Speciation of Airborne Volatile Organics in an Industrial City in Taiwan

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ABSTRACT

Characteristic speciation of airborne volatile organics in Kaohsiung, the largest industrial city in Taiwan, is present in this paper. Hourly concentration of airborne volatile organic compounds (VOCs) was monitored by on-line GC/FID and 3 hours-averaged sample was parallel conducted by canister during rush hour. Field sampling works were conducted at a traffic station (Qian-Jin) and an industrial station (Lin-Yuan) during ozone episode days (October, 2003) and non-episode days (July, 2003), respectively. The dominant volatile organics species included benzene, toluene, ethylbenzene, m,p-xylene, styrene, and o-xylene. The other species were also monitored simultaneously.

The concentration of airborne volatile organics at a traffic station during non-episode days were toluene(3.6~12.9μg/m^3), styrene(0~5.8μg/m^3), o-xylene(2.9~5.2μg/m^3), benzene (1.4~4.9μg/m^3), m,p-xylene(1.2~3.7μg/m^3), and ethylbenzene (0~3.7μg/m^3). The results in ozone episode days were toluene(30~378.8μg/m^3), ethylbenzene(3.5~72.8μg/m^3), m,p-xylene(0~41.3μg/m^3), o-xylene(0~38.2μg/m^3), benzene(0~12.9μg/m^3), and styrene (0~9.2μg/m^3). The concentration of airborne volatile organics at an industrial station during ozone non-episode days were toluene(2.2~6.3μg/m^3), o-xylene(0~3.5μg/m^3), benzene (0~2.6μg/m^3), m,p-xylene(0~1.9μg/m^3) , and ethylbenzene(0~1.2μg/m^3). The results of ozone episode days were toluene(39.5~679.9μg/m^3), ethylbenzene (2.9~40.1μg/m^3),benzene (0~21.7μg/m^3), m,p-xylene(0~20.2μg/m^3), o-xylene(0~19.8μg/m^3), and styrene (0~15.2μg/m^3). Toluene was abundant VOCs species at these two stations. However, airborne VOCs concentration at the traffic station is higher than those at industrial station regardless of rush hour or nighttime. The results show that mobile source is the dominant impact source of airborne volatile organics at streetside station in Kaohsiung.

Key words: volatile organic compounds, volatile organic hazardous air pollutants, and industrial city

INTRODUCTION

Air quality monitoring results indicate that the Kaohsiung city–Kaohsiung county–Pingtung county air basin (KKPAB), located in Southern Taiwan, has the worst air quality among the seven air basins in Taiwan. The annual number of days with criteria pollutants exceeding the national ambient air quality standards (NAAQS) at the KKPAB accounted for 20% of the monitoring days (Taiwan EPA, 1998). Since 1994, the number of days when the ozone concentration exceeded the NAAQS increased annually such that in 1997 ozone became the major subindex for this basin.[1] Therefore, the Kaoping air basin, located in Southern Taiwan, is classified as a non-attainment region for ozone. In 2000, 10.4% of the air quality data (monitoring site number times monitoring days) were classified unhealthy as its pollutant standard index (PSI) exceeded 100.The maximum hourly concentrations of ozone ranged between 126 and 203 ppb, which exceeded the maximum hourly standard of 120

ppb, at seven air monitoring stations in Kaoping Air Basin. Approximately two-fifths of the incidents were attributed to ozone episodes especially from October to December (TEPA, 2000).[2]

In order to understand the effect of atmospheric VOC distributions on the ozone formation, several investigators have conducted the field measurements of VOC concentrations in remote, rural, and urban-suburban areas (Singh and Zimmerman, 1992;Russell, 1995; Moschonas and Glavas, 1996;Riveros et al., 1998;Main et al., 1999). The objectives of this research include characterization of VOCs as well as abundant species, evaluation of the reactivity of VOCs and the OFP in air parcels, and assessment of the age of the air mass using species ratios. These results are useful for the application of photochemical kinetic mechanisms in which a quality model for the development of an ozone control strategy can be established, modeling different ozone episode events, and validating the modeling results.

For these reasons, airborne VOCs mass and major components were collected and analyzed in the industrial city of Kaohsiung, Taiwan. There are more than 1,228,429 automobiles and motorcycles and a total of 1911 factories, including two fuel power plants, two cement mills, nine sizable steel plants, and 14 large-scale petrochemical plants in Kaohsiung City. Moreover, the city is surrounded by four heavily polluted industrial parks namely Jen-wu, Ta-shei, Ta-fa, and Lin-yuan located in the adjacent Kaohsiung County. To understand the air pollution levels and their impact, airborne VOCs samples were collected at two ambient air quality sites distributed over the city during July 2003 and October 2003. The concentrations and characteristics of the major components in VOCs were measured and discussed.

METHODOLOGY

1. Field Measurement

Airborne carbonyl compounds were collected on 2 sites in the southern Taiwan air basin, including a traffic station (Qian-Jin) and an industrial station (Lin-Yuan) during ozone episode days (October, 2003) and non-episode days (July, 2003).Fig.1 shows the locations of these sites[3]. Table 1 shows the meteorological data in the air basin during the days when the field measurements were conducted. The synoptic meteorological condition was classified into the type of northeastern prevailing wind with high pressure. It was one of the typical, synoptic meteorological conditions for an ozone episode in the air basin. Sampling works were conducted on two sites simultaneously.

On each sampling site, two samples, averaging 2-hours, were taken during the periods of 07:00-09:00 and 14:00-16:00 on each sampling day. Sampling instruments were set up 10 meters above the ground at the air quality monitoring station.

2. Air Sampling and Analysis

Ambient air were collected by the active pressurized sampler (Xontech Canister Sampler 910A), with sampling flow rate of 80 ml/min, into prevacuated Summa stainless steel canisters (Scientific Instrumentation Specialists, Moscow, ID). All canisters were cleaned up in a series of pressurization/evacuation cycles at 105℃, using humidified ultra-zero air evacuated to less than 0.2 mmHg, and was shipped to the field for sampling.

Sample air was released from the canister and concentrated by a cold trap (Varian, Inc.) then purged out and analyzed by a GC/MS (Varian 3600 GC/FID, Varian Saturn 2000 MS). The

temperature of the trap system was cooled down to -160 by liquid nitrogen at first. Then the desorber was heated to 160 for purging. The gas chromatography was equipped with dual-column capillary. A fused silica capillary column (60 m, 0.32 mm ID with 1 mm DB-1, J&W) to the MS. Helium was used as the carrier gas.[4]

Fig. 1.Location map of the sampling sites (▲) in the Kaohsiung City, Taiwan, and industrial parks (●) in the adjacent Kaohsiung County.(Lin,2002)

Table 1.The meteorological data in the air basin during the sampling days (N=4)

Location	date	periods	WS(m/s)	WD(degree)	TEMP(℃)
Qian-Jin	July	07:00-09:00	1.6±0.7	204.3±61.0	31.0±1.2
		14:00-16:00	3.6±0.7	230.3±45.3	33.0±1.5
Lin-Yuan	July	07:00-09:00	1.4±0.6	238.6±141.6	31.1±1.0
		14:00-16:00	5.2±2.3	172.6±55.6	34.0±0.6
Qian-Jin	October	07:00-09:00	0.8±0.4	346.4±99.2	24.0±1.1
		14:00-16:00	3.2±0.4	294.3±25.5	27.2±0.4
Lin-Yuan	October	07:00-09:00	2.7±0.8	357.4±12.2	23.9±1.2
		14:00-16:00	4.0±0.7	233.6±8.0	28.3±0.6

RESULTS and DISSUSION

1. Concentration-based method

The observation results sorted by the CB method are classified under four classes as shown in Table 2. Among the four VOC classes at the two sites, aromatics had the highest percentage(38–90%), alkanes(3–59%) and biogenics(0–16%) being the next higher classes. The aromatics fraction at each site exhibited a comparable range of 38–63% on July and a comparable range of 88–90% on October. The alkanes fraction at each site exhibited a comparable range of 21–59% on July and a comparable range of 3–6% on October.

Biogenics and alkenes were shown to have lower concentrations for the two sites.

Table 2.VOC fractions of four classes at two sites using the concentration-based method (%) (N=4)

Locations	date	periods	Alkenes	Alkanes	Aromatics	Biogenics
Qian-Jin	July	07-09	3±3	59±23	38±22	0±0
		14-16	6±5	27±10	59±9	8±4
Lin-Yuan	July	07-09	4±4	34±8	62±6	0±0
		14-16	0±0	21±20	63±12	16±14
Qian-Jin	October	07-09	8±2	3±3	90±2	0±0
		14-16	4±5	6±7	86±10	4±5
Lin-Yuan	October	07-09	6±6	6±8	88±5	0±1
		14-16	6±10	3±6	88±9	3±3

2. A comparison of VOC concentrations with deferent locations

The VOC data sets analyzed here for comparison are listed in Table 3. The analysis includes data gathered from seven deferent urban areas and this study. Forty-one species frequently detected in these eight areas including 9 alkenes, 23 alkanes, and 9 aromatics have formed for analysis. The concentration for each VOC species in this study is the average value of four monitoring sites. Aldehydes and biogenics are exclused from the analysis due to no available data from other areas. The data listed in Table 3 is perhaps the highest quality VOC figures available, but the data are not without problem or potential flaws. Moreover, a comparison of this study with other urban centers is complicated because of differences in the measured species, sampling sites and sampling periods and the major city's activities as well as differences coupled with vehicles or vehicle's fuel compositions as described in Moschonas and Glavas (1996)[5]. Among five areas, Osaka[6] showed the highest (183 ppbv) concentration. The data shown in this study (101 ppbv) is very close to the reported concentrations in Vienna (103 ppbv)[8], Sydney (111 ppbv)[9], and Atlanta (112 ppbv)[10]. But it should be noted that the result of this study is conducted at industrial urban areas. In the values reported here the VOCs concentration is higher than other urban centers.

3. Speciation of Airborne VOCs in Ozone Episode Days and Non-episode Day

The concentration of airborne VOCs at a traffic station during non-episode days were toluene(3.6~12.9μg/m^3), styrene(0~5.8μg/m^3), o-xylene(2.9~5.2μg/m^3), benzene (1.4~4.9μg/m^3), m,p-xylene(1.2~3.7μg/m^3) , and ethylbenzene (0~3.7μg/m^3). The results in ozone episode days were toluene (30~378.8μg/m^3), ethylbenzene (3.5~72.8μg/m^3), m,p-xylene (0~41.3μg/m^3), o-xylene (0~38.2μg/m^3), benzene (0~12.9μg/m^3), and styrene (0~9.2μg/m^3). The concentration of airborne VOCs at an industrial station during ozone non-episode days were toluene (2.2~6.3μg/m^3), o-xylene (0~3.5μg/m^3), benzene (0~2.6μg/m^3), m,p-xylene (0~1.9μg/m^3) , and ethylbenzene (0~1.2μg/m^3). The results of ozone episode days were toluene(39.5~679.9μg/m^3), ethylbenzene (2.9~40.1μg/m^3), benzene (0~21.7μg/m^3) , m,p-xylene (0~20.2μg/m^3), o-xylene (0~19.8μg/m^3), and styrene (0~15.2μg/m^3).

The concentrations of speciation of VOCs on an ozone episode day were higher than those on non-episode day however sampled at a traffic station or at an industrial station. Airborne VOCs concentration at the traffic station is higher than those at industrial station regardless of rush hour or nighttime.

Table 3.VOCs in this study and other urban centers, units ppbv

Group	VOC species	Vienna	Sydney	Osaka	Atlanta	Taiwan
Alkenes	Propylene	6.3	7.4	6.1		5.1
	1-Butene					3.0
	Cis-2-butene	0.9	1	0.9		0.2
Alkanes	Isobutane	1.8	4.7	5.1		3.0
	n-Butane	4.9	7.5	11	16.9	3.0
	Isopentane	6.9	9	10.6		8.8
	Cyclopentane		0.8		1.6	0.3
	2,3-Dimethylbutane		0.9	0.8		1.3
	2-Methylpentane	3.2	2.6	3.9		2.0
	3-Methylpentane	1.9	1.6	3.1		4.9
	Methylcyclopentane	1.4	1.2	1.7	2.9	0.0
	Cyclohexane	0.6	0.9	0.8	5.4	1.1
	2-Methlyhexane	1.1	1.2	1.5	5.2	0.2
	2,3-Dimethylpentane		0.7	0.6	2.5	0.2
	n-Heptane	1.4	0.7	2		10.4
	Methylcyclohexane	0.5	0.6	0.7		0.5
	2-Methylheptane			0.6		0.0
	3-Methylheptane	0.5		0.7		1.1
	n-Octane	0.4	0.4	0.6		0.5
	n-Nonane	0.2	0.4	0.7		0.0
Aromatics	Benzene	6	2.6	5.1	8.8	7.6
	Toluene	10.9	8.9	31.1	14.7	208.6
	Ethylbenzene	1.8	1.3	3.8	2.8	23.0
	m,p-Xylene	5.7	3.9	7.7	7.6	12.3
	o-Xylene	2.3	1.5	2.8	2.8	13.2
	Isopropylbenzene					1.4
	n-Propylbenzene	0.5	0.4			2.5
	1,3,5-TMB	0.7	0.5	1.2	1.8	2.9
	1,2,4-TMB	2.4	1.3	2.9		4.2
	Alkenes,ppbv(%)	12(11)	36(32)	36(19)	9(8)	34.7
	Alkanes,ppbv(%)	61(59)	55(49)	93(51)	60(53)	7.6
	Aromatics,ppbv(%)	30(30)	20(18)	55(30)	39(34)	57.2
	Sum	103	111	183	112	393.3

Note: Vienna=anzerstorfer and Puxbaum (1990), Sydney=elson and Quigley (1982),Osaka=sujino and Kuwata (1993),Altanta=RC (1991).a This work(N=16).

4. Variation of Ozone/NMHC Concentration and Speciation of Airborne VOCs

Figure 2 shows the diurnal trend of ozone concentration and concentration of speciation of airborne VOCs at a traffic station on non-episode day. Figure 3 shows the diurnal trend of ozone concentration and concentration of speciation of airborne VOCs at an industrial station on non-episode day. The higher concentration speciation of airborne VOCs was observed in rush hour (07:00~09:00). On the other hand, the lower concentration speciation of airborne VOCs was observed in normal time (14:00~16:00). However, airborne VOCs concentration at the traffic station is higher than those at industrial station regardless of rush hour or nighttime but the ozone concentration of two stations was almost nearly.

Figure 4 shows the diurnal trend of ozone concentration and concentration of speciation of airborne VOCs at a traffic station on episode day. Figure5 shows the diurnal trend of ozone concentration and concentration of speciation of airborne VOCs at an industrial station on episode day. The higher concentration speciation of airborne VOCs was observed in rush

hour (07:00~09:00). On the other hand, the lower concentration speciation of airborne VOCs was observed in normal time (14:00~16:00).The concentration of speciation of VOCs on an ozone episode day were higher than those on non-episode day however sampled at a traffic station or at an industrial station.

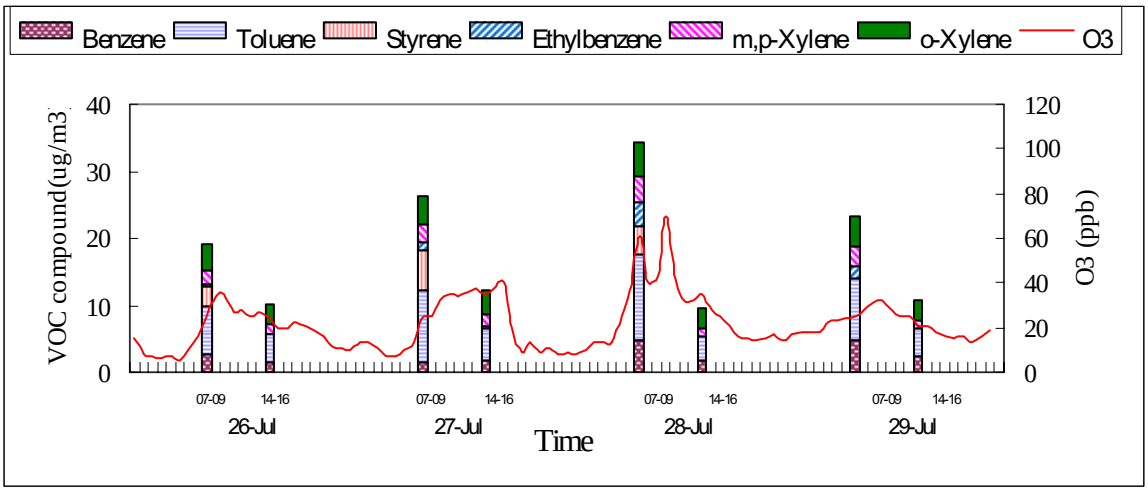

Fig.2 The diurnal trend of ozone concentration and concentration of speciation of airborne VOCs at a traffic station on non-episode

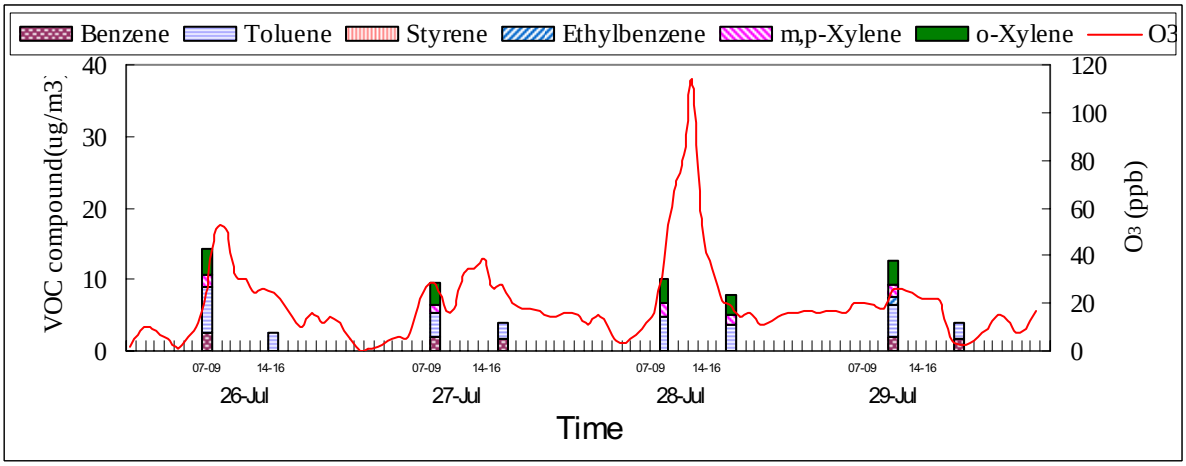

Fig.3 The diurnal trend of ozone concentration and concentration of speciation of airborne VOCs at an industrial station on non-episode day

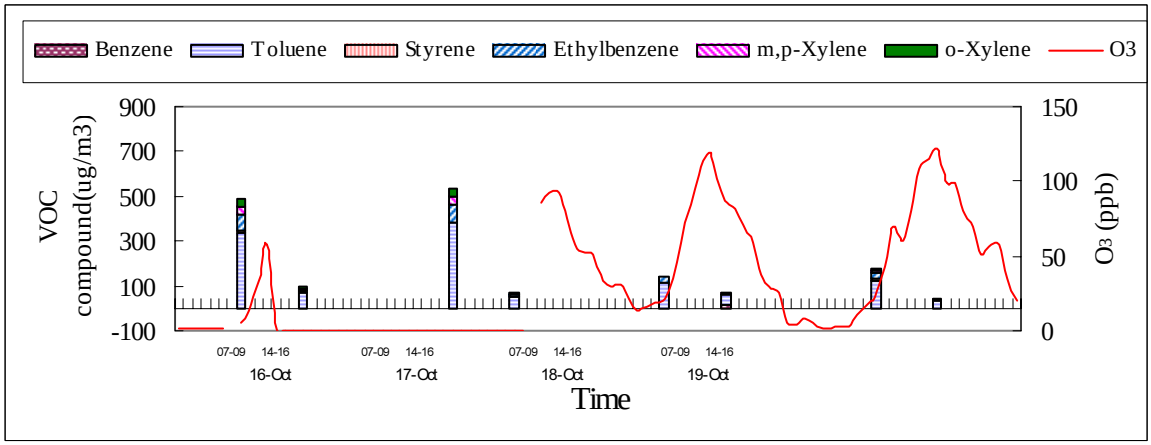

Fig.4.The diurnal trend of ozone concentration and concentration of speciation of airborne VOCs at a traffic station on episode day

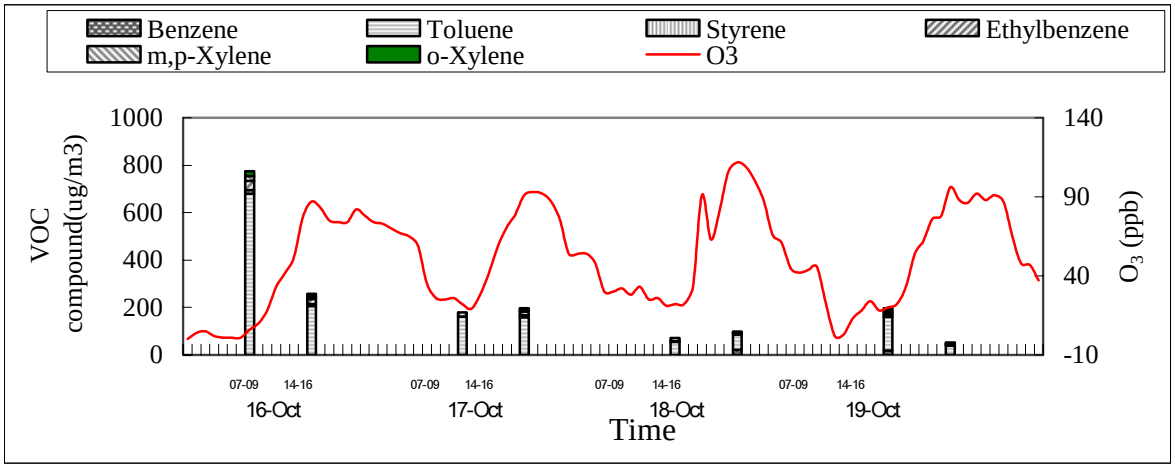

Fig.5. The diurnal trend of ozone concentration and concentration of speciation of airborne VOCs at an industrial station on episode day

CONCLUSIONS

Field measurement of airborne VOCs in the southern Taiwan air basin was conducted both on ozone episode and non-episode day. Great variation of the concentration of airborne VOCs was observed among different sites. However, the profiles of VOCs compounds on various monitoring sites in the air basin are similar to each other both on episode and on non-episode day. Aromatics had the highest percentage (38–90%).The aromatics fraction at each site exhibited a comparable range of 38–63% on July and a comparable range of 88–90% on October. Toluene was the abundant VOCs species at these two stations. However, airborne VOCs concentration at the traffic station is higher than those at industrial station regardless of rush hour or nighttime. The results show that mobile source is the dominant impact source of airborne volatile organics at streetside station in the industrial city in Taiwan. The significance of high concentration of airborne VOCs compounds on an ozone episode day in this air basin certainly will an interesting topic for future study.

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