東海大學環境科學與工程系碩士班

碩士論文

台灣中部高科技產業排放至大氣中之懸浮微粒及重金屬特性分析

Characterization of Particles and Heavy Metals in the Ambient of High-Tech Industrial Park in Central Taiwan

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係由本人指導撰述，同意提付審查。

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莊硯勛

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Abstract

The investigation of particulate matters ($PM_{10-2.5}$ and $PM_{2.5}$) was carried out through this research during period sampling data from 2008 to 2011 (including winter and summer seasons). The concentration of heavy metals (As, Cd, Cr, Cu, Mn, Ni, Pb) were analyzed by graphite furnace atomic absorption spectrometry. Moreover, the principle component analysis and hierarchical cluster analysis were used to investigate the pollutant source and profiling the spatial of $PM_{10-2.5}$ and $PM_{2.5}$.

The results show that the concentration of As was collected with an air flow in diffusion (wind speed > 2 m/s) and relative humidity between 50% to 70% in $PM_{10-2.5}$. In addition, the concentration of As was collected when air flow in diffusion and relative humidity between 50% to 80% in $PM_{2.5}$. It is interesting to noted that the probability of the high concentration of As being 13% over the standard of EU. The concentration of As in $PM_{2.5}$ trends to be increased in recent year.

Keywords: High-Tech Industrial Park, $PM_{10-2.5}$, $PM_{2.5}$, environmental characteristic analysis

Chapter 1. Introduction

The World Health Organization (WHO) statistics indicate that approximately 4 to 8% of human mortality caused by air pollution. The pollutants contribute to the air pollution are aerosol, sulfur oxides (SO_2), nitrogen oxide (NO), volatile organic compounds (VOCs), particulate matter (PM) and heavy metals. In addition, the Medical reports (Politis *et al.*, 2008) also confirmed that the high concentration level of suspended particle can lead to several health problems; such as, respiratory failure, lung disease and heart disease. The different sizes of suspended particle in the air can be affected to human health in various organs. Sánchez *et al.*, (2009) investigated that PM_{10} harm to the pulmonary functions, increase the frequency of respiratory illnesses, cardiovascular and lung cancers, increase in the attacks of asthma, pneumonia, bronchitis and chronic cough. The particle size of 10μm or greater than a majority will be deposited in the snout and 1 to 10 μm of the particles will be deposited in the bronchial region of upper respiratory tract. These suspended particles, mostly from motor vehicles, public transportation vehicles or factory chimneys in the exhaustive gases emitted into the atmosphere. Suzuki *et al.*, (2007) had analyzed 17 kinds of trace metals in the body of

a squirrel in Taiwan and Japan, found that squirrel contain high levels of heavy metals concentration in Miaoli County (Table 1-1) and most importantly, the study shown the source of these high concentrations of heavy metals maybe come from high-tech industrial area nearby Hsinchu. In order to control the risk of harm, it is necessary to understand the characteristics of adjacent areas of the particle size distribution, as well as the impact of pollutants generated by the meteorological and topographical conditions.

Table 1-1.
Trace element concentration in the kidney, liver, lung and muscle of Formosan squirrels captured in Miaoli, Taiwan.

Organ	As (μg/g)	Cd (μg/g)	Cu (μg/g)	Mn (μg/g)	Ni (μg/g)	Pb (μg/g)
Kidney	0.037	11.700	28.90	11.20	0.167	0.542
Liver	0.042	2.940	808.00	8.41	0.078	0.398
Lung	0.031	0.738	34.50	3.10	0.122	0.150
Muscle	0.035	0.201	11.70	1.91	0.074	0.036

According to the fast growing of economic and technology in Taiwan, the manufactories are unavoidably located close to urban development areas where people live and work. The most important high-tech

industrial area in central Taiwan which is consists of precision machinery, optoelectronics, integrated circuits, biotechnology, communications and computer. Thus, the emissions of hazardous air pollutants are released from area of varying the industrial activities including industrial activities, population and traffic density (Yang *et al.*, 2002). The expansion of the industrial area has potentially created high level of air pollution today and may become the problems in the future. Recently, several researches in Taiwan pay more attention to study about the pollutants in the central Taiwan science park (CTSP). There have many air pollutants in the area, especially for the particulate matters (PM) are the important pollutants. Fang *et al.*, (2003) investigated that in central Taiwan, the average concentrations of $PM_{2.5}$ and $PM_{10\text{-}2.5}$ were recorded as 42.8 and 19.4 $\mu g/m^3$, respectively in the period of 2002 (January–April). Moreover, the monthly average $PM_{2.5}/PM_{10}$ ratio was between 0.63 and 0.73. In addition, Gidhagen *et al.*, (2002) reported that the increasing of concentration of arsenic in PM_{10} at Central and Northern Chile derives from copper and gold smelters; therefore, the increasing of industrial areas also emits the fine particles which contain heavy metals to the surrounding environment.

The semiconductor process (Figure 1-1) and optoelectronics manufacturing processes (Figure 1-2) which involve many emissions of chemical (Chein *et al.*, 2004). Table 1-2 showed the pollutant ingredient and possible emissions of CTSP and arsenic is marked in toxic gas and conflagrant gas. Arsine (AsH_3), is widely used in many processes such as chemical vapor deposition, ion implantation and diffusion, epitaxy process, etc., which is the source of arsenic compounds in flue gas as well as surrounding ambient air contamination (Chein *et al.*, 2006).

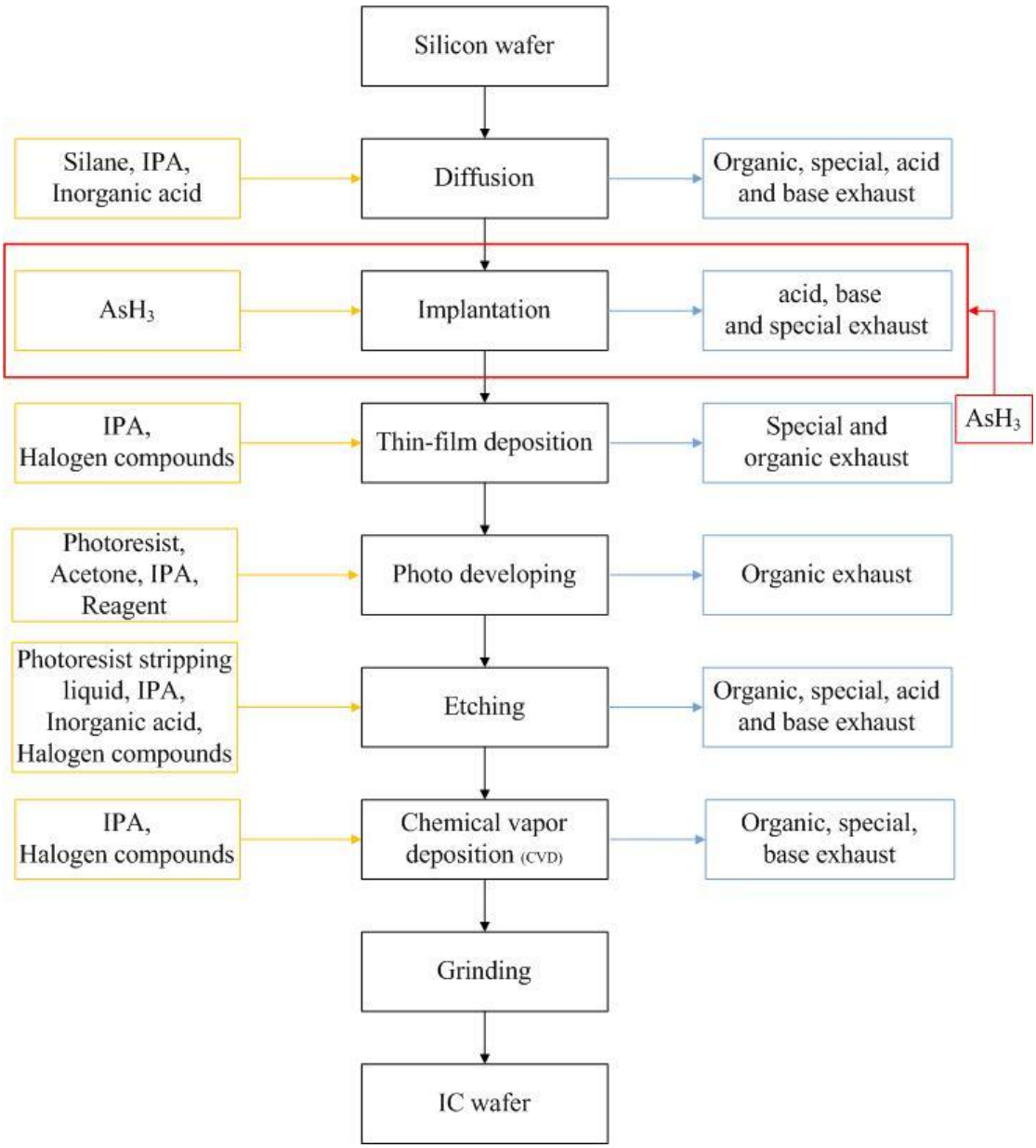

Figure 1-1. The air pollution sources of integrated circuit process

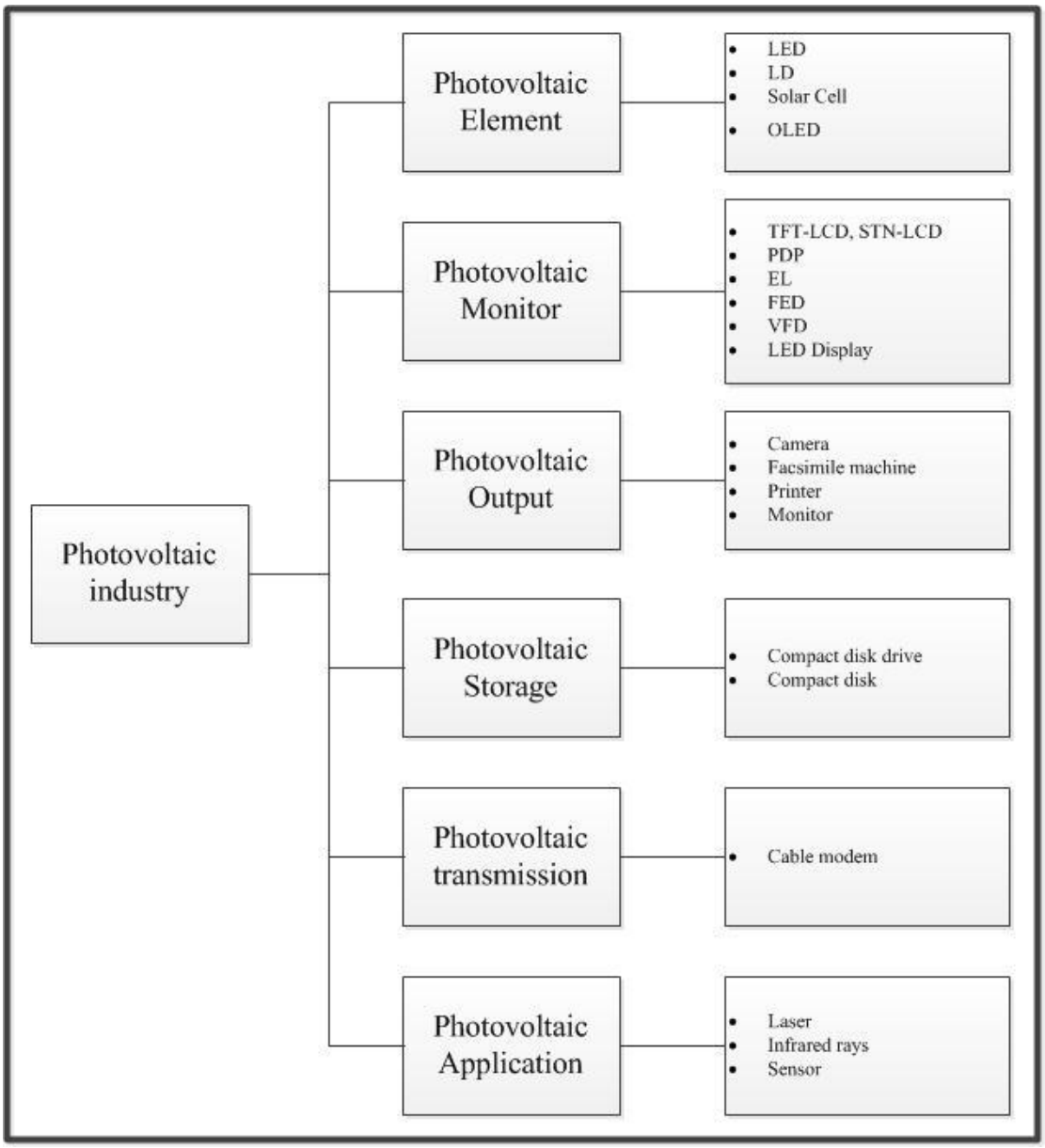

Figure 1-2. Compositions of photoelectron industries

Table 1-2.
The gas type of pollutant ingredient and possible emissions from CTSP

Pernicious gas item	Pollutant ingredient	Process	Possible emissions of CTSP
Acid and Base gas	Acid gas: HF, HNO_3, H_2SO_4,CH_3COOH, H_3PO_4, $H_2Cr_2O_7$ Base gas: NaOH	Oxidation, Reticle, Glass etching, Reactor of the cleaning, CVD	Cr
Organic gas	CH_2Cl_2,$CHCl_3$, $[(CH_3)_2CHCH_2COCH_3]$ Trans-1,2-Dichloroethene	Photoresist cleaning fluid, Imaging of clear fluid, Etched clear liquid, Wafer cleaning fluid	—
Toxic gas	AsH_3, PH_3, SiH_4, B_2H_6, B_4H_{10}, P_2O_5, SiF_4, CCl_4, HBr, BF_3, $AlCl_3$, B_2O_5, As_2O_3, BCl_3, $POCl_3$, Cl_2, HCN, SiH_2Cl_2	Oxidation, Reticle, Glass etching, diffusion, CVD, Ion implantation	**As**
Conflagrant gas	SiH_4, AsH_3,PH_3, BF_3, H_2, SiH_2Cl_2	Ion implantation, CVD, diffusion	**As**

Principal component analysis (PCA) is one of common multivariate statistical techniques that used to achieve high efficiency of data compression from the original data as well as to indicate natural associations between samples and/or variables (Astel *et. al.*, 2007; Wenning and Erickson, 1994) by gaining some information useful in the interpretation of environmental system. PCA consists of diagonalization of the covariance or correlation matrix transforming the original

measurements into linear combinations of these measurements, and then the explained variance of each principal component can be maximized. It has been wildly used to reveal the relationships among variables as well as to classify them into different latent variable, so that some special features inhered in the measured system can be characterized (Chen *et al.*, 2007; Lautre and Fernández, 2004; Lucas *et al.*, 2008 and Macciotta *et al.*, 2006). Recently, many comprehensive approaches consisted of PCA and other data analysis technologies such as geographic information system (GIS) and cluster analysis are also proposed (Lima *et al.*, 2010; Zhou *et al.*, 2007).

According to Han *et al.*, (2006), the multivariate analysis (PCA and cluster analysis (CA)) and correlation analysis were performed in the research to identify the sources of pollutants. The pollutants that significantly correlated (Cr, Cu, Pb, and Zn) were obtain from correlation analysis. The three main factors of contaminants can be classified precisely by these statistical analyses and the results show that PCA and CA can classify the sources of pollutants into three main groups; soils, industrial, and traffic source.

From past several literature (Stortini *et al.*,2009 and Pant and

Harrison, 2012), it indicates that PCA can effectively classify the pollution source. Unfortunately, there is little information covering the emission from high tech industries.

Therefore, this study attempts to apply PCA to investigate the pollution distribution and trend from a high tech industrial park.

The objectives of this study are to analyze the air emissions from Central Taiwan Science Park's (CTSP) fine particles concentrations of heavy metals (As, Cd, Cr, Cu, Mn, Ni, Pb) by Graphite Furnace Atomic Absorption Spectrometry (GFAAS). The multivariate statistical approaches used to determine pollution sources including correlation coefficient analysis, principal component analysis (PCA), and cluster analysis (CA) in the period of 2008 to 2011.

Chapter 2. Materials and Methods

The overall methodology can be illustrated as a flow chart shown in Figure 2-1. The background information was investigated at the beginning of this study and established the sampling site for ambient perimeter monitoring. The statistical analyses (principal component analysis (PCA) and cluster analysis (CA)) were used in this research to identify the pollutant species.

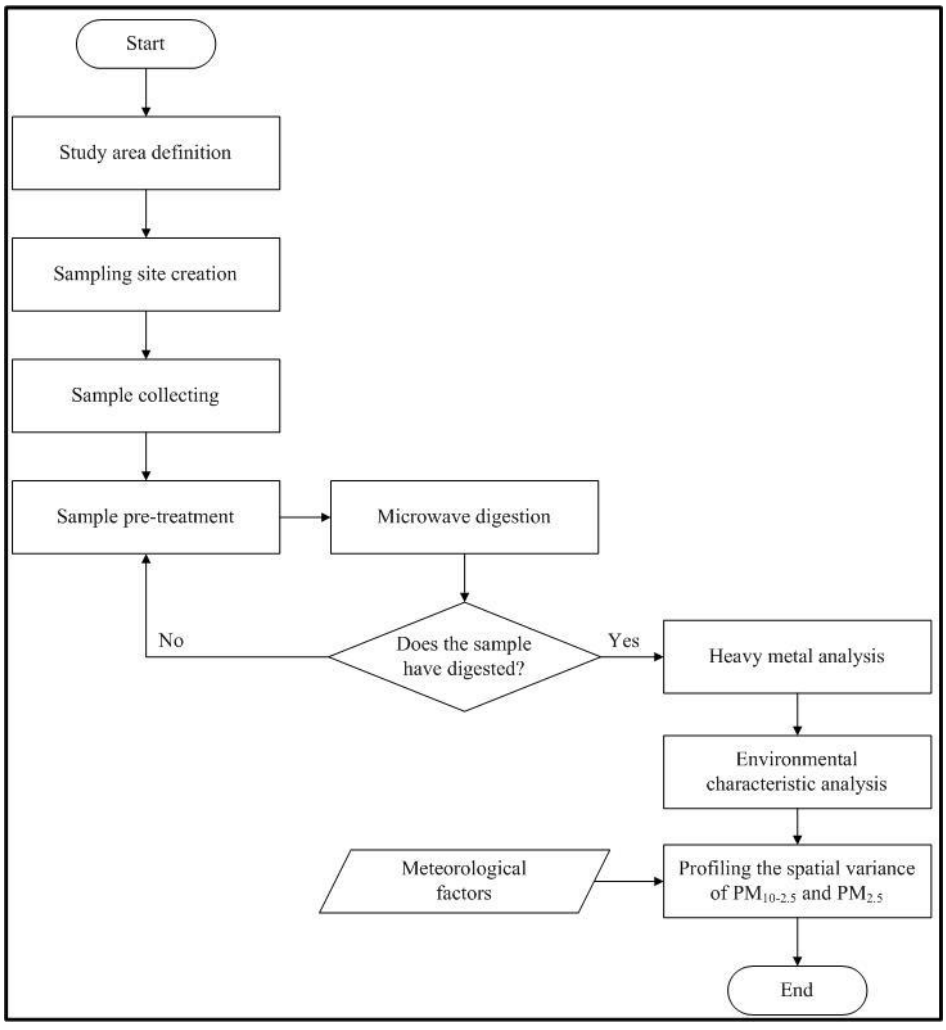

Figure 2-1. Flow chart of this study to research the ambient perimeter monitoring and spatial variance of heavy metals.

2-1 *Study area and sampling site*

There are several industrial parks were located in the central Taiwan; Tanzih Industrial Park, Taichung Industrial Park, Guan Lian Industrial Park, Taichung thermal power plant and Central Taiwan Science Park (CTSP) (Figure 2-2 (a)).

The topography of the area is not plain like other place in central Taiwan (Figure 2-2(b)). Thus, the meteorological factors are unstable in central Taiwan, and the other hand (Figure 2-2(b)) showed that the CTSP is constructed at hilltop. Because the pollutants of CTSP are difficult to investigated $PM_{10\text{-}2.5}$ and $PM_{2.5}$, therefore, this study set the sampling site in Tunghai University (THU) which is the southwest downstream from CTSP; Figure 2-3 is the history of CTSP.

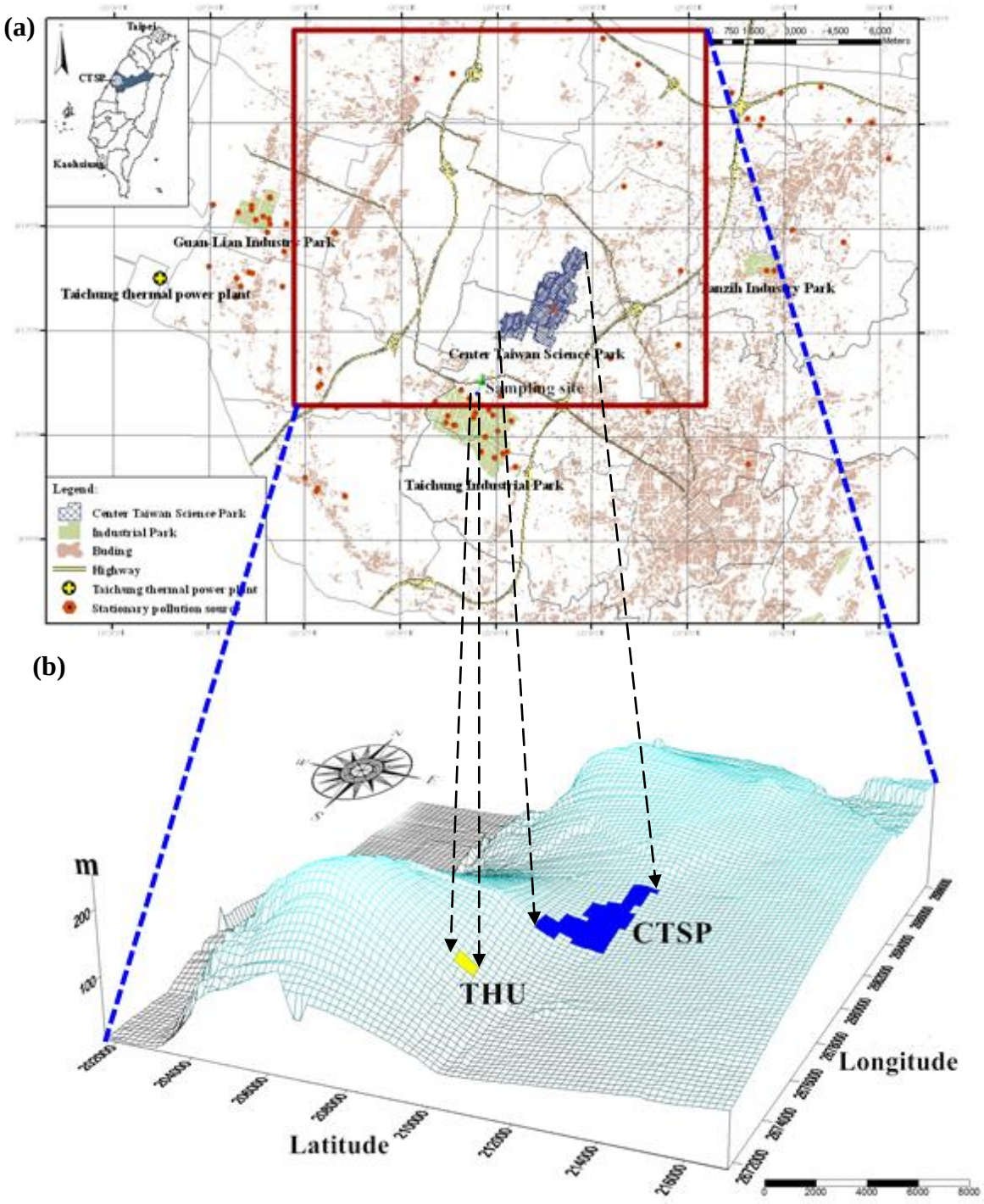

Figure 2-2. (a) Stationary industrial area in Taichung city; (b) The map of CTSP and sampling sites in 3D

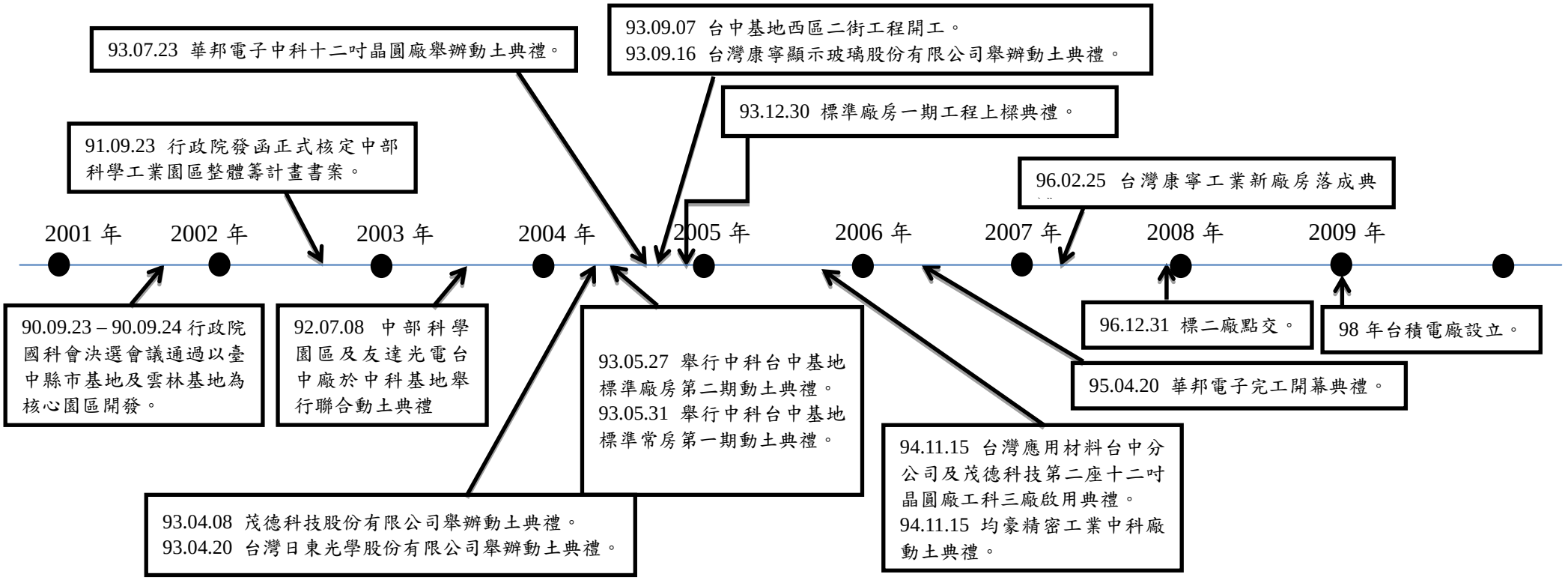

Figure 2-3. The history of CTSP in each year

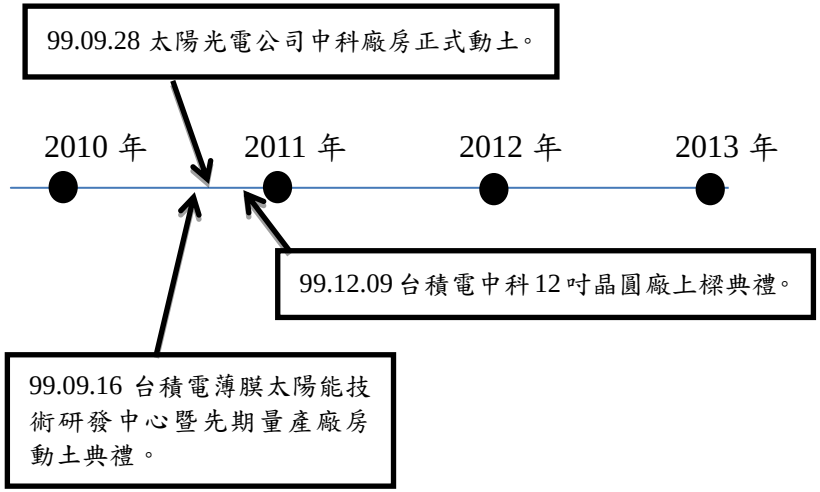

Figure 2-3. The history of CTSP in each year (continued)

2.2 *Sampling and chemical analysis*

Size-fractionated airborne particulate matters (< 2.5 μm and 2.5-10 μm) were collected on a cellulose filter paper (Whatman 47mm diameter, 20μm pore). The high-volume sampling equipped with cascade impactor (Particulate matter 10 microns and less High volume air sampler, Tisch Environmental, Inc., TE-6070 High volume MFC) for fractionate into different sizes during 24 hours at a flow rate of 1.7 m^3/min. The samplings of PMs were collected from different position of the filter; $PM_{10–2.5}$ was collected on the top of filter and $PM_{2.5}$ was obtained at the bottom of filter. The concentrations of PMs were accounted for all of $PM_{10-2.5}$ and $PM_{2.5}$ particles in this study while before the sampling; the flow rate of high volume sampler was calibrated with a calibrator.

The 45 sets of observed samples collected from the sites nearby the CTSP during the sampling period between 2008 and 2011. The samples were prepared by a microwave digestion method for subsequent spectrometric analysis.

A remolded conventional microwave oven (High technology system Corp) with a power of 200W (80℃ to 90℃) was conducted for the digestion of PMs collected in filter. The cellulose filter papers (Whatman

47mm diameter, 2.0μm pore) were soaked in a closed digestion vessels filled with 0.5 ml of HNO_3 and digested in setting microwave oven (Wang *et al.*, 1996).

After the microwave digestion and cooling, the sample solution was diluted to 10ml with deionized water for spectrometric measurement. This research applied the graphite furnace atomic absorption spectrometry (GFAAS) to analyze the heavy metal concentrations (As, Cd, Cr, Cu, Mn, Ni, Pb) of sample diluent. In order to ensure the analysis quality, a quality control program was executed during sample measurement. One standard solution and one duplicate sample were simultaneously analyzed with samples in each batch of measurements. The relative standard deviation for duplicate samples was less than 15% for all analyses. The recovery for standard solution was conducted in the range of 80% to 120%. The measured concentrations of samples were investigated more than 3 times method detection limits (MDL) and the recovery for the QC-standards ranged from 84% to 116%.

2.3 *Principle component analysis (PCA)*

More and more spatial-temporal data for pollutants are becoming available due to the increasing monitoring programs. If some useful

information inhered in these data and can be explored by data mining technologies, it will be helpful for decision makers to outline the environmental situation and to plan advantageous strategies for ambient conservation. In this respect, PCA approach is utilized in the present study to simplify high dimensional variables with retaining most of the primary information as well as to integrate some individual variables to comprehensive factors which stand for a kind of conceptual environmental characteristics.

The basis of PCA has been well-explained (Jolliffe, 2002), and is used for characterizing patterns within large sets of data by re-expressing to a rotated coordinate system in which as much variance as possible is explained by the first few dimensions. In which the eigenvectors of the variance covariance matrix are calculated, so that the principal component score, i.e. the weight of the eigenvector can be obtained. The scores of the original variables, also called principal component loadings (PC loadings), can be used to indicate the relationship between the variable and the principal component. In other word, the variable and the principal component will be stronger related if the PC loading is larger. By doing this, raw data matrix can be reduced to two or three principal

component loadings that account for the majority of the variance. Thus, these factors can be used to account for approximately required information as the original observations do. Thus, this study uses the software package SPSS for Windows to determine the structure in the relationships between ambient parameters and identify the most important factors contributing to this structure based on the eigen analysis of the correlation matrix.

2.4 *Hierarchical cluster analysis (HCA)*

Following the PCA process for grouping the characteristic parameters of objects, HCA is utilized to explore the spatial relationships among the objects by examining their distances, and then a graphic display of how these objects are clustered can be obtained. HCA measures the similarity between every pair of objects with a standardized m-space Euclidian distance that can be shown as equation (1) (Davis, 1986).

$$d_{ij} = \sqrt{\frac{\sum_{k=1}^{m}(X_{ik}-X_{jk})^2}{m}} \qquad (1)$$

In which, X_{ik} denotes the k_{th} variable measured on object i and X_{jk} is the k_{th} variable measured on object j. A low distance shows the two objects are similar or “close together”, whereas a large distance indicates

dissimilarity.

Chapter 3. Results and Discussion

3.1 *Environmental conditions*

Several investigations of the particulate emission from industrial park were shown in Table 3-1 and Table 3-2. It implies that different heavy metals were observed in different types of industries.

This study collected pollutants samples investigate from 2008 to 2011 and applied the multivariate analysis to investigate their characteristics and spatial distribution nearby CTSP.

The climate factors and heavy metal concentrations of $PM_{10-2.5}$ and $PM_{2.5}$ are displayed in Table 3-3 respectively. This study obtained that the heavy metal concentrations of $PM_{10-2.5}$ are lower than those of $PM_{2.5}$ under the same climate conditions.

Table 3-1.

The heavy metal concentrations in $PM_{10-2.5}$ from other literatures (unit: ng/m^3)

Polltant source	Lu *et al.*,(2012)	Mamane *et al.*,(2008)		Hueglin *et al.*,(2005)			Manoli *et al.*, (2002)
	Shanghai	Ashdod	Bern	Zurich-Kaserne	Basel	Chaumont	Thessaloniki
As	5.95	0.39	0.42	0.10	0.11	0.02	0.61
Cd	-	0.87	0.08	0.03	0.04	0.00	0.11
Cr	1.73	4.45	-	-	-	-	2.90
Cu	20.07	4.92	68.00	12.00	3.40	0.30	90.00
Mn	6.92	10.80	20.00	5.10	5.30	1.20	24.00
Ni	0.84	5.19	1.90	0.11	0.46	0.04	6.10
Pb	16.77	3.95	22.00	5.90	4.40	0.80	29.00

Table 3-2.

The heavy metal concentrations in $PM_{2.5}$ from other literatures (unit: ng/m^3)

Pollutant source	de la Campa *et al.*, (2010)	Storni *et al.*, (2009)	Moreno *et al.*, (2006)					Vecchi *et al.*, (2004)
	Bailén	Venice Lagoon	Tarragona	Barcellona	Huelva	Alcobendas	Llodio	Milan
As	0.73	3.58	0.50	1.10	4.20	0.60	1.50	2.00
Cd	0.21	3.51	0.20	0.60	0.80	0.30	1.00	-
Cr	2.52	-	2.20	2.90	0.90	1.10	15.80	3.33
Cu	28.40	-	31.70	31.70	32.90	23.70	29.10	11.33
Mn	7.07	5.22	2.80	9.60	3.20	4.30	39.20	10.33
Ni	13.10	12.15	3.50	5.20	3.00	2.20	20.80	4.33
Pb	22.00	18.08	17.50	40.30	26.90	19.00	76.50	30.00

Table 3-3.
The environmental condition of $PM_{10-2.5}$ and $PM_{2.5}$

Concentration	$PM_{10-2.5}$				$PM_{2.5}$			
(ng/m^3)	Max.	Min.	Mean.	Std.[4]	Max.	Min.	Mean.	Std.[4]
As	3.12	0.03	0.55	0.66	14.72	0.29	2.49	2.85
Cd	4.14	0.02	0.69	1.03	7.71	0.16	1.39	1.61
Cr	14.43	0.33	2.98	2.78	18.63	0.00	4.42	4.03
Cu	113.33	1.04	14.89	20.20	108.19	5.59	37.81	26.02
Mn	19.14	1.44	5.79	4.35	77.99	2.11	18.40	14.00
Ni	22.65	0.29	4.95	5.48	111.22	0.00	7.51	17.28
Pb	30.63	0.11	6.91	7.91	86.05	3.91	32.04	20.95
WS[1] (m/s)	5.98	1.28	2.94	1.15	5.98	1.28	2.94	1.15
Temp.[2] (℃)	30.13	11.49	20.13	4.52	30.13	11.49	20.13	4.52
RH[3] (%)	83.54	20.85	69.21	11.11	83.54	20.85	69.21	11.11

WS[1]: Wind speed; Temp.[2]: Temperature; RH[3]: Relative Humidity; Std.[4]: Standard deviation

Based upon the $PM_{10-2.5}$, it is shown that the As and Cd emission from CTSP is higher than those obtained in Europe. While $PM_{2.5}$ also indicates that CTSP has similar higher heavy metal emission than those from Europe countries.

3.2 *Environmental characteristic analysis*

The PMs ($PM_{10-2.5}$ and $PM_{2.5}$) speciation and source apportionment have been investigated by researches (Sharma and Maloo, 2005; Wu *et al.*, 2007; Kim *et al.*, 2008; Yu, 2010; Aldabe *et al.*, 2011). The apportion sources (Table 3-4) of PMs can be identified from different activities; such as, Mn, Mg, Fe, Pb, Al, V and Ni from crustal dust, road dust or

re-suspended dust (Chelani *et al.*, 2008; Kulshrestha *et al.*, 2009 and Chelani *et al.*, 2010), K, Zn and Pb from incineration process and Fe, Ni and V from oil combustion process (Allen *et al.*, 2001; Marcazzan *et al.*, 2001; Espinosa *et al.*, 2001; Miranda *et al.*, 2002; Chao and Wong, 2002 and Funasaka *et al.*, 2003).

Table 3-4.
Possible heavy metal emission sources in CTSP.

Source type	Emission of Pollution Source	Reference	Possible emission in CTSP
Industrial activities	Cd, Zn, Cu, As, Sb, V, Hg, Mn, Ni	(Sun *et al.*, 2010), (Mico *et al.*, 2006), (Karar and Gupta, 2007)	As, Cd, Cu, Mn, Ni
Traffic	Cu, Cr, Zn, Ni, Ca, Co, Pb	(Srivastava *et al.*, 2008), (Kulshrestha *et al.*, 2009)	Pb, Cr, Cu
Crustal dust, road dust, re-suspended dust	Al, Fe, Ni, Mg, Mn, Pb	(Chelani *et al.*, 2008), (Kulshrestha *et al.*, 2009) (Chelani *et al.*, 2010)	Mn, Pb, Ni

This study utilized 7 trace metal (As, Cd, Cr, Cu, Mn, Ni, Pb) concentrations data to analyze the species source of $PM_{10-2.5}$ and $PM_{2.5}$ by principle component analysis (PCA).

3.2.1 $PM_{10-2.5}$

The PCA of $PM_{10-2.5}$ showed that the variables can be divided into three groups with percentage of variation 45.300, 20.001 and 16.890, with a cumulative sum of 82.192. On the other hand, it represents that this

study can satisfactorily to use these three factors to explain all data of $PM_{10-2.5}$.

As stated earlier, the data are separated into three groups obtained by PCA; As, Cd and Mn are differentiated to factor 1, Cu and Cr are differentiated to factor 2 while Ni is differentiated to factor 3 in $PM_{10-2.5}$ (Table 3-5).

Table 3-5.
Factor analysis of $PM_{10-2.5}$

	$PM_{10-2.5}$		
Metals	Factor 1	Factor 2	Factor 3
As	**0.877**	0.062	0.311
Mn	**0.823**	0.132	-0.178
Cd	**0.814**	0.168	0.212
Cu	0.149	**0.927**	0.098
Cr	0.121	**0.915**	0.127
Ni	-0.022	0.114	**0.959**
Pb	0.489	0.166	0.681
% of Variance	45.300	20.001	16.890
Cumulative (%)	45.300	65.301	82.192

3.2.2 $PM_{2.5}$

The PCA was applied to differentiate the $PM_{2.5}$ data as well. The results showed that the variables can be divided into three groups with percentage of variation 42.472, 18.149 and 15.665, with a cumulative sum of 76.285.

This result of that As, Cd and Pb are differentiated to factor 1, Cu and Cr are differentiated to factor 2 while Mn is differentiated to factor 3 in $PM_{2.5}$ (Table 3-6).

Table 3-6.
Factor analysis of $PM_{2.5}$

	$PM_{2.5}$		
Metals	Factor 1	Factor 2	Factor 3
As	**0.880**	0.267	-0.003
Mn	0.083	0.012	**0.852**
Cd	**0.879**	0.347	-0.109
Cu	0.256	**0.831**	0.204
Cr	0.127	**0.886**	-0.053
Ni	-0.016	-0.069	-0.668
Pb	**0.848**	-0.033	0.290
% of Variance	42.472	18.149	15.665
Cumulative (%)	42.472	60.620	76.285

Compare to Table 3-4, our study defines the factors for each group, factor 1 is from stationary pollutant source which including As and Cd; factor 2 is from mobile pollutant source which including Cu and Cr. Additionally, Pb, Mn and Ni are hardly to distinguish to which pollutant source therefore, Pb, Mn and Ni were classified as other pollutant source in this study.

3.3 *Profiling the spatial variance of $PM_{10-2.5}$ and $PM_{2.5}$*

After the PCA to ensure the pollutant source, the hierarchical clustering

analysis (HCA) was applied to separate a group by stationary pollutant (As, Cd).

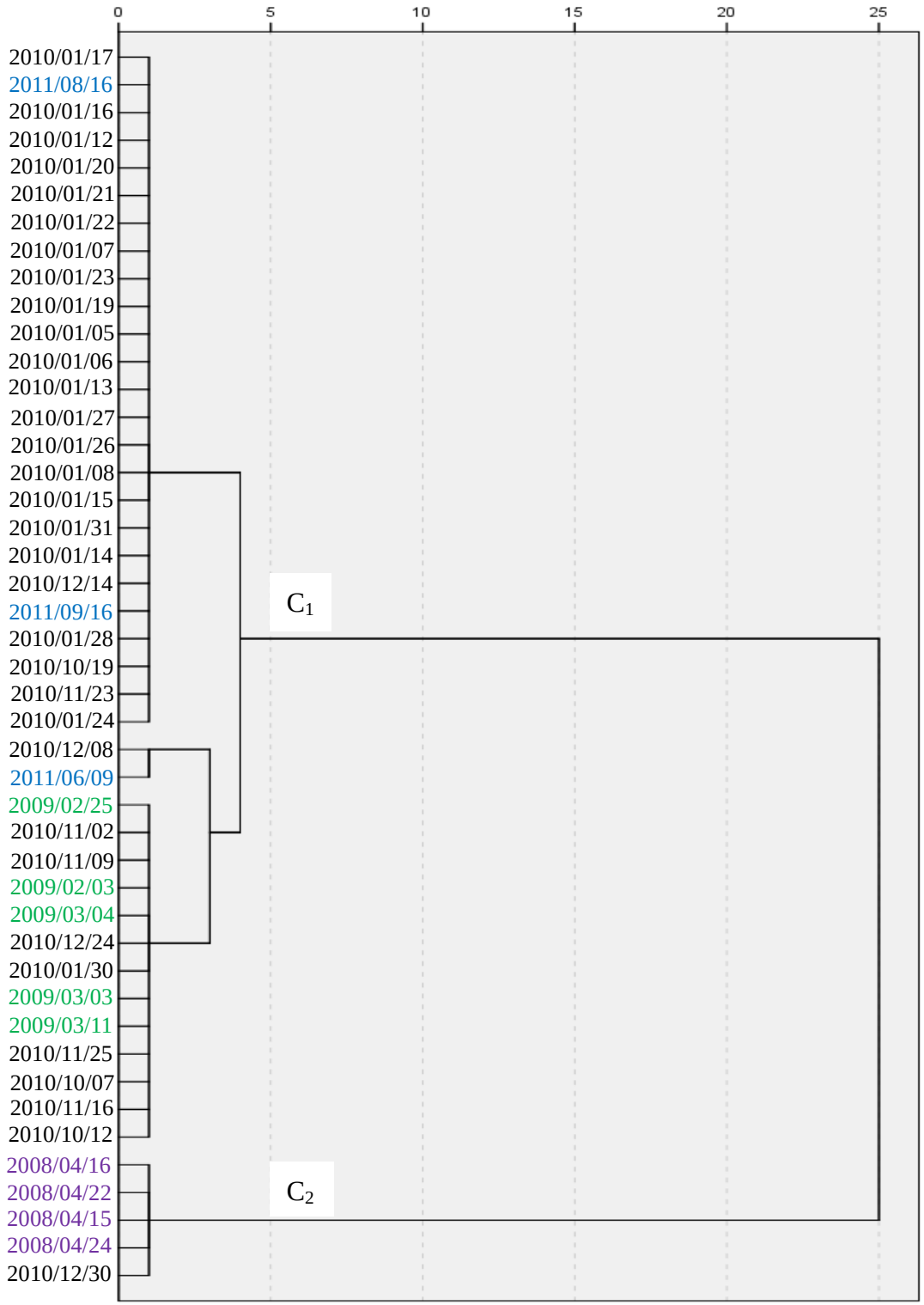

Figure 3-1. The dengrogram of stationary pollutant source of $PM_{10-2.5}$ during 2008 to 2011

Because the objective is investigating the pollutant emissions into the atmosphere of $PM_{10-2.5}$ and $PM_{2.5}$, in Figure 3-1 and 3-2 the color show the different year.

3.3.1 $PM_{10-2.5}$

In Figure 3-1, $PM_{10-2.5}$ was separated into two groups, the first group (C_1) is the low heavy metal concentration in $PM_{10-2.5}$, and second group (C_2) is high heavy metal concentration in $PM_{10-2.5}$. Therefore, this study assumes that the C_1 is the time for the factories operation and C_2 is the time during the factories development at stationary pollutant source.

The concentration of heavy metals and the climate conditions will be taken into account. Climate factors, the relative humidity, temperature, wind speed and wind direction in this two groups are almost the same; while the result show C_1 when As and Cd decrease, other heavy metals will be decrease relatively; when As and Cd increase in C_2, other heavy metals will be increase relatively (Figure 3-2).

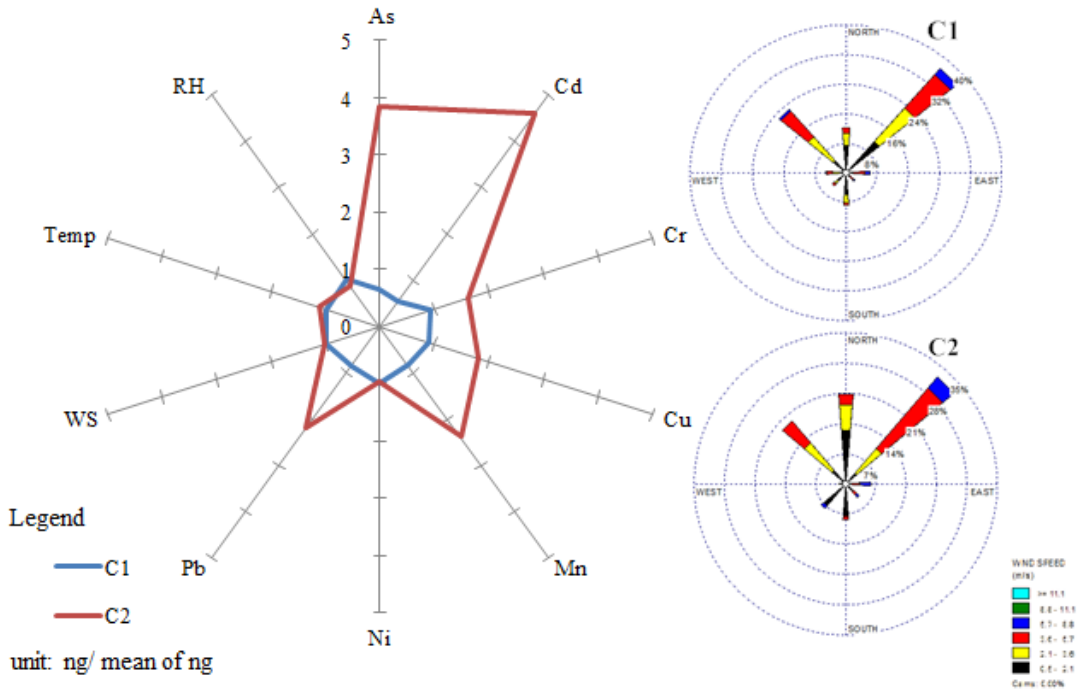

Figure 3-2. The radar chart of heavy metal with climate factors of $PM_{10-2.5}$ during the sampling period 2008~2011 nearby CTSP.

3.3.2 $PM_{2.5}$

Figure 3-3, $PM_{2.5}$ was separated into two groups, the first group (F_1) is the low heavy metal concentration in $PM_{2.5}$, and the second group (F_2) is high heavy metal concentration in $PM_{2.5}$. Thus it can be stated that the F_1 is the time during the factories development F_2 is the time for during the factories operation at stationary pollutant source (Figure 3-4).

After HCA, this study combines the heavy metals of stationary pollutant source with climate factors to analyze two groups; the result show that in climate factors, the relative humidity and temperature are almost the same, but wind speed and wind direction are not, when wind

speed increase 1.5 times (Figure 3-5) and the most of wind direction being come from northeast, As and Cd would be increase and other heavy metals would be increase relatively.

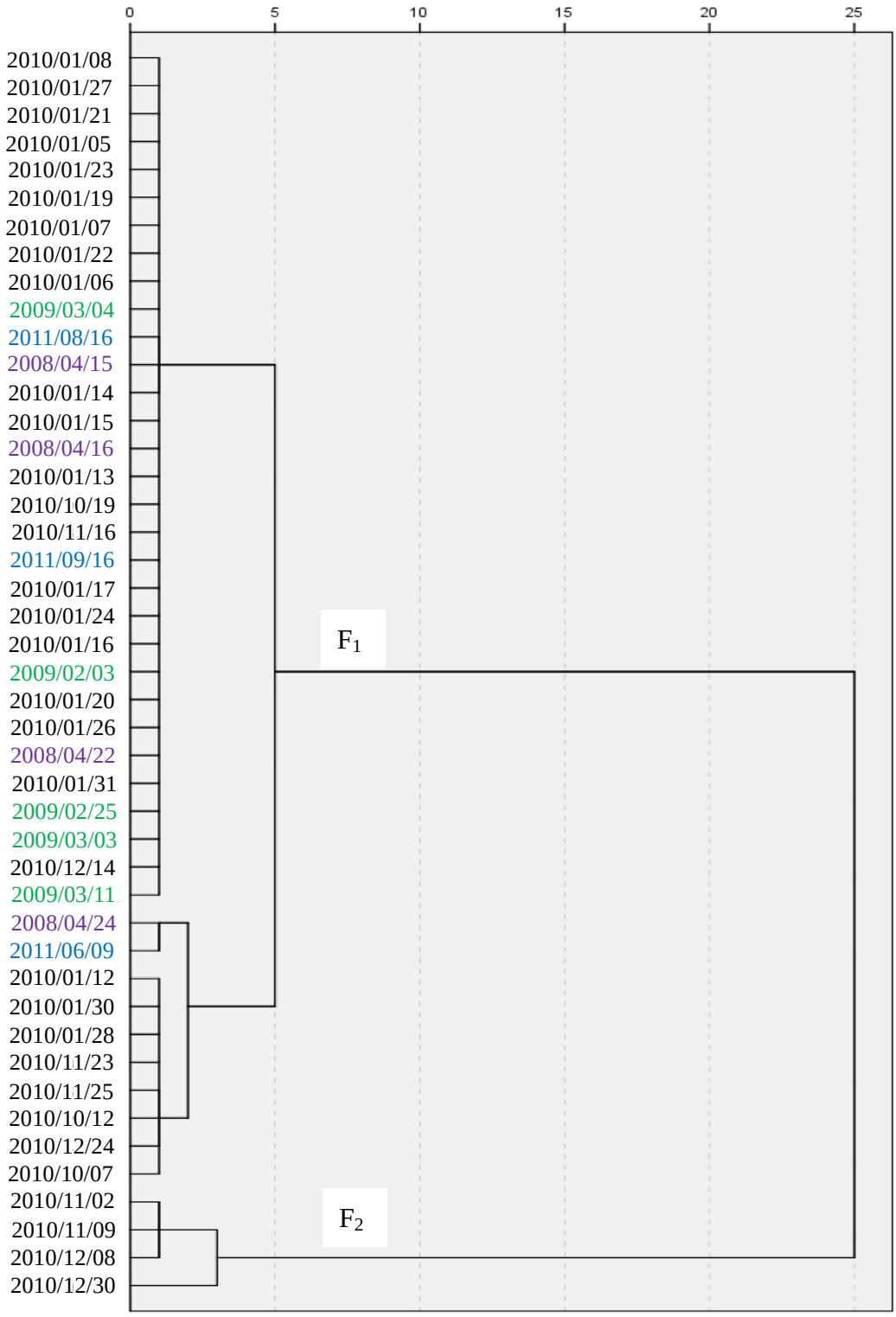

Figure 3-3. The dengrogram of stationary pollutant source of $PM_{2.5}$ during 2008 to 2011

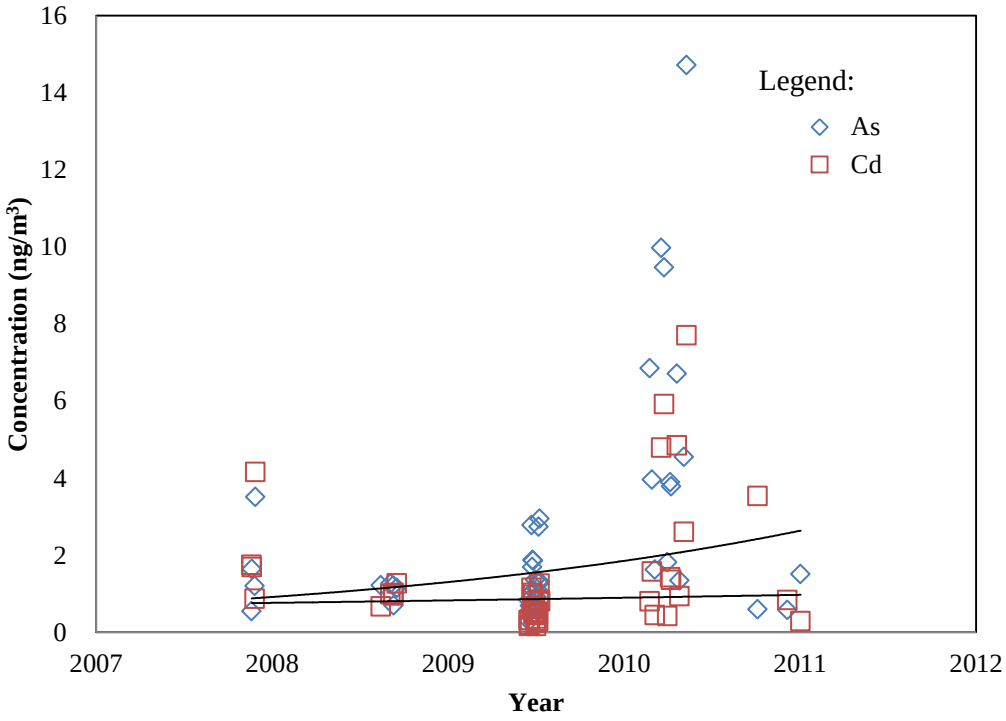

Figure 3-4. The trend of stationary pollutant species during 2008 to 2011

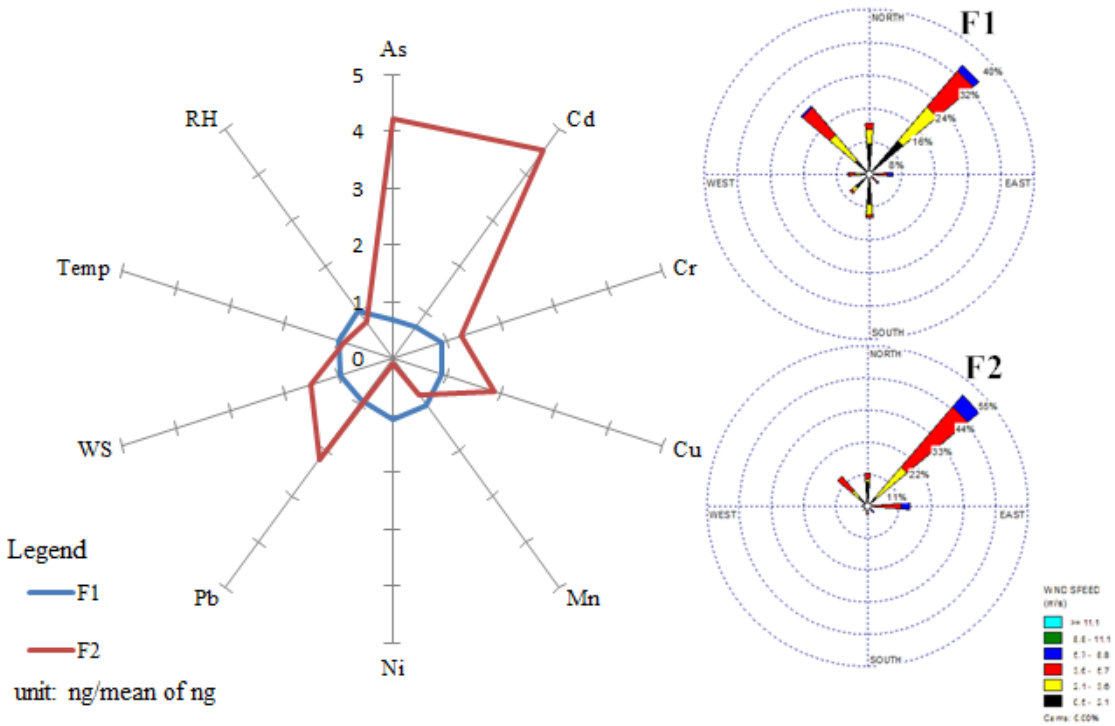

Figure 3-5. The radar chart of heavy metal with climate factors of $PM_{2.5}$

According to 3.3.1 and 3.3.2, the serious concentration of $PM_{10-2.5}$ is in early period and the pollutant sources are come from north site. In contrast for $PM_{2.5}$, the results show the more serious concentration is in later period and the pollutant source is almost come from northeast site (Figure 3-5).

3.4 *Identify As from stationary pollutant source with climate factors*

After HCA, this study combines climate conditions (relative humidity/10, wind speed and wind direction) with concentration of As. Chen *et al.*, (2010) showed that when wind speed lower than 2.0 m/s, the air flow is dispersion. In the opposite, when wind speed faster than 2.0 m/s, the air flow is diffusion. WHO show the value 1.2 ng/m^3 which value is indicated as background concentration of As in industrial sites (WHO EHC 224).

3.4.1 $PM_{10-2.5}$

In Figure 3-6, when the air flow in diffusion and RH between 50% to 70%, the concentration of As have peak; when the air flow in dispersion and RH between 50% to 70%, the concentration of As have a peak; the meaning of when the air flow in diffusion, the concentration of As may

come from further afield; fortunately, the concentration of As in $PM_{10-2.5}$ being not over than 6 ng/m^3 which value in EU standard.

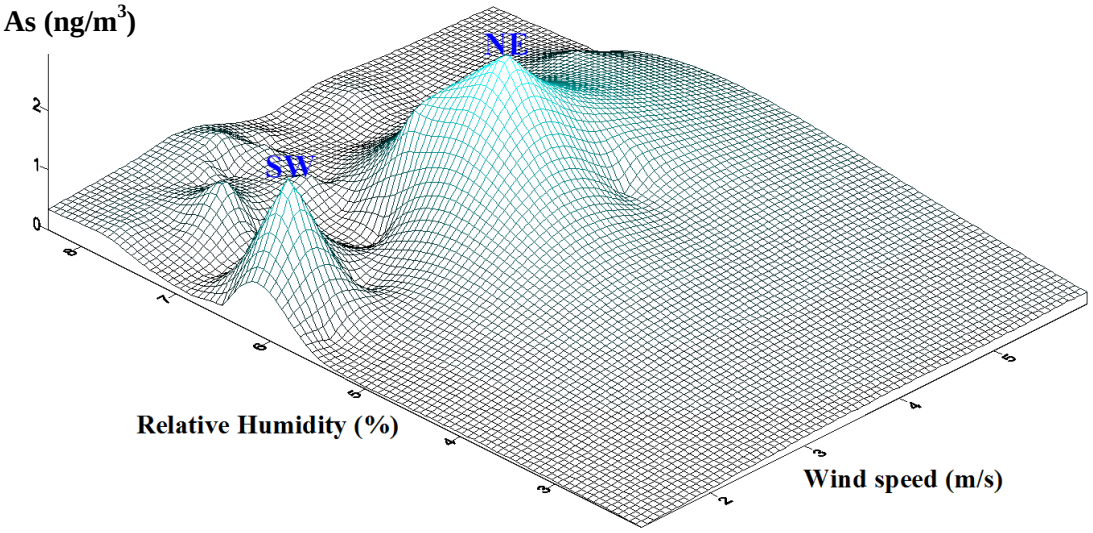

Figure 3-6. The relationship of As in $PM_{10-2.5}$, wind speed and relative humidity

3.4.2 $PM_{2.5}$

In Figure 3-7, it demonstrates that the highest concentration occurs when the RH in a range of 60%~80%. For the air flow in diffusion, the concentration of As may come from further afield, the more important is that the red part represent the value over than EU standard, and the wind direction come from northeast site. In addition, when the air flow in dispersion, the concentration of As being come from northwest.

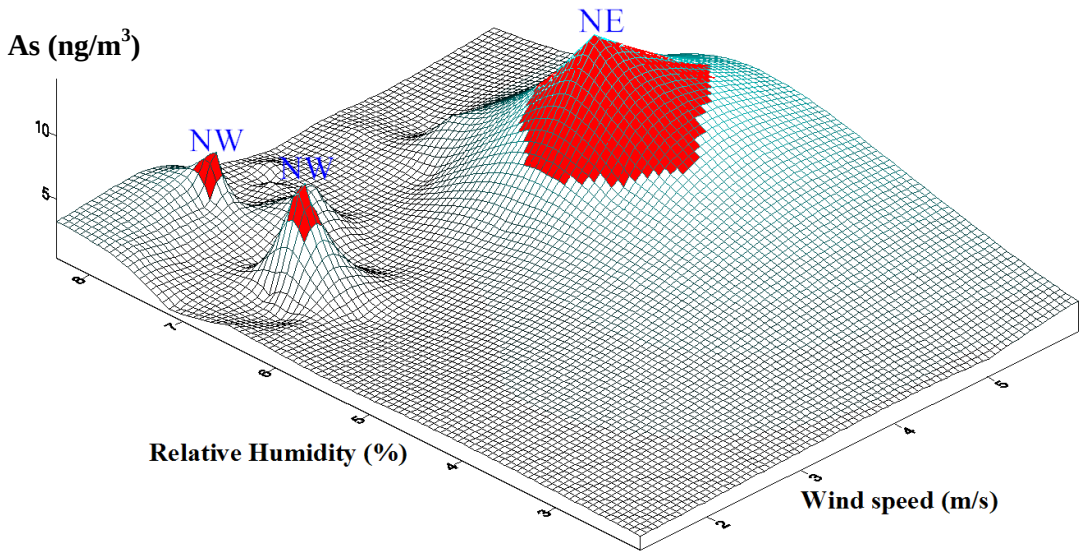

Figure 3-7. The relationship of As in $PM_{2.5}$, wind speed and relative humidity

According to previous section, the concentration of As maybe come from all the sites in $PM_{10\text{-}2.5}$, but in $PM_{2.5}$, it is a assuming that high concentration maybe cumulate on the hillside when the air flow is dispersion flow; the concentration of As in $PM_{10\text{-}2.5}$ and $PM_{2.5}$ maybe come from northeast sites when the air flow is diffusion flow. Finally, the concentration of As in $PM_{2.5}$ is higher than $PM_{10\text{-}2.5}$.

3.5 *Cumulative probability of As*

The comparison of PMs concentration of As is showed in (Figure 3-8). The probability of the high concentration of As was over 13% the standard of Europe in $PM_{2.5}$.

For the concentration of As in $PM_{10-2.5}$, the probability of $\leqq 2$ ng/m^3 was 95%; for the concentration of As in $PM_{2.5}$, the probability of $\leqq 2$ ng/m^3 was 70%, the probability of between 2 ng/m^3 to 6 ng/m^3 was 17% and the probability of $\geqq 6$ ng/m^3 was 13%.

Finally, when concentration $\leqq 2$ ng/m^3, the probability of concentration in $PM_{10-2.5}$ is higher than the concentration of $PM_{2.5}$ but when concentration $\geqq 2$ ng/m^3, the probability of concentration in $PM_{10-2.5}$ is lower than the concentration of $PM_{2.5}$, on the other hand, it represent the concentration of $PM_{10-2.5}$ was smaller than $PM_{2.5}$ during sampling period 2008 to 2011.

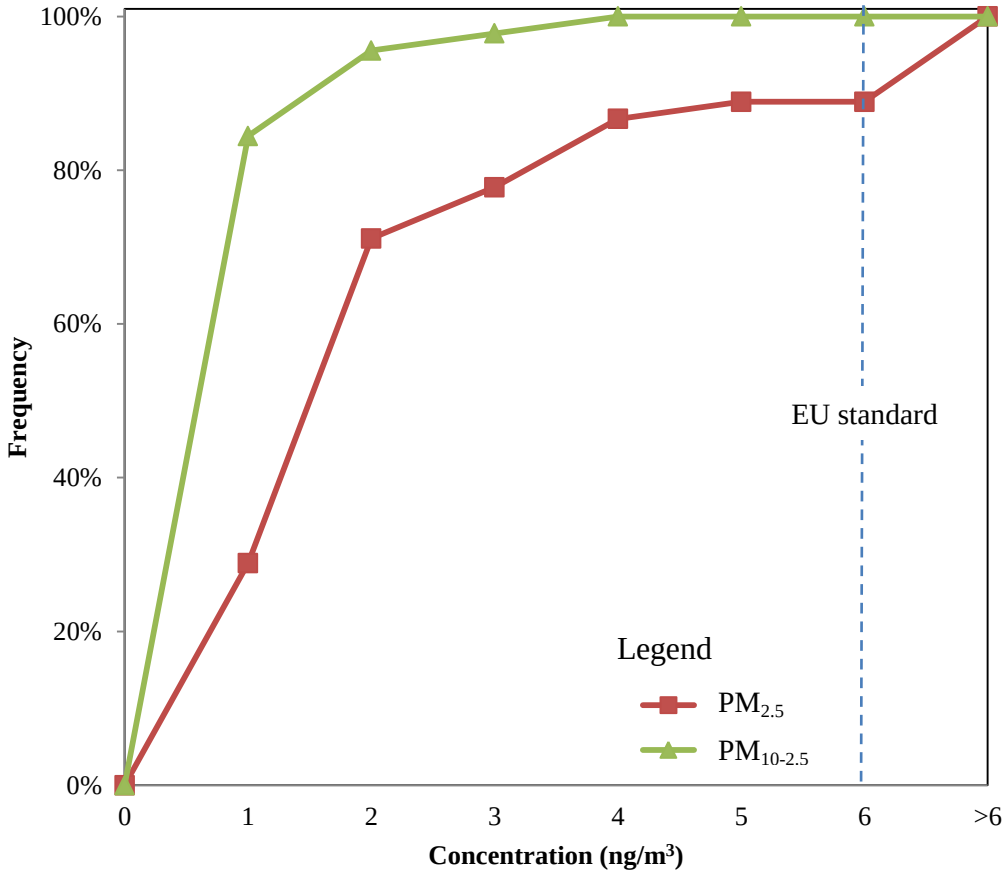

Figure 3-8. The cumulative probability of As in $PM_{10-2.5}$ and $PM_{2.5}$

3.6 *The trend of As in $PM_{2.5}/PM_{10}$ during 2008 to 2011*

The ratio of $PM_{2.5}$ with PM_{10} in this study came out the highest value all literature (Table 3-7). This study conduct the As in the distribution of particulates nearby CTSP.

During 2008 to 2009, this study finds that the ratio of $PM_{2.5}$ with PM_{10} of As increases rapidly (Figure 3-9). According to Figure 2-3, it can be explained that the factories of CTSP have operated in 2008 so the ratio of $PM_{2.5}$ with PM_{10} of As rapid increases.

Table 3-7.
Compare the $PM_{2.5}/PM_{10}$ with other countries.

Country	Site	$PM_{2.5}/PM_{10}$	Type of pollutant source	Reference
Taiwan	Taichung	0.71±0.09	High-tech science park	This study
	Taichung	0.62	Traffic	Fang *et al.*, (2008)
Hong	Hok Tusi	0.50	-	Lai *et al.*, (2007)
Kong	Hung Hom	0.68	Traffic	Cheng *et al.*, (2006)
China	Shenzhen	0.73	High-tech science park	Lai *et al.*, (2007)
	Zhuhai	0.71	High-tech science park	
Korea	Ulsan	0.55	Petrochemical industry	Hieu and Lee, (2010)
	Busan	0.56	Developing city	Kim *et al.*, (2006)
	Seoul	0.73	Developing city	
UK	Birmingham	0.66	Urban	Yin and Harrison, (2008)
Spain	Barcelona	0.64	Chemical industry	Pérez *et al.*, (2008)

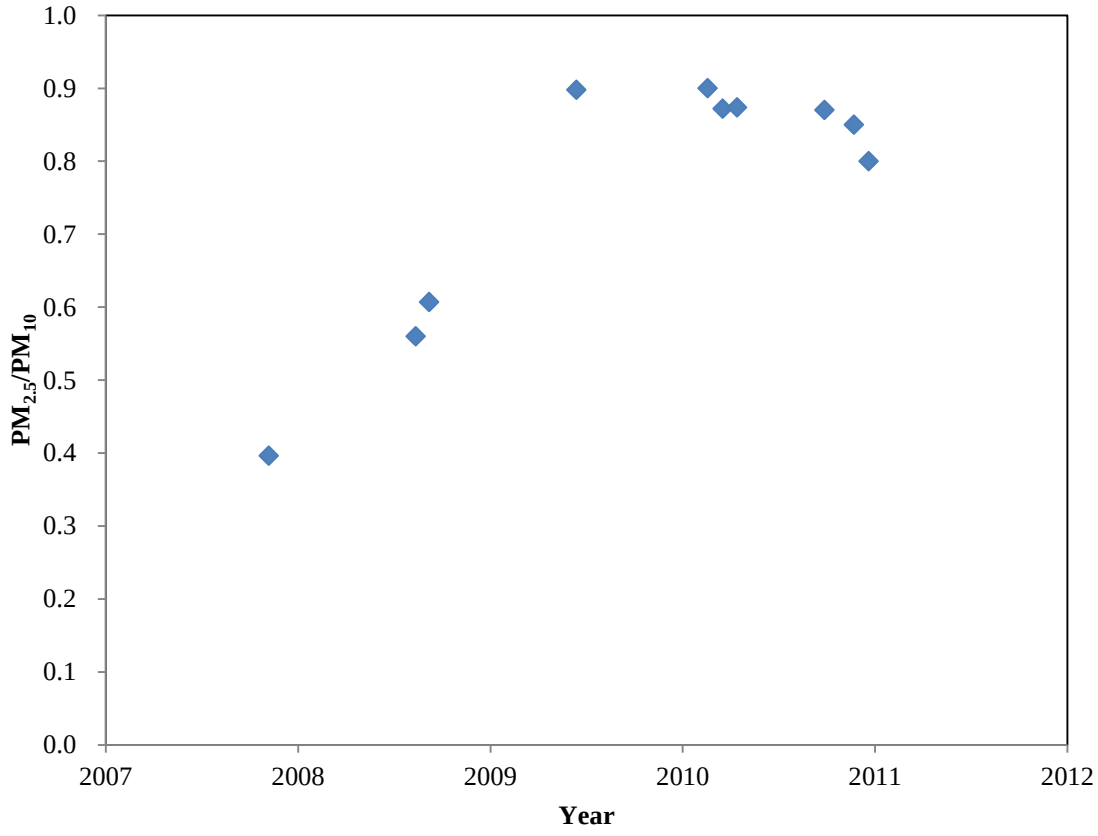

Figure 3-9. The trend of As in $PM_{2.5}/PM_{10}$ during the sampling period between 2008 and 2011

Chapter 4. Conclusions and Suggestions

4.1 Conclusions

This study has five conclusions.

1. Heavy metal concentrations of $PM_{2.5}$ higher than $PM_{10-2.5}$.
2. This study finds that As and Cd maybe come from high-tech industrial park.
3. This study finds the high heavy metal concentration of stationary pollutant source in $PM_{10-2.5}$ occur in early period (2008 to 2009) but in $PM_{2.5}$, the high heavy metal concentration of stationary pollutant source occur in later period (2010 to 2011).
4. When the wind speed faster than 2.0 m/s and the relative humidity between 50~80%, the sampling site collect the high concentration of As from northeast side.
5. During 2008 to 2011, the probability of As was over 13% the standard of EU, and the concentration of As in $PM_{2.5}$ is higher than $PM_{10-2.5}$ in recent year.

4.2 Suggestions

1. Combine sampling site with environmental factors to conduct the risk assess of nearby residents by exhausting pollution around the high-tech science park.
2. It is necessary to set up long-term heavy metals monitoring program around the Central Taiwan Science Park.

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