



Multivariate analysis of effects of diurnal temperature and seasonal humidity variations by tropical savanna climate on the emissions of anthropogenic volatile organic compounds

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HIGHLIGHTS

- The VOC distributions during the day and night in the dry and wet seasons were studied.
- The VOC data was analyzed by using principal component analysis and cluster analysis.
- The influence of humidity variation on the VOC distributions was important.
- Aromatic VOCs were likely more important under the influence of humidity variation.
- The effect of diurnal temperature change on the VOC emissions was not negligible.

ARTICLE INFO

Article history:

Received 25 June 2013

Received in revised form 24 September 2013

Accepted 29 September 2013

Available online 18 October 2013

Editor: Xuexi Tie

Keywords:

Volatile organic compounds

Temperature

Humidity

Tropical savanna climate

Principal component analysis

Cluster analysis

ABSTRACT

Volatile organic compounds (VOCs), particularly those from anthropogenic sources, have been of substantial concern. In this study, the influences of diurnal temperature and seasonal humidity variations by tropical savanna climate on the distributions of VOCs from stationary industrial sources were investigated by analyzing the concentrations during the daytime and nighttime in the dry and wet seasons and assessing the results by principal component analysis (PCA) and cluster analysis. Kaohsiung City in Southern Taiwan, known for its severe VOC pollution, was chosen as the location to be examined. In the results, the VOC concentrations were lower during the daytime and in the wet season, possibly attributed to the stronger photochemical reactions and increasing inhibition of VOC emissions and transports by elevating humidity levels. Certain compounds became appreciably more important at higher humidity, as these compounds were saturated hydrocarbons with relatively low molecular weights. The influence of diurnal temperature variation on VOC distribution behaviors seemed to be less important than and interacted with that of seasonal humidity variation. Heavier aromatic hydrocarbons with more complex structures and some aliphatic compounds were found to be the main species accounting for the maximum variances of the data observed at high humidity, and the distinct grouping of compounds implied a pronounced inherent characteristic of each cluster in the observed VOC distributions. Under the influence of diurnal temperature variation, selected VOCs that may have stronger photochemical resistances and/or longer lifetimes in the atmosphere were clustered with each other in the cluster analysis, whereas the other groups might consist of compounds with different levels of vulnerability to sunlight or high temperatures. These findings prove the complications in the current knowledge regarding the VOC contaminations and providing insight for managing the adverse impacts of the anthropogenic VOCs on the environment and public health.

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1. Introduction

The pollutions of volatile organic compounds (VOCs) have been of substantial concern and widely studied with respect to their occurrences

and relative magnitudes (Cetin et al., 2003; USEPA, 2012; Zou et al., 2003). Besides their potentials of being involved in photochemical reactions concerning ozone and particulate contaminations, a large number of VOCs are known as toxic air pollutants causing cancers and other serious health effects by inhalation (Chang et al., 2010; Guo et al., 2004; USEPA, 1995). Key symptoms associated with exposure to VOCs include various acute and chronic adverse health effects such as eye and throat irritation, headaches, loss of coordination, nausea, damages to liver, kidney, and central nervous system (USEPA, 2012). Volatile

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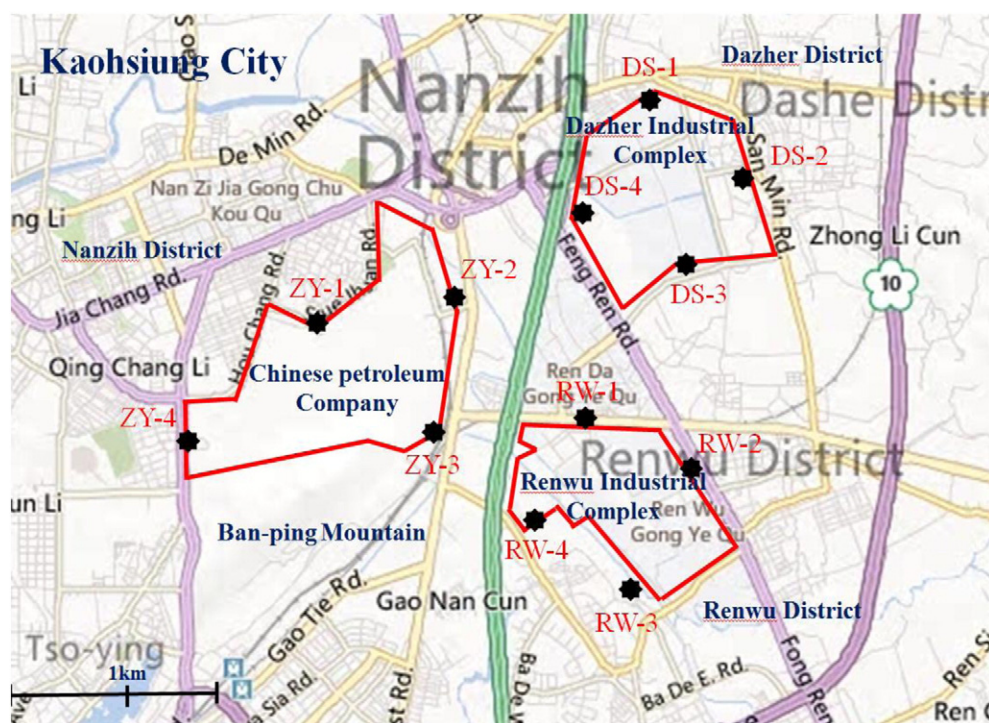


Fig. 1. Monitoring and sampling areas in this study.

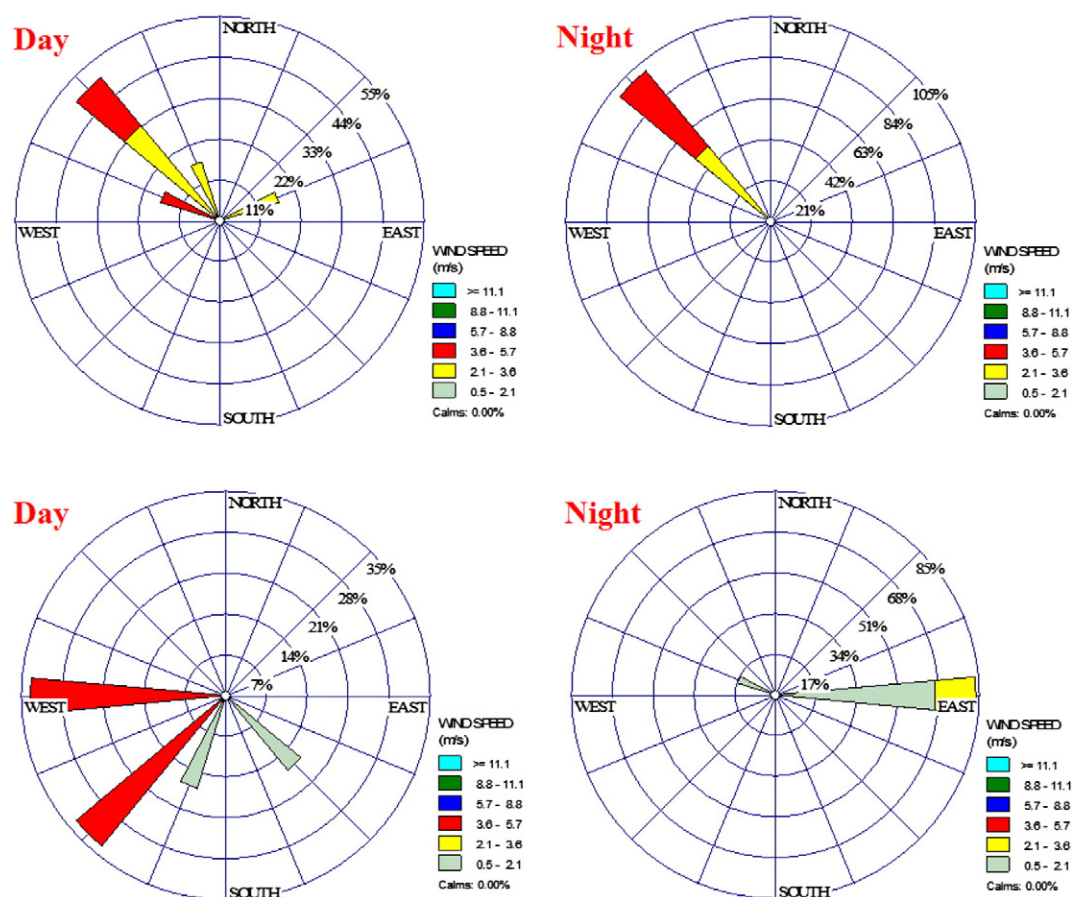


Fig. 2. Typical wind roses of the monitoring area in this study during daytime (top left and bottom left) and nighttime (top right and bottom right) in dry and wet seasons (top and bottom, respectively).

organic compounds may also be deposited onto soils and into lake and river systems, thereby affecting ecological systems and eventually human health by consumption of contaminated water and foods (Daly and Wania, 2004; Parnis and Brooks, 2001). Examples of VOCs including benzene, formaldehyde, and polypropylene, and many of VOCs have been regulated in the Clean Air Act developed by the U.S. Environmental Protection Agency (USEPA) (USEPA, 1995, 2012).

Besides natural productions such as vegetation and forest fires, VOCs can be emitted from all types of sources including motor vehicles and stationary sources that represent any facilities or installations subject to regulation for VOC emissions (Fenger, 1999; Majumdar et al., 2009; Simpson et al., 1999). Preceding studies have reported the pollutions of VOCs from different stationary sources such as industrial science parks (Na et al., 2001; Wu et al., 2006), petrochemical industries (Brock et al., 2003; Cetin et al., 2003), landfill sites (Pope and Disalvo, 1995; Zou et al., 2003), and wastewater treatment plants (Chen et al., 2013; Yang et al., 2012). As extensive studies focused on discussions with respect to the temporal and spatial distributions and source identification of VOCs, the results were found to be influenced by various environmental factors such as wind speeds and directions and physicochemical properties of compounds (Liu et al., 2008). It was suggested in our earlier study that the influence of altitude on the VOC distributions is important and is greatly impacted by the height of emission sources and the molecular weights/sizes and lifetimes of VOCs in the atmosphere (Yang et al., 2013). For example, the lifetimes of light alkanes are relatively longer and therefore are more easily accumulated in the atmosphere and transported for longer distances. As expected, the complex array of VOC pollutions due to a great number of compounds needed to be considered and the effects of different environmental (or meteorological) situations increase the challenges of developing appropriate strategies for VOC remediation.

Kaohsiung City, the monitoring area of interest in this study, is the largest industrial city in Southern Taiwan with more than three million populations and is known for its air pollution near the metropolitan areas. A dense population of pollution-intensive industries neighbors the north of the city, potentially deteriorating the ambient air quality of this area due to their high VOC emissions. In addition, the area is located within a degree to the northern tropic and possesses the characteristics of a tropical wet and dry climate (a tropical savanna climate) in Southern Taiwan, which have high temperatures in every month of the year and typically a pronounced dry season. The early studies have suggested that the influences of both temperature and humidity on the emissions of VOCs occurred and depended strongly on the type of VOCs targeted (Wolkoff, 1998; Zhang et al., 2007). As these climate parameters are typically important factors with strong temporal variations for the regions of tropical savanna climate, a full understanding of the mechanisms and extents of these factors changing the pattern of VOC pollution is rather limited and imperative for characterizing the behaviors of VOCs for their effective management in these particular areas.

Given the industries consistently being substantial VOC sources and the influences of meteorological factors (e.g., the temperature and humidity in this study), the concentrations of VOCs in the atmosphere near these anthropogenic sources during the daytime and nighttime in the dry and wet seasons were investigated in this study. Three major petrochemical industrial complexes near Kaohsiung City in Taiwan were selected as the monitoring areas. With the elevated temperatures during the daytime through the year with the occurrences of night-time lower temperatures and substantial humidity differences between the dry and wet seasons due to the tropical savanna climate, the main objective of this study is to examine the presence and magnitudes of the effects of diurnal temperature and seasonal humidity variations on the distributions of anthropogenic VOCs by monitoring and analyzing the concentration data with multivariate statistical analysis. More than one hundreds VOC species were sampled, followed by subsequent analysis using gas chromatography coupled

with mass spectrometry (GC/MS). The concentration information observed at different locations and times was used to establish the respective chemical profiles and was studied by principal component analysis (PCA) and cluster analysis. These analyses were conducted to understand the possible changes of the inherent characteristics behind different VOC distributions at varying temperatures and humidity levels.

2. Experimental methods

2.1. Monitoring and sampling area

The extents of VOC pollution in the examined areas that resulted from several major petrochemical industrial complexes near the city have been well known by the local public. The vicinities of three important petrochemical industrial complexes (China Petroleum Company (CPC), Renwu petrochemical industrial complexes, and Dazher petrochemical industrial complexes) in the north of the city were selected as the focus of this study. Total twelve monitoring and sampling sites were chosen to examine the temperature and humidity effects on the VOC concentrations and distributions at these locations, as shown in Fig. 1. Abbreviations are used to represent the names of these sampling sites and to simplify the following discussions of the results (ZY, RW, and DS denoting Chinese Petroleum Company, Renwu industrial

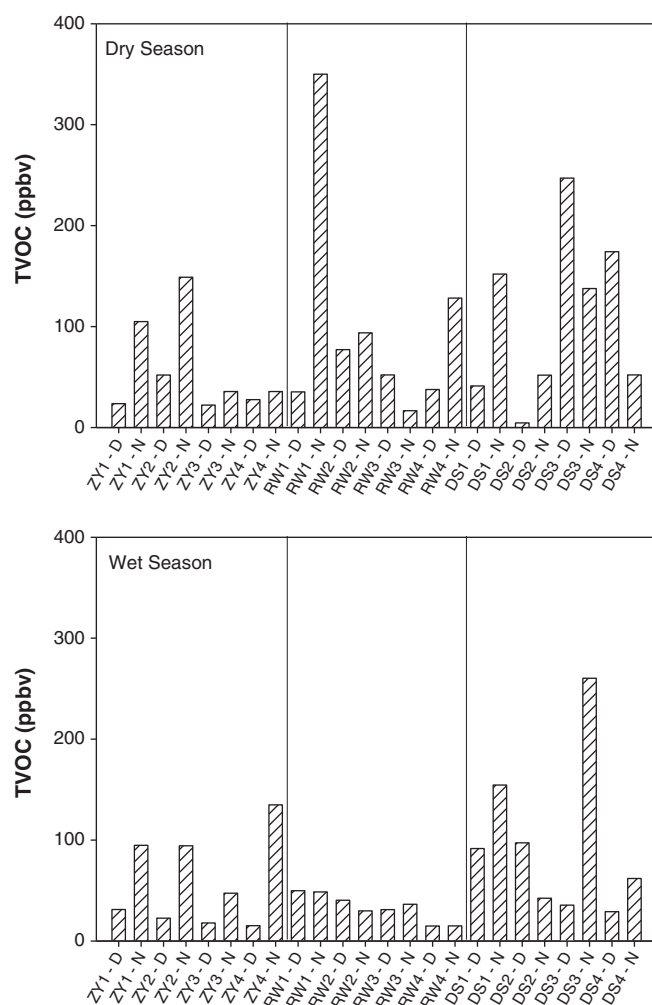


Fig. 3. Concentrations of total VOCs (TVOCs) at different monitoring sites in the dry and wet seasons. D and N denote the data observed during the daytime and nighttime, respectively.

complex, and Dazher industrial complex, respectively). The Taiwan Central Weather Bureau was used to collect the meteorological information of the area during the monitoring period (<http://www.cwb.gov.tw/V7/index.htm>). The average monthly values of relative humidity were 72% (the minimum was 39%) and 75% (the minimum was 59%) in the dry and wet seasons, respectively. Although the change of the average relative humidity between the dry and wet seasons was rather limited, the rainy season occurring between the two seasons did provide appreciably different circumstances for VOC distributions and transports with respect to the ranges of humidity variations, as indicated by the minimum humidity in these two seasons. The average temperatures in the dry and wet seasons during the period were 17.5 °C (between 11.3 °C and 25.0 °C) and 27.2 °C (between 21.2 °C and 31.9 °C), respectively.

2.2. Field sampling

The sampling was conducted twice a day in January and May 2011 to investigate the VOC concentrations during the daytime and nighttime in dry and wet seasons, respectively, given that the rainy season in this area usually last from April to June. Four sites were selected in each industrial complex considering the variations of wind speed and direction (Fig. 2), with one upwind location and three downwind locations being sampled simultaneously. The Taiwan Air Quality Monitoring Network provides the information for the wind speeds and directions of the studied areas during the monitoring period (<http://taqm.epa.gov.tw/taqm/en/default.aspx>). As shown in Fig. 2, the near-surface wind field in this area was influenced by sea and land breezes, notably in wet season. While the effect of this sea and land breeze typically occurs in the

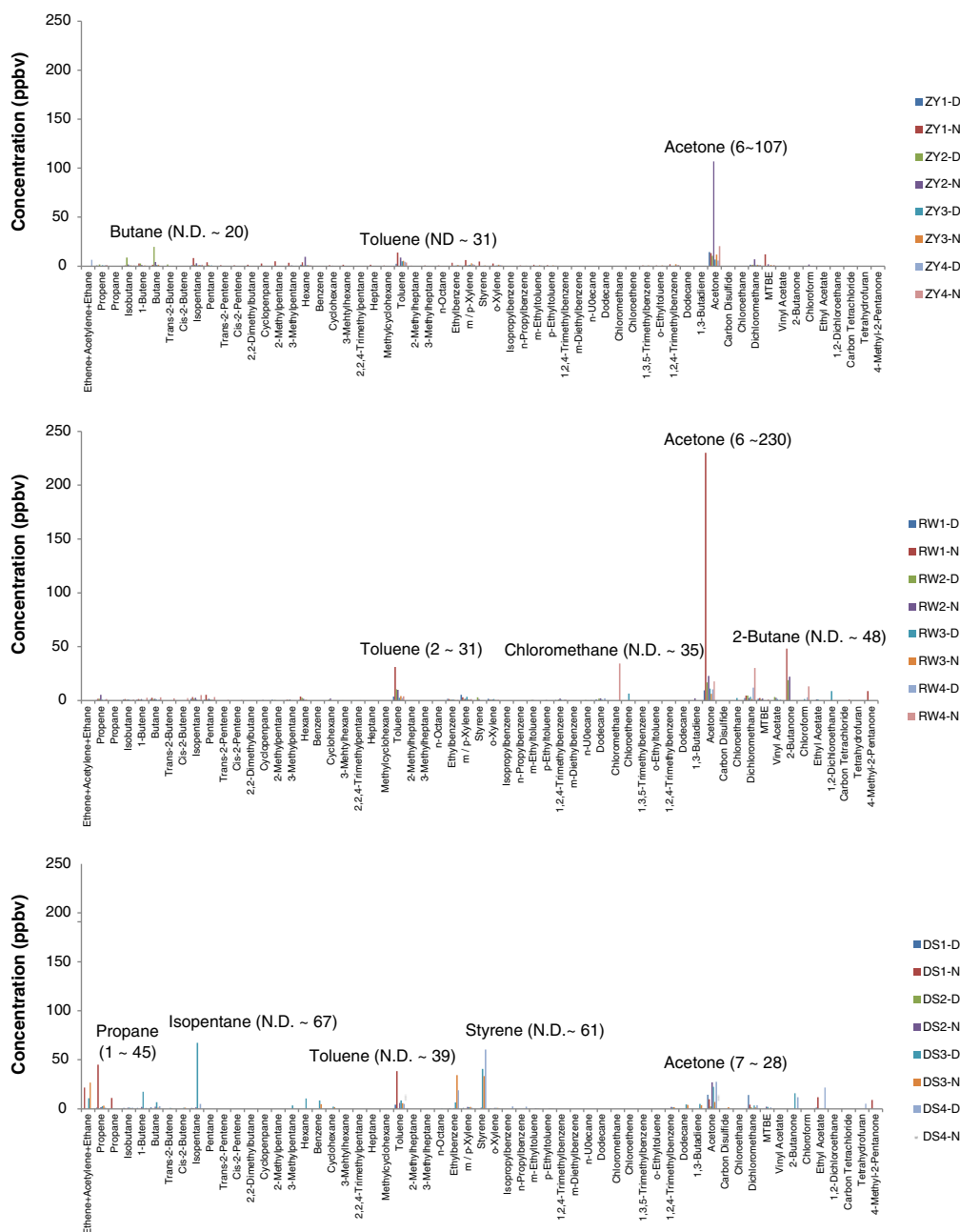


Fig. 4. Concentration distributions of the VOCs at different monitoring sites in the dry season. D and N denote the concentrations observed during the daytime and nighttime, respectively. The numbers shown in the parenthesis behind the compound's name represent the concentration ranges of the compound.

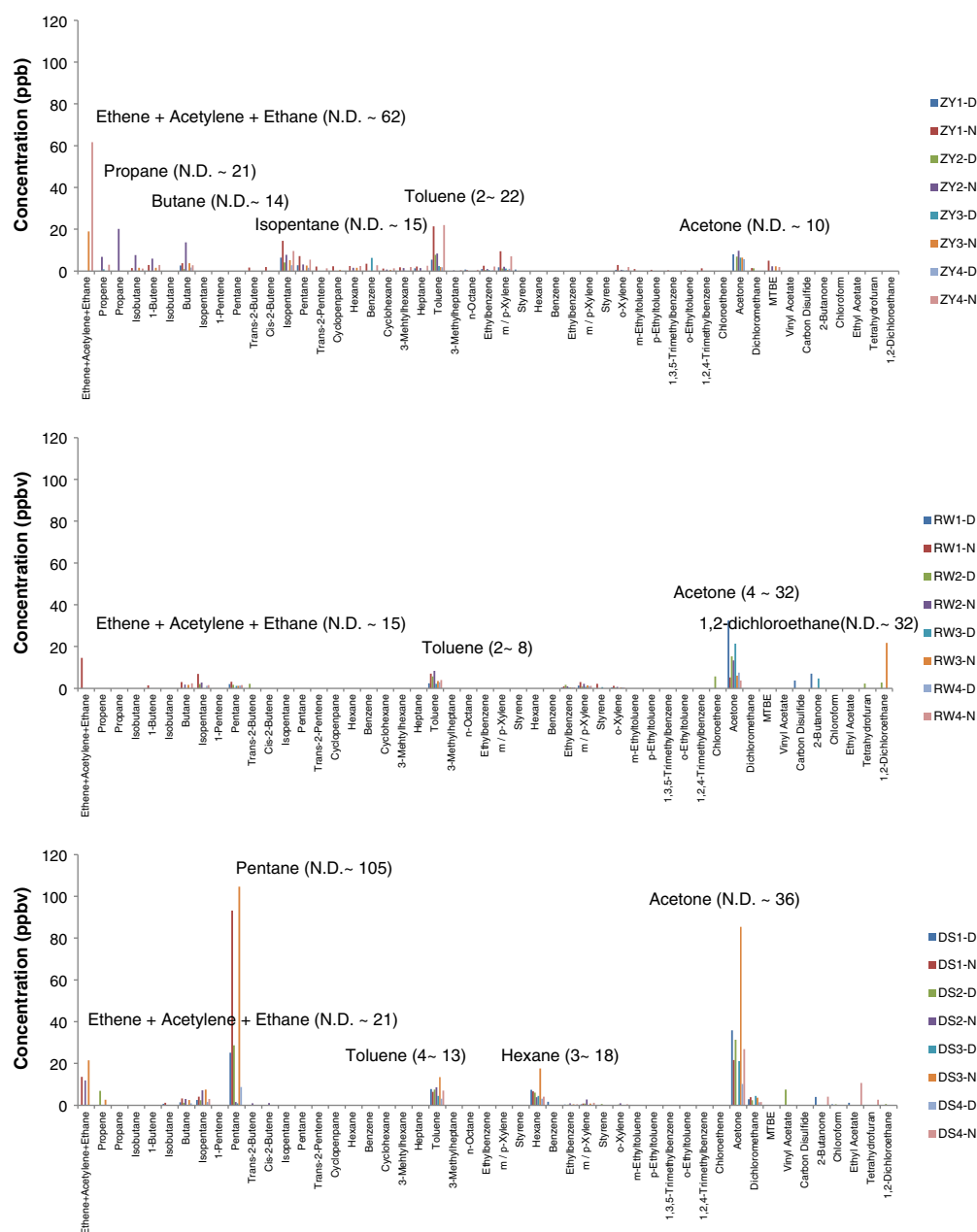


Fig. 5. Concentration distributions of the VOCs at different monitoring sites in the wet season. D and N denote the concentrations observed during the daytime and nighttime, respectively. The numbers shown in the parenthesis behind the compound's name represent the concentration ranges of the compounds.

early morning and late night, the samplings in this study were conducted in the noon or afternoon and at the beginning of night in which the wind conditions were relatively stable.

2.3. VOC analysis

The VOC concentrations in the samples were determined by following the USEPA's standard TO-15 method, which uses the air canister sampling technology followed by analysis with GC/MS. A predetermined amount of air sample was directed from a canister to the GC/MS through a solid micro-sorbent concentrator. With the target VOCs retained, the solid micro-sorbent concentrator was dry-purged with helium for concentration and drying. By heating at 150 °C, the VOCs on the concentrator were thermally desorbed, entrained in the carrier gas stream, and then trapped on a small volume multi-sorbent trap. The VOCs were then released by thermal desorption and injected into the GC/MS for analysis. A GC/MS (HP 6890N) with a thermal

desorption unit (ENTECH 7100A, TDU) was used. The GC was equipped with a 60 m × 0.25 mm I.D. DB-VRX capillary column (Chrompack, U.S.). The column temperature was programmed as follows: 40 °C as the initial temperature, increased to 180 °C at 5 °C/min and held for 2 min, and increased to 230 °C at 8 °C/min and held for 3 min. The flow rate of the carrier gas was 3 ml/min with a split ratio of 1 to 10. Mass spectrometry was performed in electron ionization mode. The acquisition mode was set to scan in the range from 29 to 300 m/z at 0.5 scan/s. In this study, the VOCs of interest contained 101 different VOC species, including various types of alkanes, alkenes, alkynes, aromatics, and halogenated compounds, as many of them are considered as Hazardous Air Pollutants (HAPs) (<http://www.epa.gov/ttn/atw/orig189.html>). All the VOC concentrations were analyzed by using the unit of ppbvC (part per billion by volume on carbon basis) for comparisons amongst different VOC species and represented using the unit of ppbv in the discussions of this study (including the figures and tables) for simplification.

Table 1

Principal component analysis of the VOCs from three monitoring areas in the dry season.

Monitoring area	1st PC	2nd PC	3rd PC
ZY	cis-2-Pentene (0.98) trans-2-Pentene (0.98) 2,2-Dimethylbutane (0.98) Cyclopentane (0.98) 2-Methylpentane (0.98) 3-Methylpentane (0.98) Heptane (0.98) Methylcyclohexane (0.98) 3-Methylhexane (0.98) 2-Methylheptane (0.98) 3-Methylheptane (0.98) 1-Octane (0.98) Styrene (0.94) Isopentene (0.95) Pentane (0.95) MTBE (0.95) Cyclohexane (0.91) Ethylbenzene (0.88) n-Propylbenzene (0.80) m,p-Xylenes (0.81) Toluene (0.75) o-Xylene (0.73)	1-Ethyl-2-methylbenzene (0.81) 12,4-Trimethylbenzene (0.79) 1-Ethyl-4-methylbenzene (0.78) 1,3,5-Trimethylbenzene (0.77)	Chloroform (0.98) n-Hexane (0.96) Acetone (0.97) Dichloromethane (0.97)
% of variance	56.4	14.8	13.5
Cumulative variance	56.4	71.1	84.6
RW	cis-2-Butene (0.99) trans-2-Butene (0.99) cis-2-Pentene (0.99) trans-2-Pentene (0.99) Chloromethane (0.99) Carbon tetrachloride (0.99) Chloroform (0.96) Dichloromethane (0.93) Isopentane (0.84) 1-Butene (0.82) n-Butane (0.71)	Toluene (0.98) Acetone (0.97) Methyl isobutyl ketone (0.96) 2-Butanone (0.94) Pentane (0.90) n-Hexane (0.87)	Propylene (0.96) Cyclopentane (0.89) Cyclohexane (0.91) 1-Ethyl-3-methylbenzene (0.81) 1-Ethyl-4-methylbenzene (0.85) 1,2,4-Trimethylbenzene (0.85) 1,3-Butadiene (0.97)
% of variance	26.6	19.3	19.0
Cumulative variance	26.6	45.9	64.9
DS	Isopentene (0.99) 3-Methylpentane (0.99) n-Hexane (0.99) 1-Butene (0.97) n-Butane (0.84) Benzene (0.84) 2-Butanone (0.79) Cyclohexane (0.75) 1,3-Butadiene (0.74)	Ethylbenzene (0.89) Ethane, ethene, ethylene (0.79) cis-2-Butene (0.70)	i-Butane (0.84) o-Xylene (0.84) m,p-Xylenes (0.83) Acetone (0.79) 1-Ethyl-3-methylbenzene (0.78) MTBE (0.72)
% of variance	27.7	17.5	16.3
Cumulative variance	27.7	45.2	61.2

2.4. Multivariate statistical analysis

Principal component analysis is an approach to investigate the air pollution data, which are typically observed and recorded in discrete forms composed of series of environmental variables and pollutants (Harrison et al., 1996). By predicting the directions in the observations along which the data have the highest variability through an eigenvalue decomposition of the variance matrix of the data, PCA is a common approach for studying air pollution issues such as dominant pollutant species, important environmental variables, or pollution source identification (Han et al., 2006; Tokalioglu and Kartal, 2006). Principal components (PCs) are determined by converting the observed variables into a set of linearly independent variables and are represented as functions of the original variables. By definition, the 1st PC (PC1) has the largest possible variance to account for as much of the variability in the observed data as possible, while the succeeding component (e.g., the 2nd PC or PC2) in turn has the largest variance uncorrelated with those of the previous components.

The PCA was carried out with SPSS 17.0 for the VOC concentration profiles observed at different monitoring sites during the daytime and nighttime in two monitoring season. The VOC data were firstly standardized to give all species the same variations, followed by calculation

of the associated eigenvalues. Varimax orthogonal rotation was applied to determine the PCs of the observation with an identical sum of eigenvalues, and the number of PCs was decided by considering the PCs with eigenvalues larger than 1, namely the Kaiser criterion. For each PC, the loading values of the original variables (different VOC species) were calculated, as a loading value larger than 0.7 indicates a strong correlation between the PC and the VOC. Additional information regarding the procedure of the PCA is available in the published early studies (Harrison et al., 1996; Larsen and Baker, 2003; Yu et al., 1998).

2.5. Cluster analysis

Given that the PCA results provide the information regarding the important VOC species such as those listed in the PCs at different locations and times, the loading values of each VOC species to different PCs were visualized by plotting 3-D loading figures and analyzed by a model-based clustering algorithm named *mclust* using the *R* statistical language. According to finite mixture modeling, the *mclust* algorithm was contributed by the Department of Statistics in the University of Washington for the purposes of classification and density estimation and was used in this study to effectively cluster the VOCs with similar characteristics with respect to their potentials interpreting the

Table 2

Principal component analysis (PCA) of the VOCs from three monitoring areas in the wet season.

Monitoring area	1st PC	2nd PC	3rd PC
ZY	cis-2-Butene (0.97) trans-2-Butene (0.97) 1-Ethyl-3-methylbenzene (0.97) 1-Ethyl-4-methylbenzene (0.97) 1,3,5-Methylbenzene (0.97) 1-Ethyl-2-methylbenzene (0.97) 1,2,4-Trimethylbenzene (0.97) Cyclopentane (0.95)	Ethane, ethene, ethylene (0.89) Cyclohexane (0.87) n-Hexane (0.80) Toluene (0.84) Heptane (0.82) Acetone (0.78) Pentane (0.76) 3-Methylhexane (0.77) m,p-Xylenes (0.75) Ethylbenzene (0.74) trans-2-Pentene (0.72) o-Xylene (0.70)	Propane (0.99) i-Butane (0.98) 1-Butene (0.88) n-Butane (0.97) Propylene (0.91)
% of variance	37.7	30.1	18.7
Cumulative variance	37.7	67.8	86.5
RW	Ethane, ethene, ethylene (0.95) 1-Butene (0.95) Styrene (0.93) Pentane (0.92) Isopentane (0.75)	Cyclohexane (0.99) Vinyl chloride (0.99) Tetrahydrofuran (0.99) Ethylbenzene (0.91)	Acetone (0.93) 2-Butanone (0.88) Carbon disulfide (0.86)
% of variance	30.8	24.7	18.1
Cumulative variance	30.8	55.5	73.6
DS	m,p-Xylenes (0.97) Cyclopentane (0.95) o-Xylene (0.95) 3-Methylpentane (0.95) Ethylbenzene (0.89) Dichloromethane (0.80)	1-Pentene (0.99) Styrene (0.99) Vinyl acetate (0.99) 1,2-Dichloroethane (0.99) Propylene (0.94)	n-Hexane (0.97) Toluene (0.95) Acetone (0.90) Ethane, ethene, ethylene (0.79) Pentane (0.76) Isopentane (0.73)
% of variance	25.6	22.6	20.7
Cumulative variance	25.6	48.2	68.9

variability in the observed concentration data. An ellipsoidal-shape model with equal data variances and a cluster size of four indicating the groups of PC1, PC2, PC3, and those having low loading values on all three PCs were used to identify the VOC groups in this study. Additional information regarding the *mclust* package can be acquired from the following link: <http://www.stat.washington.edu/mclust/>.

3. Results and discussions

3.1. Total VOC concentrations

As the total VOC (TVOC) concentrations observed at three monitored areas during the daytime and nighttime in the dry and wet seasons are illustrated in Fig. 3, the effect of seasonal humidity variation on the TVOC concentrations in different monitoring areas was observed. In the dry season, the TVOC concentration levels were between 22 and 149 ppbv (part per billion by volume), 17 and 350 ppbv, and 5 and 247 ppbv in the ZY, RW, and DS monitoring areas, respectively, while the TVOC concentrations in the wet season for these three areas ranged from 15 to 135 ppbv, from 15 to 50 ppbv, and from 29 to 260 ppbv, respectively. As the highest concentration in the dry season occurred at 350 ppbv in the RW area, the highest concentration in the wet season was 260 ppbv in the DS monitoring area. It is likely that the differences of the TVOC concentrations amongst these areas were more easily recognized in the wet season and the TVOC levels from the RW area in the wet season were appreciably lower than those in the dry season. However, the comparisons between the TVOC levels in different areas or seasons appeared to be limited by large variations in the data.

To further demonstrate the influence of seasonal humidity variation, a one-way analysis of variance (ANOVA) was conducted to determine the significant level of a factor by evaluating its F value and by comparing it with the critical value of F distribution at a specific confidence level (typically 90% or 95%). It is pointed out that the concentration distributions of TVOC were not significantly different amongst the monitoring areas in the dry season ($P = 0.43$), whereas the TVOC concentrations amongst the three areas in the wet season varied significantly at a 10% level ($P = 0.07$). By comparing the TVOC concentrations of each

monitoring area between the dry and wet seasons, only the data from the RW monitoring area showed a significant difference at a 10% level ($P = 0.09$). Although the small variation of the average relative humidity between the seasons, as mentioned in Section 2.1, possibly provided a limited effect on TVOC concentrations in the ZY and DS monitoring areas, it is indicated that the VOCs emitted from the RW areas were more readily affected by this seasonal factor assuming that the VOCs emitted in these areas were similar between the seasons.

As to the diurnal variations of TVOC concentrations, the concentrations observed at many monitoring sites in both seasons were relatively higher during the night, as expected. The highest concentration in both season, as mentioned previously, occurred during the night. In the dry season, the TVOC concentrations during the night were 1.3 to 4.4, 0.3 to 9.9 and 0.3 to 11.4 times higher than those during the daytime in the ZY, RW, and DS areas, respectively, while the concentrations in the wet season were 3.0 to 8.9, 0.7 to 1.2, and 0.4 to 7.3 times higher during the nighttime than during the daytime for the ZY, RW, and DS areas, respectively. A larger number of VOCs are known to participate in atmospheric photochemical reactions under sunlight as primary precursors to the formation of ground level ozone and particulate matter, which are the main constituents of smog, possibly reducing the TVOC levels in the atmosphere during the daytime in this study (Fenger, 1999). It is worth noting that this phenomenon was sometimes not shown at selected sites and times, mostly in the dry season (e.g., site DS3 and DS4), suggesting the presences of other possible factors such as the effect of different VOC species and the complexity of co-effect by humidity and temperature variations driving the VOC distributions in the environment.

3.2. VOC concentration distributions

As Figs. 4 and 5 exhibit the concentrations of various VOC species detected in three areas in two monitoring seasons, different VOC distributions were noticed between the dry and wet seasons. The VOCs observed at negligible levels are not included in the figures. The names of the dominant VOCs at different monitoring areas in two seasons are marked in the figures, as the parentheses behind the

Table 3

Principal component analysis of the VOCs from three monitoring areas during the daytime and nighttime in two seasons.

Area	Season	Time	1st principal component ^a	Variance ^b
ZY	Dry	Daytime	Propylene, i-Butane, 1-Butene, n-Butane, trans-2-Butene, Cyclopentene	45.5%
		Nighttime	Isopentane, Pentane, trans-2-Pentene, cis-2-Pentene, 2,2-Dimethyl butane, Cyclopentene, 2-Methylpentane, 3-Methylpentane, Cyclohexane, 3-Methylhexane, Heptane, Methylcyclohexane, 2-Methylheptane, 3-Methylheptane, 1-Octane, MTBE	62.2%
RW	Wet	Daytime	Ethylbenzene, m,p-Xylene, Acetone	51.3%
		Nighttime	Cyclohexane, Heptane, Toluene	40.1%
	Dry	Daytime	Propylene, n-Hexane, Cyclohexane, 3-Methylhexane, Styrene, 1-Ethyl-3-methylbenzene, 1-Ethyl-4-methylbenzene, Acetone, Vinyl acetate, 2-Butanone	44.8%
		Nighttime	Propylene, Cyclohexane, Styrene, 1,2,4-Trimethylbenzene, n-Hendecane, Dodecane, 1,3-Butadiene, Vinyl acetate, Ethyl acetate	35.4%
DS	Wet	Daytime	Cyclohexane, Toluene, Ethylbenzene, Vinyl chloride, Tetrahydrofuran, 1,2-Dichloroethane	50.4%
		Nighttime	Ethane, Ethene, Ethylene, 1-Butene, Pentane, Styrene	56.2%
	Dry	Daytime	Ethane, Ethene, Ethylene, 1-Butene, trans-2-Butene, cis-2-Butene, Isopentane, 3-Methylpentane, n-Hexane, Benzene, Cyclohexane, 1-Octane, 1,2,4-Trimethylbenzene, Dodecane, 1,3-Butadiene	60.4%
		Nighttime	trans-2-Butene, cis-2-Butene, Benzene, Cyclohexane, Ethylbenzene, Dodecane, 1,3-Butadiene, Carbon disulfide	43.1%
	Wet	Daytime	Propylene, 1-Pentene, Styrene, o-Xylene, Vinyl acetate, 1,2-Dichloroethane	45.6%
		Nighttime	Ethylbenzene, m, p-Xylene, Styrene	38.9%

^a The principal components listed in this table represent the constituents with loading values greater than 0.95 in the 1st principal component.^b The variance represents the contribution from all the constituents listed in the 1st principal component.

VOC's names indicate their concentration ranges. In the dry season, due to their heavy uses in petrochemical industrial processes, acetone and toluene were two major compounds with relatively higher concentrations, as expected. Of the other VOCs, butane, 2-butanone, propene, isopentane, and styrene were present in the monitoring areas with more distinguishable concentrations. As to the results for the wet season, the concentrations of acetone and toluene were significantly reduced, potentially attributed to the higher humidity levels inhibiting their emissions and transports in the atmosphere (Fig. 5). Many compounds shown in the dry seasons such as butane, chloromethane, 2-butanone, propene, isopentane, and styrene also exhibited lower or negligible concentrations in the wet season. However, the concentrations of selected VOCs, including dichloroethane, propane, butane, pentane, isopentane, and hexane, became appreciably more important in the wet season. It is worth noting that all of these compounds are saturated hydrocarbons with relatively low molecular weights. The lifetime of the light alkanes is relatively longer and therefore they may be more easily accumulated in the atmosphere and more resistant to the effect of humidity in the wet season.

Similar to the TVOC results, the influence of diurnal temperature variation on the VOC distribution in the monitoring areas was observed. The highest concentrations of these dominant VOCs, notably those listed in the results for the wet season, were mostly observed during the nighttime. Only butane from the ZY area and propane and isopentane from the DS area showed their highest concentrations during the daytime in the dry season. Because the levels of these three compounds were rather less recognizable, this unexpected finding may be explained by concentration variations at low levels during the analysis. It is also likely that the influence of diurnal variation with respect to the temperature or sunlight on VOC behaviors varied amongst different VOC species given their different physicochemical characteristics. It has been reported in the preceding study that the physicochemical properties of VOCs including their molecular weights/sizes and lifetimes affected their concentration distributions and transports in the atmosphere (Yang et al., 2013).

Nevertheless, the influence of diurnal temperature variation on the VOC distributions seemed to be less important and interacted with that of seasonal humidity variation. With the single effect by diurnal temperature variation in the dry season, most of the VOCs emitted from sources were still capable of being distributed and detected at the monitoring sites during both daytime and nighttime (e.g., the higher concentration ranges in the dry season and less obvious differences between daytime and nighttime in Fig. 4), whereas the additional contribution by the humidity effect in the wet season potentially

inhibited the transports of selected VOCs in the atmosphere, reducing the number and concentrations of VOCs analyzed during either daytime or nighttime in this season (e.g., the lower concentration ranges in the wet season and more significant differences between daytime and nighttime in Fig. 5).

3.3. Prediction of important VOCs by PCA

To verify the hypothesis regarding the existence of different important VOCs between the daytime and nighttime or between the dry and wet seasons, PCA was applied as a classification method to group the monitoring data in Figs. 4 and 5 by removing the redundant measurement during the sampling period. Tables 1 and 2 show the PCA results for the VOC concentrations observed at three sampling areas in the dry and wet seasons, respectively. While five groups of PCs were produced by considering eigenvalues greater than unity, only the information of three major PCs accounting for larger variances of the data was given. The number shown in the parenthesis after the compound's name represents its factor loading, which indicates the influence of the VOC on each PC. Tables 1 and 2 present only those with absolute loading values larger than 0.7 suggesting their strong influences.

Different VOC emission behaviors between the dry and wet seasons were noticed with respect to the percentage variances of the original data accounted for by the three PCs and the VOC species listed in each PC, suggesting the occurrence of the influence of seasonal humidity variation. In the dry season, the monitoring data in the ZY, RW, and DS areas were mainly loaded by the VOCs in three PCs, which explain 84.6%, 64.9%, and 61.2% of the original data variances, respectively. These numbers were slightly increased in the wet season (86.55%, 73.6%, and 68.9% for the ZY, RW, and DS monitoring areas, respectively). These increases primarily resulted by the changes of the PC2 and PC3, as the contributions from the PC1 became less significant, particularly for the data in the ZY area (from 56.4% for the dry season to 37.7% for the wet season). It is suggested that additional PCs such as the PC2 and PC3 in Table 2 became more important to determine the VOC observations in the wet season, indicating the potential involvement of extra VOC groups with different physicochemical characteristics at higher humidity. In addition, the VOC species included in these PCs, notably those in the PC1, were different between the dry and wet seasons. Only cyclopentane in the ZY area, 1-butene and isopentane in the RW area, and 3-methylpentane in the DS area occurred in the PC1 for both seasons. Besides these aliphatic compounds, the other species newly added in the PC1 in the wet season comprised relatively heavier

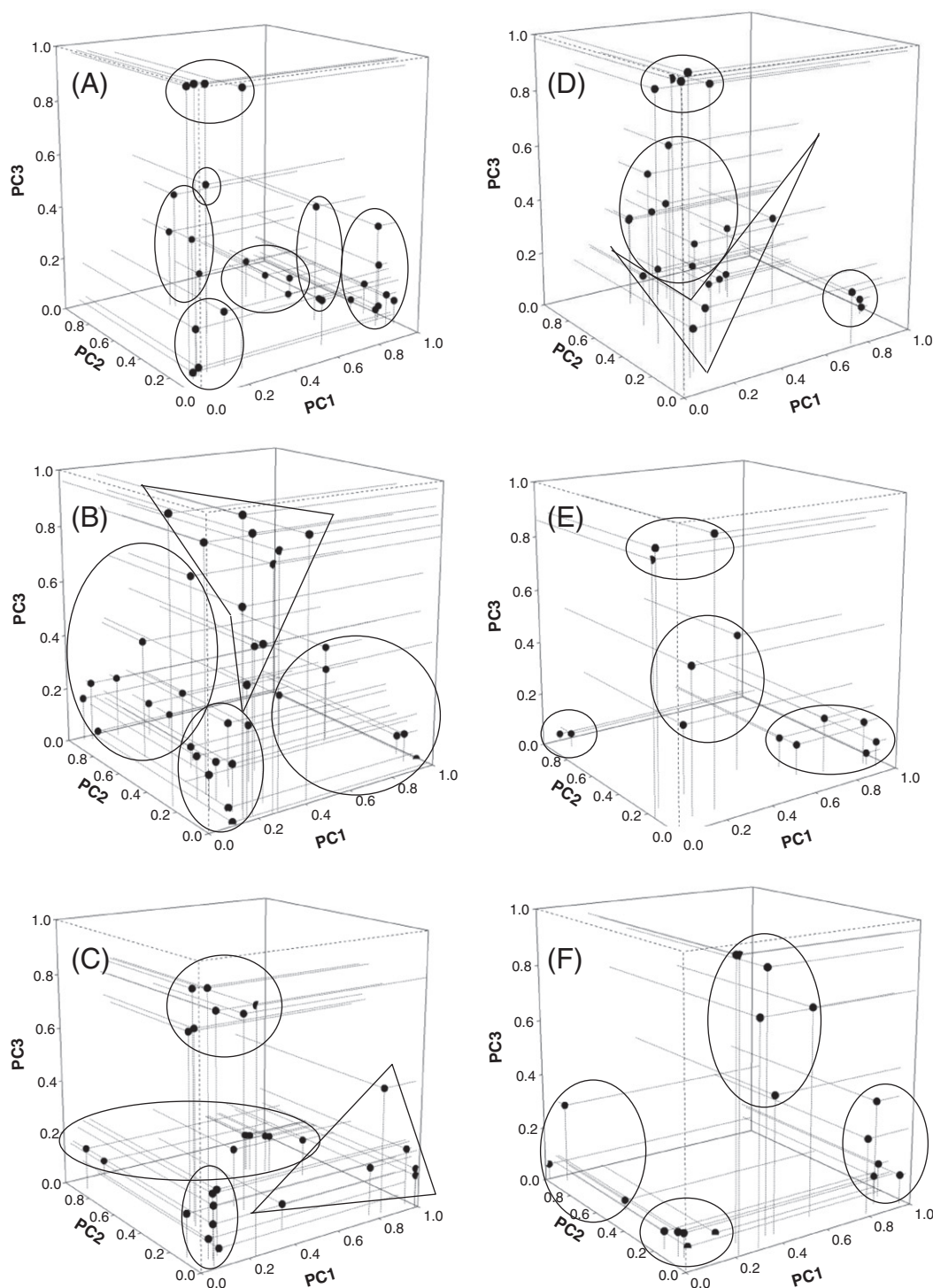


Fig. 6. Loading plots of the VOC data observed in the (A) ZY, (B) RW, and (C) DS in the dry season and in the (D) RW, (E) ZY, and (F) DS in the wet season from PCA and cluster analysis.

aromatic hydrocarbons with more complex structures. These compounds may represent those more substantial for the VOC distribution behaviors at high humidity levels.

The VOC data observed at the monitoring areas during the daytime and nighttime in both seasons were further analyzed by PCA to predict the influence of diurnal temperature variation on the VOC species listed in the major PCs and their contributions to the VOC observations (the percentages of variances), as given in Table 3. As a large number of VOCs are included in the PCs in certain cases, Table 3 only presents the important VOC species with loading values greater than 0.95 in

the PC1, and the percentage of variance represents the variability in the observed data accounted for by all the VOCs in the PC1.

Besides the ZY area in the dry season and the RW area in the wet season, the values of variance (e.g., 15 to 22% decreased) and the numbers of the VOCs in the PC1 for the data collected during the night were equal or less than those collected during the day. In this study, the daytime and nighttime samplings were conducted in the afternoon and at the beginning of night, respectively. The VOCs observed during the day might have gone through photochemical reactions prior to reaching the monitoring locations to be detected, as many other VOCs have

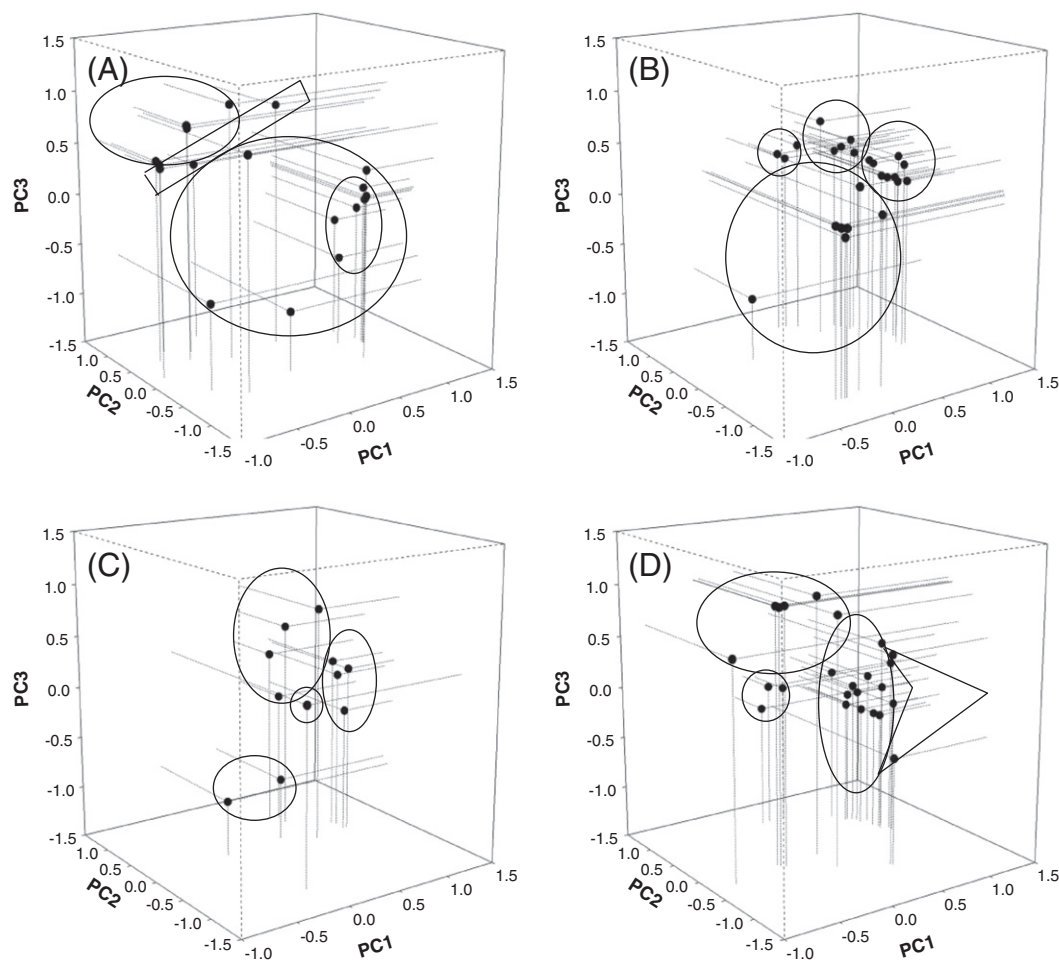


Fig. 7. Loading plots of the VOC data observed in the ZY area during the (A) daytime and (B) nighttime in the dry season and during (C) daytime and (D) nighttime in the wet season from PCA and cluster analysis.

been reacted for removal. Nevertheless, more VOCs were likely to be present during the nighttime, lowering the contributions of the PCs on the VOC concentration distributions and possibly reducing the number of VOCs included in the PCs as well. The VOCs listed for daytime in Table 3 may represent those less affected by photochemical reactions. However, these VOCs seem to be difficultly categorized just by their physicochemical properties such as their molecular structures (e.g., aliphatic or aromatic), possibly attributed to varying emission sources amongst three monitoring complexes and the effect of sea and land breezes in this area. The unexpected findings shown for the data collected in the ZY area in the dry season and in the RW area in the wet season (higher values of variances during the night) might result by their low VOC concentrations and limited diurnal variations, as shown in Fig. 3 previously.

3.4. Characterization of VOC distribution behaviors

The loading values of the VOCs in the PC1, PC2, and PC3 of the data from the dry and wet seasons were used to plot the 3-D loading plots for characterization of the humidity effect on the VOC behaviors, as shown in Fig. 6. The cluster analysis was further employed to group the VOCs with similar distribution characteristics in the plots. It is revealed in Fig. 6 that the data collected from the ZY, RW, and DS areas in the dry season were clustered into 7, 4, and 4 distinct groups, respectively. A different group number was considered for the data from the ZY area because it was the optimal number of clusters for the best model to occur in the analysis. The result of this cluster analysis is

somewhat similar to that of the PCA. For example, as the complexity of the VOC concentration distribution in the ZY area was suggested by a large number of VOCs included in the PC1 of the data (Table 1), the VOCs were clustered into seven distinct groups in the cluster analysis, more than those of the data from the other two monitoring areas. Although the data collected in the RW and DS areas was clustered into four groups (Fig. 6B and C), that is, the PC1, PC2, PC3, and the compounds with low loading values on all three PCs, the differences in the behaviors/distributions between the groups were not obvious.

However, in the wet season, as the same numbers of groups were produced for the data observed in the RW and DS areas, the spread of each cluster seemed to be smaller and the clusters can be clearly classified as the PC1, PC2, and PC3, implying more pronounced inherent characteristics of distributions in each VOC group for the data from the RW and DS areas. Also, the number of clusters for the VOC data in the ZY area was reduced from seven to four distinct groups with an elevated humidity in the wet season. It is possible by the cluster analysis that selected VOCs such as those listed in the PC1 of the data in the wet season were more resistant to the negative effect of this humidity variation on their regional dispersions and transportations, possibly attributed to their different physicochemical properties. For example, the VOCs in the PC1 for the wet season (Table 2) seemed to consist of more aromatic and cycloaliphatic compounds, as compared to those listed for the data collected in the dry season (Table 1).

Similar to the discussion for the humidity effect, the loading values of the VOCs in the three major PCs during the daytime and nighttime, as listed in Table 3, were used to develop another set of 3-D loading

plots to determine whether different distribution behaviors existed for the VOCs detected between these two time periods (Figs. 7 through 9). The VOC data in the loading plot for the RW area during the night in the wet season was not clustered because the optimal number of clusters under this circumstance occurred at the maximum choice of the model (Fig. 8B). A 2-D loading plot was prepared for the VOC data in the RW area during the nighttime in the wet season since only two PCs were present with eigenvalues greater than one (Fig. 8D).

By comparing the distribution characteristics of the VOCs between the daytime and nighttime in two seasons by cluster analysis (Figs. 7 through 9), more definite and precise grouping was noticed for the data observed during the day in either dry or wet season, notably for those in the ZY and RW areas. In the results for the data collected during the nighttime, the differences between the groups became less obvious and/or the spreads of each groups seemed to be larger, implying less pronounced inherent characteristics in each VOC groups during the nighttime. These results of cluster analysis are somehow similar to those of PCA application. In the daytime data, selected VOCs with stronger photochemical resistances and/or longer lifetimes in the atmospheric environment were possibly clustered with each other (e.g., those with relatively high loading values on the PC1), whereas the other groups may consist of VOCs having different levels of vulnerability to sunlight or high temperatures. When the sampling was conducted during the night, the impact of sunlight or high temperatures was removed, comprehensively elevating the influences of all VOCs emitted from the sources in the monitoring areas and diluting the contributions of selected compounds (e.g., those listed in the PC1 of the

data for the nighttime in Table 3) to the distribution characteristics of VOC concentrations observed in different monitoring areas.

4. Conclusion

While previous studies have reported the impacts of humidity and temperature on the emissions of few selected VOCs, the atmospheric concentrations of more than one hundred of VOCs of interest near the anthropogenic sources in an area with the features of tropical savanna climate (e.g., Southern Taiwan in this study) were studied during the daytime and nighttime in the dry and wet seasons. The influences of diurnal temperature and seasonal humidity variations caused by a tropical savanna climate on the VOC behaviors were observed and more complicated than expected. The VOC concentrations appeared to be lower during the daytime and in the wet season, possibly resulted by the stronger photochemical reactions and increasing inhibition of VOC distributions and transports by an elevating humidity. Certain compounds became appreciably more important at higher humidity, as these compounds are saturated hydrocarbons with relatively low molecular weights. Similarly, the influence of diurnal temperature variation on VOC distribution behaviors existed and varied amongst different species, but seemed to be less important than and interacted with that of seasonal humidity variation.

It is found by PCA and cluster analysis that the VOCs detected in the wet season mainly comprised several groups of compounds with different physicochemical characteristics. At high humidity, relatively heavier aromatic hydrocarbons with more complex structures and some

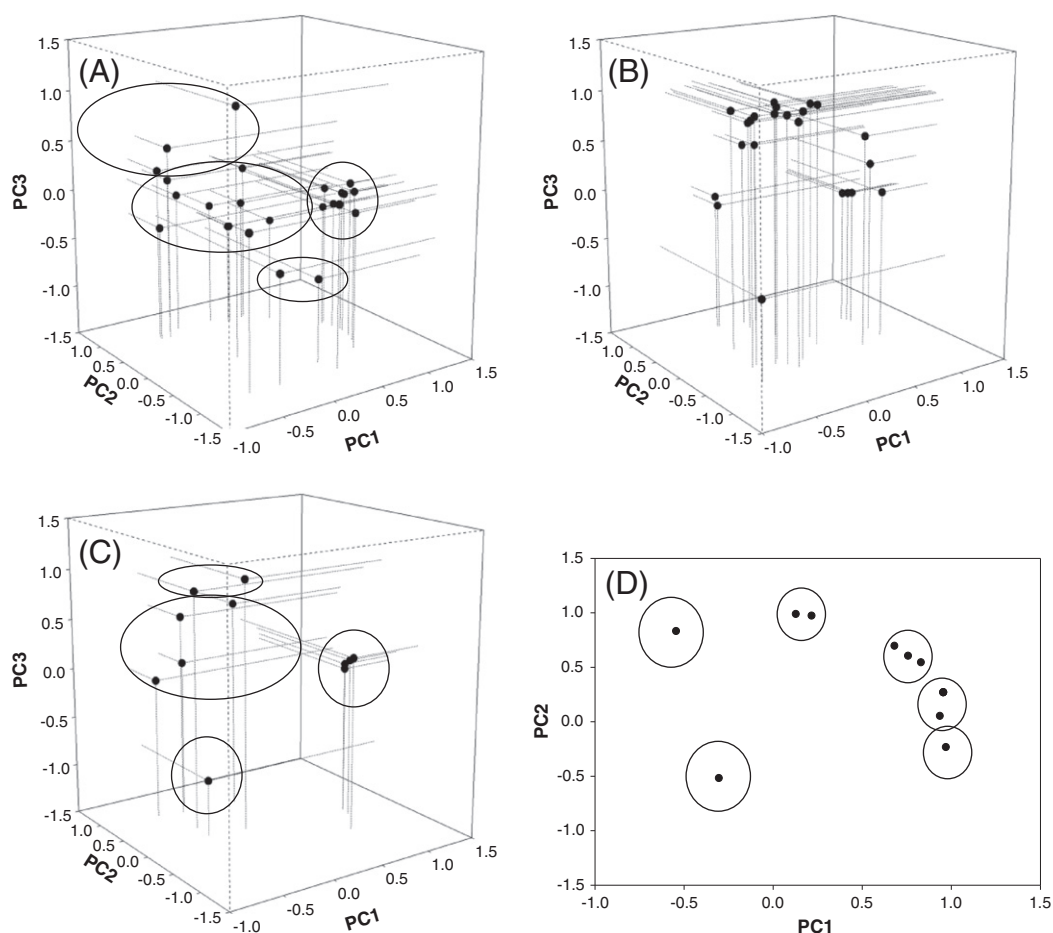


Fig. 8. Loading plots of VOC data observed in the RW area during the (A) daytime and (B) nighttime in the dry season and during the (C) daytime and (D) nighttime in the wet season from PCA and cluster analysis.

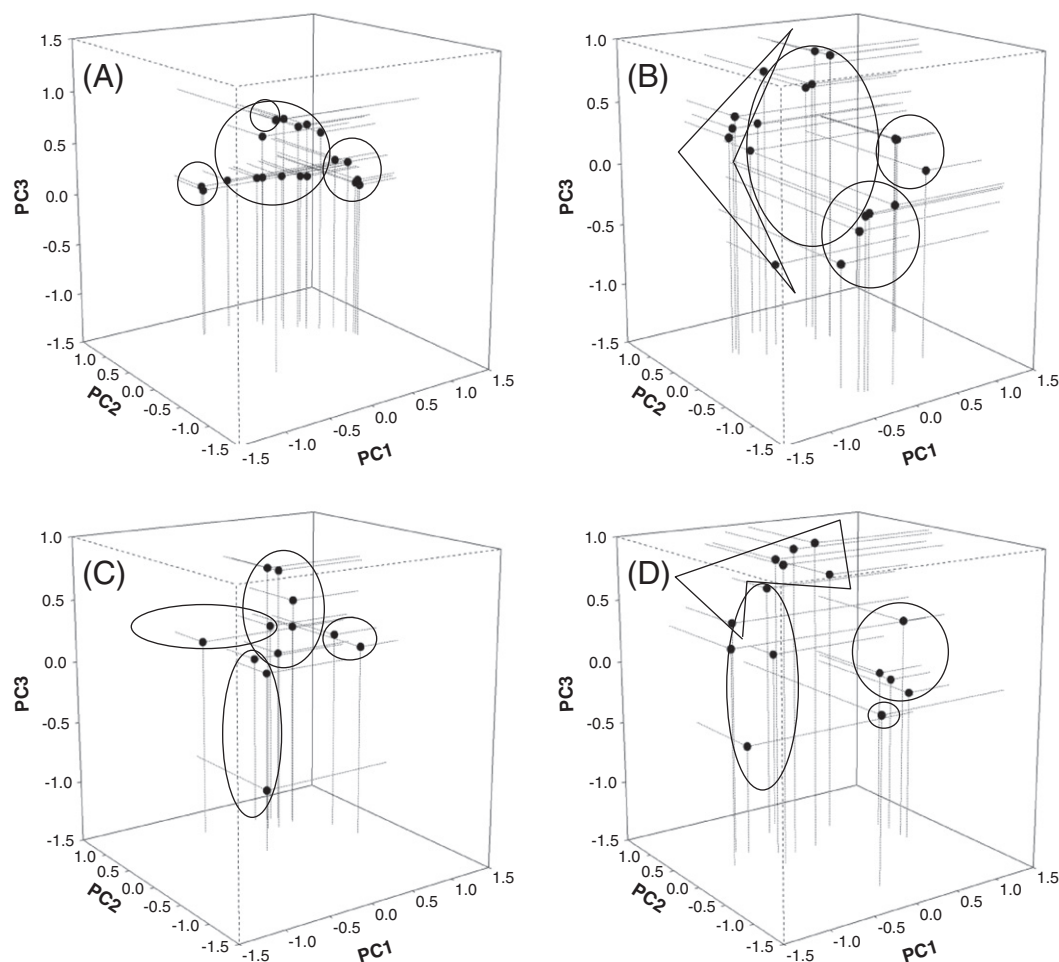


Fig. 9. Loading plots of VOC data observed in the DS area during the (A) daytime and (B) nighttime in the dry season and during (C) daytime and (D) nighttime in the wet season from PCA and cluster analysis.

aliphatic compounds were found to be the main VOC species accounting for the maximum variances of the data observed, and clearer grouping of compounds implied pronounced inherent characteristics of each group in the observed VOC distributions. Under the effect of diurnal temperature variation, selected VOCs, which may have stronger photochemical resistances and/or longer lifetimes in the atmospheric environment, were clustered with each other, whereas the other groups potentially consisted of VOCs having different levels of vulnerability to sunlight or high temperatures. The effects of diurnal temperature and seasonal humidity variations by a tropical savanna climate on the VOC emissions and distributions were demonstrated to be not negligible, as the elevated humidity and temperature (or intensive sunlight) potentially augmented the characteristics and impacts of selected VOCs from anthropogenic sources. The findings prove the complications in the current knowledge regarding the factors that influence the likelihood of VOC contamination (e.g., climate features in this study) and are of assistance to develop the effective management strategies under different environmental scenarios such as mitigating the emissions of VOC species with strong dispersions and long lifetimes at high humidity and temperatures.

Acknowledgment

This study was conducted under the auspices of Taiwan National Science Council (Taiwan NSC) under contract number (NSC 99-EPA-M-004-001). This study was also supported in part by the Environmental

Protection Bureau in Kaohsiung, Taiwan. The authors are grateful to these two institutions for their financial support.

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