Particulate Composition Characteristics under Different Ambient Air Quality Conditions

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Particulate Composition Characteristics under Different Ambient Air Quality Conditions

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ABSTRACT

Particulate compositions including elemental carbon (EC), organic carbon (OC), water-soluble ionic species and elemental compositions were investigated during the period from 2004 to 2006 in southern Taiwan. The correlation between the pollutant standard index (PSI) of ambient air quality and the various particle compositions was also addressed in this study. PSI revealed a correlation with fine (r=0.74) and coarse (r=0.80) particulate matter (PM). PSI manifested a significant correlation to the amount of analyzed ionic species (r about 0.80) in coarse and fine particles and a moderate correlation to carbon content (r=0.63) in fine particles; however, it showed no correlation to elemental content. While the ambient air quality ranged from good to moderate, the ionic species including Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+} and Ca^{2+} increased significantly (1.5-3.7 times increase for Daliao and1.8-6.9 times increase for Tzouying) in coarse particulate matter. For fine particles, NO_3^-, SO_4^{2-}, NH_4^+, and K^+ also increased significantly (1.3-2.4 times for Daliao and 2.8-9.6 times for Tzouying) when the air

quality went from good to moderate. For meteorological parameters, temperature evidenced a slightly negative correlation with PM concentration and PSI value, which implied a high PM concentration in the low-temperature condition. This reflects the high frequency of PM episodes in winter and spring in southern Taiwan. In addition, the mixing height increase from 980 to 1450 m corresponds to the air quality condition changing from unhealthy to good.

Keywords: Pollutant standard index (PSI), water-soluble ionic species, elemental carbon, organic carbon, elemental composition

IMPLICATIONS

The study investigates particulate compositions including elemental carbon (EC), organic carbon (OC), water-soluble ionic species and elemental compositions during the period from 2004 to 2006 in southern Taiwan. The relationship between the pollutant standard index (PSI) of ambient air quality and the various particle compositions was also addressed in this work. While the ambient air quality deteriorated, the ionic species including Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+} and Ca^{2+} increased significantly in coarse particulate matter and NO_3^-, SO_4^{2-}, NH_4^+, and K^+ also increased significantly in fine particles. In addition, the mixing height decreased corresponds to the poor air quality conditions.

INTRODUCTION

Numerous epidemiological studies have been published on the health risks associated with PM that is 10 μm or less in diameter[1]. Some studies have also shown an association between coarse PM and cardiovascular and respiratory disease [2-5]. Furthermore, a few studies have associated particles with inflammatory responses in susceptible people [6-8]. Therefore, the effects of PM on human health are important issues for air quality management.

Many studies have shown that EC, OC, ionic species (i.e., SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Na^+ etc.), crustal elements, and water are the major constituents in particulate matter [9-12]. Sulfate, nitrate and ammonium are the common components of secondary inorganic aerosols in the atmosphere, and the particles are formed via the reactions of the precursors of SO_2, NOx (NO and NO_2), and NH_3 in the atmosphere. In addition, OC and EC particles are released from the incomplete combustion of carbonaceous fuels. Elemental carbon is a primary pollutant, emitted directly during the combustion processes. Organic carbon comprises both primary and secondary carbons; primary organic carbon is emitted in the particulate phase, and secondary organic carbon is formed via gas-to-particle processes of volatile organic compounds in the atmosphere. Trace elements are important fingerprints to identify the emission sources of particulate matter. Therefore, the characteristics of particulate compositions are important information in implementing control measures for air quality management.

Furthermore, Asia dust storms come from the Loess Plateau, which affects air quality, health and visibility in Taiwan. The average PSI value in the Kaohsiung-Pintung air basins was between 64 and 68 during the period from 1998-2007, and the percentage of episode days of air quality ranged from 6.7-13.6%. Particle-caused ambient air quality episodes ranged from 28-42% during 2004-2008, except for ozone[13]. Therefore, PM is one of the important issues of air quality management in the area. Few studies have

focused on the chemical composition characteristics following ambient air quality variation. Therefore, work is needed to evaluate the detailed chemical compositions of coarse and fine particles under different ambient air quality conditions to enable implementation of PM control measures in the future.

Kaohsiung is an urban and industrial metropolitan city in southern Taiwan, and it also is the second largest city in the country. According to the emission inventory issued by the Taiwan Environmental Protection Administration (TEPA) in 2006[14], emissions from the Kaohsiung-Pingtung air basin contributed to over 20% of the total air pollutant emissions in Taiwan. Of the total emissions in Taiwan, 20% of the $PM_{2.5}$ (34 thousand ton yr^{-1}), 18% of the non-methane hydrocarbon (157 thousand ton yr^{-1}), 35% of the SOx (66 thousand ton yr^{-1}), and 26% of the NOx (164 thousand ton yr^{-1}) were emitted in the Kaohsiung-Pingtung area. Seventy-eight percent of the air pollutants was emitted from stationary sources (power plant, oil refinery plant, iron and steel industry, petrochemical industry and others) and 22% from mobile sources (motorcycles, gasoline vehicles, diesel vehicles and off-road vehicles). The Kaohsiung-Pingtung area, a mix of industrial and urban uses, contains over 50% of the traditional and heavy industries in Taiwan[14].

The environmental loading of air pollutants in Kaohsiung was nearly two times higher than that in other air basins in Taiwan[14]. Although there have been many control programs implemented in the air basin of Kaohsiung to resolve the air quality problem, it still had the highest frequency of air quality episodes (pollutant standard index, PSI > 100) in Taiwan during the past ten years. Therefore, detailed ambient air pollutant composition is important baseline information for the formulation of effective control measures for ambient air quality improvement. But few studies present comprehensive and detailed information about air pollutants (i.e., particulate compositions and gas pollutants) and meteorological effects related to the air quality indicator (i.e., pollutant

standard index). Therefore, the study provides an integrated insight to investigate the relationships among the variation of air pollutants, meteorological parameters and PSI values.

In this study, coarse and fine particulate compositions, including elemental carbon, organic carbon, water-soluble ionic species and elemental compositions were investigated from 2004 to 2006 in southern Taiwan. In addition, the correlation between the PSI of ambient air quality and the various particle compositions was addressed in this study. It is useful to understand the relationship between chemical composition and ambient air quality deterioration in this air basin.

EXPERIMENTAL METHODS

Sampling Location

Two stations of the Taiwan Air Quality Monitoring Network (which was established by the TEPA in 1993), Daliao and Tzouying, were chosen as sampling sites for the experiment (**Figure 1**). Tzouying station is located in Kaohsiung City, and Daliao station is located in Kaohsiung County. Both stations are near industrial districts. Kaohsiung City had a population of 1.5 million in 2006 within approximately 154 km^2. Kaohsiung County's population is 1.2 million within an area of approximately 2793 km^2. Tzouying and Daliao have population densities of 9200 and 1500 people km^{-2}, respectively. Daliao is 12 km from the coastline, and it is near a rural-industrial complex area with various agricultural activities and heavy industrial districts--i.e., Da-Fa (less than 0.3 km east, a mixed industrial area, i.e., metal industry, scrap metal recovery, chemical industry, etc.), Lin-Hai (approximately 6.5 km west, iron and steel industry, petrochemical industry, etc.) and Lin-Yuan (approximately 4.5 km southwest, the main petrochemical industrial

district in Taiwan). Conversely, Tzouying is 3.3 km from the western coastline, and the major pollution sources in the region include the largest oil refinery plant in Taiwan (3.5 km north of the station), the electronics industry in the Kaohsiung Export Processing Zone (5.3 km north of the station), cement plants (2-3 km north of the station), and the Mass Rapid Transit construction zone (approximately 0.6 km north of the station).

The experiment was conducted during the periods from 22 October to 3 November 2004, 25 January to 5 February 2005, 31 May to 5 June 2005, and 16-21 January 2006. At each site, two, 12-h (8a-8p and 8p-8a) particulate samples were taken per day and average to get 24-h average data. The same sampling schedule was followed for the two sites in this study.

The meteorological stations were also located in the sample building of the air quality monitoring station. The prevailing wind direction during the sampling periods was WNW and NW in winter and S in summer at both sampling sites. Summer and autumn comprise the rainy season (May to September), and the average rainfall and wind speed were about 1900 mm yr^{-1} and 2.4 m s^{-1}, respectively, in the period from 1981 to 2010 in the Kaohsiung area. The wind direction is affected by the land-sea breeze, monsoons, and topography.

Particulate Matter Sampling Method

Ambient PM was taken by a dichotomous sampler (Graseby Adenson G 241, USA) equipped with an inlet of 10 μm cutpoint. PM below 10 μm aerodynamic diameter (PM_{10}) was divided into two size fractions upon entering the sampler using a virtual impactor with a 2.5 μm cutpoint. The two size fractions were classified as a coarse fraction (2.5 μm < aerodynamic diameter < 10 μm, $PM_{10-2.5}$) and a fine fraction (aerodynamic diameter < 2.5 μm, $PM_{2.5}$). The total flow rate of the dichotomous

sampler was 16.7 l min^{-1}. It was split into 1.67 and 15 l min^{-1} for coarse and fine flow, respectively.

PM was collected using 37-mm quartz fiber filters (Pallflex 2500 QAT-UP, 37 mm) supported by polyolefin rings. Filters were pre-treated before sampling at 900^{o}C for 3 h to reduce the background level of carbonaceous species and other volatile species in the filter and to reduce the artifact effect of the filter. The pre-treated filters were placed in clean polyethylene Petri dishes; the dishes were then wrapped with Teflon tape and aluminum foil and stored in a freezer until field sampling. The weight of the filters and the collected particulate mass concentration was measured by a microbalance (Mettler Toledo, MX5) with a reading of 1 μg. The precision of the quartz filter is ± 10 μg under the condition of 40% relative humidity at 25^{o}C. Prior to weighing, the filters were conditioned at 25±2^{o}C and 40±5% relative humidity for 48 h. Filter samples were stored in a refrigerator at 4^{o}C before chemical analysis to limit losses of volatile components. In addition, the quartz filter was preheated to reduce interference, and blank samples and other quality assurance and quality control samples were also analyzed in this study to minimize the artifact effect of the filter.

Chemical Analysis

Three-fourths of the PM filter was used for chemical analysis, including one-fourth each for ionic species, elemental analysis and carbon analysis (one-eighth of the filter for TC and one-eighth of the filter for EC). The remaining one-fourth of the PM filter was storage for duplicate analysis. Generally, the weighted filter samples were stored in a refrigerator at 4^{o}C, and the cutting and analysis procedures were carried out within 72 h to avoid the artificial loss of the samples, i.e. NH_4^+, organic carbon, etc.

1. Ionic species

193 The collected aerosol filters were ultrasonically extracted for 2 hr into 20 ml of
194 deionized, distilled water and filtered through a Teflon filter of 4.5 μm nominal pore size.
195 Ion chromatography (Dionex, 120) was used to analyze the concentration of anions (Br^-,
196 F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}). The separation of
197 anions was accomplished using an IonPac AS 12A (Dionex, Corp) (4×200 mm)
198 analytical column, an AG 14 guard column, with a 10 μl sample loop, and an anion
199 self-regenerating suppressor-ultra. A solution of 2.7 mM Na_2CO_3/0.3 mM $NaHCO_3$ was
200 used as an effluent at a flow rate of 1.5 ml min^{-1}. The separation of cations was
201 accomplished using an IonPac CS 12A (Dionex, Corp) (4×250 mm) analytical column,
202 and a CG 14 guard column (Dionex, Corp), with a 50 μl sample loop, and a cation
203 self-regenerating suppressor-ultra. A solution of 20 mM methanesulfonic acid was used
204 as the eluent at a flow rate of 1 ml min^{-1}. Applying this analysis method, the detection
205 limits of analyzed ionic species were in the range of 0.005 (Mg^{2+})-0.010 (NO_2^-) μg m^{-3}. In
206 addition, the recoveries of ionic species were between 87 (Na^+) and108 %(NH_4^+).

207 2. Element analysis

208 One-fourth of the particulate filter sample was mixed with a 20-ml acid mixture
209 (HNO_3:$HClO_4$:HF = 5:3:2, v/v) in a Teflon-lined closed-vessel and placed in a
210 high-pressure digestion oven at 170^oC for 5 hr. The digested acid mixture was analyzed
211 to determine the trace elements. A Perkin Elmer OPTIMA 3000 ICP-AES (inductively
212 coupled plasma atomic emission spectrometer) was used to determine the Al, Ca, Fe, K,
213 Mg, Na, S and Zn concentrations. Additionally, a SCIEX Elan Model 5000 ICP-MS
214 manufactured by Perkin-Elmer was employed to determine the As, Ba, Cd, Cr, Cu, Mn,
215 Ni, Pb, Sb, and V fractions.

216 To validate the digestion method, the NIST Standard Reference Material, SRM 1648,
217 was used to simulate the particles. About 0.1 mg of SRM 1648, which approximates the

composition of the road dust particulate matter, was used to examine the accuracy and reliability of the digestion method. Al, As, Ba, Co, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Sb, Se, V, and Zn were recovered in the acceptable range (recovery: 88-105%); however, Cr was recovered at a rate of only 63%. The major error in Cr determination was due to the Cr loss incurred through volatilization during sample digestion. Many investigators have reported the volatility effect on Cr(VI), e.g., CrO_2Cl_2 (b.p. 117^oC) formation from the digestion and evaporation process. Interference problems due to argon gas, filter media, and/or acid-derived background ions, specifically, $^{40}Ar^{12}C^+$, $^{38}Ar^{14}N^+$, $^{35}Cl^{16}OH^+$, and $^{35}Cl^{17}O^+$ ions, inhibit detection of the $^{52}Cr^+$ isotope[15].

3. Organic and elemental carbon

Particulate samples that were intended for carbon analysis were collected on quartz-fiber filters that had previously been heated in air at 900^oC for 3 hr to lower their carbon blank level. The particulate filter sample was stored below 4^oC until analysis. Total carbon (TC) and elemental carbon (EC) were measured with a C/H/N elemental analyzer (Carlo Erba EA 1110, Corlo Erba Instruments). The procedure performed in this study to determine particulate carbon content is similar to the method described by Cachier et al. (1989)[16]. The filters were cut after sampling, and one-eighth of the filter was taken for analysis. The samples were heated in advance in a 340^oC oven for 100 min to expel the organic carbon (OC) content, then fed into the elemental analyzer to obtain the elemental carbon content. Another one-eighth sample was fed directly into the elemental analyzer without pre-treatment to obtain the TC concentration. The OC value was taken as the difference between TC and EC.

RESULTS AND DISCUSSION

Particulate Mass Concentration

Based on the U.S. EPA classification[17], the ambient air quality was divided into

three groups for different PSI ranges: good (0-50), moderate (51-100), and unhealthy for sensitive groups (101-150) in this study.

The PM concentration was 17±14 μg m^{-3} for coarse particles and 40±26 μg m^{-3} for fine particles under the PSI value of 36±5 at Daliao. For moderate ambient air quality, the coarse particles were 32±9 μg m^{-3}, and the fine particles were 57±21 μg m^{-3}. In the unhealthy ambient air condition, the coarse and fine particles were 51±7 and 95±19 μg m^{-3}, respectively, at Daliao.

At Tzouying, the coarse particle concentrations were 14±2 μg m^{-3}, and the fine particle concentrations were 21±5 μg m^{-3} when the ambient air quality was good. For moderate ambient air quality, the coarse and fine particulate matter concentrations were 31±9 and 45±26 μg m^{-3}, respectively. Under unhealthy air quality conditions, the particulate concentration was high, reaching 46±13 μg m^{-3} for coarse particles and 78±22 μg/m^3 for fine particles.

Based on Taiwan's emission data system, the emission sources of PM_{10} were 40% by re-suspended particles of on-road vehicles, 32% by industry, 10% by construction, 5% by diesel vehicles, and the rest by others (open burning, surface erosion, etc.) in the Kaohsiung-Pingtung air basin for primary particulate matter[14].

In addition, the PSI revealed a correlation with fine (r=0.74) and coarse (r=0.80) particulate matter. Therefore, the increase in fine and coarse particulate matter could reflect deterioration of the ambient air quality (**Figure 2a**). A comparison of the PM concentration did not yield a statistically significant difference between the two stations. But based on the average concentration, the PM mass concentration was high at Daliao. In addition, the particulate mass concentration revealed a higher increase in fine particles than in coarse particles, although the coarse particulate mass also increased during the ambient air quality deterioration. The PM concentration increase could be attributed to the variation of emission sources and meteorological parameters. The effects of

meteorological parameters on air quality will be discussed in detail later.

Chemical Composition

PSI revealed a correlation (r=0.77) to the amount of analyzed ionic species of coarse particles (**Figure 2b**) but did not evidence a good correlation to element content (r= 0.14-0.48) (**Figure 2c**) or total carbon content (r=0.41-0.63) (**Figure 2d**). In addition, the PSI evidenced significant correlation with the amount of analyzed ionic species (r=0.77-0.82) and a moderate correlation with carbon content (r=0.63) in the fine particles, but the trend of element content did not reflect the PSI value variation. Therefore, the ionic species increase in coarse and fine particles and the carbon content increase in fine particles is indicative of air quality deterioration. The PSI values correlated with ionic species and carbon content in fine particles, which reflects the fact that photochemical reaction is an important mechanism for transitioning pollutants from the gas to the particulate phase.

1. Carbon

Carbon content was 20-30% and 23-27% of particulate mass for coarse and fine particles, respectively, at Daliao. For Tzouying, carbon contributed 24-32% of coarse particulate mass and 25-37% of fine particulate mass (**Figure 3**). The correlation between the variation in carbon content and that of ambient air quality conditions was insignificant.

In good and moderate air quality conditions, the EC and OC content increased significantly (50-100%), while the PSI changed from good to moderate. But the carbon content increase was insignificant in the air quality change from moderate to unhealthy. Generally, organic carbon in particulate organic matter is emitted directly into the atmosphere (primary pollutant) or formed by the condensation of products generated via photooxidation of volatile organic compounds (secondary pollutant)[18]. Traffic sources, combustion sources, and photochemical reactions were the major sources of organic

carbon reported by Buzcu-Guven et al. (2007)[19], and similar results were found in southern Taiwan[20]. The average hydrocarbon concentration (precursor of secondary organic aerosol) of nine air quality monitoring stations in the vicinity of both particle sampling stations was 2.08, 2.66 and 2.78 ppm for PSI<50, 50<PSI<100, and PSI>100, respectively. The precursor concentration would be one of the important reasons for the insignificant carbon content increase, when the air quality deteriorated from moderate to unhealthy, but further study is necessary to clarify why the carbon content increase was insignificantly in the air quality change from moderate to unhealthy. Future work should address such issues as the intensity of solar radiation and the reaction characteristics of aerosol compositions under different air quality conditions.

OC increased significantly during air quality deterioration, especially in the fine particles. But the trend of OC increase did not completely reflect the deterioration of ambient air quality. Generally, secondary organic aerosols in the ambient atmosphere are produced by ozone or radical-initiated reactions of hydrocarbon precursors, generating nonvolatile and semivolatile organic species that undergo nucleation reactions to form new particles or condense onto the pre-existing particulate matter[21]. Therefore, low transport flux (based on the low wind speed and low mixing height) associated with the air quality deterioration could cause the precursor accumulation of organic carbon or enhance organic carbon formation in the particles.

2. Element

Figure 4 shows the element composition in coarse and fine particulate matter at Daliao and Tzouying. The element fraction in coarse and fine particulate mass was not significantly affected by the variation of ambient air quality at either station. In the coarse particles, the Al and Fe increased significantly, and Ca, K and Mg increased somewhat, but the other elements did not change significantly with air quality deterioration.

Analysis of the element composition of coarse and fine particulate matter showed that most of the elements did not significantly increase/decrease following the unhealthy/good ambient air quality changes. But the element content in coarse particles increased when the air quality deteriorated at both stations, especially Al and Fe, which could come from the soil or road dust re-suspension. About 10% of the high coarse particle content could be attributed to low wind speed (WS< 1.2 m s^{-1}), and 10% occurred under the low mixing height condition (MH< 850 m). About 80% could not be clearly identified; composite meteorological parameters could be associated with high coarse particle level, and more data should be analyzed to assess this possibility.

In addition, an increase in sulfur content in fine particles could reflect poor air quality conditions, with the sulfur coming from oil combustion, i.e., motor vehicles and boiler combustion and manufacturing processes of industry. V increased in the fine particles during air quality deterioration at both stations; these elements could be emitted from an oil refinery plant or coal combustion, as the important heavy industries of Taiwan are associated with high emission loading. Fe, Ni and Zn levels increased during the poor air quality at Tzouying, which may be attributed to motor vehicles, a metal refinery plant, or heavy fuel oil and wood-fired boilers in the area [22].

3. Ionic species

Table 1 shows the ionic species content in coarse and fine particulate matter at Daliao and Tzouying. Ionic species content ranged from 34 to 50% for coarse particles and from 42 to 56% for fine particles, which corresponded to PSI values from 36 to 113 at Daliao (**Figure 3a and b**). At Tzouying, the ionic species content ranged from 30 to 45% for coarse particles and from 21 to 62% for fine particles, corresponding to PSI values from 34 to 111 (**Figures 3c and d**). The ionic species content fraction increased with the increase of PSI value at both stations. In addition, the mass concentration of

ionic species in the particles also increased with the increase of PSI value.

Table 1 shows the results of some studies in southern Taiwan[20, 23]. The PM concentration and the level ionic species were in the range of moderate to unhealthy air quality compared to this study. Sulfate, nitrate, ammonium, chloride ion and sodium ion were the major water-soluble species in PM constituents in both of these studies.

When the ambient air quality went from good to moderate, the ionic species including Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+} and Ca^{2+} increased significantly (an increase of 1.5-3.7 times for Daliao and1.8-6.9 times for Tzouying) in the coarse particulate matter. Furthermore, when the ambient air quality went from moderate to unhealthy, NO_3^-, SO_4^{2-} and NH_4^+ increased (2.2-4.0 times for Daliao and 1.7-5.1 times for Tzouying) in the coarse particles.

For fine particles, the NO_3^-, SO_4^{2-}, NH_4^+, and K^+ increased significantly (1.3-2.4 times for Daliao and 2.8-9.6 times for Tzouying) when the air quality went from good to moderate. When the ambient air quality went from moderate to unhealthy, the ionic species including Cl^-, NO_3^-, SO_4^{2-}, $NH_4^+$and K^+ increased significantly in the fine particulate matter (an increase of 1.4-2.6 times for Daliao and 2.0-3.0 times for Tzouying).

In addition, the PSI values revealed a correlation to ammonium (r=0.78), sulfate (r=0.74), nitrate (r=0.74), and potassium ions (0.71), but not with the other species, in the fine particles. Based on this study, the increase of ionic species content in the PM could be the main factor contributing to of ambient air quality deterioration in the air basin.

According to the data collected from monitoring stations in Taiwan, the SO_2/NO_2 concentrations of Daliao were 6±4/12±4, 11±4/27±9, and 11±10/45±11 ppb for PSI<50, 50<PSI<100 and PSI>100, respectively. In Daliao, an increase of SO_2 was observed when the air quality conditions went from healthy to moderate, and an increase in NO_2 was observed when the air quality deteriorated, with a direct correspondence between the

increase in NO_2 concentration and the increase in PSI value. In addition, the SO_2/NOx concentrations were 6±2/21±5, 8±3/31±7, and 10±3/41±4 ppb for PSI<50, 50<PSI<100 and PSI>100, respectively at Tzouying. In Tzouying, the slight increase of SO_2 was observed for different PSI conditions, and the increase of NO_2 was significant for different air quality conditions. The increase of ionic species (i.e. sulfate, nitrate etc.) in particulate matter was attributed partially to the increase of gaseous precursors.

Relationship of Particulate Compositions

1. Coarse particle

For coarse particles, ammonium evidenced a high correlation to sulfate (r=0.95) and nitrate (r=0.80); sulfate also correlated highly with nitrate (r=0.81) (**Figure 5a**). Over 77% of the analyzed anions were nitrate and sulfate. For the equivalent molar ratio (or neutralization ratio, NR[24]) of $\frac{[NH_4^+]}{[NO_3^-]+nss[SO_4^{2-}]}$ (where $[NH_4^+]$ is μeq m^{-3}, $[NO_3^-]$ is μeq m^{-3} and nss $[SO_4^{2-}]$ is non-sea-salt sulfate μeq m^{-3})[25] was 0.39, indicating that other cationic species, i.e., Na^+, K^+, Ca^{2+} and Mg^{2+}, are also important fractions in coarse particles for ionic balance.

In addition, the high correlation (r=0.91) between Mn and Ni indicated that the sources of the elements were re-suspended road dust mixed with traffic-related (tire tread, brake-drum abrasion, fuel additives, etc.) or industrial-related (i.e., iron and steel plants) particles [26-30]. In addition, a slight correlation (r=0.60) was noted between As and V, which could be emitted from coal and residual oil combustion[9, 31-32] in the region and mixed with coarse particulate matter.

2. Fine particle

Ammonium revealed a high correlation to nitrate (r=0.92), and sulfate correlated to ammonium (r=0.91) and potassium (r=0.87) in the fine particles (**Figure 5b** and **c**).

About 90% of the anions were nitrate and sulfate in fine particulate matter. In the winter, the equivalent molar ratio of $\frac{[NH_4^+]}{[NO_3^-]+nss[SO_4^{2-}]}$ was 0.97±0.12; but the $\frac{[NH_4^+]}{[NO_3^-]+nss[SO_4^{2-}]}$ was 0.52±0.22 in summer. An NR of unity, or higher, indicates the presence of sulfate and nitrate predominantly as their ammonium salts, NH_4NO_3 and $(NH_4)_2SO_4$ could be the main species in the winter, based on the equivalent molar ratio of $[NH_4^+]$, $[NO_3^-]$ and $[SO_4^{2-}]$. In contrast, lower values of NR imply the presence of acidic sulfate and nitrate, which are then neutralized by Na^+, Ca^{2+}, Mg^{2+}, etc. [33]. In addition, the high temperature in the summer could enhance the volatilization of ammonium nitrate and reduce the NR ratio, but chemical reactions in the atmosphere could also account for this effect, so the high-temperature effect cannot be definitively identified as the cause for the shift in the ratio [34]. Other cationic species could be more important in summer than in winter for ionic balance.

In addition, the Mg^{2+} correlated to Ca^{2+} (r=0.82), which would imply that these ionic species come from the same sources, i.e., soil or road dust. The element composition of As correlated to V (r=0.91), which could imply that they come from the same sources, i.e., oil refinery industry or oil combustion [35-36]. Mn correlated to Ni (r=0.84) in fine particulate matter, which could be emitted from the steel industry[37] or gasoline[38].

Meteorological Effect

At PSI less than 50, the temperature, wind speed (WS) and relative humidity (RH) were 27.0±0.9^{o}C, 1.6±0.4 m/s, and 86±3%, respectively. In addition, the temperature was 24.3±2.8/22.8±2.2^{o}C, WS was 1.8±0.8/1.5±0.4 m/s, and RH was 71±5/73±6% for 50<PSI<100/PSI>100, respectively. There was insignificant WS different for the three

423 grades of PSI; however, relatively low temperature and low RH were observed at high
424 PSI value conditions.

425 Generally, the WS, temperature, and RH did not reveal a significant relationship
426 with PM concentration and their compositions. However, the temperature revealed a
427 slightly negative correlation to PM concentration and PSI value, which implied a high
428 PM concentration in the low-temperature condition (in the winter and spring). This
429 reflects the high frequency of PM episodes in the winter and spring in southern Taiwan.

430 The mixing height was measured by the Central Weather Bureau of Taiwan. For
431 the mixing height effect on the PSI value, results indicated that high mixing height
432 (1450±330 m) reflected good ambient air quality (PSI< 50). But at moderate and
433 unhealthy ambient air quality conditions, there was no significant difference in the
434 mixing height (1020±280 and 980±220 m, respectively). The overall conclusion here is
435 that the mixing height was about 40-50% higher under good ambient air quality than
436 when the ambient air quality was moderate or unhealthy. Low mixing height and low
437 wind speed revealed low transport flux, which could be one of the important causes of
438 ambient air quality deterioration.

439 **Figure 6** shows the wind speed and direction under the different PSI conditions.
440 At Daliao station, the wind directions were primarily northeast (NE), south (S) and
441 northwest (NW); the emissions from traffic and from the Da-Fa and Lin-Yuan industrial
442 districts could be the main sources of pollution when the PSI <50. For 50<PSI<100, the
443 winds were from NW and NE, and traffic and Da-Fa industrial district were the main
444 sources of air pollution. When the PSI>100, the wind was coming mainly from
445 west-southwest (WSW), SW and NW, and the traffic and the Lin-Hai, Lin Yuan and
446 Da-Fa industrial districts were the major sources of air pollution. These conditions were
447 associated with low mixing height.

448 For Tzouying station, winds from the southeast (SE) indicated that the air

449 pollution was coming from downtown of Kaohsiung city and associated with high mixing
450 height when the PSI<50. During the high PSI conditions, NW and WNW were the main
451 wind directions, suggesting that the air pollution was being transported from sea
452 (long-distance transport from Mainland China or local circulation-land sea breeze could
453 affect the local air pollution).
454
455 **CONCLUSIONS**
456 This study investigated the chemical composition characteristics as they relate to the
457 ambient air quality in this air basin of southern Taiwan. Results indicated that fine and
458 coarse particulate matter manifested a high correlation with PSI value. PSI was
459 correlated with the amount of analyzed ionic species of coarse and fine particles but was
460 not well correlated with element content and total carbon content. Ionic species
461 including Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+} and Ca^{2+} increased significantly in coarse
462 particulate matter, and NO_3^-, SO_4^{2-}, NH_4^+, and K^+ increased in fine particles.
463 Ammonium was highly correlated with sulfate and nitrate, and sulfate was also highly
464 correlated with nitrate in coarse and fine particles. Based on the molar equivalent ratio
465 of $\frac{[NH_4^+]}{[NO_3^-]+nss[SO_4^{2-}]}$, other cationic species, i.e., Na^+, K^+, Ca^{2+} and Mg^{2+} are also
466 important fractions in coarse particles for ionic balance. But ammonium was the most
467 important cationic species in fine particles. Wind speed and relative humidity did not
468 significantly affect the PSI value, but the temperature manifested a slight negative
469 correlation with the high episode frequency in the winter and spring seasons in southern
470 Taiwan. Furthermore, the mixing height was about 40-50% higher under good ambient
471 air quality than when the ambient air quality was moderate or unhealthy. The study
472 successfully determines the gas pollutants, particulate compositions and meteorological
473 effects under various air quality conditions. However, while source fingerprints and

source contributions are important issues in air quality management, it is a limitation of this study that we have not provided detailed fingerprints of sources or identified source contribution to air pollutants.

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