study was to assess the levels of urine Tertiary Butyl Alcohol (TBA) as an index of biological monitoring for exposure to Methyl Tertiary Butyl Ether (MTBE) among road toll station workers in Bangkok metropolitan area. The subjects of this study consisted of 35 road toll station workers as study group. The Airborne MTBE was measured throughout the work with a VOCs diffusive sampling device (VOC-SD) attached on the breathing zone of each subject. The urine samples were collected after work. The Airborne MTBE was analyzed by gas chromatography equipped with MS and the urine samples were done by one with headspace GC-FID. The geometric mean of Airborne MTBE was 21.9 ppb for road toll station workers. The geometric mean of urine TBA level, a metabolite of MTBE, was 232.7 μg/l for road toll station workers. The correlation between MTBE exposure and urine TBA levels was 0.233 ($p=0.033$). From these results, TBA in urine may be used as biological exposure marker for occupationally exposed workers to MTBE in Bangkok. However, a bigger sample size in future study may provide stronger significant findings.

Key words: Methyl tertiary-butyl ether (MTBE), Tertiary butyl alcohol (TBA), Road toll station workers, Bangkok

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Introduction

The Methyl Tertiary Butyl Ether (MTBE) was originally introduced as an octane enhancer in unleaded gasoline in the 1970s. The U.S. Clean Air Act Amendments (CAAAs) of 1990 recommend the use of oxygenated gasolines, fuel blends that meet specific content requirements including a minimum percentage of oxygen by weight to reduce carbon monoxide and tropospheric ozone in several metropolitan area.[1] To achieve the minimum oxygen content specified in CAAAs using MTBE, MTBE must comprise 11-15% of oxygenated gasoline by volume.[2] An increase in the use of these oxygenates has risen the concerns on its health effects. Prompted research was made in several fields. Short-term effects have been studied in response to complaints by service station customers.[3, 4] The effects on humans of long-term exposure to low levels of MTBE are unknown.[5] The MTBE has also been reported to cause cancer in animal studies, and it should be considered as a possible carcinogen to humans as well.[6] In Thailand, 5.5-11% of MTBE has been added to gasoline since the early 1995s, as a gasoline additive and an octane booster and replacement for lead in gasoline, mainly to reduce carbon monoxide in the exhaust.[7] In Bangkok, the capital of Thailand, where traffic jam is violent in the metropolitan area, road toll station worker group may be the occupationally group greatly exposed to MTBE during their works. They are performing their duties about 8-10 hours per day. However, MTBE exposure levels and the urine Tertiary butyl alcohol (TBA) levels, a metabolite of MTBE, as an index of biological monitoring to MTBE exposure levels for road toll station workers in Bangkok metropolitan area have never been assessed. Ultimately, we designed the present study to assess the levels of exposure to Airborne MTBE among road toll station workers via the collection of breathing zone samples during the work. The urine samples were studied to measure TBA, a metabolite of MTBE, as a biomarker of MTBE exposure levels.

Materials and Methods

Study subjects

The study group consisted of road toll station workers (only male) (n=35) from 2 road toll stations. They performed their duties in the booth from 06:00 AM to 14:00 PM (morning shift) on the study day.

Working conditions

During the study day, there were additional measurement of temperature and humidity in the road toll booths by using hot wire anemometer (Model Testo 452).

Collection and analysis of air samples

The MTBE in breathing zone (personal sampling) was collected with an VOCs Diffusive Sampling Device (VOC-SD) during the period of the work (8 hrs.) among the road toll station worker group (n=35). After the sampling, the samples were kept in a refrigerator at the laboratory before analysis. As Determination of MTBE in the samples was carried out by desorption with a solvent (1 mL Dichloromathane) and measured by gas chromatography (GC) using a Mass Selective Detector (MS).

Collection and analysis of urine samples

All subjects in the study group agreed to provide the urine samples. The urine sampling was performed after the finishing the work. The urine specimens were kept a refrigerated at 4°C until the analysis. Before the analysis, the urine specimens in plastic bottoms were decanted (2 ml) into vials and added Hydrochloric acid (0.5 ml) sealed with Teflon faced septa and then incubated at 60°C for 30 min. The urine specimens were analyzed in the same laboratory as Airborne MTBE was analyzed.

The urine TBA levels were measured using the head-space (Model 7694 headspace Sampler) connected to the GC-Flame Ionization Detector (FID).

Administration of questionnaires

The study subjects were interviewed by using a questionnaire after work. We checked the characteristics of subjects, for example, sex, age, etc., and the working conditions among the study group.

Statistical analyses

A logarithmic transformation was performed before statistical analysis because the variables were not normally distributed. Correlation coefficient was used for correlation between MTBE exposure levels and urine TBA levels among all subjects and for correlation between Airborne MTBE and the number of cars during working time among road toll station workers. Linear simple regression was used for predicting the Airborne MTBE levels from the vehicle flow rate. Any P values less than 0.05 were considered statistically significant.

Results

Characteristics and working conditions

The characteristics and working conditions of subjects in the study group were shown in Table 1. All study subjects were male. The mean age of the road toll station worker group was 33.4 years for station 1 and 35.3 years for station 2. They had 5 working days of each week.

The sampling day for investigation in the both road toll station worker groups found that ambience workplace temperature were between 27.3 -31.9°C and ambience workplace humidity was between 75.8-99.7% for station 1 and temperature between 30.8-33.1°C and ambience workplace humidity was between 68.0 – 81.2% for station 2.

Table 1 Characteristics and working conditions

Variables	Road toll station workers group	
	Station 1 (n=24)	Station 2(n=11)
Age (years)	33.4 ± 5.8	35.3 ± 4.1
Smokers	8 (33.3)	3 (27.3)
Drinkers	17 (70.8)	7 (63.6)
Working careers workers		
More than 10 years3	3 (12.5)	0 (0)
5 to 10 years	10 (41.7)	7 (63.6)
Less than 5 years	11 (45.8)	4 (36.4)
Working days of each week		
5 days	24 (100.0)	11 (100.0)
6 days	-	-

Values are means ± SD and number (percentages).

Air samples

Airborne MTBE levels ranged from 11.8 to 38.2 ppb for the road toll station worker group (n= 35). The concentration of Airborne MTBE was summarized in Table 2. Because of the skewed distributions of individual samples, the geometric mean value (GM) was used as the central value. The geometric mean of Airborne MTBE was 21.9 ppb (ranged from 11.8 to 38.2 ppb) for the road toll station worker group. Figure 1 shows the relationship between MTBE exposure levels and the number of cars during working time in road toll station workers (r=0.500, p=0.007). The number of personal air samples were 28 (7 were missing due to technical problem). This study yielded moderate relationship with the following regression result of MTBE level in airborne; y = 0.0044 x + 14.302 (R^2= 0.25, n=28).

Table 2 Concentration of Airborne MTBE

Items	Road toll station workers group (ppb) (n=35)
Mean ± SD	22.7 ± 6.3
GM ± GSD	21.9 ± 1.3
Median	21.6
Minimum	11.8
Maximum	38.2

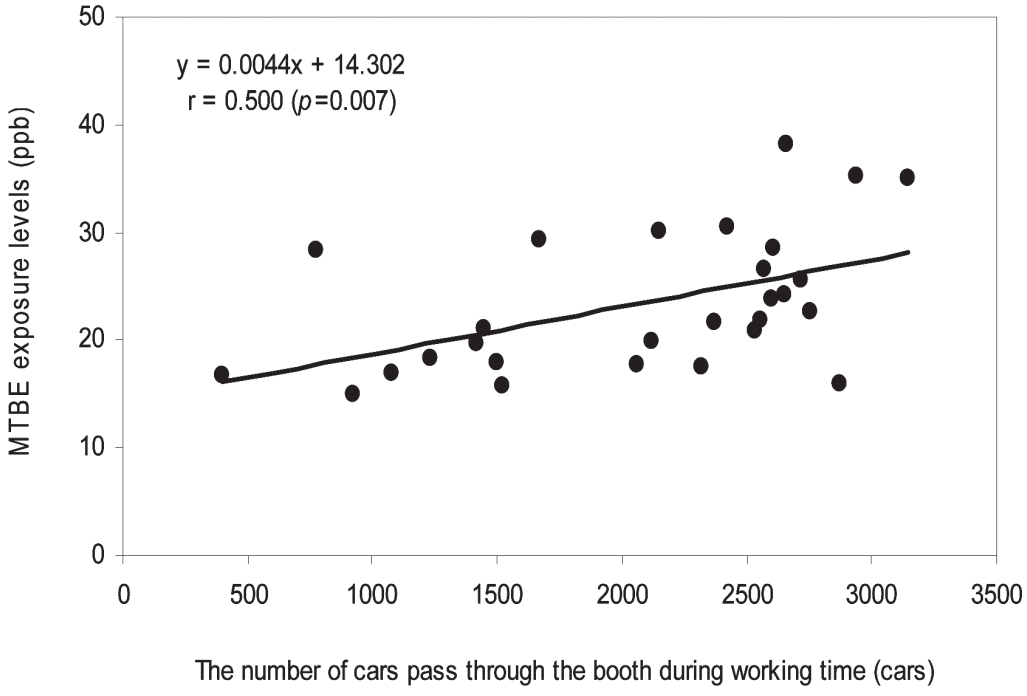

Fig. 1 Relationship between MTBE exposure levels and the number of cars during working time among road toll station workers

Urine samples

The concentration of TBA in urine samples were summarized in Table 3. The geometric mean of urine TBA levels was 232.7 μg/l for the road toll station worker group. The concentrations of Airborne MTBE were slightly related to urine TBA levels. Figure 2 shows the coefficient correlation between log-MTBE exposure levels and log-urine TBA levels in workers (r= 0.233, p=0.033).

Table 3 Concentration of urine TBA levels

Items	Road toll station workers group (μg/l) (n=35)
Mean ± SD	269.1 ± 171.1
GM ± GSD	232.7 ± 1.7
Median	201.7
Minimum	124.1
Maximum	756.0

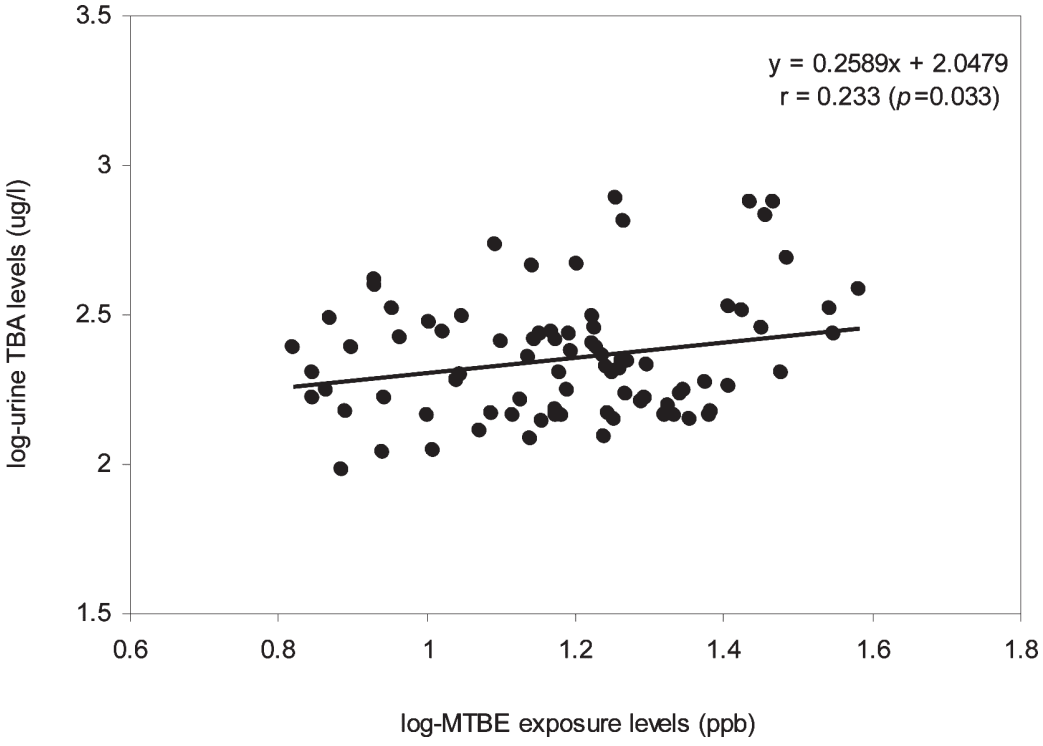

Fig. 2 Correlation between MTBE exposure levels and urine TBA concentration in workers

Discussion

This article revealed that the road toll station workers were certainly exposed to Airborne MTBE. The total exposure to MTBE during the working day (morning shift) was measured; therefore, the measured values are commensurate with any 8-h threshold value. The road toll station workers sometimes has combined shift on the day. They are easily exposed to Airborne MTBE. However, the value did not exceed the threshold limit value of MTBE (50 ppm, TWA 8 h) recommended by American Conference of Governmental Industrial Hygienists (ACGIH).[8]

We found that geometric mean of concentration of MTBE levels of road toll workers were lower than those directly associated with gasoline vapor emission, such as petroleum refinery workers (MTBE = 0.58 ppm),[9] dispatch tank truck driver (MTBE = 1.44 ppm),[10] and gas station workers (MTBE = 0.30 ppm).[11] Nevertheless, the exposure levels found in this study were higher than bus commuter (MTBE = 5.92 ppb),[12] traffic police officer (MTBE = ND ppb).[13] Our results of the present study were still much higher than those found in the general ambient environments in Taiwan.[14] Although Thai gasoline contain MTBE levels less than the minimum oxygen content specified in CAAAs.[7]

This study shows the moderate relationship between MTBE exposure levels and the number of vehicles during working time in booth attendant of road toll station workers. The regression coefficient was found to have positive values indicating that an increase in the vehicle flow rate would lead to increase in the MTBE exposure level. Same results were shown in the result of Lee CC *et al.*[14] R^2 value was 0.25 indicating that vehicle flow rates were able to explain the variations in exposure levels of booth attendants for target MTBE. This study, it might be concluded that the vehicle flow rate can be used as an indirect indicator for predicting the booth attendants' MTBE exposure level. Besides, the results of this study might be used a basis for road toll station managers to assess the exposure levels of booth attendants under various conditions with different vehicle flow rates.

From TBA, a major metabolites of MTBE, undergo conjugation to form a glucuronide, we analyzed the concentration of TBA level in urine with hydrolysis technique by added HCL of 0.5 ml and incubating at 60°C for 30 min. This method made break down the conjugation of TBA which increased occurrence of free TBA in urine although the urinary excretion of TBA was less than 1% of the absorbed dose.[15]

The weak correlation was found between Airborne MTBE and urine TBA levels in workers which it was significant. Our result did not agree with those of Vainiotalo S *et al.*[16] They reported that no correlation was found between the TBA metabolite in blood or urine and MTBE in air.

TBA is more suitable as biological exposure marker for MTBE than the parent ether itself. Therefore, this study shows that TBA is an index for biological monitoring of MTBE exposure. Nihlen A *et al.*[15] showed same results. It may be explained by at least two reasons. First, MTBE has several fast elimination phase, whereas TBA has a relatively show monoexponential decay. Second, MTBE is high volatile, whereas TBA has a low volatility and high hydrophilicity. The present study had some limitation inherent in its the sample size.[17] Unfortunately, we do not have details information on activities during the work.

Finally, we would like to emphasize that the road toll station workers in Bangkok are exposed to MTBE added in gasoline. However, we should follow up to expose by using biological monitoring for their works. Therefore, TBA in urine may be used as biological exposure marker for occupationally exposed workers to MTBE in Bangkok. Consequently, they should get occupational health education and follow up to health management.

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บทคัดย่อ

การประเมินระดับความเข้มข้นของ TBA ในปัสสาวะที่เป็นดัชนีทางชีวภาพของสาร MTBE ในพนักงานด่านเก็บเงินในเขตกรุงเทพมหานคร

ศรีรัตน์ ล้อมพงษ์

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วัตถุประสงค์ของการศึกษาวิจัยเพื่อที่จะประเมินระดับความเข้มข้นของ TBA ในปัสสาวะซึ่งใช้เป็นดัชนีทางชีวภาพของการสัมผัสสาร MTBE ในพนักงานด่านเก็บเงินของกรุงเทพมหานคร ในการศึกษานี้มีพนักงานด่านเก็บเงิน จำนวนทั้งสิ้น ๓๕ คน มีการใช้อุปกรณ์ VOCs ในการเก็บตัวอย่างอากาศในขณะปฏิบัติงาน แบบติดตัวบุคคล พร้อมกับการเก็บตัวอย่างปัสสาวะหลังจากเลิกงาน ปริมาณระดับความเข้มข้นของสาร MTBE ในบรรยากาศนำมาวิเคราะห์ด้วย GC-MS และ GC-FID สำหรับการวิเคราะห์ระดับปริมาณความเข้มข้นของสาร TBA ในปัสสาวะ จากการศึกษาพบว่า ค่า GM ของปริมาณความเข้มข้นของสาร MTBE ในบรรยากาศมีค่าเท่ากับ ๒๑.๙ ppb และระดับความเข้มข้นของสาร TBA ในปัสสาวะมีค่าเท่ากับ ๒๓๒.๗ μg/l และพบว่ามีความสัมพันธ์ระดับต่ำระหว่างระดับปริมาณความเข้มข้นของสาร MTBE ในบรรยากาศกับระดับปริมาณความเข้มข้นของ TBA ในปัสสาวะอย่างมีนัยสำคัญทางสถิติ (ค่าพี = ๐.๐๓๓) จากผลการศึกษาวิจัยนี้ทำให้พบว่า ระดับปริมาณความเข้มข้นของสาร TBA ในปัสสาวะอาจจะนำมาใช้เป็นดัชนีทางชีวภาพของผู้ประกอบอาชีพที่มีการสัมผัสกับสาร MTBE ได้แต่อย่างไรก็ตามในอนาคตของการศึกษา ควรมีจำนวนตัวอย่างที่เพิ่มมากขึ้นเพื่อให้เกิดความสัมพันธ์กันอย่างแท้จริง

คำสำคัญ: MTBE, TBA, พนักงานด่านเก็บเงิน, กทม.