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BTEX and MTBE Concentrations in Residential Indoor Air Near Industrial Complex, Korea

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공단지역 인근거주지의 실내 휘발성유기화합물류 농도

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요 약

대기 중 휘발성유기화합물류(VOCs)의 배출원은 매우 다양하며, 특히, 공단에서 배출되는 VOCs 노출로 인한 공단 주변거주지역 주민에게 배출특성 및 물질별 독성에 따라 유해한 건강 영향을 끼칠 가능성이 있다. 또한 일반가정에서의 자체 실내 오염원 또한 휘발성유기화합물류의 노출의 한 원인이다. 본 연구에서는 공단 주변 거주지역 및 동일 행정구역상의 비교지역을 선정하여 공단배출로 인한 실내유입 VOCs 노출 및 자체 실내오염원으로 인한 농도분포 및 기여정도를 조사하였다. 본 연구에서 공단주변 거주지역 및 비교지역의 조사된 실내 평균 농도는 MTBE 2.24, 2.47 μg/m^3, benzene 9.82, 8.51 μg/m^3, toluene 103.80, 83.57 μg/m^3, ethylbenzene 36.45, 15.52 μg/m^3, xylene 26.27, 1.00 μg/m^{3}로 비교지역 거주지에 비해 공단지역 주변거주지의 실내공기 중 VOCs의 농도가 높은 것으로 나타났다. 최종적으로 I/O ratio를 비교한 결과 조사 거주지 모두 자체 실내오염원이 있는 것으로 관찰되었고, 공단지역 주변거주지의 경우 공단의 VOCs 배출로 의해 추가 노출이 되는 것으로 각각 조사되었다.

Key words : BTEX, MTBE, indoor, outdoor, residence, industrial complex

INTRODUCTION

Volatile organic compounds (VOCs) are an important public health problem. Humans are exposed to these contaminants by inhalation, ingestion, and dermal contact. However, very little is known about the health effects of individual compounds, and still less about the sources of these compounds that contribute to daily exposures. It is well known that industrial sources and vehicle exhaust contribute to ambient VOC levels in urban areas (Singh and Zimmerman, 1992; Vega *et al.*, 2000; Chan *et al.*, 2002). Other sources include combustion by-products, cooking, construction material, furnishes, solvents, adhesives, caulks, office equipment and consumer products (Guo *et al.*, 2003). Among the volatile indoor air pollutants,

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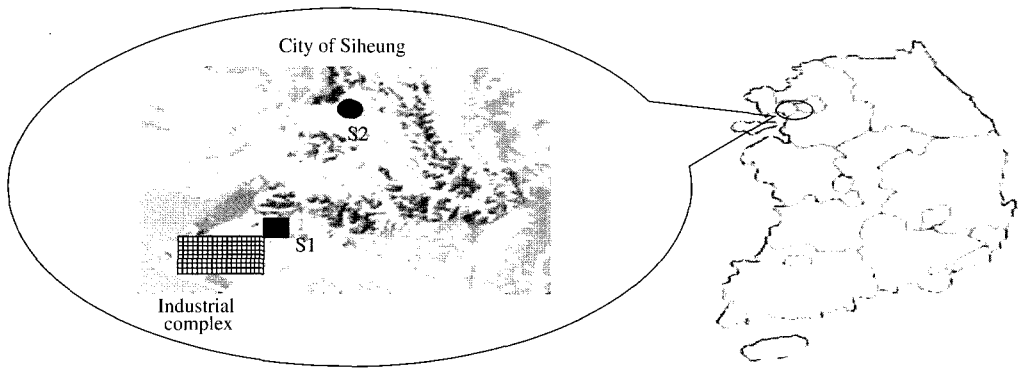

Fig. 1. Location of Siheung.

aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and xylene (BTEX) investigated in this study, are particularly abundant in the indoor environment (Krause *et al.*, 1991). In addition to BTEX, MTBE (methyl tertiary butyl ether) has also been intensively investigated (Perng-Jy *et al.*, 2002; Jo *et al.*, 2004). MTBE (methyl tertiary-butyl ether) is a chemical compound that is manufactured by the chemical reaction of methanol and isobutylene. MTBE has been used in U.S. gasoline at low levels since 1979 to replace lead as an octane enhancer (helps prevent the engine from "knocking") (IRIS., 2005). MTBE has been widely used in many countries as a fuel additive for reducing motor vehicle carbon monoxide, and hydrocarbon emissions (Perng-Jy *et al.*, 2002). While some VOCs may be present at concentrations not considered acutely harmful to human health with short-term exposure, long-term exposure may have mutagenic and carcinogenic effects. The occurrence and concentrations of VOCs in homes can be affected by outdoor atmospheric conditions, indoor sources, indoor volume, human activities, removal by reaction, ventilation rates, and seasonal factors. Furthermore, VOC concentration can vary due to chemical reactions in the presence of ozone, temperature changes, and humidity (Van der wal *et al.*, 1997).

Like many other industries, the dyeing industry is associated with VOC emissions from the solvents employed in the dyeing and finishing processes (Wicks *et al.*, 1994).

This study was conducted to establish the analytic procedure of MTBE & BTEX (benzene, toluene, ethylbenzene, xylene) in industrial complex discharge and the relationships among VOCs concentration.

MATERIALS AND METHODS

1. Sampling period and locations

Target compound sampling was conducted in city of Siheung, at residences adjacent to the Siwha dyeing industrial complex and at residences far from the complex. Seventeen subjects in industrial complex sites (S1), and 16 reference sites (S2) were selected for the final exposure sample. A total of 33 participants were recruited from S1 (industrial complex sites) and S2 (reference sites). S1 sites were within 100 m and 500 m of the boundary of the industrial complex, while S2 were 20 km and 25 km away (Fig. 1). The Siwha industrial complex was established in 1986, approximately 30 km west of Seoul and there are some 8,000 migrant workers in about 2,500 factories. The participants answered a detailed questionnaire on characteristics such as house type and age, area, indoor smoking, ventilation, new furniture purchases within the past 6 months, and possible exposure through indoor and outdoor contact as well as their present and former locations. This study carried out an intensive MTBE and BTEX measurement

from December 2003 until January 2004 at sites in Siwha, one in the industrial area and the other in a residential area.

2. Sampling and analytical methods

Surveys were conducted to measure the concentrations of four aromatic VOCs (benzene, toluene, ethlybezene, xylene) and methyl tertiary-butyl ether (MTBE) in the industrial outdoor and indoor air within Siwha and in residential indoor and outdoor air.

For indoor air, Samplers were located in the center of the living-room at a height about 1.5 m above floor level. The outdoor air was sampled at fixed stations at a height about 1.5 ~ 2.0 m, in the garden of the apartments.

MTBE & BTEX samples were adsorbed to Perkin Elmer Tenax TA adsorbent tubes connected at a flow rate of 0.1 L/min with a low-volume air sampler. The MTBE & BTEX were analyzed by coupling a thermal desorption system (TDS, Tekmar Model Aerotrap 6016) to a gas chromatograph (GC-MSD HP 6890 series) using a 0.32-mm-ID by 60-m-length and 1 μm phase film thickness HP-1 capillary column (Agilent Tec.) The trap was thermally desorbed at 240°C for 3 min and the target compound cryo-focused at −110°C on a internal-trap (0.1mm glass bead). The cold trap was rapidly heated on 225°C flushed the cryo-focusing module of the TDS. The cryo-focusing module was then heated to 225°C and flushed to transfer the target compounds to a GC. The initial oven temperature was set 40°C for 10 min and ramped at 5°C/min to 200°C. The established calibration curves for the five investigated MTBE & BTEX were found with R^2-values > 0.995. The Desorption efficiencies for the five target compounds were greater than 80%. The accuracy was checked seven duplicate samples to test the precision of the sampling and analytical techniques. We found that relative standard deviation for the target VOCs were consistently less than 20%.

Half the limit of detection (LOD) was as follows: benzene, 0.17 μg/m^3; toluene, 0.21 μg/m^3; ethylbenzene, 0.29 μg/m^3; xylene, 0.26 μg/m^3 and MTBE, 0.22 μg/m^3.

Table 1. General characteristics of participants in this study

	S1 (n=17)	S2 (n=16)	Total (n=33)
House type			
Apartment	17 (100%)	16 (100%)	33 (100%)
Other	0 (0%)	0 (0%)	0 (0%)
House age			
≤3 year	0 (0%)	4 (25%)	4 (12.1%)
≥3 year	17 (100%)	12 (75%)	29 (87.9%)
Indoor smoking			
Yes	9 (52.9%)	8 (50.0%)	17 (51.5%)
No	8 (47.1%)	8 (50.0%)	16 (48.5%)
Ventilation			
Yes	14 (82.4%)	14 (87.5%)	28 (84.8%)
No	3 (17.6%)	2 (12.5%)	5 (15.2%)
New furniture (within 6 month)			
Yes	0 (0%)	3 (18.8%)	3 (9.1%)
No	17 (100.0%)	13 (81.3%)	30 (90.9%)

3. Statistical methods

Statistical analyses were performed using the SAS program (version 8.1). The paired sample data were analyzed with a paired t-test. The geometric mean (GM) and geometric standard deviation (GSD) characterized the log-normally distributed data. The criterion for significance in the Mann-Whitney-U (Wilcoxon Rank-Sum) test was $P < 0.05$.

RESULTS

1. General characteristics

Table 1 presents a summary of the general characteristics of participants in this study. Different categories such as house type, house age, indoor smoking, ventilation and new furniture purchased were compared. The house types were wholly apartments (100 %) and there were no single detached houses. Apartments were for the most part constructed more than 3 years ago (87.9%) and most new furniture was pur-

chased more than 6 months ago (90.9%). Overall, 51.5% of households contained at indoor-smoker, while 48.5% contained no indoor-smoker. In addition, a higher proportion of households had ventilation (84.8%), compared with 15.2% with no ventilation. Average ventilation was 1 ~ 2 times per day. Housing and characteristics in S1 and S2 were generally similar.

2. Measurements of MTBE and BTEX

The results for MTBE & BTEX for both areas are summarized in Table 2. The geometric mean outdoor concentrations were 6.86, 8.35, 105.60, 14.56, and 19.96 μg/m^3, for MTBE, benzene, toluene, ethlybenzene and xylene, respectively for S1, and 2.51, 7.50, 65.15, 10.06 and 9.20 μg/m^3, respectively, for S2. Meanwhile, the geometric mean indoor concentrations were 2.24, 9.82, 103.80, 36.45, and 26.27 μg/m^3, respectively, for S1 and 2.47, 8.51, 83.57, 15.52 and 1.00 μg/m^3, respectively, for S2. Outdoor air concentrations of MTBE were significantly higher for S1 than for S2 ($P<0.05$), whereas no significant difference was found in the outdoor air concentrations of the other target compounds between the two sites. Indoor air concentrations of xylene were significantly higher for S1 than for S2 ($P<0.05$), but no significant difference was found in the indoor air concentrations of the other target compounds between the two sites. This is consistent with the observation that indoor and outdoor air pollution in S2 is substantially higher than that in S1.

Indoor/Outdoor (I/O) concentration ratios of VOCs ranged from 0.32 to 2.50 and 0.11 to 1.54 for S1 and S2, respectively. In the case of S1, higher indoor concentrations of benzene, ethylbenzene, and xylene suggest that indoor sources exist for these compounds. For S2, high I/O values for benzene, toluene and ethylbenzene suggest that indoor sources exist for these compounds.

3. Concentrations according to indoor smoking at sites

Table 3 presents the geometric mean indoor BTEX and MTBE concentrations in the smoking households

Table 2. GM and GSD concentrations (μg/m^3) at industrial complex sites (S1) and reference sites (S2)

	S1 (n=17)			S2 (n=16)		
	Indoor GM±GSD	Outdoor GM±GSD	I/O	Indoor GM±GSD	Outdoor GM±GSD	I/O
Benzene	9.82±13.69	8.35±14.43	1.18	8.51±18.83	7.50±10.46	1.13
Toluene	103.80±60.03	105.60±63.47	0.98	83.57±58.03	65.15±56.61	1.28
Ethyl-benzene	36.45±56.12	14.56±24.87	2.50	15.52±15.73	10.06±14.27	1.54
Xylene	26.27±44.88*	19.96±56.07	1.32	1.00±3.32	9.20±17.13	0.11
MTBE	2.24±5.00	6.86±16.54*	0.32	2.47±4.92	2.51±4.28	0.98

* $P<0.05$

Table 3. GM and GSD concentrations (μg/m^3) according to indoor smoking at industrial complex sites (S1) and reference sites (S2)

	S1 (n=17)			S2 (n=16)		
	Smoking (n=9) GM±GSD	Nonsmoking (n=8) GM±GSD	S/N	Smoking (n=8) GM±GSD	Nonsmoking (n=8) GM±GSD	S/N
Benzene	20.47±1.79	24.90±1.29	0.82	20.90±1.56	4.76±40.35	4.40
Toluene	73.24±2.80	88.88±2.09	0.82	32.25±7.30	80.84±1.66	0.40
Ethyl-benzene	18.57±4.09	33.64±3.81	0.55	14.03±2.99	13.31±2.36	1.08
Xylene	65.85±2.39	14.83±9.60	4.44	13.14±1.00	2.89±1.00	4.53

versus the nonsmoking households. Target VOCs (benzene, toluene, ethylbenzene, xylene) in S1 and S2 smoking households did not have significantly higher indoor concentrations compared to the nonsmoking households. However, there were elevated levels of benzene, ethyl-benzene and xylene in the smoking homes, at S2. In contrast, there were elevated xylene concentrations in the smoking homes, at S1.

DISCUSSION

Volatile organic compounds (VOCs) commonly found in occupational or non-occupational environments are potential causes of acute symptoms such as allergies, asthma, mucous irritation, headaches and tiredness and may substantially contribute to the increase of cancer incidence in the population (Grazia *et al.*, 2006)

The indoor and outdoor air quality in residences adjacent to the dyeing industrial complex and residences far from the complex were characterized. Finally, Indoor and outdoor air concentrations of target compounds were generally higher at industrial complex sites than the reference sites. This result is possibly due to the influence of other unidentified sources of VOCs from the industrial complex and indoor. Source identification is also possible by determining the indoor/outdoor (I/O) concentration ratio (Ilgen E *et al.*, 2001). When I/O values are greater than 1, indoor sources must be present (Elke *et al.*, 2001). The ratio of the indoor (I) to the outdoor (O) air concentration of different compounds, i.e. the I/O value, reflects the importance of outdoor versus indoor sources even better than the absolute concentration. This study could be interpreted as an indication of weak indoor sources for this compound. In the case of S1, higher indoor concentrations of benzene, ethyl-benzene, and xylene suggest that indoor sources exist for these compounds. For S2, high I/O values for benzene, toluene and ethyl-benzene suggest that indoor sources exist for these compounds.

The ratio of the indoor to outdoor air concentrations for toluene (S1) and MTBE (S2) were both close to 1. This result is similarity with previous study. For MTBE, since no significant.

Sources were identified inside the homes surveyed, the indoor levels appeared to result primarily from the penetration of MTBE emitted from outdoor sources, such as service stations, gasoline-powered motor vehicles, and other gasoline uses, into the homes (Jo *et al.*, 2004).

A number of investigators have demonstrated that the indoor concentrations of VOC in dwellings are usually higher than outdoor concentration (Kiyoshi *et al.*, 2004). In this study, indoor benzene concentrations of 9.82 $\mu g/m^3$ (industrial complex sites) and 8.51 $\mu g/m^3$ (reference sites) were reported. This compares to mean indoor concentrations of 39.8 and 11.0 $\mu g/m^3$ reported for Seoul and an industrial complex in Korea (Son *et al.*, 2003; Jo *et al.*, 2004) and 4.0 and 8.3 $\mu g/m^3$ reported for California (Sheldon *et al.*, 1991; Wilson *et al.*, 1993).

Benzene is emitted during its production and from coke ovens. Besides these industrial sources, emission also occurs from different combustion sources, such as motor engines, wood combustion and stationary fossil fuel combustion (WHO, 2000). Average indoor concentration of toluene in this study of 103.8 $\mu g/m^3$ (S1) and 83.6 $\mu g/m^3$ (S2) were observed. In Germany, an average concentration of 25.7 $\mu g/m^3$ was recorded in an urban area (Elke *et al.*, 2001) and in private homes in Hong Kong mean toluene values of 59.1 $\mu g/m^3$ were reported (Guo *et al.*, 2003). In residences adjacent to a dyeing industrial complex in Korea, a geometric mean of 290 $\mu g/m^3$ was determined (Jo *et al.*, 2004). It has a number of industrial uses: as a solvent, carrier, or thiner in the paint, rubber, printing, cosmetic, adhesives and resin industries, as a starting material for the synthesis of other chemical and as a constituent of fuels (Low *et al.*, 1988). In the case of ethyl-benzene, indoor concentrations of 36.5 $\mu g/m^3$ (S1) and 15.5 $\mu g/m^3$ (S2) were reported. Guo *et al.* (2003) reported average toluene concentrations in different indoor environments in Hong Kong: 2.72

Table 4. Outdoor results of other studies of BTEX and MTBE are summarized

Outdoor	MTBE	Benzene	Toluene	Ethyl-benzene	Xylene
China urban[1)]	–	33.8	62.0	15.6	56.3
China landfill 1[1)]		73.0	113.0	24.0	45.7
U.S. Los Angeles[1)]		19.5	45.0	10.2	20.3
Taiwan urban[2)]	0.03	0.5	0.92	0.17	0.5
Hong Kong[3)]	–	26.7	77.2	6.7	31.3
Brazil urban[4)]	–	24.6	43.1	13.7	39.0
This study (S1)	6.9	8.4	105.6	14.6	20.0
This study (S2)	2.5	7.5	65.2	10.1	10.6

[1)]Zou a *et al.*, 2003, [2)]Perng-Jy Tsai *et al.*, 2002, [3)]Chan *et al.*, 2002, [4)]Grosjean *et al.*, 1998
S1: industrial complex sites, S2: reference sites

$\mu g/m^3$ in private homes, in offices 7.81 $\mu g/m^3$, schools 4.12 $\mu g/m^3$, shopping mall 11.86 $\mu g/m^3$, and restaurant 8.59 $\mu g/m^3$. Ethyl-benzene is used primarily in the production of styrene. It is also used as a solvent, as a constituent of asphalt and naphtha, and in fuels (ATSDR, 1999). The average indoor concentration of xylene observed in this study was 26.3 $\mu g/m^3$ (S1) and 1.0 $\mu g/m^3$ (S2). In Germany, an average concentration of 27.6 $\mu g/m^3$ was reported in an urban area (Elke *et al.*, 2001). Mean indoor concentrations of 60.9 and 20.1 $\mu g/m^3$ were reported for Seoul and an industrial complex in Korea (Son *et al.*, 2003; Jo *et al.*, 2004). The term xylene refers to mixtures of the three xylene isomers (o-, m-, p-) and ethyl-benzene. m-xylene is commonly the predominant component (40~77%) in commercial preparations of xylene, with the other components each comprising roughly up to 20% of the mass. The use of xylene as a solvent, in paints and coatings, and in gasoline is widespread (IRIS, 2005).

Outdoor results of other studies of benzene, toluene, ethyl-benzene, xylene and MTBE are summarized in Table 4. These results are similar to previous studies in other countries (Grosjean *et al.*, 1998; Chan *et al.*, 2002; Perng-Jy Tsai *et al.*, 2002; Zoua *et al.*, 2003).

Smoking has been identified as one major indoor sources and contributes on average 2~3 $\mu g/m^3$ to the total indoor concentration, as revealed in other studies (Wallace, 1989; Krause *et al.*, 1991). In addition, cigarette smoke is an important source of benzene in indoor air, and median benzene levels have been found to be higher in the homes of smokers (10.5 $\mu g/m^3$) than those of nonsmokers (7 $\mu g/m^3$). Toluene is a major component of tobacco smoke and concentrations can vary greatly (WHO, 2000). In this study, there were elevated benzene, ethylbenzene and xylene concentrations in the smoking homes, at S2.

As expected, the indoor concentrations of BTEX and MTBE in industrial complex sites are the higher. However, housing and characteristics in S1 and S2 are very similar on many points except for house new buildings (25%) and new furniture purchased within 6 months (19%), while S1 has none. This situation could bias the results, since new buildings and new furniture could emit VOCs. While some of the influences, such as industrial complex activities, are temporal at ventilation, and therefore, sampling sites in homes and act to limit of our approach. In addition, the sources of indoor and outdoor VOC may vary in different countries, different areas of a country, and different socioeconomic strata (Kiyoshi *et al.*, 2004). Other important sources for personal exposure must be examined, particularly traffic and other indoor factors not measured in this study. Further studies are needed to assess of the VOCs emission from industrial complex.

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