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Characteristics of Water-Soluble Ionic Species in Fine (PM_{2.5}) and Coarse Particulate Matter (PM_{10-2.5}) in Kaohsiung, Southern Taiwan

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ABSTRACT

Eleven ionic species and fine and coarse particle mass concentrations of fine (PM_{2.5}) and coarse (PM_{10-2.5}) particulate matter were investigated in Kaohsiung, southern Taiwan. The PM_{2.5} and PM_{10-2.5} particulate concentrations were 49–64 and 34–37 $\mu\text{g}\cdot\text{m}^{-3}$, respectively. Fifty-five to 64% of the particulate matter less than 10 μm in aerodynamic diameter (PM₁₀) mass was attributed to the PM_{2.5}. PM_{2.5} concentrations at Daliao (a rural and industrial complex area) were higher than at Tzuoying (an urban and industrial complex area). Ionic species contributed 45–53% and 42–45% of PM_{2.5} and PM₁₀, respectively. Potassium ions (K⁺), sulfate (SO₄²⁻), and ammonium (NH₄⁺) were predominant in PM_{2.5}, whereas sodium, calcium, and magnesium ions were foremost in PM_{10-2.5}. Nitrate (NO₃⁻) existed in both the PM_{2.5} and PM_{10-2.5}. Chloride (Cl⁻), NO₃⁻, and NH₄⁺ concentrations were higher at night than during the day, and they were easily transferred into the gas phase by photochemical reactions and temperature-induced volatilization. The NH₄⁺/SO₄²⁻ ratios were 2.6 and 2.5 at Daliao and

Tzuoying, respectively, which indicated that both sampling sites were rich in NH₄⁺. Therefore, ammonium nitrate would be present in the area.

INTRODUCTION

Ambient particles are a concern because they not only reduce visibility but also have a negative impact on human health. Some epidemiological evidence suggests that mortality may be linked to particulate matter (PM) and its fraction compositions, especially in urban areas.¹⁻³

In the southern Taiwan air basin (Kaohsiung-Pingtung area), air quality reports show that 14–16% of the time in recent years the value of the pollutant standard index was above 100.⁴ PM has been the dominant pollutant in the air basin and is due to motor vehicles, industrial emissions, and other sources. Therefore, an understanding of the characteristics of particulate compositions is essential to the development of a safe implementation plan.

Many studies have indicated that ionic species outweigh others in particulate compositions. In addition, most of the sulfate (SO₄²⁻) and nitrate (NO₃⁻) attributed to the photochemical reaction of sulfur dioxide (SO₂) and nitrogen dioxide (NO₂) forms a secondary aerosol in the atmosphere. Turpin et al.⁵ revealed that SO₄²⁻, organic carbon (OC), and soil were the major components of the fine aerosol at Meadview, AZ. McCulloch et al.⁶ indicated that particulate mass was attributed to the serious ionic species loading in PM and ammonia (NH₃) transfer into PM. The ammonium (NH₄⁺) concentration was higher than in other areas because of farming in eastern North Carolina. In the Southeastern Aerosol and Visibility Study (SEAVS),⁷ Andrews et al. found that the fine particulate mass

IMPLICATIONS

Water-soluble ionic species were the major compounds in all PM_{2.5} except carbon. In southern Taiwan, the atmosphere is a high-frequency air-quality episode in winter that is usually due to particulate matter and ozone. Therefore, this study investigated the ionic compositions of PM_{2.5} and PM_{10-2.5} to understand the ionic species characteristics during the day and night of the particulate episode period.

fractions of SO_4^{2-} , OC, and NH_4^+ were 33–39%, 8–13%, and 6–10%, respectively. Loy et al.⁸ found that the PM less than 2.5 μm in aerodynamic diameter (fine PM [$\text{PM}_{2.5}$]) mass was $20.3 \pm 9.5 \mu\text{g} \cdot \text{m}^{-3}$, and the mass contribution of the SO_4^{2-} fraction as ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) was more than 50% in winter and less than 30% in summer in 1998–1999. Hansen et al.⁹ showed that the mass contribution of SO_4^{2-} , NO_3^- , and NH_4^+ was 36–44% of $\text{PM}_{2.5}$ in the Southeastern Aerosol Research and Characterization Study (SEARCH) in 1999–2001. In California, NH_4^+ , NO_3^- , SO_4^{2-} , OC, and elemental carbon (EC) were the most abundant components of $\text{PM}_{2.5}$.^{10–13} In general, ionic species also contributed to PM in many areas. Results indicated that SO_4^{2-} , NO_3^- , and NH_4^+ were the main water-soluble ionic species in $\text{PM}_{2.5}$ in Korea, Hong Kong, and Switzerland, and three species accounted for more than 30% of the mass in $\text{PM}_{2.5}$.^{14–16} Therefore, we focused on the ionic species in PM for this study, although the elemental and carbonaceous contents are also important.

In Taiwan, air pollution episodes are most often caused by PM and ozone. Therefore, the control of PM is important for the improvement of air quality. Lin investigated $\text{PM}_{2.5}$ compositions and established that SO_4^{2-} , NO_3^- , and NH_4^+ were the major ionic species, occupying 42.2% of the $\text{PM}_{2.5}$ mass and 90% of the total water-soluble ionic species.¹⁷ Chen et al. investigated the acid aerosol concentrations in Taipei and determined that the concentrations of SO_2 , nitric acid (HNO_3), nitrous acid (HONO), SO_4^{2-} , NO_3^- , and nitrite (NO_2^-) were 3.3–8.7 ppb, 0.2–3 ppb, 0.5–5.1 ppb, 4.6–33.9 $\mu\text{g} \cdot \text{m}^{-3}$, 0.8–6.6 $\mu\text{g} \cdot \text{m}^{-3}$, and 0.2–0.9 $\mu\text{g} \cdot \text{m}^{-3}$, respectively.¹⁸ These papers established that ionic species were important components of particulate mass, especially in NH_4^+ , SO_4^{2-} , and NO_3^- .

Some previous studies have investigated the composition characteristics of PM, but few have considered the day and night variations in particulate compositions.^{19–21} Furthermore, water-soluble ionic species were the major compounds in all $\text{PM}_{2.5}$ except carbon. In southern Taiwan, the atmosphere is a high-frequency air-quality episode air basin, usually because of PM and ozone pollution. Therefore, it is important to investigate the ionic compositions of $\text{PM}_{2.5}$ and coarse PM (or $\text{PM}_{2.5} \mu\text{m} < \text{aerodynamic diameter} < 10 \mu\text{m}$ [$\text{PM}_{10-2.5}$]) to understand the ionic species characteristics of air quality episodes both during the day and at night.

EXPERIMENTAL PROCEDURES

Sampling Program

Samples were collected from two stations (Tzuoying and Daliao) in Kaohsiung, southern Taiwan. These stations are part of the Taiwan Air Quality Monitoring Network established by the Taiwan Environmental Protection Agency in 1993. Tzuoying is located in Kaohsiung City, and Daliao is located in Kaohsiung County. A map of sampling sites and pollution sources is shown as Figure 1. The distance between the sampling station and the coast is approximately 3.3 km for Tzuoying and approximately 12 km for Daliao. The major pollution sources near Tzuoying include an oil refinery plant (O; ~3.5 km northeast of the Tzuoying station); a power plant (P1, ~4 km south of the Tzuoying station); the Kaohsiung export processing zone (IC5), where the electronics industry predominates (~5.3 km northeast of the Tzuoying station); cement plants (2–3 km north of the Tzuoying station); and the Kaohsiung mass rapid transit station construction zone (~0.6 km north of the Tzuoying station). The Daliao sampling station is in the south near the Da-Fa industrial district (IC3), which is

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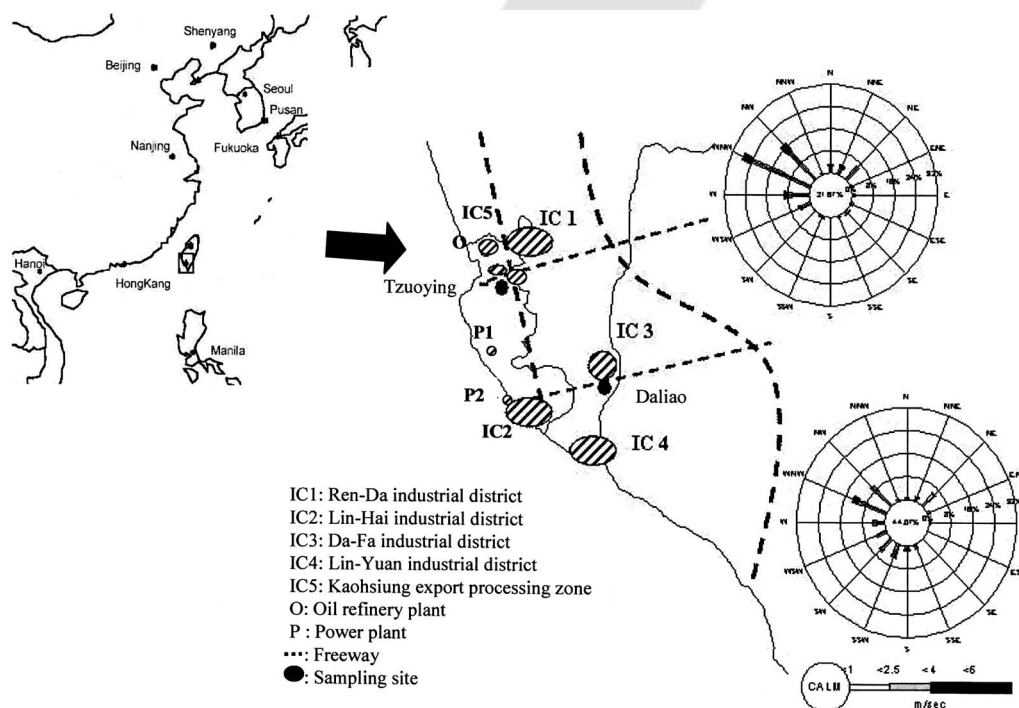


Figure 1.

an important air pollution source. Furthermore, the Lin-Yuan petrochemical industry (IC4) is approximately 4.5 km south of the Daliao station, the Lin-Hai industrial district (IC2; heavy industries, e.g., iron and steel plants) is approximately 6.5 km southwest of the Daliao station, and P2 (a power plant) is located in the vicinity of IC2. Additionally, the Daliao area is a rural-industrial complex area with various agricultural activities.

Twelve-hour samples were collected from October 22 to November 3, 2004 during two sampling time periods at each site, 7:00 a.m. to 7:00 p.m. and 7:00 p.m. to 7:00 a.m., to distinguish between the concentrations caused by daytime activities and those at night, especially motor vehicle exhaust and industrial emissions. In general, there are two rush intervals (7:00–9:00 a.m. and 5:00–7:00 p.m.) for motor vehicle activity during the daytime period.

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 west-northwest (WNW) and northwest (NW) at both sampling sites. Therefore, sea salt and local emissions could have been a source of the particulates. In addition, the wind speed at Tzuoying was higher than at Daliao, which may cause high sea salt contribution at Tzuoying during the daytime.

The wind direction was significantly different between daytime (7:00 a.m. to 7:00 p.m.) and nighttime (7:00 p.m. to 7:00 a.m.). During the daytime, over 70% of the winds were west (W), WNW, and NW; in contrast, at night, 75% were north (N), north-northeast (NNE), northeast (NE), and northeast-east (NEE) (data not shown). The wind direction was affected by the land-sea breeze, monsoons, and topography.

PM Sampling Method

Ambient PM was taken by a dichotomous sampler (Graseby Adenson G 241) equipped with an inlet of a 10- μm cut point. PM less than 10 μm in aerodynamic diameter (PM_{10}) was divided into two size fractions when entering the sampler using a virtual impactor with a 2.5- μm cut point. The two size fractions were classified as a coarse $\text{PM}_{10-2.5}$ fraction and the $\text{PM}_{2.5}$ fine fraction. Particulate mass concentration of PM_{10} is the sum of $\text{PM}_{2.5}$ and $\text{PM}_{10-2.5}$ in this study. The total flow rate of the dichotomous sampler was $16.7 \text{ L} \cdot \text{min}^{-1}$. It was split into 1.67 and $15 \text{ L} \cdot \text{min}^{-1}$ for coarse and fine flows, respectively. Twenty-six samples were taken for each cut size ($\text{PM}_{2.5}$ and $\text{PM}_{10-2.5}$), with a total of 104 samples for both cut size particles at the two stations.

PM was collected using 37-mm quartz fiber filters (Pallflex 2500 QAT-UP, 37 mm) supported by polyolefin rings. Filters were pretreated before sampling at 900°C for 2 hr to reduce the carbonaceous species background level and interference by other volatile species in the filter and reduce the artifact effect caused by the filter. The background concentration of ionic species in the filter was low. Fluoride (F^-), bromide (Br^-), SO_4^{2-} , and magnesium (Mg^{2+}) were not detectable; the other ionic species were $0.07 \mu\text{g}/\text{m}^3$ (chloride [Cl^-]) to $0.10 \mu\text{g}/\text{m}^3$ (calcium [Ca^{2+}]) (on the basis of the sampling volume

of air) in the filter. The pretreated 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 collected mass particulate concentration were measured by a microbalance (Mettler Toledo, MX5) with a reading of $1 \mu\text{g}$. The precision of quartz filter filters is about $\pm 10 \mu\text{g}$ under the condition of 40% relative humidity (RH) at 25°C . Before weighing, the filters were conditioned at $25 \pm 2^\circ\text{C}$ and $40 \pm 5\%$ RH for 48 hr. Filter samples were stored in a refrigerator at 4°C before chemical analysis to limit losses of volatile components.²²

Sampling artifacts for water-soluble ions were not quantified in this study. The quartz filter was preheated to reduce the interference, and the blank samples and other quality assurance and quality control samples were also included in this study to minimize the artifact effect of the filter.

Chemical Analysis

The collected aerosol filters were ultrasonically extracted for 2 hr into 20 mL of deionized distilled water and filtered through a Teflon filter of 4.5- μm nominal pore size. Ion chromatography (Dionex, 120) was used to analyze the concentration of anions (Br^- , F^- , Cl^- , NO_2^- , NO_3^- , SO_4^{2-}) and cations (sodium [Na^+], NH_4^+ , potassium [K^+], Mg^{2+} , Ca^{2+}).

The separation of anions was accomplished using an IonPac AS 12A ($4 \times 200 \text{ mm}$) analytical column, an AG 14 guard column with a 10- μL sample loop, and an anion self-regenerating suppressor-ultra. A solution of 2.7 mM sodium carbonate (Na_2CO_3)/0.3 mM sodium bicarbonate (NaHCO_3) was used as an effluent at a flow rate of $1.5 \text{ mL} \cdot \text{min}^{-1}$. The separation of cations was accomplished using an IonPac CS 12A ($4 \times 250 \text{ mm}$) analytical column, a CG 14 guard column with a 50- μL sample loop, and a cation self-regenerating suppressor-ultra. A solution of 20-mM methanesulfonic acid was used as the effluent at a flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$. The method detection limits of Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-} , F^- , Br^- , and NO_2^- were 0.06, 0.04, 0.02, 0.005, 0.03, 0.07, 0.05, 0.06, 0.05, 0.04, and $0.10 \mu\text{g} \cdot \text{m}^{-3}$, respectively.

The ionic species standard mixed solution was spiked into the quartz fiber filter, and the filter was then dried at room temperature. The dried filter followed the analysis procedures of the samples to measure the ionic species concentration. In addition, the recovery of Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-} , F^- , Br^- , and NO_2^- was 90, 115, 104, 106, 110, 112, 99, 97, 113, 97, and 102%, respectively. Some recovery variations of ionic species were 10–15%, which is in the acceptable range.^{23,24} In addition, the ion charge balance was checked in every filter sample, and the anion-to-cation charge ratio was 0.96–1.11. According to the literature,^{25,26} some ionic imbalance was encountered due to the carbonate species, especially in $\text{PM}_{10-2.5}$ (high dust condition). In this study, the anion-to-cation charge ratio was in the range of 1 ± 0.15 . Therefore, the carbonate content could not affect the ionic balance of particulate composition in this study.

Table 1. PM_{2.5} and PM₁₀ concentrations at different sampling sites.

Sampling Period	Sampling Sites	PM _{2.5}	PM ₁₀	PM _{2.5} / PM ₁₀	References	
1996–1997	Kaohsiung, Taiwan	12–112	19–152	0.66 ± 0.20	Chen et al., 1999 ²⁷	
2000–2001	Southern Taiwan	71 ± 21(31–107)	111 ± 44(41–232)	0.69 ± 0.09(0.37–0.73)	Chen et al., 2004 ²⁸	
1999–2000	Southern Taiwan	Day	65 ± 25(24–139)	109 ± 42(47–230)	0.61 ± 0.12(0.34–0.83)	Lin and Tai, 2001 ¹⁹
		Night	71 ± 27(22–151)	113 ± 40(41–222)	0.64 ± 0.12(0.31–0.83)	
		Whole day	68 ± 24	111 ± 38	0.62 ± 0.10	
2004	Daliao	24-hr average	64 ± 24(17–103)	98 ± 26(26–136)	0.64 ± 0.09(0.47–0.79)	This study
		Day (n = 13)	52 ± 15(23–86)	90 ± 18(17–103)	0.57 ± 0.06(0.47–0.65)	
		Night (n = 13)	76 ± 26(17–103)	107 ± 31(26–136)	0.70 ± 0.06(0.60–0.79)	
	Tzuoying	24-hr average	49 ± 24(11–99)	86 ± 33(23–166)	0.55 ± 0.11(0.24–0.68)	
		Day (n = 13)	36 ± 18(11–63)	73 ± 23(46–107)	0.47 ± 0.13(0.24–0.60)	
		Night (n = 13)	59 ± 25(11–99)	96 ± 37(23–166)	0.60 ± 0.06(0.53–0.68)	

Notes: Values in parentheses indicate range of mean values of each sampling period.

RESULTS AND DISCUSSION

PM Concentration

Table 1 shows the particulate concentrations in Daliao and Tzuoying. PM_{2.5} and PM₁₀ concentrations were 64 ± 24 and 98 ± 26 μg · m⁻³, respectively, in Daliao. The mass concentrations of PM_{2.5} and PM₁₀ in Tzuoying were 49 ± 24 and 86 ± 33 μg · m⁻³, respectively, which are comparable to values obtained in other studies done in the area.

The ratios of PM_{2.5}/PM₁₀ of Daliao and Tzuoying were 0.64 and 0.55, respectively. The percentage of PM_{2.5} in PM₁₀ was higher than that of the PM_{10–2.5}. The result is the same as those reported in Table 1. The particle mass concentration from October 1996 to June 1997 was reported by Chen and co-workers.²⁷ Lin and Tai¹⁹ reported measurements taken from November 1998 to April 1999. In addition, data from the Asian dust storm periods in 2000 and 2001 were reported by Chen et al.²⁸ In Taiwan, the rainy season runs from May to September, and high pollution episodes can be found from October to February in the following year. All sampling periods covered the high particulate concentration period in southern Taiwan.

In addition, the PM_{2.5}/PM₁₀ ratio and particulate concentrations at night were slightly higher than those measured during the day. This could be because the mixing height at night (<800 m) is lower than during the day (>1000 m; mixing height not shown). The wind speeds were 2.3 and 1.7 m/sec at Tzuoying and Daliao, respectively. The average wind speed at night was approximately 0.7 m/sec lower than during the day. On the basis of wind speed and mixing height, the transportation flux was higher during the daytime than at night. PM_{10–2.5} may not be as easily transported at night (lower transport flux). In addition, further work is required to identify the various sources contributing to the PM.

The PM₁₀ correlation coefficient between filter sampling and the Taiwan Environmental Protection Agency (TEPA) monitoring data was 0.89 and 0.95 for Daliao and Tzuoying, respectively. The particulate mass ratios of dichotomous sampling and TEPA data were 0.97 and 0.89 for Daliao and Tzuoying, respectively. The particulate

concentration measured by filter sampling was approximately 10% lower than the TEPA data, suggesting that the data in this study are representative.

Ionic Species Concentration

Figure 2 illustrates the ionic species concentrations in Daliao and Tzuoying. The sequence of the major ionic species in the PM_{2.5} at both sites was SO₄²⁻ > NO₃⁻ > NH₄⁺ > Cl⁻ > Na⁺ > K⁺. On the other hand, NO₃⁻ was higher than SO₄²⁻ in PM_{10–2.5} at both stations. Xiu et al.²⁹ also investigated the inorganic ions in size-fractionated PM at the Shanghai campus; results indicated that the sequence of concentration was SO₄²⁻ > NO₃⁻ ≈ NH₄⁺ > Cl⁻ > F⁻ in each size fraction. The sequence of ionic species evidenced the same trend as this study, which may be attributed to the similar emission sources and near the coast. Generally, SO₄²⁻, NO₃⁻, and NH₄⁺ are major ionic species in PM.^{10–16} The ionic species contributed 45 ± 6% and 42 ± 6% for the PM_{2.5} and PM₁₀ mass, respectively, at Daliao. In addition, 53 ± 14% and 45 ± 7% were contributed to the PM_{2.5} and PM₁₀ mass, respectively, at Tzuoying.

According to the mass fraction of the ionic species, SO₄²⁻, NH₄⁺, and K⁺ were predominant in the PM_{2.5}. NO₃⁻ existed in both the PM_{2.5} and PM_{10–2.5}. In addition, Na⁺, Ca²⁺, and Mg²⁺ predominated in the PM_{10–2.5}. This is consistent with the work by Wall et al.,³⁰ which showed that Na⁺ peaks at around 1–10 μm and primarily in the PM_{10–2.5}. In addition, SO₄²⁻ and NH₄⁺ were foremost in aerodynamic diameters less than 2 μm (PM_{2.5}).²⁸

NO₃⁻ was found in both the PM_{2.5} and PM_{10–2.5}. According to the results reported by Wall et al.,³⁰ the aerodynamic diameters of NO₃⁻ peaks were 0.2, 0.7, and 3 μm. More than half of the NO₃⁻ is found in the PM_{10–2.5} together with most of the Na⁺ and Cl⁻. In addition, Jonson et al.³¹ found that a large fraction of NO₃⁻ in sea salt was in the form of sodium nitrate (NaNO₃) because of its low volatility compared with that of ammonium nitrate (NH₄NO₃). De Leeuw et al.³² reported that NaNO₃ is formed on the surface of an existing PM_{10–2.5} sea salt or mineral dust particle, and NaNO₃ and calcium nitrate (Ca(NO₃)₂) can be collected in the PM_{10–2.5}. Nitrogen oxides (NO_x) were most often

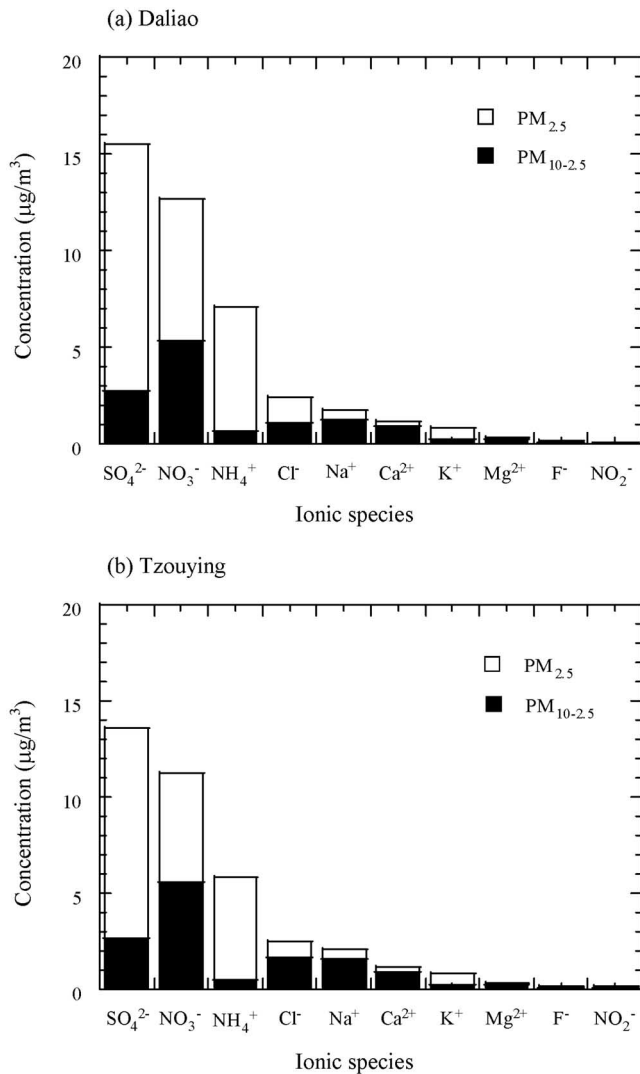


Figure 2.

the precursor of NO_3^- . NO_x can be converted into HNO_3 and combines with NH_3 to form NO_3^- as a secondary aerosol by photochemical reactions.^{33,34} Therefore, NaNO_3 existed mainly in the $\text{PM}_{10-2.5}$ but was also found in the $\text{PM}_{2.5}$, resulting from the reaction of gas-phase HNO_3 with sea salt particles under insufficient NH_4^+ condition or local pollution in $\text{PM}_{2.5}$ (i.e., coal combustion in the steel industry)^{35,36}. The Kaohsiung-Pingtung area is the most important industrial area in Taiwan, and there are many emission sources near the sampling station.

Kaneyasu et al.³⁶ also found that NO_3^- and non-sea salt are predominant in $\text{PM}_{2.5}$ because of local pollution. The Kaohsiung industrial metropolitan area is an ozone nonattainment region with a power plant, industries (petrochemical industry, iron, steel plant, etc.), and motor vehicles being the major sources of NO_x . Therefore, local combustion sources (i.e., coal and heavy oil consumption) are important sources of gaseous precursors of NO_3^- in $\text{PM}_{2.5}$.

Solar radiation induces photochemical reactions that create hydroxyl radicals that react with atmospheric constituents. Gas emissions of precursor gases such as SO_2 ,

NO_x , and NH_3 convert to particles of NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, ammonium bisulfate (NH_4HSO_4), and sulfuric acid (H_2SO_4).

In this study, the $\text{PM}_{2.5}$ always dominated the distribution of SO_4^{2-} . Neither condensation of vapor nor coagulation of smaller PM was verified as the formation mechanism for particles of around 0.5–0.7 μm , because the growth time scale of condensation particles to residual size is much shorter than the removal time scale.³⁷ SO_4^{2-} is most often converted from the photochemical oxidation of sulfur-containing precursors such as SO_2 , hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), and carbon disulfide (CS_2). SO_2 is the largest contributor of SO_4^{2-} among the sulfur-containing compounds.³⁴ Sulfur oxide (SO_x) can be oxidized to H_2SO_4 by gas-phase, aqueous-phase, or multiphase reactions of oxidants or radicals by condensation or nucleation of H_2SO_4 on particulate or to form a new aerosol. Partial H_2SO_4 was neutralized by NH_3 to form $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 . In general, SO_4^{2-} is mainly in the $\text{PM}_{2.5}$, particularly particle size less than 1 μm .^{5,38,39}

The non-sea-salt sulfate (nss-sulfate) was 2.41 ± 0.65 and $2.26 \pm 0.71 \mu\text{g}/\text{m}^3$ for Daliao and Tzuoying, respectively, for $\text{PM}_{10-2.5}$. The fractions of sea-salt sulfate were 11 and 15% for Daliao and Tzuoying, respectively, for $\text{PM}_{10-2.5}$. The sea-salt sulfate contributed less than 1% to $\text{PM}_{2.5}$ SO_4^{2-} at both stations.

In this study, K^+ was the main component in the $\text{PM}_{2.5}$ because of burning of vegetative material (i.e., rice straw) during the sampling period in Daliao. Ryu et al.⁴⁰ investigated biomass burning aerosols and found that Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , and K^+ were the major ionic species in the particles. K^+ is a highly useful tracer for pyrogenic aerosols in plants. It is the major electrolyte in cell cytoplasm, released in large amounts of K-rich particulates in the submicron size fraction.^{41,42}

Day and Night Variation of Ionic Species

Figure 3 shows the ionic species concentrations with day and night variations. In general, there were no significant differences in the mass concentrations of SO_4^{2-} , Na^+ , K^+ , and Ca^{2+} between day and night. Na^+ content in the $\text{PM}_{10-2.5}$ was approximately 20–30% higher in the daytime for both stations. But the difference was insignificant using the Student's *t* test method (taking $p < 0.05$ as significant; the *p* value is 0.01 for the two stations). However, the concentrations of Cl^- , NO_3^- , and NH_4^+ were higher at night than during the day.

During the day, the NO_3^- concentrations were predominant in $\text{PM}_{10-2.5}$, whereas at night they were higher in $\text{PM}_{2.5}$. For the $\text{PM}_{2.5}$, the NO_3^- concentrations at night were 5 and 5.5 times higher than the concentrations during the day at Daliao and Tzuoying, respectively. This may be attributed to the photochemical reaction during the day, which consumed the NO_3^- in the $\text{PM}_{2.5}$. In addition, the Cl^- concentration at night was higher than during the day. Cl^- concentration in $\text{PM}_{2.5}$ at night was approximately 8.6 and 9.6 times higher than the day concentration in Tzuoying and Daliao, respectively. In addition, the meteorological parameters (i.e., mixing height [the average mixing height was >1000 m during the day and <800 m at

F3

AQ: E

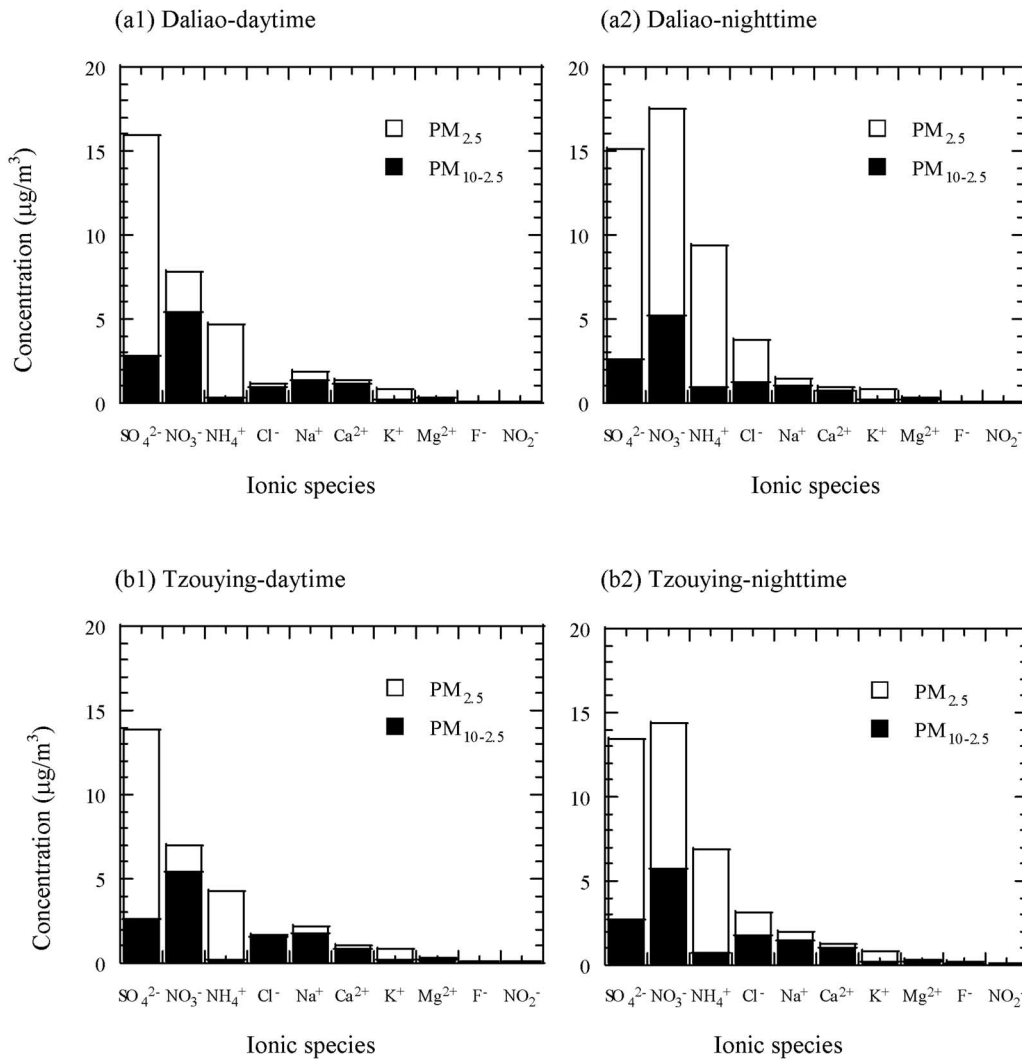
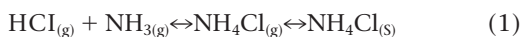


Figure 3.

night during the sampling periods) and wind speed were another reason to except source emission and chemical reactions in the atmosphere.

Furthermore, the NH_4^+ concentration in $\text{PM}_{2.5}$ at night was higher than during the day. The night/day ratio of NH_4^+ concentration was 1.5 at Tzouying and 1.9 at Daliao in $\text{PM}_{2.5}$.

Kadowaki⁴³ and Yao et al.⁴⁴ revealed that Cl^- depletion in sea salt because of higher gaseous HNO_3 may lead to the reduction of $\text{PM}_{10-2.5}$ Cl^- . A higher NO_3^- percentage may also be due to the formation of NaNO_3 . Generally, $\text{PM}_{10-2.5}$ was not the dominant NO_3^- mode. Therefore, the Cl^- must have another significant formation mechanism besides sea salt. Furthermore, Cl^- is an important secondary pollutant produced by the reaction of hydrochloric acid (HCl).



In addition, Cl^- depletion in the $\text{PM}_{10-2.5}$ commonly produces HCl or nitrosyl chloride (NOCl), which may also promote ammonium chloride (NH_4Cl) formation in

$\text{PM}_{2.5}$,^{43,44} $\text{PM}_{10-2.5}$ Cl^- might have two formation mechanisms. One is sea salt transport; the other might result from photochemical reactions on the $\text{PM}_{10-2.5}$ surface or direct reaction of gaseous Cl^- with a component of the PM. Wall et al.³⁰ indicated that Cl^- peaks were around 0.1, 0.7, and 2–11 μm , particularly in $\text{PM}_{10-2.5}$. In addition, some Cl^- compounds were emitted from the polyvinyl chloride plant in the Ren-Da petrochemical industrial district (near the Tzouying station) and the chlorine industry (producing chloralkali, liquid chlorine, HCl, etc.) in the Lin-Hai industry district (near the Daliao station).⁴⁵ Emissions from these processes may be the sources of Cl^- in the particles.

According to sea salt composition,³⁷ the mass concentration ratio and molar ratio of Cl^- and Na^+ are approximately 1.8 and 1.17, respectively. Assuming that the Na^+ can be attributed to sea salt, the theory of Cl^- concentration would be measured by the Cl^-/Na^+ molar ratio, and the relationship could be used to measure the Cl^- loss.³⁷

The $\text{PM}_{10-2.5}$ loss of Cl^- is $0.04 \pm 0.02 \mu\text{mol} \cdot \text{m}^{-3}$ during the day and $0.02 \pm 0.01 \mu\text{mol} \cdot \text{m}^{-3}$ at night at

Table 2a. Correlation of PM_{10-2.5} ionic species in Tzuoying during the day.

Ionic Species	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
F ⁻	1.0									
Cl ⁻	-0.25	1.0								
NO ₂ ⁻	0.04	-0.06	1.0							
NO ₃ ⁻	0.32	-0.47	0.21	1.0						
SO ₄ ²⁻	0.27	-0.27	0.23	0.96	1.0					
Na ⁺	-0.39	0.80	-0.26	-0.03	0.13	1.0				
NH ₄ ⁺	0.34	-0.41	0.44	0.64	0.60	-0.38	1.0			
K ⁺	0.59	-0.19	-0.20	0.70	0.70	0.08	0.38	1.0		
Mg ²⁺	-0.25	0.80	0.09	0.14	0.33	0.91	-0.06	0.13	1.0	
Ca ²⁺	0.63	-0.23	-0.11	0.58	0.57	0.01	0.08	0.89	0.01	1.0

AQ: C Daliao. At Tzuoying, the PM_{10-2.5} loss of Cl⁻ was 0.04 ± 0.03 μmol·m⁻³ during the day and 0.03 ± 0.02 μmol·m⁻³ at night. Results indicated that Cl⁻ loss occurred more easily during the day than at night.

Cl⁻ loss during the day was higher than at night, and the Cl⁻ loss at night may be caused by the acids (i.e., HNO₃ and H₂SO₄) and NO₂ reacting with sodium chloride (NaCl) to produce HCl and NOCl gas, respectively.⁴⁶⁻⁴⁸

According to the *t* test, the day and night concentrations of Cl⁻, NO₃⁻, and NH₄⁺ were significantly different (taking *p* < 0.05 as significant; *p* < 0.001 for three ionic species) in PM_{2.5} at Daliao. In PM_{10-2.5}, NH₄⁺, Ca²⁺, and Mg²⁺ were also different during the day and at night at Daliao. Daliao is an industrial rural area, with many agricultural and industrial activities. NH₄⁺, Ca²⁺, and Mg²⁺ can be emitted from the agricultural activities (i.e., fertilizer, cultivation, and soil) in Daliao. At Tzuoying, the differences in PM_{10-2.5} ionic species were insignificant between the day and night periods. But the Cl⁻, NO₃⁻, and NH₄⁺ concentrations in PM_{2.5} during the day and at night were significantly different at Tzuoying. In PM_{2.5}, Cl⁻, NO₃⁻, and NH₄⁺ were different during the day and at night at both sampling sites. This may be caused by a chemical reaction in the atmosphere and emission variations between day and night. In addition, the ambient temperature in the daytime was 26.4 and 27.2 °C at Tzuoying and Daliao, respectively. At night, the temperature was 2-3 °C lower than during the day. Therefore,

the temperature could be a factor in the day and night difference of NH₄⁺, NO₃⁻, and Cl⁻ in PM_{2.5}.

Ionic Species Correlation

Correlation of Ionic Species in PM_{10-2.5}

Table 2 shows the correlation of mass concentration of ionic species during the day and at night for PM_{10-2.5}. For PM_{10-2.5}, the sequence of relative contribution of cations was Na⁺ (29-44%) > Ca²⁺ (23-34%) > NH₄⁺ (12-33%) > Mg²⁺ (11-14%) > K⁺ (3.3-3.8%) for both stations.

There was a high correlation between Na⁺, Mg²⁺, and Cl⁻ for PM_{10-2.5} ionic species in the daytime, especially in Tzuoying (Table 2a). They may come from the same sea salt source (chemical composition of sea salt as a reference data). In Tzuoying, NO₃⁻, SO₄²⁻, Ca²⁺, and K⁺ analysis revealed a moderate to high correlation, especially at night (Table 2b). This may be due to a sea-salt/soil- or road-dust aggregation

In addition, there was a high correlation between Ca²⁺ and K⁺ that may come from soil or road dust, especially in Tzuoying (Table 2, a and b). Generally, K⁺ comes from biomass burning and forms in PM_{2.5}. But K⁺ was in the PM_{10-2.5} in this case; therefore, the soil may be a source of K⁺. Sea salt and road dust contribute to PM_{10-2.5}; the chemical constituents of road dust include Ca²⁺ and K⁺, and sea salt includes K⁺. Generally, K⁺ is the main element in soil and crustal rock, and it is also found in sea salt.³⁷ There is a proposed high correlation of

Table 2b. Correlation of PM_{10-2.5} ionic species in Tzuoying at night.

Ionic Species	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
F ⁻	1.0									
Cl ⁻	0.39	1.0								
NO ₂ ⁻	-0.29	-0.005	1.0							
NO ₃ ⁻	0.57	0.14	0.20	1.0						
SO ₄ ²⁻	0.70	0.41	-0.01	0.89	1.0					
Na ⁺	0.21	0.69	0.09	0.40	0.46	1.0				
NH ₄ ⁺	0.16	0.14	0.23	0.59	0.48	0.21	1.0			
K ⁺	0.73	0.33	-0.12	0.84	0.92	0.32	0.48	1.0		
Mg ²⁺	0.64	0.71	0.06	0.67	0.81	0.83	0.22	0.68	1.0	
Ca ²⁺	0.82	0.26	0.05	0.73	0.83	0.03	0.26	0.84	0.57	1.0

Table 2c. Correlation of PM_{10-2.5} ionic species in Daliao during the day.

Ionic Species	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
F ⁻	1.0									
Cl ⁻	0.42	1.0								
NO ₂ ⁻	-0.45	-0.38	1.0							
NO ₃ ⁻	-0.30	-0.35	0.27	1.0						
SO ₄ ²⁻	-0.28	-0.30	0.27	0.92	1.0					
Na ⁺	0.09	0.82	-0.14	-0.03	-0.02	1.0				
NH ₄ ⁺	-0.002	-0.13	-0.05	0.84	0.70	0.02	1.0			
K ⁺	0.55	-0.04	-0.20	0.33	0.36	-0.18	0.42	1.0		
Mg ²⁺	0.06	0.61	-0.09	0.24	0.28	0.80	0.14	-0.16	1.0	
Ca ²⁺	0.08	-0.37	0.22	0.63	0.77	-0.35	0.40	0.49	0.02	1.0

Mg²⁺ and SO₄²⁻ at night in Tzuoying. The high correlation of Mg²⁺ with Na⁺, Cl⁻, and SO₄²⁻ indicates that they may be emitted from the same source, and sea salt contains these ionic species.

In Daliao, NO₃⁻, SO₄²⁻, and NH₄⁺ also displayed a high correlation (Table 2, c and d), indicating they may be formed from source or reaction mechanisms. NH₃ undergoes sorption on the aerosol and reacts with SO₄²⁻ and NO₃⁻ to form (NH₄)₂SO₄, (NH₄)HSO₄, and NH₄NO₃. These reactions may occur at night.

Correlation of Ionic Species in PM_{2.5}

Table 3 illustrates the mass concentration correlation of ionic species during the day and at night for PM_{2.5}. For the PM_{2.5}, the relative contribution of cations of NH₄⁺ was approximately 80%. The relative contribution of NH₄⁺ in cations was 10% higher at night.

In the daytime, Mg²⁺ displayed a high correlation with Na⁺ in both sampling stations during the day (Table 3, a and c). Especially in Tzuoying, Mg²⁺ displayed a moderate-to-high correlation with Na⁺. A moderate-to-high correlation was seen between Ca²⁺ and SO₄²⁻, NH₄⁺ and K⁺ in Tzuoying (Table 3, a and b). In Daliao, K⁺, NO₃⁻, SO₄²⁻, and NH₄⁺ exhibited a moderate-to-high correlation in the daytime (Table 3c). According to the correlation coefficient, potassium sulfate (K₂SO₄), potassium nitrate (KNO₃), NH₄NO₃, (NH₄)HSO₄, and (NH₄)₂SO₄ were the potential compounds during the day in Daliao. In addition, calcium sulfate (CaSO₄),

(NH₄)HSO₄, and (NH₄)₂SO₄ were the potential compounds in Tzuoying.

At night, Cl⁻ had a high correlation to NO₃⁻, NH₄⁺, and Ca²⁺ at both sampling stations (Table 3, b and d). K⁺ showed a high correlation to NO₃⁻, SO₄²⁻, and NH₄⁺ in Daliao (Table 3, c and d). Therefore, NH₄Cl, NH₄NO₃, CaCl₂, K₂SO₄, KNO₃, NH₄NO₃, (NH₄)HSO₄, and (NH₄)₂SO₄ were the potential compounds in the PM_{2.5}. There was a high NH₄⁺ correlation to Cl⁻, NO₃⁻, and SO₄²⁻ in Tzuoying (Table 3b). Ca²⁺ maintained a moderate correlation to Cl⁻, NO₃⁻, and K⁺ at night (Table 3b). In Tzuoying, CaCl₂, NH₄Cl, Ca(NO₃)₂, NH₄NO₃, (NH₄)HSO₄, and (NH₄)₂SO₄ were the potential chemicals at night. Shimohara et al.⁴⁸ investigated the chemical form and reaction of airborne gaseous and PM in northern Kyushu, Japan. Results indicated that NaNO₃, Ca(NO₃)₂, (NH₄)₂SO₄, (NH₄)HSO₄, NH₄Cl, and NH₄NO₃ formed the main chemical particulate compositions.

Reactions of SO₂ to particulate SO₄²⁻ and NO_x to particulate NO₃⁻ compete with each other for available hydroxyl radicals and NH₃. NH₄⁺ reacts preferentially with H₂SO₄ to form (NH₄)HSO₄ and (NH₄)₂SO₄, and the amount of NH₄NO₃ formed is significant only when the total NH₃ exceeds the SO₄²⁻ by a factor of 2 or more on a mole basis.

In PM_{2.5}, SO₄²⁻ is balanced by NH₄⁺ and strong acid. However, some NH₄⁺ can be associated with NO₃⁻. Pathak et al.⁴⁹ found that acidity, NH₄⁺, and SO₄²⁻ can be

Table 2d. Correlation of PM_{10-2.5} ionic species in Daliao at night.

Ionic Species	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
F ⁻	1.0									
Cl ⁻	0.58	1.0								
NO ₂ ⁻	0.33	-0.17	1.0							
NO ₃ ⁻	-0.16	-0.15	0.04	1.0						
SO ₄ ²⁻	0.23	0.16	0.26	0.70	1.0					
Na ⁺	0.63	0.80	0.04	0.13	0.25	1.0				
NH ₄ ⁺	0.17	0.30	0.18	0.80	0.87	0.35	1.0			
K ⁺	0.49	0.24	0.28	0.60	0.73	0.45	0.67	1.0		
Mg ²⁺	0.47	0.34	-0.03	0.36	0.42	0.53	0.41	0.31	1.0	
Ca ²⁺	0.37	-0.15	0.24	0.58	0.65	0.09	0.47	0.76	0.39	1.0

Table 3a. Correlation of PM_{2.5} ionic species in Tzuoying during the day.

Ionic Species	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
F ⁻	1.0									
Cl ⁻	-0.05	1.0								
NO ₂ ⁻	0.14	-0.63	1.0							
NO ₃ ⁻	-0.10	0.16	-0.57	1.0						
SO ₄ ²⁻	-0.51	-0.65	0.10	0.27	1.0					
Na ⁺	-0.43	0.67	-0.30	-0.31	-0.25	1.0				
NH ₄ ⁺	-0.41	-0.48	-0.22	0.42	0.93	-0.23	1.0			
K ⁺	-0.68	0.18	-0.55	0.43	0.62	0.41	0.72	1.0		
Mg ²⁺	-0.48	0.58	-0.51	-0.08	0.06	0.87	0.19	0.73	1.0	
Ca ²⁺	-0.50	-0.27	-0.44	0.51	0.78	-0.08	0.87	0.70	0.23	1.0

categorized into two regimes on the basis of the particulate NH₄⁺ to SO₄²⁻ molar ratio NH₄⁺/SO₄²⁻. The NH₄⁺-rich particles (2 ≥ NH₄⁺/SO₄²⁻ > 1.5) were mostly neutralized; little free acid through NH₄NO₃ was present. The NH₄⁺-poor particles (1.5 ≥ NH₄⁺/SO₄²⁻) have a significant amount of free acid and little or no NH₄NO₃.

The molar ratios of NH₄⁺/SO₄²⁻ were 2.62 ± 1.09 and 2.54 ± 0.80 for PM_{2.5} at Daliao and Tzuoying, respectively. The value of the molar ratio at night was higher than during the day. At Daliao, the ratios were 1.72 ± 0.33 and 3.52 ± 0.67 during the day and at night, respectively. In addition, the day and night ratios were 1.80 ± 0.72 and 2.98 ± 0.70, respectively, at Tzuoying. For PM_{10-2.5}, the ratio was smaller than for the PM_{2.5}.

The NH₄⁺/SO₄²⁻ ratios were 1.19 ± 0.87 and 1.00 ± 0.77 at Daliao and Tzuoying, respectively, for PM_{10-2.5}. The ratios were 0.29 ± 0.24 and 0.90 ± 0.38 during the day and at night, respectively, at Daliao. Furthermore, the ratios were 0.22 ± 0.19 and 0.67 ± 0.36 during the day and at night, respectively, at Tzuoying. The NH₄⁺/SO₄²⁻ ratio during the day was lower than at night, possibly caused by the NH₄⁺ compounds

Principle Component Analysis for Ionic Species in Particles

Principle component analysis was applied to investigate the correlation of ionic species in PM (data not shown). For PM_{2.5} in the daytime, NO₃⁻, SO₄²⁻, NH₄⁺, and K⁺ revealed a high loading in factor 1 for both stations; the pollution would come from chemical reactions (NO₃⁻,

SO₄²⁻, and NH₄⁺) and biomass burning (K⁺). Factor 2 includes Cl⁻, Na⁺, and Mg²⁺, which were attributed to sea salt. For PM_{2.5} at night the ionic species in factors were similar to the daytime, but high Cl⁻ loading occurred together with NO₃⁻, SO₄²⁻, NH₄⁺, and K⁺ in factor 1, which also reflected the high Cl⁻ concentration at night at both stations. The chemical reaction, sea salt, and biomass burning affected the ionic species profile in PM_{2.5}.

For PM_{10-2.5}, high factor loading of NO₃⁻, SO₄²⁻, NH₄⁺, and Ca²⁺ could be measured in factor 1 reflecting the chemical reaction and road dust (Ca²⁺) effects on the ionic species in the particles. Sea salt (Na⁺, Mg²⁺, and Cl⁻) was an important source in factor 2. In Tzuoying, chemical reactions (NO₃⁻, NH₄⁺ and SO₄²⁻) and sea salt (Cl⁻, Na⁺, and Mg²⁺) were found in the same factor, which may be attributed to the sea salt as an important source of PM_{10-2.5} (Tzuoying is located near the coast).

On the basis of the principle component analysis, there were three factors that could explain 81–91% and 80–89% of the variances for PM_{2.5} and PM_{10-2.5}, respectively.

CONCLUSIONS

Eleven ionic species and PM_{2.5} and PM_{10-2.5} concentrations were investigated in Kaohsiung, southern Taiwan. Of the two sampling sites, the PM mass concentration at Daliao (a rural-industrial-agricultural complex area) was slightly higher than that at Tzuoying (an urban-industrial complex area). SO₄²⁻, NO₃⁻, and NH₄⁺ were the ionic species in the PM_{10-2.5} and PM_{2.5}. In addition, SO₄²⁻,

Table 3b. Correlation of PM_{2.5} ionic species in Tzuoying during the night.

Ionic Species	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
F ⁻	1.0									
Cl ⁻	0.25	1.0								
NO ₂ ⁻	-0.002	-0.25	1.0							
NO ₃ ⁻	0.17	0.86	-0.16	1.0						
SO ₄ ²⁻	-0.02	0.56	0.21	0.71	1.0					
Na ⁺	-0.27	-0.27	0.26	-0.22	0.11	1.0				
NH ₄ ⁺	0.03	0.80	-0.07	0.94	0.86	-0.19	1.0			
K ⁺	0.39	0.53	0.10	0.48	0.68	0.30	0.53	1.0		
Mg ²⁺	-0.41	0.12	0.17	0.11	0.39	0.51	0.27	0.53	1.0	
Ca ²⁺	0.35	0.76	0.32	0.70	0.62	0.08	0.65	0.76	0.36	1.0

Table 3c. Correlation of PM_{2.5} ionic species in Daliao during the day.

Ionic Species	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
F ⁻	1.0									
Cl ⁻	0.17	1.0								
NO ₂ ⁻	-0.09	-0.34	1.0							
NO ₃ ⁻	0.14	0.45	-0.49	1.0						
SO ₄ ²⁻	-0.15	-0.06	-0.49	0.69	1.0					
Na ⁺	0.62	0.62	0.03	0.07	-0.40	1.0				
NH ₄ ⁺	-0.26	0.09	-0.54	0.80	0.95	-0.38	1.0			
K ⁺	-0.13	0.04	-0.25	0.73	0.81	-0.71	0.81	1.0		
Mg ²⁺	0.46	0.40	-0.002	-0.35	-0.58	0.85	-0.60	-0.49	1.0	
Ca ²⁺	0.68	0.12	-0.27	0.53	0.42	0.40	0.30	0.52	0.15	1.0

Table 3d. Correlation of PM_{2.5} ionic species in Daliao at night.

Ionic Species	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
F ⁻	1.0									
Cl ⁻	-0.01	1.0								
NO ₂ ⁻	-0.21	0.29	1.0							
NO ₃ ⁻	-0.06	0.72	0.60	1.0						
SO ₄ ²⁻	-0.33	0.67	0.34	0.70	1.0					
Na ⁺	0.48	-0.07	-0.24	-0.33	-0.02	1.0				
NH ₄ ⁺	-0.16	0.86	0.41	0.91	0.89	-0.19	1.0			
K ⁺	-0.12	0.48	0.31	0.74	0.81	-0.02	0.79	1.0		
Mg ²⁺	-0.29	-0.21	-0.21	-0.28	0.30	0.58	-0.07	0.17	1.0	
Ca ²⁺	0.07	0.73	0.09	0.48	0.69	0.28	0.70	0.64	0.22	1.0

NH₄⁺, and K⁺ were found mainly in PM_{2.5}, which may be attributed to chemical reactions and combustion in the atmosphere. Ca²⁺, Na⁺, and Mg²⁺ predominated in the PM_{10-2.5}, possibly because of sea salt and road dust or soil erosion. NO₃⁻ existed in both the PM_{2.5} and PM_{10-2.5}. The PM_{2.5} NO₃⁻ may be caused by ambient chemical reactions (HNO₃ + NH₃ = NH₄NO₃), and the PM_{10-2.5} NO₃⁻ (NaNO₃) may be due to the NO₃⁻ reacting with sea salt or crystal alkali and alkali-earth metals. NO₃⁻, NH₄⁺, and Cl⁻ concentrations were higher at night than during the day at both sampling sites. NH₄NO₃ and NH₄Cl are volatilized more easily during the day than at night because of the temperature and photochemical reactions. In the sampling periods, the molar ratio of NH₄⁺ and SO₄²⁻ was higher than 2 at both sampling sites, which indicated that the ambient particles were rich in NH₄⁺. Therefore, (NH₄)₂SO₄, (NH₄)HSO₄, and NH₄NO₃ might be the particulate chemical compositions, especially in PM_{2.5}. Although the study proposes some potential species in PM_{10-2.5} and PM_{2.5}, further work is needed to collect additional data and enable meaningful conclusions to be drawn regarding the reaction mechanisms.

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1

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