Spatial and Temporal Distribution of Volatile Organic Compounds around an Industrial Park of Taiwan

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Abstract

The results of spatial and temporal distribution of volatile organic compounds (VOCs) in ambient air surrounding the Hsinchu Science-Based Industrial Park (SBIP), Taiwan during February 2001 to November 2001 are presented. The sampling was performed at 13 different sites around the SBIP for 24 hrs once every month, and a total of 130 samples were collected. The effects of geographical and meteorological conditions and production volume of the SBIP on the variation of pollutant's concentration were investigated. The spatial distribution shows that a comparatively higher concentration of VOCs was found at the sites, which are in the southwestern part of SBIP, downwind of or close to factories. When the wind velocity was low (i.e. below 2 m/s), the concentration of pollutant tended to increase and became uniformly distributed around the science park. The temporal distribution shows a decrease in ambient concentration of pollutants from February to June 2001, mainly due to the decline in the production volume of the SBIP in this period. During the whole period of investigation, the concentration of most of the compounds (except acetone and IPA) was found to be lower than the factory-surrounding air quality standard of Taiwan, but in some cases it was higher than the AALG (ambient air level goal).

Keywords: volatile organic compounds, industrial park, spatial distribution, temporal distribution, meteorological and geographical effect.

1. Introduction

Volatile organic compounds (VOCs) are important in atmospheric chemistry as they play major role from urban to global scales. Knowledge of individual chemical compounds is required to

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characterize the VOCs emission as atmospheric behaviors of individual species vary enormously. VOCs are introduced in the urban environment due to vehicular traffic, industrial processes, gasoline evaporation and natural gas emission. The VOCs are considered to be responsible for formation of ozone and other photochemical oxidants leading to urban smog. Several VOCs have been identified as toxic, carcinogenic or mutagenic at concentration levels in urban environment (Edgerton et al., 1989). These compounds may also contribute to global warming (Derwent, 1990, Fishman, 1991).

Several researchers have attempted VOC monitoring studies over different parts of world considering VOCs increasing importance in environmental issues (Son et al. 2003, Heavner et al. 1996, Bortoli et al. 1986). Na et al. (2003) have measured diurnal characteristics of VOCs in central Seoul and found higher concentrations during morning and evening with low concentration during afternoon. They have also estimated the participation of individual VOCs in ozone formation. The variations of the strength of these sources along with meteorological conditions and photochemical activities cause diurnal, seasonal, and annual variations of the VOC concentrations (Na and Kim, 2001; Borton et al., 2002). Shrivastava (2004) has studied ambient VOCs at residential, commercial, industrial, traffic junctions and petrol pumps in the industrial city of Mumbai. High level of VOCs has been reported in several Asian countries by Hussam et al. (2002) and Ivan et al. (1998).

During the past two decades, Taiwan has been progressed rapidly in the hi-tech semiconductor manufacturing industry. However the emission by these industries causes air quality problems. Taiwan Environmental Protection Administration (TEPA) (1999) has defined the semiconductor manufacturing industry as those who engaged in integrated circuits (IC) wafer production, wafer package, epitaxial, photo-mask production, and wire frame production. Chein and Chen (2003) have studied the emission characteristics of VOCs from semiconductor industries in Hsinchu Science based Industrial Park (SBIP), Taiwan. They have reported isopropyl alcohol (IPA) as the dominant compound in most of the semiconductor industries. The monitoring of VOCs in ambient air was conducted at several different locations in SBIP, Hsinchu during 2000-2003 by Chiu et al. (2005). No definite seasonal variation in VOCs was found. However, stagnant weather condition with low wind speeds contribute to the accumulation of toxic species at ground level. Lo (2005) and Lo et al. (2004) have measured VOCs concentration in ambient atmosphere of Kaohsiung Refinery in Taiwan to study seasonal variation of VOCs. Tsai et al (2004) have studied the relationship between volatile organic profiles and emission sources in ozone episode region in Southern Taiwan.

Air pollution monitoring studies around an industrial area are important for developing emission control strategies, determining applicability of permitting and control programs, and ascertaining the effects of sources and appropriate mitigation strategies, and a number of other related applications by the governments, local agencies, consultants and industries. This study is to investigate the level of VOCs in the ambient air of the SBIP in Hsinchu, Taiwan. The VOCs namely acetone, IPA, MEK, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene were monitored at 13 different sites of the SBIP for 24 hrs each every month during February 2001 to November 2001. The simultaneous measurements of acidic and basic air pollutants made during this study were reported by Tsai et al.

(2003). The spatial and temporal variation in concentration levels and the effects of geographical and meteorological conditions, and the production volume of the SBIP on the concentration levels were studied. The monitoring data were compared with the factory-surrounding air quality standard of Taiwan (Taiwan EPA, 1999) and Ambient Air Level Goal (AALG) (Calabrese and Kenyon, 1991).

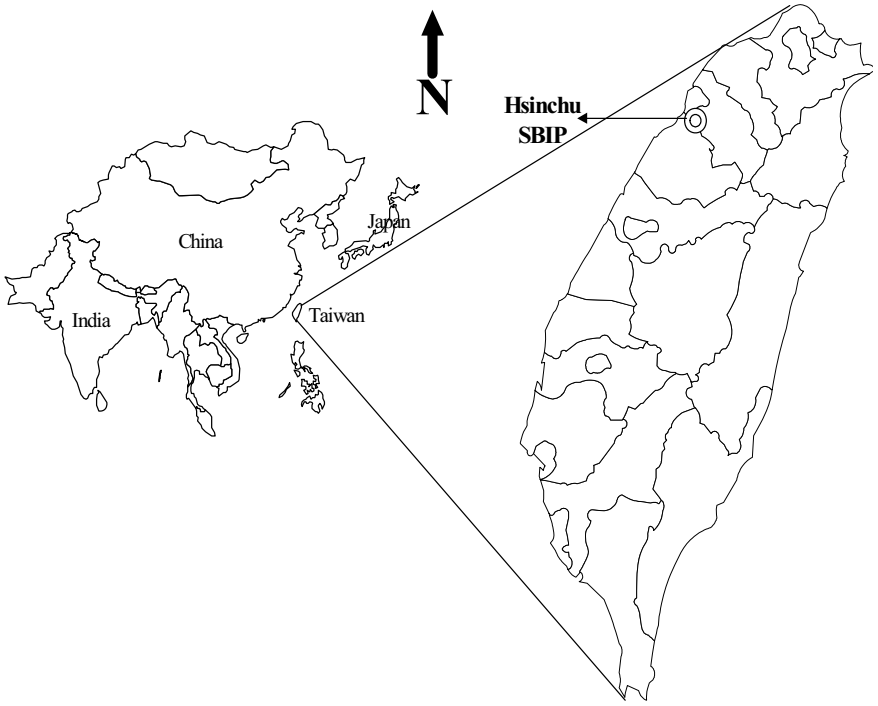


Figure 1. Location of the SBIP in Taiwan.

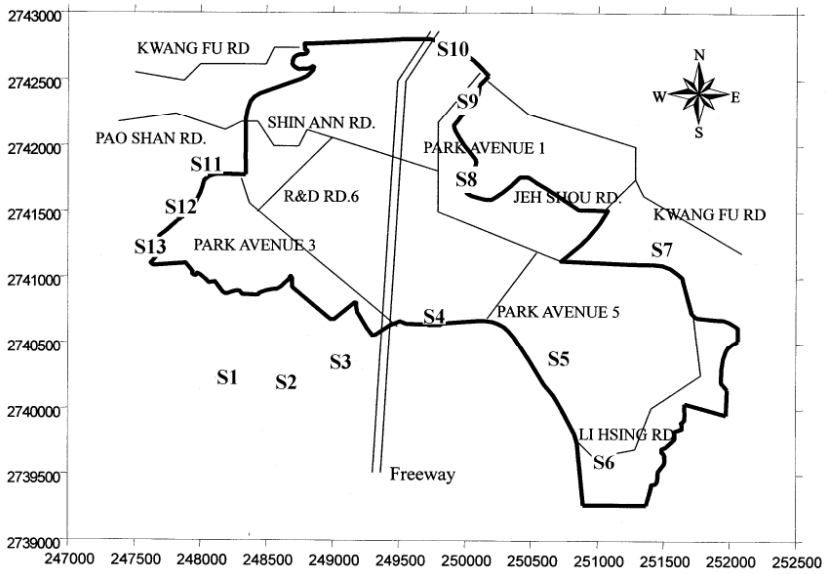


Figure 2. Sampling sites in the SBIP.

2. Material and Methods

The site

The Hsinchu Science-Based Industrial Park was developed mainly after 1980. As of December 2001, a total of 312 hi-tech companies, were operating in this park, including: integrated circuits (123), computer and peripherals (51), telecommunications (57), optoelectronics (51), precision machinery (11), and biotechnology (19). Many of these companies, mainly integrated circuits related, use various VOC-related chemicals and inorganic acids in their cleaning or etching processes (Chein and Chen, 2003), and the annual consumption of HCl, HF, HNO_3, H_2SO_4, H_3PO_4 and mixed acids (concentrated acids) of the semiconductor industry is reported to be about 1288, 2121, 427, 7135, 1125 and 1368 thousand liters, respectively, in the year 2001. Most of the companies use wet scrubbers to control the emission of these inorganic pollutants. In contrast, the yearly emission of VOC related compounds amounts to a total of 237.987 tons in the year of 2003.

The Hsinchu city, situated nearby northwest coast of Taiwan, covers an area of about 100 km^2. The population of the city is about 0.35 million (as of December 2001). The city is mainly known for the Science-Based Industrial Park (SBIP), which is located at the northern side of the city lying between 2739000 to 2743000 m latitude and 247000 to 252000 m longitudes (Figures 1 and 2). The southern side of the park surrounded by the urban area (i.e. residential colonies, commercial complexes and universities campuses), whereas the northern side of the park is mainly rural, agriculture farm, and etc. Ambient aerosol samples were collected at 13 different sampling sites (S1-S13) of the Hsinchu SBIP. The altitude of the SBIP is about 50-120 m above sea level and is extended over an area of about 605 hectares.

3. Sampling

The sampling of VOCs was conducted by using an absorption tube system (Perkin-Elmer Inc.). The system works on diffusion and permeation theory to collect ambient VOCs. It consists of a stainless steel tube of 0.635 cm outer diameter and 9 cm length with cross sectional area of 0.181 cm^2. Figure 3 shows the schematic diagram of the absorption tube. Adsorbent of 163 mg Tenax TA was filled inside the adsorption tube containing stainless steel gauze and glass wool. The tube was shacked well so that the absorbent will fill in the space inside the tube. The tube was preheated up to 300 ^{0}C to remove organic gases/particles. Nitrogen gas with flow rate of 100 mL/min is used as carrier gas**.** Since the concentrations of contaminants in the ambient air are very low, the highly sensitive thermal desorption method is used. Proper care was taken by using storage caps while transporting and handling of the tube. The Dual-Mode Low-Flow Air Samplers, model LFS-113, from Gilian Inc. were used for pumping air.

Samplers were placed at schools and residential buildings at an average height of 1.5 to 2 m above the ground level. The sampling was performed simultaneously in all 13 sites around the Hsinchu SBIP once every month for a period of 24 hrs during the whole study period (i.e. February 2001 to November 2001). Sampling day and time, and meteorological data are given in Table 1. Figure 4 shows the typical wind direction at the Hsinchu SBIP during the sampling period. The meteorological data were collected from the Hsinchu Environmental Bureau. The typical variable wind with wind speed less than 3 m/s was observed from March 2001 to August 2001 (Figure 4 a) and dominant north east wind with wind speed more than 5 m/s was observed for February 2001 and after September 2001 (Figure 4 b).

4. Analysis

After sampling, the samplers were wrapped in Parafilm and brought to the laboratory. Before analysis, a standard concentration of 20 ng/µl is used for quality control cycle. The automatic thermal desorption system (ATD-400, Perkin-Elmer Inc.) was used to analyze the samples. It works as a 2-stage desorption system. The Gas Chromatograph, GC (HP5890, Series II, Hawlett-Packard, Inc. B) was used with column of DB-624. Capillary column of 30m x 0.53mm, ID 3µm (J and W Scientific Inc., C) was used. Nitrogen was used as the carrier gas. The standard operating conditions were maintained during the analysis.

The QA/QC measurements (detection limit, recovery test, data reproducibility test, etc.) were carried out to ensure the accuracy and reliability of analysis. All chemicals used were of analytical grade reagent (Merck).

The desorption efficiency test was done to ensure complete desorption of the compound after the automatic thermal desorption (ATD) test. Each sample was absorbed 3 times during this test and it was found that complete absorption occurs after first desorption except benzene. The desorption efficiency of benzene was found to be about 83% with low concentration and 98-99 % for other compounds in all concentrations and it is comparable with the other literature referred in this paper.

The additive recovery efficiency was also examined during this experiment to understand the accuracy and precision of VOC after thermal desorption and analysis through the absorptive tube. It was tested for 1 ng/µl, 10 ng/µl, 40 ng/µl solutions and it was found that the additive recovery efficiency for 1 ng/µl of IPA and MEK it is not constant however it is satisfactory for other VOCs. It may be due to the fact that the addition of low concentration is affected by the background of the sampling tube.

The calibration was done using 1 ng/µl, 10 ng/µl, 20 ng/µl, 40 ng/µl solutions using TDS (Thermal Dynamic Stripper) with standard method at the flow rate of 100 ml/min. The calibration results found to be satisfactory. The detection limit of this method is very low (for example, 0.04 ppb for xylene) and is better than other methods. The quality control tests were done using same operating conditions of ATD/ GC / FID with standard concentration of 20 ng/ µl.

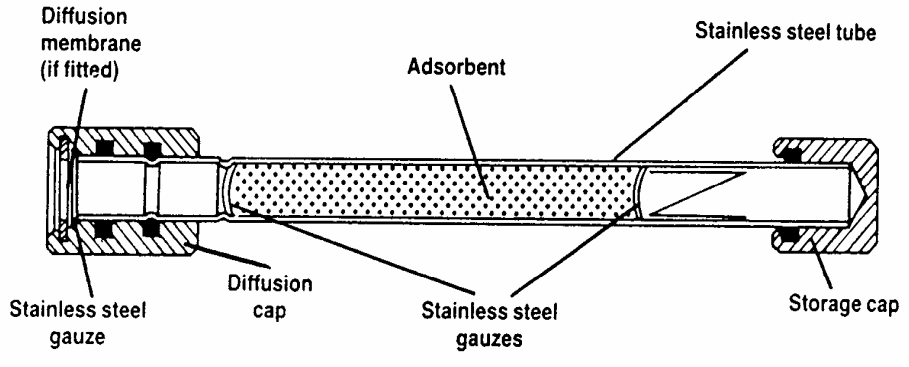


Figure 3. Schematic diagram of the absorption tube.

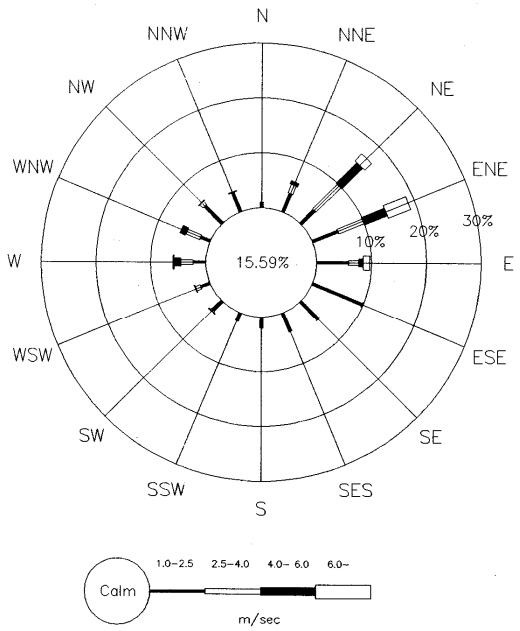


Figure 4. a

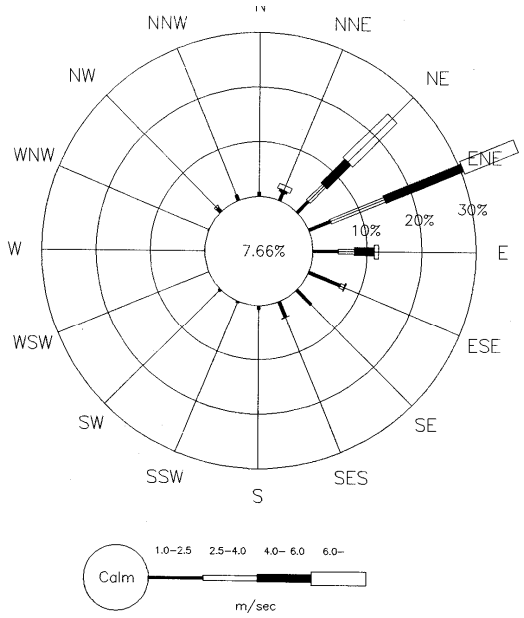


Figure 4. b

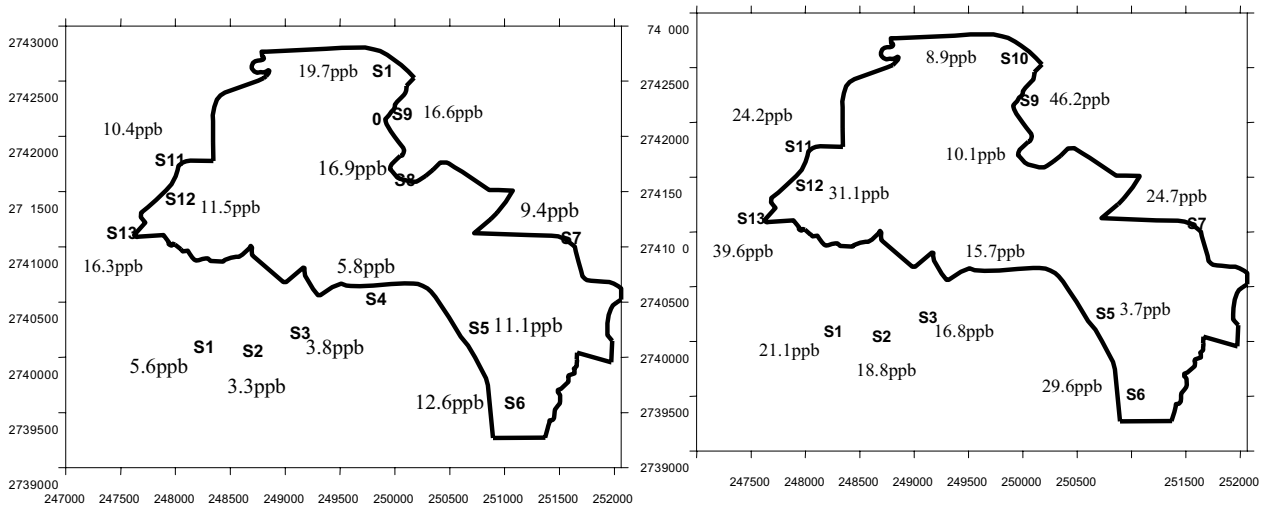
Figure 4. Typical wind direction of the park (a) during May 2001 (b) during October 2001 (the data were collected from Hsinchu Environmental Bureau).

5. Results and Discussion

5.1. Spatial variation in average concentration of VOCs

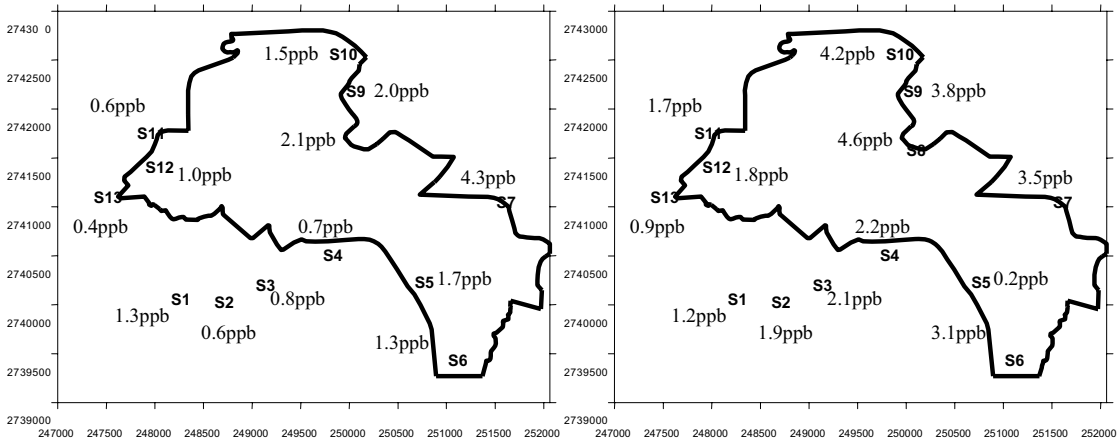
A total of 130 samples for VOCs (i.e. acetone, IPA, MEK, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene) were collected from all 13 sites during the period of investigation. Wind speed was found to affect significantly the concentration level of pollutants. Figures 5 (a), (b) and 6 (a), (b) show the influence of wind speeds recorded in two consecutive months August 2001 (comparatively low wind speed, 1.7 m/sec, and random wind direction) and September 2001 (comparatively high wind speed, 7.7m/sec, and Northeastern wind) on the spatial variation in concentration of acetone and IPA, respectively. The meteorological data shown in Table 1 indicate the random nature of the wind

direction in the low wind condition. In the low wind condition, the concentration of pollutants was higher and became uniformly distributed around the park. The prevailing wind in the NE and ENE direction from September to April is usually strong (Figure 4). Strong prevailing NE wind reduces pollutant concentrations and the downwind locations (sites S1-S6) usually had higher concentrations than the upwind sites. The measurements of acidic and basic pollutants made along with VOCs also showed similar variation in these pollutants associated with wind speed (Tsai et al., 2003). The stagnant weather conditions with low wind speeds aid accumulation of toxic species at ground level (Chiu et al., 2005).



(a) **(b)**

Figure 5. Concentrations of acetone at 13 sites in (a) August 2001 (wind speed = 1.7 m/sec) (b) September 2001 (wind speed = 7.7 m/sec).



(a) **(b)**

Figure 6. Concentrations of IPA at 13 sites in (a) August 2001 (wind speed = 1.7 m/sec) (b) September 2001 (wind speed = 7.7 m/sec).

The concentration of acetone and IPA in all 13 sites was found to be 2.2 to 42 and 2.1 to 45 fold, respectively, higher in low wind condition (August, 2001) than the high wind condition (September, 2001).

5.2. Temporal variation in average concentration of vocs

Figures 7 (a)-(h) show the temporal distribution of the pollutants measured at the 13 sites during February 2001 to November 2001. The concentration level of pollutants was found to be comparatively lower during February to June 2001 mainly due to the decline in production in this period. The production volume is directly related to the corporate sale of the SBIP. The corporate sale of the SBIP (in US dollars) during the period of this study was obtained from the SBIP authority and it was moderately constant from February 2001 up to June 2001. However it was continuously increasing from July 2001 to November 2001.

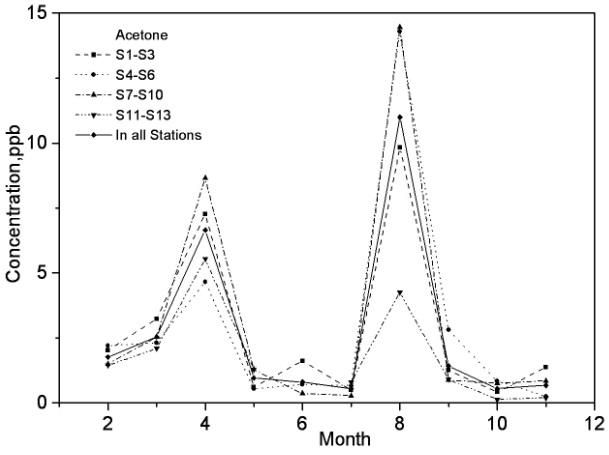
The concentrations of acetone and IPA were found to increase significantly in the month of April and August 2001, Figure 7(a) and (b), as compared to the same during rest of the observational period. These concentrations are maximum in August 2001 due to mainly significant increase in production volume in this month and low wind. The increase in concentration of acetone and IPA found in the month of April 2001 is mainly associated with the low wind conditions as there is no significant increase in production volume in this month. It is worth to mention that the usage of acetone and IPA is maximum among all VOCs in semiconductor industry.

The utilization of MEK, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene is less as compared to that of acetone and IPA in the semiconductor factories thus their concentrations show maximum in April 2001, associated with low wind conditions (Figures 7 (c)-(h)). However, during the other months of the study, its concentration was found to be spatially uniform and low.

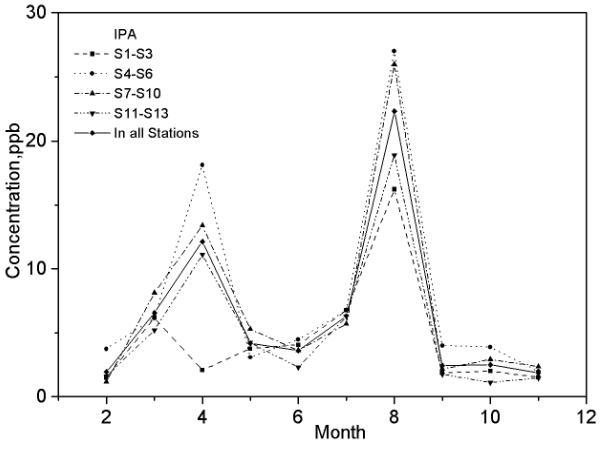
The site S1-S3 is southwest to SBIP and there are no big factories in the vicinity. Also there are no busy roads around the sites causing mobile pollution. The sites are well surrounded by natural trees. Thus minimum VOC concentrations are found at S1-S3 during entire period of observation. As site S4-S6 are in the vicinity of big semiconductor factories using acetone and IPA in their processing, busy roads inside SBIP, the concentration of VOCs especially acetone and IPA is found to be higher. The sites S7-S10 are upwind of SBIP and have water treatment park of SBIP in the area. Thus moderate concentrations are found at these sites. The sites S11-S13 are far way from major factories and busy roads thus lower concentration is observed at these places.

The semiconductor industries manufacture integrated circuit chips for electronic communication devices. The processes involved in semiconductor manufacturing use various VOC-related chemicals as photoresist solution, photoresist stripping solution, developer etc. The emission profiles of few semiconductor industries were studied by the GC/MS analysis by Chein and Chen, (2003). IPA used in cleaning and drying processes was found to be the most dominant chemical emitted from these factories. The acetone emission is also identified as significant from wafer manufacturing fabs. Our

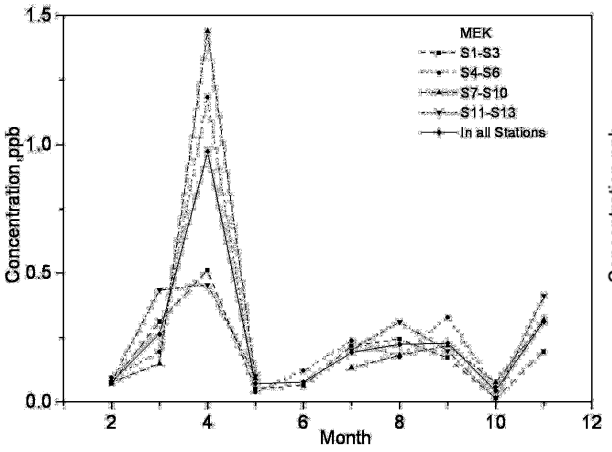
measurements of higher concentration of acetone and IPA in SBIP confirm earlier results of such high emission close to the semiconductor industries by Chein and Chen (2003) and Chiu et al. (2005).



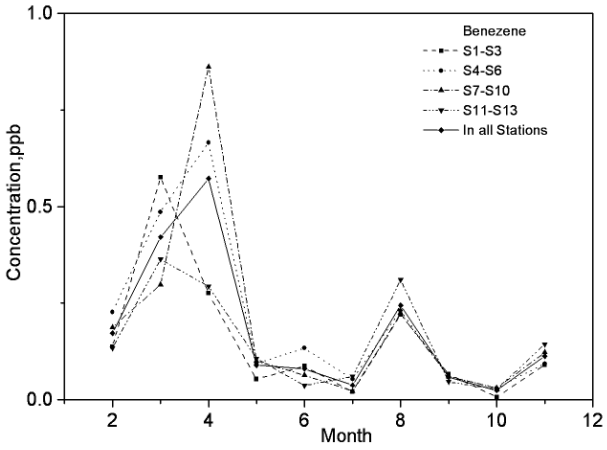
(a)



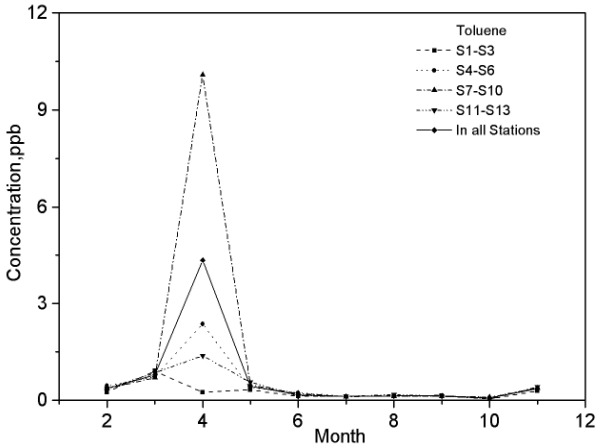
(b)



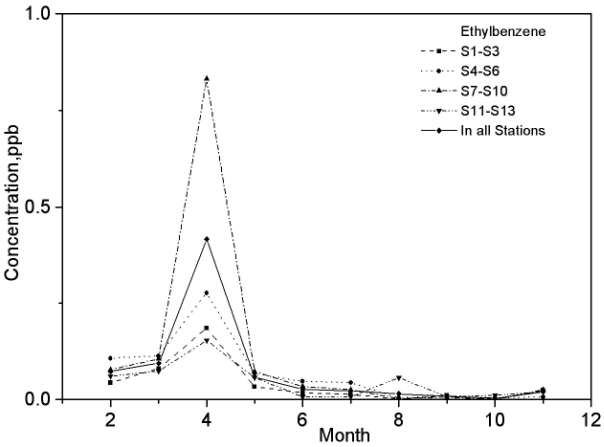
(**c**)



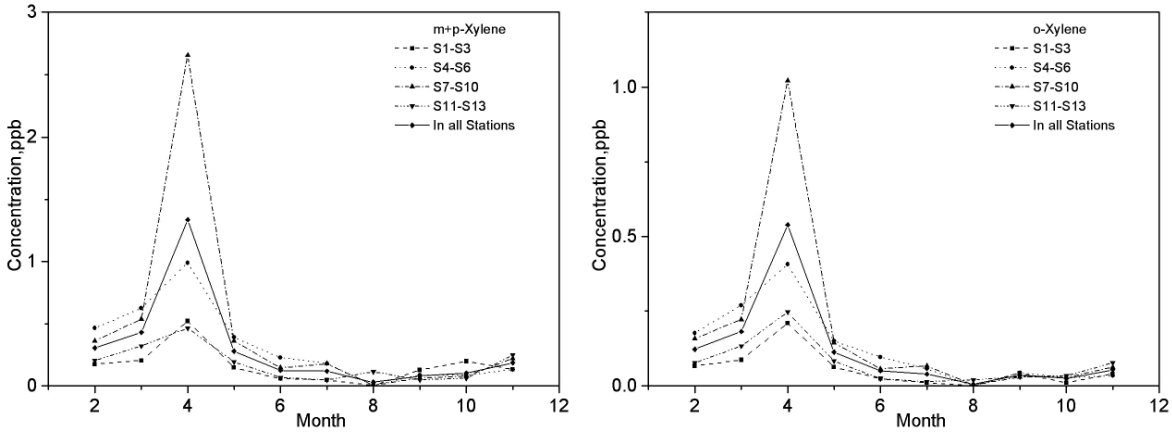
(d)



(**e**)



(f)



(g) **(h)**

Figure 7. Monthly (from February 2001 to November 2001) variation in average concentration of (a) acetone, (b) IPA (c) MEK (d) benzene (e)toluene, (f) ethylbenzene, (g) m+p-xylene, (h) o-xylene.

Table 2. Comparison of air quality standards.

Species	Factory-surrounding air quality standard of Taiwan (Taiwan EPA, 1999)	Ambient Air Level Goal (Calabrese and Kenyon, 1991)
Acetone	15 ppm	15 ppm 8-hr TWA[a]
IPA	8 ppm	8 ppm 8-hr TWA[a]
Benzene	0.5 ppm	0.03 ppb 8-hr TWA[a]
Toluene	2 ppm	0.38 ppm 8-hr TWA[a]
Xylene	2 ppm	1.2 ppm 8-hr TWA[a]
Ethyl Benzene	1 ppm	0.03 ppm 8-hr TWA[a]

[a]Time Weighted Average

Table 3. Comparison of VOC concentrations in Hsinchu SBIP.

	Chiu et al. SBIP (39 sites) May 12-16, 2000		Present study SBIP (13 sites) May 24, 2001			
	Average	SD	Average	SD	Max.	Min.
acetone	19.1	26.7	0.95	0.98	3.64	0.23
IPA	3.3	1.6	4.17	1.12	6.28	2.92
benzene	8.2	10.5	0.08	0.05	0.21	0.02
toluene	11.4	14.6	0.43	0.19	0.78	0.12
m+p xylene	1.5	2.5	0.27	0.14	0.62	0.13

5.3. Comparison with factory air quality standard of Taiwan

Table 2 shows the factory-surrounding air quality standard of Taiwan and AALG. During the period of investigation, the concentration level of most of the species was found to be lower than the factory-surrounding air quality standard of Taiwan. Table 2 shows that although the level of VOCs was found to be lower than the factory-surrounding air quality standards of Taiwan, in some cases acetone and IPA was higher than the AALG. However, reduction in total amount of VOC emission over the year from 2000 to 2003 is reported by Chiu et al. (2005).

5.4. Comparison of the VOC concentration with other measurements in SBIP

The VOC concentration in ambient air was also examined during the year 2000-2003 at several locations in SBIP by Chiu et al. (2005). The comparison of average VOC concentration made by them during May 12-16, 2000, was done with observations made on May 24, 2001 in same locality of SBIP (Table 3). The comparison shows that the values of VOC concentration measured in SBIP by the present study in 2001 were smaller by one order of magnitude than those observed in 2000. Moreover, the VOC concentration measured in 2000 shows large variation. The main reason for such difference is sampling density. It should be noted that we had 13 sampling locations around the periphery of the SBIP whereas the dense sampling at 39 locations, in the close vicinity of several semiconductor factories, were selected in other study. Also, our observations were of day and those of Chiu et al. were average of 5 days. The VOC emission profiles of four semiconductor factories were determined to understand the emission characteristics by Chein and Chen (2003). Their results show large variation in different VOC species emission profiles from different factories. The decrease in VOC concentration at SBIP over a period of 1 year, if at all it exists, is worth reporting. The results support the earlier finding of reduction in amount of VOC from 2000 to 2003 in SBIP by Chiu et al. (2005), attributing to the strict implementation on the use and discharge of organic solvents in industries by Taiwan EPA.

6. Conclusions

The spatial and temporal distribution of VOCs concentration around the SBIP was found to be dependent mainly on wind speed, direction of wind, and the production volume of the park. The spatial distribution showed that the concentration level of VOCs was found to be higher on the sites situated in the WS part of the SBIP, in the downwind location or close to the factories. The prevailing winds, blown from NE and ENE from September to February, were strong enough to reduce VOC concentrations.

The results of temporal distribution showed that the concentration level of acetone and IPA were found to be low from February to June, 2001 mainly due to the decline in production at

semiconductor industries in this period. This study also concludes that acetone and IPA were dominant VOCs emitted from SBIP and their sources were local. The concentrations of MEK, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene was found to be spatially uniform and low except for a maximum concentration observed in April 2001.

During the investigation period the concentration level of most of the species was found to be lower than the factory-surrounding air quality standard of Taiwan. Comparison with earlier observation of VOCs in Hsinchu SBIP showed a decrease in VOC concentration at SBIP over period of one year.

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