Characteristics and Source Apportionment of Atmospheric PM$_{2.5}$ at a Coastal City in Southern Taiwan

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ABSTRACT

Fine particulate matters (PM$_{2.5}$) has been identified as one of the major air pollutants in urban areas, which are responsible for the adverse effects on public health and the deterioration of visibility. New PM$_{2.5}$ air quality standards were promulgated in Taiwan on 14th May 2012, as well as the standard sampling and analytical method for atmospheric PM$_{2.5}$ (NIEAA205.11C) on 24th April 2012. In this study, the atmospheric levels and characteristics of PM$_{2.5}$ in Tainan during 2013 were evaluated by measuring the mass concentration of PM$_{2.5}$ and analyzing the water-soluble ionic, carbon, and metal components. Additionally, a Chemical Mass Balance (CMB) receptor model was used to identify possible sources of PM$_{2.5}$ and their contributions. Based on results of this study, the current PM$_{2.5}$ levels in Tainan in spring and winter (41–49 µg m$^{-3}$) were substantially higher than the yearly average PM$_{2.5}$ air quality standards (15 µg m$^{-3}$). According to chemical composition analysis, secondary aerosols (NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$) contributed approximately 50% and 60% of PM$_{2.5}$ mass in spring and winter respectively; but were responsible about 40% by mass in summer at both Tainan and Xinying stations. From the results of CMB model, the main contribution sources to the PM$_{2.5}$ in Tainan are traffic emissions (31.5%), ammonium sulfate (25.5%), ammonium nitrate (12.5%), and crustal elements (11%). Consequently, to improve PM$_{2.5}$ of Tainan City, the priority control pollutants (or sources) are primary PM$_{2.5}$ (open burning, construction sites and road dust by vehicles), NO$_x$ (diesel vehicle emissions), and SO$_x$ (fuels).

Keywords: PM$_{2.5}$; Chemical composition; Chemical mass balance; Source apportionment; Emission controls.

INTRODUCTION

Atmospheric particulate matter (PM), has been identified as one of the major air pollutants in urban areas, which are responsible for the adverse effects on public health and the deterioration of visibility as well as influencing global climate change (Diaz, 2008; Pope, 1996; Tsai and Cheng, 1999; Choi et al., 2012; Chang et al., 2013). PM basically constitutes a heterogeneous mixture of different components with varying physiochemical properties depending on the sources as well as the meteorological conditions (Janssen et al., 2011). Additionally, commonly PM can be categorized as PM$_{2.5}$ constituting fine particulate matter with aerodynamic diameter less than 2.5 µm and PM$_{10}$ with aerodynamic diameter less than 10 µm (Lin et al., 2015).

From results of various studies PM$_{2.5}$ is reported to lead to adverse health effects such as premature deaths in children, rising hospital admissions and increasing respiratory problems in minors (Bell et al., 2007; Hemann et al., 2009; Dai et al., 2015; Lv et al., 2015). Specifically, PM can potentially cause lung inflammation and related cancer, asthma, and cardiopulmonary injury (Pope et al., 1995; Gouveia and Fletcher, 2000; Silva et al., 2010; Hung et al., 2012). Fine particles have the capacity to penetrate the gas-exchange membranes and even transfer across the circulatory system (Yang et al., 2015). Both short- and long-term exposure to PM$_{2.5}$ could lead to functional decline of organs (Rosenthal et al., 2008; Tillett, 2012).

As mentioned earlier the PM is composed of various organic and inorganic components. On the other hand, Janssen et al. (2011) and Bell et al. (2007) notes that certainly not all PM constituents are uniformly responsible in triggering health problems. Nevertheless, the chemical contents of PM$_{2.5}$ might lead to different potential health effects by toxic elements and nonspecific toxicity of...
particles (Saldarriaga-Norena et al., 2009; Wang et al., 2014; Liao et al., 2015). In terms of source differences, the combustion generated PM are more toxic compared to non-combustion particulate matter (Janssen et al., 2011). Previously, Ebisu and Bell (2012) found out that metal constituents including Al, Ca, EC, Ni, Si, Ti and Zn posed greater harm to expectant mothers compared to As, Cd, Cr, Hg, Pb, V, and ions such as Na⁺, NH₄⁺, NO₃⁻, and SO₄²⁻ as well as carbonaceous OC.

Recently, Pereira et al. (2014) reported that a 1 µg m⁻³ increase in PM₂.₅ exposure for Western Australian pregnant women resulted in a 3% risk in prelabor rupture of membranes, while in an earlier study the same research group reported that a 1 µg m⁻³ increase in PM₂.₅ exposure resulted in a 5% risk increase for Connecticut pregnant women (Pereira et al., 2013). Another study by Bell et al. (2009) shows that the relative risks for cardiovascular and respiratory hospital admissions are dependent on the species present in the PM₂.₅ such that for various regions and seasons the relative risks were higher with increasing elemental carbon, nickel and vanadium PM₂.₅ content.

Currently the World Health Organization (WHO) and several leading countries have promulgated the PM₂.₅ air quality standards for regulating the emissions and protecting the public health. In Taiwan, the new PM₂.₅ standards in the ambient air were announced in 2012, with 35 and 15 µg m⁻³ as 24-hour and annual mean standards, respectively. However, considering the complexity of pollutant contributions from the numerous air pollution indicators, the PM₂.₅ can be used as the most important surrogate to understand the complicated air quality problem (Boldo et al., 2006). A comprehensive understanding of the local PM₂.₅ properties might be the first step for improving the overall air quality.

There are three major directions to analyze the local atmospheric PM₂.₅ source apportionment. First, collect the reliable sampling or reference data to setup an emission inventory. Taiwan Emission Data System (TEDS8.1, 2010) has local, comprehensive, and latest PM₂.₅ emission data in Taiwan. Furthermore, the air quality models, such as simple Gaussian diffusion and photochemical reaction consideration models, could be employed to identify the concentration increase by various emission sources. There were several researches accomplished by this modeling process (Held et al., 2004; Karamchandani et al., 2006; Mao et al., 2006; Pekney et al., 2006; Queen and Zhang, 2008; Yu et al., 2008; Smyth et al., 2009; Wang et al., 2009; Nompengkol et al., 2012; Elangasinghe et al., 2014). The second step is to analyze the contribution characteristics of emission sources at receptor sites by using a receptor model. Chemical-Mass-Balance (CMB 8.2) is a widely used statistical regression model to analyze the contribution of each factor, emission sources or classifications (Querol et al., 2001; Chow and Watson, 2002; Watson et al., 2002; Zheng et al., 2002; Lewis et al., 2003; Marcuzzan et al., 2003; Zheng et al., 2005; Heo et al., 2009; Matawh et al., 2014). The last one is to evaluate the long-term monitoring database by receptor model such as Positive Matrix Factorization (PMF) (Maykut et al., 2003; Jaekels et al., 2007; Vecchi et al., 2008; Pandolfi et al., 2011; Sofowote et al., 2015). This kind of multi-regression model is an effective way to analyze the contribution without limitation of sources and their composition profile data; however, the sample number should be higher to improve the modeling accuracy.

In Taiwan, the major cities are all located close to the ocean for the transportation demand of economic development. Tainan is the most representative coastal city in southern Taiwan (as shown in Fig. 1), with a population of about 1.88 million. On average, the population density is 860 people km⁻² and in some areas the population density goes up to 14,072 people km⁻² in the coastal region, which is similar to those of Tokyo and New York. Additionally, the motorcycles have a high contribution to the traffic volume in Taiwan. There are approximately 1.94 million vehicles (motorcycles, cars, buses, and trucks) in Tainan City, indicating that there is more than one vehicle for each citizen. Moreover, there are over 9,000 factories around the city. Therefore, heavy traffic and industry can be easily identified as sources of emission problem. Nevertheless, the open burning is another potential emission source, since a wide agricultural region (about 7,000 acre) is located at the north of Tainan City. Additionally, the monsoon winds coming from the North and South during the dry seasons of fall and spring as well as the wet season of summer brings it share of pollution from Southeast Asia and China via long range transport.

This study seeks to elucidate the characteristics of PM₂.₅ in Tainan city by identifying the sources using CMB model, evaluating the long-term patterns to understand the seasonal variations and analyzing major constituents of PM₂.₅ such as EC, OC, water-soluble anions including Cl⁻, NO₃⁻, and SO₄²⁻ and cations including Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺ to determine their contribution to PM₂.₅ mass. Therefore the study aims to provide useful information for air quality control in such a densely populated and multi-emission city.

MATERIALS AND METHODS

Research Design

The overall research scheme is as shown in Fig. 2. To monitor the air quality for Tainan City, there are four auto-monitoring stations set up by Environmental Protection Administration (TWEPA), including Xinying, Shanhua, Annan, and Tainan from north to south, when two of them (Xinying and Tainan) monitor and collect the PM₂.₅ data (as shown in Fig. 1). Xinying site was located at more rural area and Tainan site was at urban center, which were both only 15 kilometers far from coastline. These two places were chosen to represent the atmospheric condition of a coastal city in this study. Nevertheless, the relative locations of them might indicate the pollutant transports by seasonal north or south wind in Taiwan. This research first analyzed the long-term variation of PM₂.₅ by manual and automating records. The manual one is the standard and reliable method of TWEPA; however, the auto-monitoring has begun much earlier than the manual one. Therefore, the comparison and regressions were then carried out in this study. The chemical compositions of PM₂.₅ were then analyzed from the samples.
Due to financial and resources constraints, the sampling procedure for CMB model was classified into three seasons, including spring (March 29th–April 19th, 2013), summer (June 17th–July 6th, 2013), and winter (November 27th–December 15th, 2013). On the other hand, for auto and manual data 24-hr samples were collected once per three days during the whole year of 2013. Furthermore, the soluble ions, carbon, and metal components were analyzed and discussed for identification of primary and secondary aerosol constituents. Chemical-Mass-Balance (CMB) model was finally employed to estimate the contributions from potential sources.
**Sampling Equipment and Methods**

The PM$_{2.5}$ sampling in this study followed the standard procedure (NIEA A205.11C) announced by TWEPA. Particulate samples were collected by two parallel low-volume air samplers with a flowrate of 16.7 L min$^{-1}$ ± 5% at 1 atm, which consisted of one-stage filter packs placed after very sharp cut cyclones (VSCCs, BGI) with particle size 10 and 2.5 µm each (PQ200 series). The polytetrafluoroethylene (PTFE, Teflon$^\text{a}$) fiber filter, with 46.7 mm diameter, was used to collect the accurate mass of PM$_{2.5}$ by using an electronic microbalance (METTLER TOLEDO Model XP2U) with sensitivity of ±1 µg after 24 h equilibration at 23 ± 1°C with relative humidity at 40 ± 5%. Each filter sample was pre- and post-weighed three times to ensure the variance for each one was less than 10 µg. The net mass was thus calculated by subtracting initial weight from final weight, and further divided by sampling volume (about 24 m$^3$) to obtain PM$_{2.5}$ concentration.

**Chemical Analyses for PM$_{2.5}$ Compositions**

The specifics of PM$_{2.5}$ chemical composition analyses are as follows and listed in Table 1.

**Water-Soluble Ions**

Three water-soluble anions (Cl$^-$, NO$_3^-$, and SO$_4^{2-}$) and five cations (Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$) were analyzed using Ion Chromatography (IC). For sample pretreatment, 1/2 of each collected PTFE filter was shaken for 30 minutes in a 15 mL ultrapure deionized water and then extracted ultrasonically for another 90 minutes in order to completely release the water soluble species. Anions were analyzed using a Dionex ICS-1000 with ASRS-ULTRA suppressor, Ion Pac AS4A-SC column and a Na$_2$CO$_3$/NaHCO$_3$ eluent with a flowrate of 2 mL min$^{-1}$. Cations were analyzed by a Dionex DX-900 with CSRS-ULTRA suppressor, Ion Pac CS12, using a 0.1 M sulfuric acid (H$_2$SO$_4$) eluent. The standards of anions and cations were used in different calibrations to control the quality of analysis. The concentrations in blank sample filters were below limit of detection (LOD) of each ion. Thus, no subtraction was done for data calibration.

**Metal Elements**

Analysis of metal elements, including Zn, Cd, Ni, Pb, As, Fe, Mn, Cr, Mg, Ca, Al, utilized the other 1/2 PTFE sample filter for acid digestion and instrument analysis. The digestion took place in Teflon vessels with concentrated nitric acid (HNO$_3$), hydrochloric acid (HCl), and hydrofluoric acid (HF). Determination of sample concentration was performed by high-resolution inductively coupled plasma in series with a mass spectrometer (ICP-MS, Jobin Yvon ULTIMA 2000). The calibration line were checked by standard solution with the absolute error < 10%. The recovery of the method was checked every 10 samples by an extra standard sample solution with the value in rage of 80–120%. The methodological blank sample were quantified and found less than LOD.

**Elementary and Organic Carbon**

On the other hand, the parallel quartz fiber filters were used to capture and determine the elementary carbon (EC) and organic carbon (OC) contents and determined by using Thermal Optical Reflectance (TOR) analysis, Interagency Monitoring Protection Visual Environment (IMPROVE). The TOR carbon analyzer consists of a thermal system and an optical system. The thermal system consists of a quartz tube installed inside a coiled heater. Current through the heater is controlled to approach and maintain pre-set temperatures for certain time periods. A part of the quartz filter sample is placed in the heating zone and heated to different temperatures under non-oxidizing and oxidizing atmospheres. Additionally, the optical system is composed of a He-Ne laser, a fiber optic transmitter and receiver, and a photocell. The filter deposit should face a quartz light tube, resulting to that the reflected laser intensity can be monitored throughout the analysis. The OC were volatilized from the filter in a non-oxidizing (He) condition, while the EC is not oxidized, as the temperature first increases to 580°C. Furthermore, the oxygen was added to the He when temperatures greater than 580°C, and caused the EC burns and released to the sample stream. The gas stream then passed through a heated MnO$_2$ bed, where they were oxidized to CO$_2$, and further were reduced to CH$_4$ by crossing a heated Ni catalyst. Finally, the methane is then quantified with a flame ionization detector (FID). Please refer to DRI Standard Operating Procedure for more detail information of TOR analysis (DRI, 2012).

**Chemical Mass Balance Receptor Model**

Receptor models use the chemical and physical characteristics of PM$_{2.5}$ measured at sources (reference data) and receptor (samples in this study) to both identify the presence of and to quantify the source contributions to receptor concentrations. The Chemical Mass Balance (CMB) receptor model, which was first used in the early 1970's (Hanzel and Durham, 2005), can provide a least-square

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**Table 1.** Instruments, analyses, and principles.

<table>
<thead>
<tr>
<th>Item</th>
<th>Instruments</th>
<th>Principle</th>
<th>Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass concentration</td>
<td>METTLER TOLEDO Model XP2U</td>
<td>electromagnetic induction</td>
<td>PM$_{2.5}$</td>
</tr>
<tr>
<td>Water-soluble ions</td>
<td>Dionex ICS-1000</td>
<td>Ion Chromatography</td>
<td>Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$</td>
</tr>
<tr>
<td>Metal components</td>
<td>Jobin Yvon ULTIMA 2000 (ICP)</td>
<td>Atomic mass spectrometry</td>
<td>Zn, Cd, Ni, Pb, As, Fe, Mn, Cr, Mg, Ca, Al</td>
</tr>
<tr>
<td>EC and OC</td>
<td>Thermal Optical Carbon Analyzer, DRI Model 2001A</td>
<td>Thermal desorption Optical calibration</td>
<td>Elemental carbon and organic carbon</td>
</tr>
</tbody>
</table>

EC: elementary carbon; OC: organic carbon.
solutions to sets of linear equations (Watson et al., 1994) that represents for each receptor chemical concentration as a linear sum of products of source profiles and source contributions. The model fits speciated data from a source group to corresponding receptor data (sample) and the output data consists of the amount contributed by each emitter type represented by a profile to the total mass concentration (Begum et al., 2007). According to (Watson et al., 1994) the model requires a sufficient number of samples at receptor sites, analysis of receptor sites samples for chemical species present in the source emissions, identification of potential sources and their profiles and the number of noncollinear sources be less than the number of measured species. The mass balance equation is shown as follows.

\[ C_i = \sum_{j=1}^{n} a_{ij} s_j, i = 1, 2, \ldots, n \]  

(1)

where \( C_i \) is the concentration of species \( i \) measured at the receptor site in \( \mu g \text{ m}^{-3} \)

\( a_{ij} \) is the mass fraction of species \( i \) in the profile of the source \( j \) (%)

\( n \) is the number of species

\( s_j \) is the mass concentration at the receptor site of all species assigned to the source \( j \) (\( \mu g \text{ m}^{-3} \))

The CMB model assumes that the compositions of the source emissions are constant over the sampling duration, the chemical species do not react with each other, all sources are identified, the number of sources are less than the chemical species, the source profiles are linearly independent and that any uncertainties are uncorrelated and normally distributed (Watson et al., 1994). According to “EPA-CMB8.2 User’s Manual”, all the uncertainty check, output statistics, and criteria were reported in Table 2, indicating the modeling results were statistical reliability. The PM2.5 composition fingerprints of emission sources were selected in the following priority: local studies in last 15 years in Taiwan, international study in last 10 years, and data from the Interagency Monitoring of PROtected Visual Environment (IMPROVE) and the Speciation Trends Network (STN).

**RESULTS AND DISCUSSION**

**Annual and Long-Term Variation of PM\(_{2.5}\) in Tainan City**

This study collected manual station and auto-station data, and calculate the concentration ratio to discuss the difference between manual and auto monitoring method. PM\(_{2.5}\) could be sampled by two major method, Beta-ray decay and impaction gravity. Beta-ray method could be employed for a continuous and long-term monitoring; however, the on-site monitoring has the humidity effect, leading to overestimate the PM\(_{2.5}\) concentration. Fortunately, the gravity method could avoid that problem by condition the filter in a desiccator with constant temperature, pressure, and humidity. However, this method takes time and lead to a non-continuous sampling.

For seasonal variation in 2013, the manual and auto-monitoring PM\(_{2.5}\) concentrations in two sites were derived from 24-hour sampling averages per three days (as shown in Fig. 3). There were only three months (June, July and August) fitting the TWEPA 24-hour standard (35 \( \mu g \text{ m}^{-3} \)), while the PM\(_{2.5}\) concentrations were extremely higher in two periods, January to May (averaging at 43 \( \mu g \text{ m}^{-3} \) at Tainan and 41 \( \mu g \text{ m}^{-3} \) at Xingying, respectively) and September to December (averaging at 49 \( \mu g \text{ m}^{-3} \) at Tainan and 46 \( \mu g \text{ m}^{-3} \) at Xingying, respectively). The results of auto-monitoring and manual-sampling have good linear regression with the slope of 1.01 and 1.07 at Tainan and Xingying sites, respectively, as well as R\(^2\) were both over 0.95. This indicated good agreement between each other, when the long-term monitoring data could be calibrated to the manual one (for air quality standard). Additionally, the chemical composition from manual samples could inform the PM\(_{2.5}\) conditions by monitoring data.

Additionally, from the annual data there is seasonal variation in the differences between auto (higher) and manual (lower). At Tainan station, the average difference between auto and manual results in summer was highest (45\%), while those of spring, fall and winter were 28\%, 26\% and 11\%, respectively. Similarly, at Xingying Station the highest difference was in summer 41\%, while the auto-manual differences for spring, fall and winter were 21\%, 19\% and 9\%, respectively. The differences are due to humidity and summer it is more humid, while it is less humid in winter. Furthermore, the Tainan station is nearer to the ocean compared to Xingying station, therefore the effect of humidity at Tainan station is more pronounced.

Fig. 4 shows the manual/auto ratios derived from 24-hour sampling per three days for Tainan City in 2013. For both Tainan and Xingying Stations, Fig. 4 shows three distinct periods with varying ratios. The lowest ratios occurred in the period from May to August for both stations averaging at 0.56 and 0.61 for Tainan and Xingying, respectively. The ratios for rest of the year averaged at 0.81 and 0.86, for Tainan and Xingying, respectively. The seasonal variations of humidity effect were then indicated. In summer, the

| Table 2. Output statistics and criteria of CMB model. |
|---------------------------------|-----------------|
| **Output statistics** | **Criteria** |
| Chi-square | 0.0 to 4.0 (close to 0) |
| R-square | 0.8 to 1.0 (close to 1) |
| Percent Mass Explained | 80% to 120% |
| T statistic | > 2.0 |
| Ratio of Calculated to Measured (C/M) | 0.8–1.2 (close to 1) |
| Ratio of Residual to Uncertainty (R/U) | < 2.0 to 2.0 (close to 0) |
| Degrees of Freedom | > 5 (maximized) |
Man/Auto ratios were relatively lower than those in the dry seasons, since the overestimation by Beta-ray auto-method caused by the higher humidity in summer. Fortunately, summer is always not the warning season for air pollution. Therefore, in the season with high PM$_{2.5}$ levels in Tainan could utilize the auto-method to continuous monitor the worse air quality with lower cost and man power.

Long-term trends of PM$_{2.5}$ in Tainan City are as shown on Fig. 5. The auto-data are adjusted by using aforementioned regression equation to manual state but still over the regulated standard. Fortunately, the long-term trend indicated the PM$_{2.5}$ level in Tainan City is improving year by year.
The annual mean concentrations decrease by 18.3% from 2006 to 2012, while the 24-hr mean concentrations decreased by 28.6%. The steady decline in PM$_{2.5}$ levels from 2006 to 2013 may be attributed to reduced emissions from sources owing to improving air quality control strategies.

**Chemical Compositions**

Figs. 6(a) and 6(b) show the water-soluble ion compositions of PM$_{2.5}$ at Tainan and Xinying site, respectively, during 2013. The equivalent ratios of anion/cation were 0.79–1.12, which were in the range of normal data quality (0.8–1.2%). The most dominant anions were sulfate and nitrate, while the cations were dominated by ammonium. These three ions accounted for over 70% mass of total ionic composition similar to other studies (Yao et al., 2002; Hsu et al., 2008; Chang et al., 2013; Li et al., 2013). These results are similar to those obtained by Yin et al. (2012) and Souza et al. (2014) whereby SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ were the dominants ions in PM$_{2.5}$ during a major haze even in Yong’an China. Similarly, Bell et al. (2007) identified NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ as the major species in PM$_{2.5}$ in addition to EC, OC, Si, and Na$^+$. Furthermore, the secondary inorganic ions NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ were the dominant species in PM$_{2.5}$ evaluated recently in Beijing China by Wang et al. (2015).

Seinfeld et al. (1998) determined the index “$I$” is equal to the mole ratio of ammonium and sulfate ions. Different “$I$” indicates different sulfate components in PM$_{2.5}$. Chu (2004) determined the index “$J$” as the equivalent ratio of the ammonium over sulfate and nitrate that should be balanced. NH$_4^+$ is not enough to balance all the NO$_3^-$ and SO$_4^{2-}$, while $J$ is less than 1.0. These parameters are good indicators of the acidity of the PM$_{2.5}$ (Choi et al., 2012).

\[
I = \frac{NH_4^{+}_{eq}}{SO_4^{2-}_{eq}}
\]

\[
J = \frac{NH_4^{+}_{eq}}{2 \times SO_4^{2-}_{eq} + NO_3^-_{eq}}
\]

Fig. 7 shows “$I$” and “$J$” value of this study. When “$I$” were greater than 2 in both Tainan and Xinying site, it indicated that the ammonium was capable to balance the sulfate and form ammonium sulfate. The rich ammonium might be emitted from the agricultural and livestock farming in the suburban and rural area around Tainan city. The case, $J < 1$, while $I > 2$, means the NH$_4^+$ was enough to neutralize the SO$_4^{2-}$, but could not capture all the NO$_3^-$ Therefore, the excess NO$_3^-$ could couple with the other cation, such as Na$^+$, Mg$^{2+}$, and Ca$^{2+}$. Thus, controlling NOx is better than SO$_x$ to reduce secondary PM$_{2.5}$ level.

For carbon contents, as shown on Fig. 8, the levels of OC and EC were highest in winter than summer and spring similar to observations made by Wang et al. (2015). Meanwhile, OC/EC ratio was over 2.2, the result might indicate that the main carbon component is secondary organic carbon (Jihua et al., 2009). Elemental carbon is emitted majorly from anthropogenic activities utilizing carbonaceous fuels, while organic carbon may be from both emission sources and secondary transformation of gases in the atmosphere. Therefore, OC/EC ratios help to identify the major sources of carbon in the aerosols (Choi et al., 2012; Yin et al., 2012; Souza et al., 2014). The EC/OC ratio was relatively higher in summer than in other seasons at Tainan site, which might be resulted from the stronger photosynthesis and humidity leaded to formation of the secondary aerosol in summer. Additionally, the atmospheric boundary layer was lower in winter and cause the inhibit the diffusion of primary EC, leading to a much lower EC/OC in urban area with multiple emission sources. The above phenomenon could not found in Xinying site, which has less population and primary EC emissions. Furthermore, information on OC and EC is useful for understanding the light scattering capacity of the aerosol and the visibility of the atmosphere (Souza et al., 2014).

For the overall chemical composition of PM$_{2.5}$, as shown on Fig. 9, the secondary content ratios were higher than primary ratios during the high pollution seasons, while conversely, the primary content dominated the PM$_{2.5}$ mass in the low pollution season. At both Tainan and Xinying stations, the secondary fractions increased by 12% and
Fig. 6. Water-soluble ionic composition of Tainan Station.

Fig. 7. $I$ and $J$ value at Tainan and Xinying sites.
22.7%, respectively, during the high pollution seasons. This can be attributed to higher oxidation rates experienced during high pollution episodes of NOx, SOx and Ammonium from NO2, SO2 and Ammonia, respectively. These results are similar to those reported by Yue et al. (2015) for the Pearl Delta Region whereby the seasonal average total contributions of NH4+ NO3 and SO42– to PM2.5 varied from 46.0% (summer) to 64.3% (winter).

Specifically, the highest seasonal variability was noted for NO3 with difference between the high pollution and
low pollution seasons ranging about 13.2% and 15.5%. According to Choi et al. (2012), the high NO$_3^-$ concentration in winter (high pollution season) can be explained by the shift from gas phase (nitric acid) to particle phase (ammonium nitrate) which is dependent on the temperatures and humidity.

On the other hand, SO$_4^{2-}$ had the similar trend in low temperature seasons, which could secondary formed by the SO$_2$ emitted from the stationary sources in distance. Actually, Jihua identifies SO$_4^{2-}$ and NO$_3^-$ as secondary aerosol arising from atmospheric transformations from SO$_2$ and NO$_x$, respectively (Jihua et al., 2009). Additionally, the ratio of NO$_3^-$/SO$_4^{2-}$ is a good indicator of the contribution of sulfur and nitrogen by mobile and stationary sources (Souza et al., 2014).

The above results indicate that a most probable direction for more effective PM$_{2.5}$ control should be seasonal and more targeted to constituents with high contributions in different seasons since Yin et al. (2012) noted that the ions and the carbonaceous matter including EC and OC are majorly responsible for PM$_{2.5}$-related health problems.

**CMB Source Apportionment**

Fig. 10 displays the simulation result of CMB model. The main contributions on PM$_{2.5}$ were ammonium sulfate and ammonium nitrate, which are secondary PM, and traffic, which is primary aerosol. The sulfate and nitrate in PM$_{2.5}$ were mostly emitted from the stationary sources and diesel vehicles. Crustal elements, which could be considered as the background components were varied between different sampling sites. Notably, the traffic contribution is 32~50% in the high pollution season, especially at the urban area (Tainan site). Seasonal variations were evident whereby open burning, secondary organic carbon and suspended dust were highest contributors of PM$_{2.5}$ in summer. On the other hand, the sea salts contributed less than 10% of atmospheric PM$_{2.5}$ since the aforementioned multiple emissions. The secondary NO$_x$, Secondary SO$_4$ and traffic were dominant sources in spring and winter. As mentioned earlier, especially for scenarios where $J < 1$ and while $I > 2$, the best control strategies would be to control the secondary contributions and NO$_x$ emissions from traffic.

**CONCLUSIONS**

This study was carried out to elucidate the characteristics of PM$_{2.5}$ in a coastal city of Tainan, Taiwan. The results obtained in the present study for PM$_{2.5}$ are useful for the policy makers in evaluating and formulating the best control strategies concerning air quality measures using PM$_{2.5}$ as a surrogate for the complex air pollution problem.
The currents PM$_{2.5}$ levels in Tainan City during low temperature seasons were substantially higher than the yearly average PM$_{2.5}$ Air Quality Standard of 15 µg m$^{-3}$. Specifically, from January to May the average concentrations at Tainan and Xinying were 43 µg m$^{-3}$ and 41 µg m$^{-3}$, respectively, while from September to December the PM$_{2.5}$ averaging at 49 µg m$^{-3}$ at Tainan and 46 µg m$^{-3}$ at Xinying, respectively.

The results of auto-monitoring and manual-sampling showed good linear regression. Comparison of the daily monitoring data of PM$_{2.5}$ from auto and manual methods showed that auto data was higher than manual data due to onsite humidity effect. At Tainan station, the average difference between auto and manual results in summer was highest (45%), while those of spring, fall and winter were 28%, 26% and 11%, respectively. Similarly, at Xinying Station, the highest difference was in summer 41%, while the auto-manual differences for spring, fall and winter were 21%, 19% and 9%, respectively.

According to overall chemical composition analysis, there were about 50% and 60% of secondary aerosols (with high SO$_4^{2-}$ content) in Tainan station and Xinying station, respectively in spring and winter; meanwhile, there were only 40% of secondary PM$_{2.5}$ for Tainan and Xinying station in summer.

Based on the simulated results of CMB, I and J values, the main contribution sources are Traffic emissions (31.5%), Ammonium sulfate ((NH$_4$)$_2$SO$_4$) (25.5%), Ammonium nitrate (NH$_4$NO$_3$) (12.5%), and crustal elements (11%). This study indicates that a city with high population density would lead to a higher PM$_{2.5}$ level contributed by traffic sources even located near to the coastline. The sea salt effect does not dominate the PM$_{2.5}$ compositions anymore. The sea salt effect does not dominate the PM$_{2.5}$ compositions anymore. Nevertheless, open burning provides part of the PM$_{2.5}$ emissions in this area. Consequently, the priority control pollutants (or sources) are primary PM$_{2.5}$ (open burning, construction sites and road dust by vehicles), NO$_x$ (diesel vehicle emissions), and SO$_x$ (fuels).

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