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Ambient BTEX and MTBE in the neighborhoods of different industrial parks in Southern Taiwan

Lien-Te Hsieh [a,b,*], Hsi-Hsien Yang [c], Ho-Wen Chen [c]

[a] Department of Environmental Engineering and Science, National Pingtung University of Science and Technology, Nei Pu 912, Ping Tung 91201, Taiwan

[b] Environmental Toxics and Plasma Technology Laboratory, NPUST, Ping Tung, Taiwan

[c] Department of Environmental Engineering and Management, Chaoyang University of Technology, 168 Jifong E. Rd, Wufong, Taichung County, Taiwan

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Abstract

This study assessed the concentrations of five volatile organic compounds (VOCs), including BTEX (the acronym for benzene, toluene, ethylbenzene, and xylene) and methyl *tertiary*-butyl ether (MTBE), in six different industrial park neighborhoods in southern Taiwan, including the Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi industrial parks. The concentrations of MTBE and BTEX ranged from undetectable to 145.6 $\mu g/m^3$. Average MTBE–BTEX ratios of Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi were (13.4:3.6:4.7:1.0:7.4), (2.9:1.0:1.7:1.3:2.9), (3.0:1.0:2.7:1.0:2.7), (5.2:1.0:8.6:1.7:4.9), (3.1:3.1:2.8:1.0:3.3) and (4.3:1.2:3.6:1.0:3.8), respectively. Moreover, average T/B ratios in Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi were 1.3, 1.7, 2.6, 8.6, 0.9 and 2.9, respectively. High T/B ratio (8.6) in the neighborhood of the Ren-Wu industrial park suggested that the emission of large additional sources of toluene from this industrial park, or the existence of major differences in the auxiliary fuels used. Average X/E ratios in Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi were 7.4, 2.2, 2.7, 2.9, 3.3 and 3.8, respectively. The lower X/E ratio (2.2) in the Ping-Tung neighborhood compared to elsewhere indicates an aged air parcel. Furthermore, principal component analysis also confirmed that the dominant influences in the six different industrial park neighborhoods were related to the emissions of MTBE, benzene and toluene.

Keywords: MTBE; BTEX; Industrial park neighborhood; T/B ratio; X/E ratio

1. Introduction

Methyl *tertiary*-butyl ether (MTBE) is an oxygenate first synthesized in Italy in 1968 [1]. Since the 1970s, MTBE has become a common ingredient in gasoline owing to its excellent octane rating and low impact on air quality in large cities [2–6]. The benefits of MTBE include reduced particulate emissions, unburnt hydrocarbons, CO and exhaust emissions. However, both environment pollution by MTBE, and the possible adverse effects of MTBE exposure are issues of public concern [7–9]. Because MTBE is released to the atmosphere as an unburned hydrocarbon, especially during cold engine starts or from evaporative sources (such as, breathing losses or refueling). The presence of MTBE in fuel is also associated with increased emissions of its by-products, especially formaldehyde. In Taiwan, MTBE is blended into gasoline in ratio of up to 11% by volume to improve the oxygen content. MTBE is added to gasoline in Taiwan not because of clean air related laws, but rather to increase octane values.

Other common VOCs, including aromatic hydrocarbons such as benzene, toluene, ethylbenzene, *m*,*p*-xylene and *o*-xylene (BTEX), are widely used in industry and exert serious adverse effects on environmental air quality. BTEX are frequently produced from industrial sources, including printing and laminating facilities, foundries, electronics, and paint manufacturing units. Especially, BTEX frequently occur together at hazardous waste sites [10]. Public health risks from exposure to either MTBE or BTEX are best assessed via an approach that considers both the mechanism and toxic

* Corresponding author. Tel.: +886 8 7740521; fax: +886 8 7740256.
E-mail address: Lthsieh@mail.npust.edu.tw (L.-T. Hsieh).

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consequences of the joint action of the whole mixture, particularly the presence or absence of interactions that affect the responses of the critical target-organs [11]. Therefore, during the past several decades, both MTBE and BTEX have been intensively studied [12–21]. As far as ambient air legislations are concerned, the Expert Panel on Air Quality Standards (EPAQS) of the United Kingdom has recommended an ambient air standard of 16 $\mu g/m^3$ as an annual rolling mean for benzene [22]. A short-term (30 min) ambient air quality standard of 30 $\mu g/m^3$ for benzene has been established in Texas, USA [23].

Differentiating between different pollution sources is difficult for samples taken from ambient air, and so it is difficult to forecast the true influence of different emission sources. However, toluene/benzene (T/B) or xylene/ethylbenzene (X/E) ratios can clarify the characteristics of BTEX emission. Nelson and Quigley [24,25] demonstrated that the ratio between ($m + p$)-xylene and ethylbenzene (X/E) can indicate the extent of atmospheric photochemical reactivity. Subsequently, Monod et al. [18] identified the X/E ratio as a useful tool for estimating the photochemical age of air mass and confirmed this method proposed by Nelson and Quigley [24]. Recently, Hsieh and Tsai [26] noted that the species ratios (T/B and X/B) were useful tools for estimating the photochemical age of air mass and confirmed the method proposed by Nelson and Quigley [24] and Monod et al. [18]. Xylenes are considered a highly reactive species while ethylbenzene is considered a low reactivity species. Low X/E ratio suggests an aged air parcel.

MTBE and BTEX emit from various sources, transport or disperse across the source boundary, and then mix into the ambient air. Most related VOC studies have focused on pollutants emission related to the different sources, the target place or special receptors. This study focuses on the perspective of the source boundary. Since MTBE, benzene and toluene were the major cancer causing pollutants from vehicle and industrial exhaust, it is necessary to examine the different boundaries and industrial neighborhoods for such toxic compounds. Consequently, this study investigated MTBE and BTEX concentration variation in the neighborhoods of six different industrial parks, and attempted to characterize the source profiles of MTBE and BTEX in southern Taiwan.

2. Methods

2.1. Sampling sites and descriptions

Southern Taiwan is located on the lee side of the central mountain range of Taiwan. This region has stable atmosphere, clear skies and a distinct pattern of diurnal land-sea breeze circulations. To examine the spatial distribution of VOCs in different industrial park neighborhoods, six sites were chosen based on their different industrial or manufacturing types and traffic densities. In this study, the six sampling sites, namely the Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi industrial parks, were chosen for VOC monitoring. The conceptual descriptions of six industrial parks were presented as follows:

Nei-Pu industrial park: The park is an industrial park with very low population and traffic density. Park buildings are few and widely scattered. The total area of the park is approximately 99 ha, and the park contains a total of 61 factories. The industrial types in the park can be divided into three categories: (1) food-processing industry; (2) food manufacturing industry; and (3) electrical appliances industry.

Ping-Tung industrial park: The park is an important industrial park near the Ping-Tung city (commercial area). The park has high traffic density and there are numerous high-rise commercial buildings located nearby. The total area of the park is approximately 113.2 ha, and some 143 are located within the park. The industrial types in the park can be divided into three different categories: (1) machining manufacturing industry; (2) metalworking industry; and (3) food manufacturing industry.

Ping-Nan industrial park: It is a newly developed area close to both Fang-Liao and Dong-Gang, which has slowly industrialized during recent years. The area contains a mixture of old low-rise residential buildings and newly built low-rise factory buildings. The total area of the park is approximately 278 ha, and the park contains some 97 factories. The park contains two major industry types: (1) iron and steel industry and (2) refrigeration manufacturing industry.

Ren-Wu industrial park: This is a typical petroleum park in southern Taiwan. This park has a very high traffic density. The total park area is approximately 127 ha, and the park contains some 50 factories. Three industry types exist in the park: (1) petrochemical industry and (2) general manufacturing industry.

Lin-Yuan industrial park: This park is an important exclusive petroleum zone in southern Taiwan. The park has a high traffic density, and is in an area of newly built low-rise residential buildings and low-rise factory buildings. The total area of the park is about 395 ha and the park contains a total of 29 factories. Two industry types exist in the park: (1) special oil industry and (2) petroleum industry.

Nan-Zi industrial park: This park is similar to Ren-Wu industrial park. This park is set in an area containing both old and new high-rise residential buildings, as well as newly built high-rise office and factory buildings. The area has high traffic density. The total park area is about 170 ha and the park contains a total of 30 factories. Two industry types exist in the park: (1) petroleum industry and (2) petrochemical industry.

In this study, the industrial park neighborhoods were selected according to their activities. They are not near according to their far distances between them and, therefore, would be little influence between them. Furthermore, Southern Taiwan experiences both humid and hot weather, since it is located in a semi-tropical region and is affected by the alternate northeastern and southwestern seasonal currents.

2.2. Sampling and analytical methods

Sampling was performed at six selected sites (Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi) at three times of the day (7:00–11:00 a.m., 1:00–5:00 p.m. and 7:00–11:00 p.m.) from July 2003 to December 2004 to clarify the characterization of VOCs in the ambient air of different industrial park neighborhoods in southern Taiwan. Four samples were taken simultaneously during each period at each site, including the up-, down-, left- and right-streams based on the direction of prevailing wind during the sampling period. The average of those four samples at the up-, down-, left- and right-stream was taken as a representative sample of the industrial park neighborhood. Sampling height was 1.5 m for each site. Besides, the basic meteorological condition was obtained by using portable meteorological machines (LM-8000 type) and was recorded during sampling times.

A portable sampling pump (SKC 224-XR Series Pumps, SKC Inc.) was used to draw in the air. The pump was calibrated by a standard SKC flow meter (SKC UltraFlo™, SKC Inc.) before and after sampling. The sampling airflow rate was 200 ml/min. The sampling duration ranged from 60 to 120 min depending on the anticipated VOC levels in the air of the sampling sites. In this study, the sampling was active and the sorbents were the activated carbon material (ORBO-32). For the individual sampling duration, the sample volume ranged from 1.2 to 2.4 l. During sampling periods (7:00–11:00 a.m., 1:00–5:00 p.m. and 7:00–11:00 p.m.), we replace new ORBO tube every two hours to ensure the sampled volume within the confidence volume (under the breakthrough condition). Our experimental results indicates the mean calculated sampling efficiency is higher than 93%.

For each collected sample, MTBE and BTEX (including benzene, toluene, ethylbenzene, *m*/*p*-xylene and *o*-xylene) were analyzed by gas chromatography with a flame ionization detector (GC/FID; Agilent Technologies, 6890N Network GC System) using the NIOSH Method 1615 [27]. The identification and quantification of VOCs was accomplished by using a GC (Agilent Technologies, 6890N Network GC System) with a Agilent Technologies capillary column (DB-1 30 m × 0.53 mm i.d., 3.0 μm film thickness), a flame ionization detector (FID) (Agilent Technologies, 6890N). This GC/FID was control by a computer workstation and equipped with an Agilent Technologies 7683 Series automatic sampler. The GC oven temperature was initially at 30 °C for 5 min. It was then raised at 15 °C/min to 90 °C and kept for 2 min, and then raised at 20 °C/min to 200 °C and kept for 5 min. The stock solution was prepared using VOCs Mix 2 (Supelco, from Liu-Ho Co., Taiwan). The established calibration curves for the six investigated VOCs were found to have *R*-square-values >0.996. Seven replicate analyses were performed on a sample, using the lowest previously specified concentrations for establishing calibration curves for the five VOCs. The resultant standard deviation (STD) for each VOC compound was used to estimate its method detection limit (that is, MDL = 3 × STD). The analytical results displayed that the MDLs for the five VOC compounds of the MTBE, benzene, toluene, ethylbenzene, and *m*/*p*-xylene and *o*-xylene were 1.25, 0.38, 1.024, 0.833, 0.404 and 0.404 $\mu g/m^3$, respectively. Three replicate analyses were performed on each of the three samples with known specified concentrations, and the relative standard deviations (R.S.D.s) thus obtained were employed to assess the accuracy of the method.

3. Results and discussion

3.1. MTBE and BTEX concentrations

Six different industrial park neighborhoods (Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi) were selected to represent the food processing, machine manufacturing, iron and steel, general manufacturing, special oil and petroleum, and petrochemical industries, respectively. Table 1 lists the measured basic meteorological condition in six different sampling sites. We obtained these meteorological data simultaneously in the sampling sites during sampling period. These averages are calculated during all sampling period in this study.

Table 2 lists the descriptive statistics of the MTBE and BTEX measured in the six different industrial park neighborhoods (with sample size $n = 129$). Generally, the mean concentration of MTBE was 3–5 times higher than that of benzene (except for the Lin-Yuan sample area about 1.0). This is associated with the fact that two stroke scooters continue to comprise approximately 1/3 of the motorcycle fleet in Taiwan, and are notorious for their low burning efficiency, meaning that the evaporative emissions were expected to contribute a significant fraction to the ambient of industrial neighborhoods.

Table 1
Measured basic meteorological condition in six different sampling sites

Sampling site	Temperature (°C)	Relative humidity (%) (mean)	Atmospheric pressure (mmHg) (mean)	Sunlight lux (mean)	Wind speed (m/s) (mean)
Nei-Pu	24.8 ± 3.3	56.1 ± 7.9	766.4 ± 2.6	5604.1 ± 138.1	0.7 ± 0.5
Ping-Tung	28.2 ± 3.3	48.5 ± 9.1	767.1 ± 2.5	12183.2 ± 111.2	0.8 ± 0.4
Ping-Nan	28.3 ± 4.6	46.6 ± 10.5	767.4 ± 1.7	11436.4 ± 190.3	1.4 ± 0.6
Ren-Wu	26.7 ± 3.8	46.1 ± 7.0	768.7 ± 1.4	7635.3 ± 193.8	1.5 ± 0.8
Lin-Yuan	22.3 ± 3.7	58.4 ± 9.6	772.5 ± 2.4	9929.2 ± 106.1	1.6 ± 0.7
Nan-Zi	25.4 ± 4.0	50.1 ± 7.1	770.1 ± 2.3	7813.6 ± 194.3	0.9 ± 0.4

Table 2
Descriptive statistics of the MTBE and BTEX measured in different industry park neighborhoods in southern Taiwan (sample size $n = 129$)

Concentration (μg/m^3)	Mean	Median	S.D.	Min.	Max.
MTBE					
Nei-Pu	24.97	29.18	11.22	ND	41.27
Ping-Tung	17.06	17.10	9.10	ND	40.30
Ping-Nan	18.41	15.82	8.33	6.84	35.96
Ren-Wu	34.11	18.77	34.10	12.70	145.61
Lin-Yuan	25.92	22.70	14.09	13.74	74.39
Nan-Zi	25.43	20.76	10.91	13.04	59.47
Benzene					
Nei-Pu	6.72	7.34	3.13	ND	12.39
Ping-Tung	5.86	5.04	3.38	ND	13.73
Ping-Nan	6.54	6.73	2.98	1.73	12.54
Ren-Wu	6.57	5.92	2.78	4.00	16.26
Lin-Yuan	25.84	8.40	34.67	3.69	120.56
Nan-Zi	7.16	6.08	6.04	3.91	36.81
Toluene					
Nei-Pu	8.86	6.80	8.81	ND	37.19
Ping-Tung	9.70	5.15	12.77	ND	54.56
Ping-Nan	16.90	6.53	22.71	1.03	73.60
Ren-Wu	56.63	49.20	20.02	36.06	101.04
Lin-Yuan	23.47	17.77	20.26	6.82	73.83
Nan-Zi	21.09	17.09	14.78	3.37	67.52
Ethylbenzene					
Nei-Pu	1.87	2.13	0.94	ND	3.16
Ping-Tung	7.79	7.03	4.10	3.22	19.65
Ping-Nan	6.24	6.40	2.61	2.41	10.91
Ren-Wu	10.95	9.23	4.48	6.95	23.31
Lin-Yuan	8.44	6.80	3.94	5.54	17.39
Nan-Zi	5.86	5.04	3.38	1.96	13.73
m,*p*-Xylene					
Nei-Pu	10.04	10.40	5.51	ND	17.11
Ping-Tung	11.11	10.33	5.59	ND	26.93
Ping-Nan	12.16	9.31	5.46	5.45	23.05
Ren-Wu	22.79	21.27	5.44	15.18	35.36
Lin-Yuan	19.90	19.00	4.06	14.50	30.70
Nan-Zi	15.70	16.75	5.05	7.08	25.77
o-Xylene					
Nei-Pu	3.71	3.21	1.63	ND	6.53
Ping-Tung	6.07	5.76	3.16	ND	16.67
Ping-Nan	4.55	3.32	3.35	ND	13.40
Ren-Wu	9.31	8.22	3.22	6.17	17.41
Lin-Yuan	7.78	6.24	4.06	4.21	16.87
Nan-Zi	6.56	5.80	2.35	4.23	14.80

Table 2 reveals that the highest mean concentrations for MTBE and benzene were measured at Ren-Wu and Lin-Yuan, respectively. Furthermore, the highest mean concentrations for toluene, ethylbenzene, *m*,*p*-xylene and *o*-xylene were measured at Ren-Wu. In certain sampling neighborhoods (such as Nei-Pu and Ping-Tung), higher concentrations of toluene might result from nearby construction work (such as painting) and evaporation from car-painting plants and industrial areas during the sample period.

MTBE, benzene, and toluene ranged widely. For example, the range for MTBE at Ren-Wu was from 12.7 to 145.6 μg/m^3, the range for benzene at Lin-Yuan was from 3.69 to 120.6 μg/m^3, and the range for toluene at Ren-Wu was from 36.1 to 101.0 μg/m^3. The difference between different industrial types at different sampling locations produced complications of VOCs in the different neighborhoods. Although these complications occurred at every site, two main reasons for the difference occur at the six different locations. One reason for the difference is that higher concentrations of MTBE, toluene and benzene suggest that traffic emissions simultaneously occurred with the industrial emissions in the park and pollutant transportation disperses in the neighborhood atmosphere. Another reason for the high levels of benzene or toluene relates to the fact that these pollutants have longer lifetimes in the atmosphere than other pollutants do. Assuming [OH] = 10^6 rad cm^{-3}, the estimated lifetimes of benzene, tolueene, ethylbenzene, *m*-xylene, *p*-xylene and *o*-xylene are 9.4 days, 1.9 days, 1.6 days, 11.8 h, 19.4 h and 20.3 h, respectively [18,28]. The relatively longer lifetime of benzene and toluene indicated that these materials have lower reactivity or are more stable in the atmosphere of the neighborhoods. Table 3 lists some average MTBE and BTEX concentrations for various cities taken from the recent literature. The table reveals that the levels of BTEX measured in the six industrial park neighborhoods differed from other Asian samples.

In this study, daytime covers both 7:00–11:00 a.m. and 1:00–5:00 a.m., and night time covers 7:00–11:00 p.m. Thus, daylong time covers all (7:00–11:00 a.m., 1:00–5:00 a.m., and 7:00–11:00 p.m.). Fig. 1 compares mean MTBE and BTEX concentrations at daytime, nighttime and throughout the day (daylong time) in six different industrial park neighborhoods in southern Taiwan. Both MTBE and BTEX displayed higher nighttime compared to daytime concentrations in most of the sampling locations. This trend appears to be mostly associated with the influence of climate on VOC removal. VOC removal is faster in summer than in winter because more sunlight and higher temperatures produce higher chemical removal reaction rates [29]. Thus, the winter VOC concentrations exceeded the summer concentrations, consistent with the findings in many other cities [30–32]. In fact, all six different sampling sites have strong daytime solar heating owing to southern Taiwan lying between the Tropic of Cancer and the equator. Consequently, MTBE and BTEX removal is faster in the daytime compared to the nighttime because more sunlight and higher temperatures result in higher chemical removal reaction rates.

MTBE is more suitable than other VOCs as a reference compound for indicating traffic emissions owing to the fact that it is the such compound consumed in the formation of gasoline. Besides some minor leakage from gas stations during pumping, MTBE in ambient air is assumed to derive almost exclusively from car exhaust and evaporative emissions [20]. However, a small number of process related to the recycled motor repair factory and agriculture working machine in parks may contribute to the release of MTBE because of using the gasoline as their working fuel. Fig. 2 shows the percentage of MTBE and BTEX for a daylong

Table 3
Summary of average MTBE and BTEX concentrations for different cities in the literatures

Sampling site	Brief type description	MTBE	Benzene	Toluene	Ethylbenzene	*m*,*p*-Xylene	*o*-Xylene	Unit	Reference
Taiwan (toolbooth at highway tool station)	Bus/truck lane (dayshift)	2.70 ± 1.45	3.13 ± 1.23	13.91 ± 1.33	2.05 ± 1.26	4.52 ± 1.29	(here are reported as *m*,*p*-Xylene plus *o*-Xylene)	ppb	[35]
	Car-lane/ticket (dayshift)	5.63 ± 1.25	6.23 ± 1.29	21.93 ± 1.25	3.24 ± 1.21	8.56 ± 1.25			
	Car-lane/cash (dayshift)	6.04 ± 1.35	5.98 ± 1.26	21.74 ± 1.31	3.55 ± 1.22	8.59 ± 1.22			
	Background	0.03 ± 1.13	0.45 ± 1.21	0.92 ± 1.35	0.17 ± 1.37	0.50 ± 1.26			
Finland (self-service stations)	Station 1	(7.5, 4.1)							
	Station 2 in June, October)	(12.4, 14.1)	–[a]	–	–	–	–	μg/m^3	[14]
Helsinki (Urban air quality monitoring stations)	Site 1 (city)	2800	2100	6600	1300	4100	1600		
–	Site 2 (sports filed)	1500	1000	3000	600	1900	740		
–	Site 3 (suburban station)	2400	1900	6018	1430	4600	1730		
–	Site 4 (industrial area)	1100	950	2700	590	1900	730	ng/m^3	[36]
Bangkok	Industries + residential	–	18.2 ± 13.7	186 ± 198	36.6 ± 55.2	81 ± 90.2	28.9 ± 27.6	μg/m^3	[37]
Hong Kong									
Mong Kok	Residential area	–	15.11 ± 22.95	137.15 ± 195.14	11.65 ± 18.98	22.45 ± 36.99	10.63 ± 14.62	μg/m^3	[19]
Causeway Bay	Commercial area	–	10.05 ± 7.24	71.10±65.13	13.70 ± 20.71	13.47 ± 13.23	7.67 ± 6.45	μg/m^3	[19]
Kwai Chung	Industrial area	–	15.07 ± 16.60	139.35 ± 263.98	24.68 ± 68.56	27.88 ± 54.32	13.39 ± 26.55	μg/m^3	[19]
Yuen Long	Newly developed area	–	10.53 ± 10.81	45.20 ± 50.97	7.44 ± 8.51	12.27 ± 19.06	5.12 ± 6.34	μg/m^3	[19]
Hok Tsui	Background area	–	2.75 ± 1.51	4.58 ± 3.26	2.20 ± 4.11	2.68 ± 2.40	1.45 ± 0.99	μg/m^3	[19]
PolyU campus	Campus (winter)	–	5.07 ± 2.28	26.44 ± 10.71	2.61 ± 1.67	2.78 ± 1.30	2.03 ± 0.96	μg/m^3	[29]
	Campus (summer)	–	2.97 ± 1.10	26.22 ± 8.48	3.18 ± 2.11	3.99 ± 1.82	3.06 ± 1.99	μg/m^3	[29]
Kwun Tong	Industries (winter)	–	4.92 ± 2.01	26.42 ± 18.55	2.53 ± 2.34	2.23 ± 1.76	1.66 ± 1.19	μg/m^3	[29]
	Industries (summer)	–	1.74 ± 0.69	64.34 ± 36.77	2.17 ± 0.78	2.31 ± 0.66	1.61 ± 0.47	μg/m^3	[29]
Hok Tsui	Background (winter)	–	2.07 ± 0.62	3.23 ± 2.58	0.24 ± 0.19	ND[b]	ND	μg/m^3	[29]
	Background (summer)	–	0.32 ± 0.17	1.05 ± 1.31	ND	ND	ND	μg/m^3	[29]
Manila (Philippines)	Traffic, city	–	–	168 ± 268	21.9 ± 25.5	55.8 ± 56.9	16.8 ± 16.9	μg/m^3	[37]
Rome	Traffic, city	–	35.5	99.7	17.6	54.6	25.1	μg/m^3	[34]
Sao Paulo (Brazil)	Traffic, city	–	16.7 ± 10.1	28.1 ± 17.9	6 ± 3.2	18.5 ± 10.1	6.2 ± 3.6	μg/m^3	[37]
Santigao (Chile)	Traffic, city	–	14.8 ± 10.8	29.8 ± 13.7	6.5 ± 2.7	25.2 ± 14.9	8.9 ± 5.6	μg/m^3	[37]

[a] (–) Denotes not available.
[b] ND denotes under the detectable limitation.

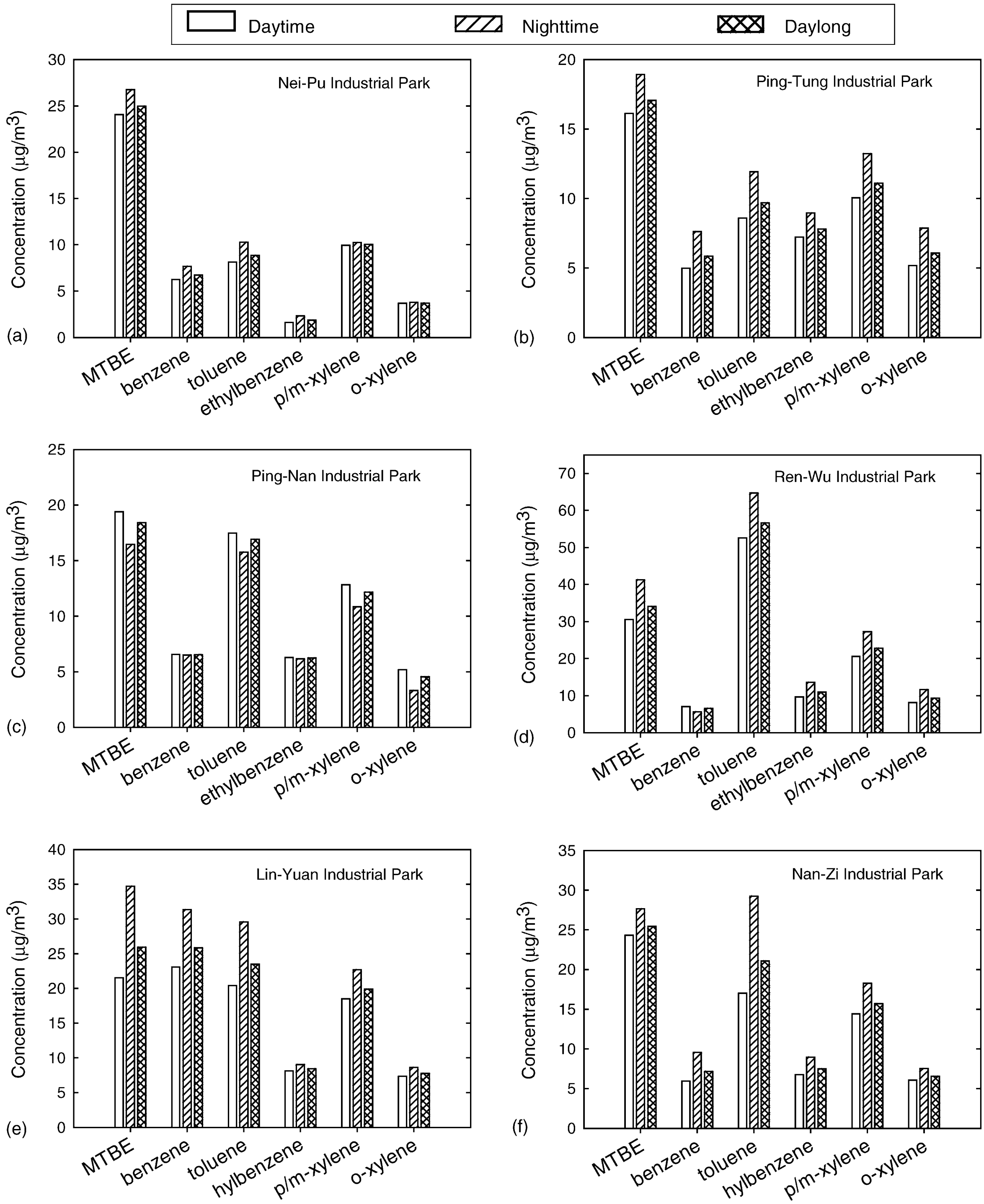

Fig. 1. Comparison of mean MTBE and BTEX concentrations at daytime, nighttime and daylong time in different industrial park neighborhoods in southern Taiwan.

sample period in the six sampling industrial park neighborhoods. MTBE, toluene and benzene are the three most common species in all the six sites and contribute approximately 24–44, 16–40 and 5–23%, respectively, of the total MTBE and BTEX at these sampling sites. This phenomenon demonstrated that not only traffic emissions but also different industrial sources are complicatedly mixed in the sampling neighborhoods in southern Taiwan. Therefore, we hypothesize that many factors influence the VOC profiles in southern Taiwan, representing a complex scenario that can only be understood by obtaining more data and conducting intensive measurements.

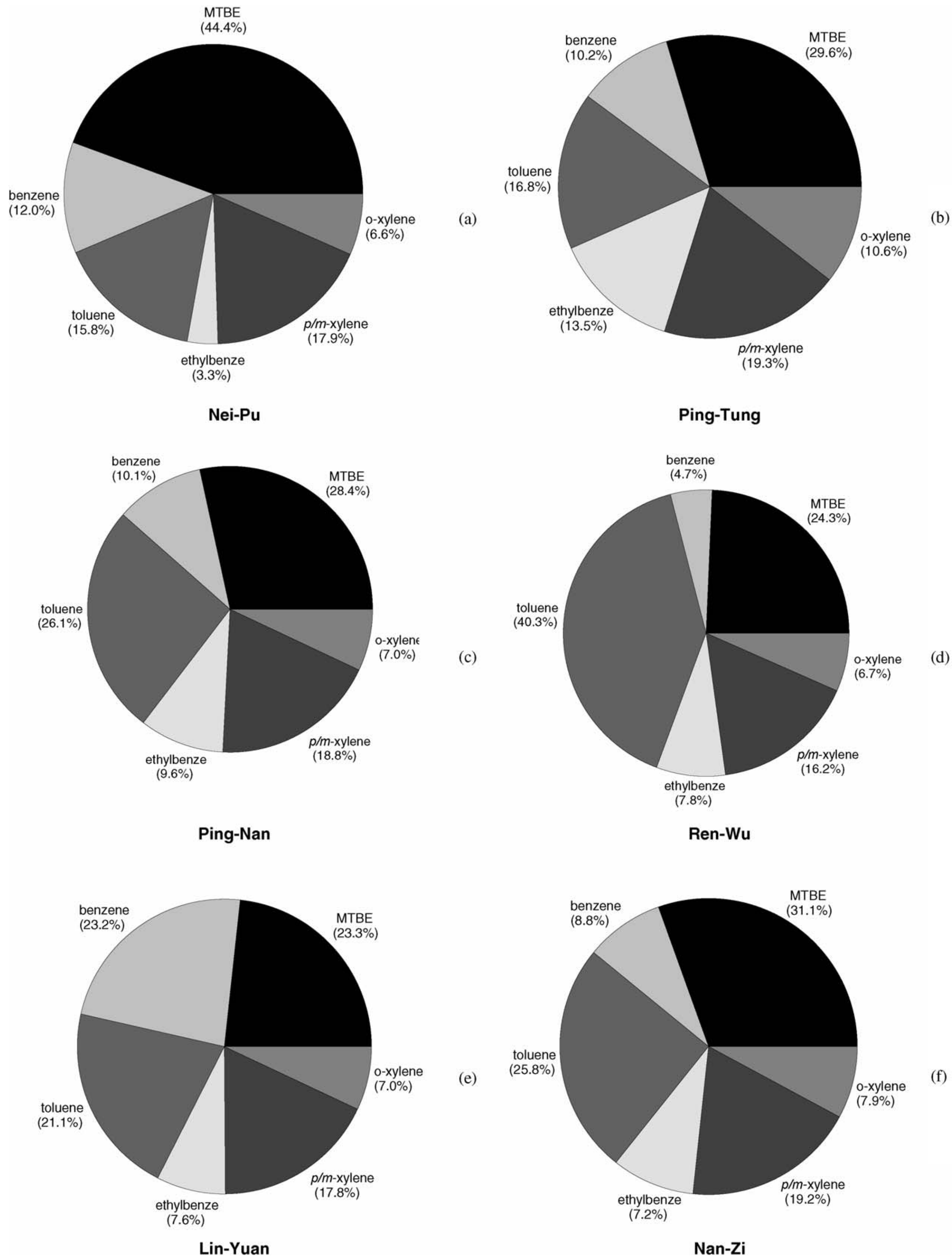

Fig. 2. Percentage of MTBE and BTEX in the six sampling industrial park neighborhoods.

3.2. MTBE–BTEX ratios

Average MTBE–BTEX ratios were calculated to compare the VOC emissions among the six sampling industrial parks. In this study, the MTBE–BTEX ratio means the ratios between MTBE, benzene, toluene, ethylbenzene, and xylene (*m*,*p*-xylene + *o*-xylene) concentrations based on the normalization by minimum level. The average MTBE–BTEX ratios of Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi were (13.4:3.6:4.7:1.0:7.4), (2.9:1.0:1.7:1.3:2.9), (3.0:1.0:2.7:1.0:2.7), (5.2:1.0:8.6:1.7:4.9), (3.1:3.1:2.8:1.0:3.3) and (4.3:1.2:3.6:1.0:3.8), respectively. The ratios at different sampling neighborhoods reflected the possible existence of different sources in different neighborhoods. In neighborhoods where multiple sources of VOCs coexist, the concentration ratio of MTBE to any VOC tends to be smaller than when traffic is the main source, as the contribution of VOC from these multiple sources is superimposed upon the traffic emissions, whereas MTBE comes only from traffic.

Lee et al. [19] demonstrated that, in the atmosphere of Hong Kong, the BTEX ratios in Mong Kok, Kwai Chung, Yuen Long, Causeway Bay and Hok Tsui were (1.3:11.5:1.0:2.8), (1.0:10.6:2.1:3.1), (1.4:6.1:1.0:2.6), (1.0:6.9:1.3:2.1) and (3.3:6.3:1.3:1.0), respectively. Different ratios of BTEX were also reported in other studies on vehicle exhaust, such as (3:5:1:3), (3:14:1:4), (4:11:1:3) and (7:11:1:3) in the Lincoln Tunnel (USA), at Newark, Elizabeth and Camden, respectively [33]. The difference in BTEX ratios between this work and those above studies demonstrates that difference between the sources in the different sample areas. Furthermore, the climate, topography, characteristics of vehicle fuel used, and the orientation and alignment of buildings, industries roads, and so on may also influence the MTBE and BTEX profiles in southern Taiwan.

3.3. Toluene/benzene (T/B) ratios

In addition to BTEX ratios, most studies have also reported toluene to benzene ratio (T/B). Lee et al. [19] suggested that T/B ratio increases with increasing traffic volume, industrial emissions and other urban sources in denser areas. T/B ratio ranged from 0.1 to 5.2, from 0 to 5.5, from 0.2 to 8.2, from 4.1 to 16.3, from 0.2 to 4.6 and from 0.7 to 9.4 in the Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi industrial park neighborhoods, respectively. Moreover, average T/B ratios in Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi were 1.3, 1.7, 2.6, 8.6, 0.9 and 2.9, respectively. Higher average T/B ratio (8.6) was found in Ren-Wu compared to other industrial park neighborhoods, while Lin-Yuan and Nei-Pu both had low average T/B ratios. The high T/B ratio in Ren-Wu indicated that large additional sources of toluene are emitted from this industrial park, or alternatively that the auxiliary fuels used differ significantly. In the six different industrial park neighborhoods in southern Taiwan, the average T/B ratio was approximately 3, while Hong Kong and the other cities have T/B ratios of 2–10 and 2.0–3.3, respectively [19,34]. However, high or low T/B ratio was found in six different industrial park neighborhoods. This observation result indicates that VOCs measured along the boundary of the industrial park should be considered a blend concentration associated with nearby land use, traffic density, site type and industrial activities.

3.4. Xylene/ethylbenzene (X/E) ratio

The study used the xylene/ethylbenzene (X/E) ratio to assess the relative age of the air parcels. X/E ratio ranged from 1.5 to 260, from 0.6 to 2.9, from 1.1 to 2.9, from 1.5 to 2.9, from 1.5 to 2.6 and from 1.3 to 3.4 in Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi industrial park neighborhoods, respectively. In Nei-Pu, the maximum X/E ratio was 260 because of the release of metal and printing solvent upwind during the sampling day. The average X/E ratios, namely (*m*,*p*-xylene + *o*-xylene)/ethylbenzene ratios, in Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi were 7.4, 2.2, 2.7, 2.9, 3.3 and 3.8, respectively. The concentrations of MTBE and BTEX in the atmosphere of the six different industrial park neighborhoods were mainly influenced by direct emissions from various industrial sources within the parks, fuel evaporation, photochemical reactions and small quantities of vehicles emissions. The comparison of the X/E ratios in the six different sampling neighborhoods suggested there is the situation about the photochemical reactivity of xylenes. The average X/E ratio (7.4) in Nei-Pu exceeded that in the other five sampling sites (average values from 2.2 to 3.8). This phenomenon indicated that the freshly emitted xylene in the transportation decayed at different rates to OH-oxidation in the atmosphere. Notably, the lower X/E ratio (2.2) in the Ping-Tung neighborhood implies an aged air parcel. Overall, the X/E ratios measured in the different industrial park neighborhoods in southern Taiwan are higher than those observed in Hong Kong (average values from 1.5 to 2.2) [29]. This study suggests that VOCs crossed the neighborhoods and are away from industrial sources, the reaction/degradation of the more reactive isomers of xylene is markedly.

3.5. MTBE and BTEX correlations

Statistical analysis was applied to identify the relationship between the MTBE and BTEX species in six industrial park neighborhoods. Generally, the level of correlation (r) has three cases: (1) high correlation (if $|r| \geq 0.8$); (2) moderate correlation (if $0.5 \leq |r| < 0.8$); (3) weak correlation ($|r| < 0.5$). High to moderate MTBE and BTEX correlations were noted in the Ping-Tung industrial park neighborhood. This Ping-Tung site, with some nearby point sources to skew the correlation, received pollution predominantly related to the multi-processes from the park region, as well as automobile related pollution from nearby roads. Notably, the Ping-Tung and Ren-Wu industrial park neighborhoods

Table 4
Factor analysis of MTBE and BTEX in different industrial park neighborhoods in southern Taiwan

Compounds	Factor-1	Factor-2	Factor-3	Communality
MTBE	–	0.948	–	0.934
Benzene	–	–	0.977	0.998
Toluene	0.853	–	–	0.758
Ethylbenzene	0.879	–	–	0.807
m,p-Xylene	0.757	–	–	0.776
o-Xylene	0.892	–	–	0.865
Eigenvalue	2.95	1.18	1.04	–
% of variance	49.22	19.75	17.33	–
Cumulative (%)	49.22	68.97	86.30	–

Extraction method: principal component analysis. Rotation method: varimax with Kaiser normalization. Factor loadings ≥6 listed.

displayed significant correlations in BTEX. Moreover, good correlations in TEX and poor correlations between benzene and TEX were observed in the neighborhood of the Lin-Yuan industrial park. TEX mainly derived from the vaporization of industrial solvents, manufacturing and painting emissions, while benzene mainly derived from nearby traffic.

Since two complicated sources of BTEX, related to the petroleum and petrochemical industries and traffic emissions, existed near the Nan-Zi industrial area, it was reasonable to expect a low correlation coefficient. Nei-Pu exhibited poor BTEX correlation coefficient. This poor correlation can be explained by the mixed sources of BTEX that appeared at different times, or by the fact that some sources of BTEX only emitted at certain times, for example the evaporation of solvents during cleaning. Expecting a poor correlation appeared reasonable, since some batch emissions were related to the electric appliance industry in the surrounding area. Furthermore, the poor correlation between MTBE and other VOCs in certain sampling neighborhoods implies the air is poor or initial mixed and the small difference in MTBE content in the exhaust and evaporative emissions is obscured by this mixing.

3.6. Principal component analysis

Principal component analysis was performed on valid measured data. This analysis was intended to reduce the number of VOCs by extracting some factors that could explain the common variance of these VOCs. Table 4 lists the results of PCA. Three factors were extracted for all sampling sites in this investigation. The number of factors extracted depended on the eigen value (>1.000). For the measured data, the three factors explained 86.30% of the common variance in the data set. The first factor (Factor-1) explained approximately 49.22% of the variance, while the second factor (Factor-2) and third factor (Factor-3) explained approximately 19.75 and 17.33%, respectively, of the variance. Among the measured VOCs, toluene, ethylbenzene and xylenes had the highest loadings (>0.6) for the first factor. The second and third factors comprised of MTBE and benzene with high factor loadings, respectively. This PCA result is expected based on general chemical knowledge. Owing to ambient conditions in the troposphere, MTBE reacts with OH radicals (usually at the methoxy side of the MTBE molecule) to form primarily *tert*-butyl formate (TBF) and formaldehyde, with smaller amounts of benzene (minor product) or without the formation of TEX. Furthermore, although poor correlations between MTBE and BTEX were observed in certain sampling sites since these compounds are primarily released from industry-related emissions, these compounds were the result of combination of industry-related emissions from nearby parks and traffic sources. Principal component analysis could confirm that the dominant influences in the six different industrial park neighborhoods were MTBE, benzene and toluene.

4. Conclusion

The concentrations of MTBE and BTEX in six different industrial park neighborhoods in southern Taiwan were quantified using GC with FID detector following the NIOSH Method 1615. Concentrations of MTBE and BTEX ranged from undetectable to 145.6 $\mu g/m^3$. The existence of mixed sources were reflected in the widely differing T/B ratios. The ratios of T/B (average T/B ratio = 8.6) were higher in the Ren-Wu (petrochemistry and multiple-producing industry) neighborhood than in any of the other sampling neighborhoods (average T/B ratio = 2–5). These observation results suggest that VOCs measured along the boundary of industrial park should be considered a blend concentration influenced by nearby land use, traffic density, site type and industrial activities. The average X/E ratio (5.4) in the Nei-Pu sample site (which was dominated by metal-manufacturing) exceeded that in the other five sampling sites (average values from 1.4 to 2.4). This indicated that the freshly emitted xylene in the transportation decayed at different rates from atmospheric OH-oxidation. The lower X/E ratio (1.4) in the Ping-Tung neighborhood implies an aged air parcel. Principal component analysis was performed on the valid measured data, and three factors were extracted for all sampling sites in this study. The analytical results indicated that the dominant influence in the six industrial park neighborhoods was MTBE, benzene and toluene. Long-term measurements are required to assess the progress achieved through applying control strategies.

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