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ABSTRACT

Gaseous pollutants and $PM_{2.5}$ aerosol particles were investigated during a tropical storm and an air pollution episode in southern Taiwan. Field sampling and chemical analysis of particulate matter and gaseous pollutants were conducted in Daliao and Tzouying in the Kaohsiung area, using a denuder-filter pack system during the period of 22 October to 3 November 2004. Sulfate, nitrate and ammonium were the major ionic species in the $PM_{2.5}$, accounting for 46 and 39% of the $PM_{2.5}$ for Daliao and Tzouying, respectively. Higher $PM_{2.5}$, Cl^-, NO_3^- and NH_4^+, HNO_2 and NH_3 concentrations were found at night in both stations, whereas higher HNO_3 was found during the day. In general, higher $PM_{2.5}$, HCl, NH_3, SO_2, Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ concentrations were found in Daliao. The synoptic weather during the experiment was first influenced by Typhoon NOCK-TEN, which resulted in the pollutant concentrations decreasing by about two-thirds. After the tropical thunderstorm system passed, the ambient air quality returned to the previous condition in 12 to 24 hours. When there was a strong subsidence accompanied by a high-pressure system, a more stable environment with lower wind speed and mixing height resulted in higher $PM_{2.5}$, as well as HNO_2, NH_3, SO_4^{2-}, Cl^-, NO_3^-, NH_4^+ and K^+ concentrations during the episode days. The rainfall is mainly a scavenger of air pollutants in this study, and the stable atmospheric system and the high emission loading are the major reasons

for high air pollutant concentrations.

Keywords: $PM_{2.5}$, acid-base gases, water-soluble ions, denuder sampling system

1. Introduction

The health effects of $PM_{2.5}$ have been reported to be greater than those of larger particulate matter because $PM_{2.5}$ can go deeper into the unciliated and alveolar areas of the lungs when inhaled (Spengler et al., 1990). Many epidemiological studies focusing on $PM_{2.5}$ and acid gas concentrations have discussed the occurrence of allergy, asthma and cardiovascular diseases (Glodberg et al., 2001; Hoek et al., 2002; Gauvin et al., 2002; Jalaludin et al., 2004; Kappos et al., 2004) . However, various emission sources, meteorological conditions and local topography may affect the concentrations and compositions of $PM_{2.5}$ and their gas precursors (Lee et al., 1999; Pathak et al., 2003; Bari et al., 2003a and 2003b).

In general, direct emissions from the sources as well as reactions between primary pollutants in the atmosphere contribute to the generation of ambient particulate matter. Through photochemical reactions in the atmosphere, NO_x and SO_2 emitted from natural and artificial sources lead to the formation of nitrate and sulfate (Buhr et al., 1995; Hazi et al., 2003; Pathak and Chan, 2005). HCl is mainly emitted from municipal and industrial waste incineration and factories in urban and industrial areas, and HCl could be formed via the reaction of HNO_3 with aqueous or solid NaCl in sea-salt particulate matter (Matsumoto and Tanaka, 1996; Casado et al., 1996; Encinas and Casado, 1999; Shimohara et al., 2001; Bari et al., 2003a; Encinas et al., 2004). NH_3 is emitted from natural and anthropogenic sources, as well as artificial sources, which can include the fertilizer industry, agricultural fermentation, and farm animal waste (Walker et al., 2003; Plessow et al., 2005). In addition, NH_3 may easily transfer into the particulate phase as NH_4^+ through reaction in the atmosphere (Walker et al., 2003; Plessow et al., 2005).

Numerous studies have measured ionic species in particulate matter (Lee et al., 1999; Pathak et

al., 2003 and 2004; Bari et al., 2003a and 2003b; Pathak and Chan, 2005). Sulfate and nitrate generally contribute more to the particulate mass than other components. Some studies have reported similar measurements of gases and ionic species in particulate matter, but few of these studies measured all of the compounds in detail. In addition, water-soluble ionic species contribute a large portion of particulate mass; therefore, this article focused on the water-soluble ions in $PM_{2.5}$, although elemental and other species are also important for particulate compositions, such as the organic fraction of $PM_{2.5}$ which can contribute up to 40% of the mass of $PM_{2.5}$ in polluted area (Lin, 2002).

Kaohsiung, an urban and industrial metropolitan city in southern Taiwan, is the second largest city in Taiwan. According to the emission inventory investigated by the Taiwan Environmental Protection Administration (TEPA) in 2004, emissions from the Kaohsiung air basin contributed over 20% to total air pollutant emissions in Taiwan (TEPA, 2005). The environmental loading of air pollutants in Kaohsiung was nearly twice that of other air basins in Taiwan (TEPA, 2006). Although many control programs have been implemented in the air basin of Kaohsiung to resolve the air quality problem, the area has continued to have the highest air quality episodes (pollutant standards index, PSI > 100) in Taiwan during the past ten years.

Of the total emissions in Taiwan in 2003, 20% $PM_{2.5}$ (34 thousand ton/yr), 18% (157 thousand ton/yr) non-methane hydrocarbon, 35% SOx (66 thousand ton/yr), and 26% (164 thousand ton/yr) NOx were emitted in the Kaohsiung-Pingtung area (TEPA, 2006). 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) (TEPA, 2006). The Kaohsiung-Pingtung area is a mixed industrial and urban area that contains over 50% of the traditional and heavy industries in Taiwan.

Although particulate matter accounts for a large portion of the air pollution in this area, meteorological variations also contribute to bad air quality episodes. In addition to air pollutant emission, the subtropical weather and island topography may affect secondary aerosol formation. In Taiwan, the rainy season runs from May to September, and high-pollution episodes often occur

between October and February during the following year. Therefore, it is important to understand the relationships among gaseous precursors, aerosol particles and meteorological conditions. In addition, few studies have focused on the effects of the tropical storm system on the particulate concentration and compositions.

In this study, a sampling program was carried out over Kaohsiung during the period of 22 October to 3 November 2004. Chemical analyses (i.e., HNO_2, HNO_3, HCl, SO_2, NH_3, and ionic species including anions (NO_3^-, SO_4^{2-}, Cl^-, F^-, NO_2^-, Br^-) and cations (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+})) made it possible to investigate the detailed characteristics of $PM_{2.5}$ and gaseous pollutants under various weather conditions. High-pressure systems (22-23 Oct and 27 Oct-3 Nov) and a tropical storm system (Typhoon NOCK-TEN, 24-26 Oct) affected the air quality during the sampling period, providing interesting circumstances for work to elucidate the effect of local air pollution sources on air quality. Therefore, the study could determine the influence of meteorological effects, including a high-pressure system and a tropical storm system on the particulate concentration and compositions in southern Taiwan.

2. Experimental methods

2.1 Sampling locations

Tzouying station is located in Kaohsiung City (downtown of Kaohsiung), and Daliao station is located in Kaohsiung County (rural area of Kaohsiung). Both stations are near industrial districts. Kaohsiung County has a population of 1.2 million in an area of approximately 2793 km^2. The population of Kaohsiung City, which is the second largest city in Taiwan and occupies an area of approximately 154 km^2, was 1.5 million in 2004. Tzouying and Daliao have population densities of 9200 and 1500 people/km^2, respectively. Daliao is 12 km away from the coastline, and it is near a rural-industrial complex area with various agricultural activities and heavy industry--i.e., Da-Fa (less than 0.3 km east), Lin-Hai (approximately 6.5 km west) and Lin-Yuan (approximately 4.5 km southwest). Conversely, Tzouying is 3.3 km away from the western coastline, and the major pollution

sources in the region include an oil refinery plant (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 in Kaohsiung in southern Taiwan during the period of 22 Oct to 3 Nov 2004. Two stations of the Taiwan Air Quality Monitoring Network (which was established by the Taiwan Environmental Protection Agency in 1993), Daliao and Tzouying, were chosen as sampling sites for the experiment (**Figure 1**). At each site, samples were collected during the periods of 7 am-7 pm and 7 pm-7 am the following day to enable characterization of air pollutants during the day and night, respectively. Weather systems that affected air quality during the sampling period included high-pressure systems (22-23 Oct and 27 Oct-3 Nov) and a tropical storm system (Typhoon NOCK-TEN, 24-26 Oct).

2.2 Denuder and filter sampling

The denuder system employed in this study was composed of a cyclone with a cut-off diameter of 2.5 μm (University Research Glassware; URG, Chapel Hill Inc., USA) followed by four annular denuders (URG-2000-30EH), a filter pack, a flow controller and a pump (USEPA, 1998). Airflow was set at a constant rate of 16.7 l min^{-1}.

The first denuder was coated with 10 ml of 0.1 % (w/v) NaCl in 1:9 methanol/deionized water solutions for the absorption of HNO_3 gas (Perrino et al., 1990; USEPA, 1998). The second and third denuders were coated with 10 ml 1:1 (v:v) mixtures of 2% (w/v) Na_2CO_3 in deionized water and 2% (w/v) glycerol in methanol solution for the absorption of HCl, HNO_2 and SO_2 gas. The fourth was coated with 10 ml of 1% (w/v) citric acid in methanol solution for the absorption of NH_3 gas. Three filters placed in series followed the denuders. The first Teflon filter (Pallflex, 47 mm, pore size: 2 μm, USA) was set up to collect particulate matter with diameters < 2.5 μm. In order to collect acid gas that evaporated from particles or that was not completely absorbed by the denuder, the next quartz filter was coated with Na_2CO_3 solution. The last quartz filter was coated with a citric acid solution

and designed to collect NH_3 evaporated from particles. After sampling, each denuder tube and filter was extracted with deionized water and analyzed by ionic chromatography. Two denuder sampling systems were analyzed for the same sampling site for quality assurance and quality control procedures, and the relative error for all gas species and particulate ions ranged from 5-17%. In addition, the additives of HNO_3, SO_2 and NH_3 gases were used to measure the recovery of the denuder adsorption system. Recoveries were 89±10%, 95±8% and 102±7% for HNO_3, SO_2 and NH_3, respectively. The gas collection efficiency was similar to that reported in other studies (Sioutas et al., 1996; Bai et al., 2003; Acker et al., 2005).

2.3 Chemical analysis

The collected aerosol filters were ultrasonically extracted for 2 h into 20 ml of deionized distilled water and passed 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 (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}). The separation of anions was accomplished using an IonPac AS 12A (4×200 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 Na_2CO_3/0.3 mM $NaHCO_3$ was used as an effluent at a flow rate of 1.5 ml min^{-1}. The separation of cations was accomplished using an IonPac CS 12A (4×250 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 eluent at a flow rate of 1 ml min^{-1}. This analysis method yielded detection limits between 0.005 (Mg^{2+}) and, 0.10 (NO_2^-) μg m^{-3} and recoveries from 87(Na^+) to 115% (NH_4^+). In addition, the particulate ion balance of A/C (anion/cation) ratio was 1.08±0.08 for Daliao and 1.04±0.07 for Tzouying.

2.4 Weather analysis

The synoptic environment was illustrated by weather charts from the Central Weather Bureau (CWB) in Taiwan. Hourly surface meteorological data including temperature, dew point, humidity, pressure, precipitation, solar radiation, wind speed and wind direction in the CWB Kaohsiung station

were analyzed during the experiment as well. In addition, a sounding launched at Kaohsiung station at 12-h intervals was employed for analyzing the mixing heights, following the procedures reported by Holzworth (Holzworth, 1972).

To determine the atmospheric stability associated with the dispersion of atmospheric contaminants, an estimation of "Pasquill stability categories" was adopted in this study (Turner, 1969). This classification scheme generally describes the degree of atmospheric turbulence. Categories range from extremely unstable (A) to neutral (D) to extremely stable (F).

3. Results and discussion

3.1 Composite pollutant concentration

The average concentrations of gaseous pollutants and ionic species in $PM_{2.5}$ sampled in Daliao and Tzouying are listed in **Table 1**. The ratio of anions and cations (AC ratio) was 0.92-1.20 (average 1.08 for daytime and 1.01 for nighttime) for all samples in Daliao and 0.93-1.21 (average 1.07 for daytime and 1.00 for nighttime) for all samples in Tzouying. The AC ratios did not exhibit a significant difference between daytime and nighttime.

In general, the $PM_{2.5}$ mass concentration in Daliao was slightly higher than that in Tzouying. The concentration of the gaseous pollutants HCl, NH_3 and SO_2 in Daliao was about 1.45-2 times higher than that of those sampled in Tzouying during the same sampling period. The ionic concentration of Cl^-, NO_3^-, SO_4^{2-}, and NH_4^+ in Daliao was also 1.13-1.74 times higher than that in Tzouying. The higher concentration of gaseous pollutants and ionic species in sampled particulate matter probably contributed to the higher pollutant emission in the Daliao area (TEPA, 2005); far from the coastline, the pollutants are not transported as easily as they are in Tzouying. Overall, three major soluble inorganic species (sulfate, nitrate, and ammonium) accounted for 45.7 and 38.8% of the $PM_{2.5}$ mass concentration at Dalia and Tzouying sites, and around 90.0% of the total dissolved ionic concentration measured at both sites. The unidentified portion of $PM_{2.5}$ mass included water content, elemental, and carbonaceous species (Lin, 2002).

202 The ratio between the day and night $PM_{2.5}$ concentrations was nearly the same (0.75-0.76) for both
203 stations. Sulfate, nitrate and ammonium were the major ionic species in the $PM_{2.5}$. Collectively, they
204 contributed 46% and 39% of the $PM_{2.5}$ mass in Daliao and Tzouying, respectively. The mass fraction
205 of these three major ionic species in $PM_{2.5}$ at night was 8% and 6% higher than that during the day for
206 Daliao and Tzouying, respectively. The variations were calculated based on the fact that $PM_{2.5}$ mass
207 concentration was generally 30% higher at night than during the day. The concentrations of Cl^-, NO_3^-
208 and NH_4^+ in $PM_{2.5}$ sampled at night at both sites were 10, 6 and 1.8 times higher than of those
209 sampled during the day. There were no significant concentration variations during the day or at night
210 for other $PM_{2.5}$ ionic species. Chloride ion concentration at night was higher than during the day in
211 this study. In addition, the meteorological parameters, i.e., mixing height (low mixing height at
212 night) and wind speed (low wind speed at night), were another reason to expect source emission and
213 chemical reactions in the atmosphere. In addition, the ambient temperature in the daytime was 26.4
214 and 27.2^oC at Tzouying and Daliao, respectively. At night, the temperature was 2-3^oC lower than
215 during the day. Therefore, the temperature could be a factor in the day and night difference of NH_4^+,
216 NO_3^-, and Cl^- in fine particles. Generally, chloride depletion was higher during the day than at night.
217 The chloride depletion at night may be caused by acids (such as HNO_3 and H_2SO_4) and NO_2 reacting
218 with NaCl to produce HCl and NOCl gas, respectively (Shroeder and Urone, 1974; Hitchcock et al.,
219 1980; Shimohara et al., 2001). During the day, photochemical reactions and temperature could be the
220 reasons for chloride depletion. In addition, chloride compounds could be emitted from the polyvinyl
221 chloride (PVC) plant in the Ren-Da petrochemical industrial district (near the Tzouying station) and
222 the chlorine industry (producing chloralkali, liquid chlorine, hydrochloric acid, etc.) in the Lin-Hai
223 industry district (near the Daliao station) (TEPA, 2000). In addition, the chloride ion concentration at
224 night was also higher than during the day. Chloride ion concentration in fine particles at night was
225 about 8.7 and 11 times higher than the day concentration in Tzuoying and Daliao, respectively. The
226 meteorological parameters, chemical reaction in atmosphere, and emission sources could affect the
227 Cl^- concentration in PM. But the different of chemical reactions could be the main reason to cause

high Cl^- at night.

In the fine particles, the nitrate concentration at night was 5.7 and 6.0 times higher than the concentration during the day at Daliao and Tzuoying, respectively. This may be attributed to the photochemical reaction during the day, which consumed the nitrate in the fine particles. Furthermore, the ammonium concentration in fine particulate at night was higher than during the day. The night/day ratio of ammonium concentration was 1.7 at Tzuoying and 1.8 at Daliao in $PM_{2.5}$. In addition, the meteorological parameters, i.e., mixing height and wind speed, were another reason to expect source emission and chemical reactions in the atmosphere.

In addition to HNO_3, the concentrations of HCl and SO_2 were slightly higher during the day, but the variation was less than 10% (0.2 $\mu g/m^3$) and 30% (5 $\mu g/m^3$) for HCl and SO_2, respectively, in Daliao. In Tzouying, the daytime concentrations of HCl and SO_2 were, respectively, 3% and 17% higher than the nighttime concentrations.

The concentration of HNO_3 during the day was about 8 and 6 times higher than that at night for Daliao and Tzouying, respectively. The concentration of HNO_3 was higher than that of HCl during the day (**Table 1**). The reaction of $NaCl_{(s)}$ and $HNO_{3(g)}$ may have produced HCl near the coastal area (Seinfeld and Pandis, 1998). Hence, this reaction cannot explain the higher HNO_3 concentration that occurred during the day. NO_2 reacts with hydroxyl radicals during the day and produces HNO_3, which could be one of the dominant mechanisms after sunrise (Russell et al., 1984 and 1985). In contrast to HNO_3, the concentrations of HNO_2 and NH_3 at night were about two times higher than those during the day. High HONO at night could come from source emissions, i.e., combustion engines (diesel vehicles) (Kurtenbach et al., 2001), or heterogeneous NO_2-HONO chemical conversion (Su et al., 2008; An et al., 2009; Yu et al., 2009) In addition, nitrous acid was rapidly photolyzed at wavelengths ≤ 400 nm during the day (Calvert et al., 1994). Thus, HNO_2 accumulated mostly at night and was photolyzed by "OH push" after sunrise (Platt and Perner, 1980; Staffelbach et al., 1997; Acker et al., 2005).

Total NH_3 emissions in Kaohsiung were 1.7×10^5 tons in 2005, with contributions of 43% and

254 40% from agricultural activity and the livestock industry, respectively. Additionally, 17% of the
255 NH_3 emission was attributed to industrial processes and biological sources (TEPA, 2005). Generally,
256 the retention time of NH_3 may be a few hours in the lower atmosphere, but it could be weeks in a
257 calm environment (Asman and van Jaarsveld, 1992; Kapoor et al., 1992). Although a relatively small
258 amount of NH_3 is emitted from industrial processes, the higher NH_3 concentration at night in this
259 study may still be closely related to the industrial activities near the sampling sites. Another reason
260 for higher NH_3 may be the stable atmosphere at night (Cadle et al., 1982; Singh et al., 2001).

261 Some reference data were selected from other studies--i.e., Hong Kong (Pathak et al., 2003 and
262 2004) and Korea (Lee et al., 1999) for similar weather conditions; New York (Bari et al., 2003) for
263 metropolitan comparison; and other studies in Taiwan (Tsai et al., 2000; Hsu et al., 2008) to compare
264 the gaseous pollutants and ionic species in $PM_{2.5}$. **Table 2** compares the acid and base gas
265 concentrations and ionic species concentrations in $PM_{2.5}$ sampled in different areas. The $PM_{2.5}$
266 concentration in the current study was similar to that sampled in Korea (Lee et al., 1999). However,
267 vehicles were the major source of particles, which is different from the Kaohsiung air basin, where
268 only 13% of $PM_{2.5}$ was from vehicles and 87% was from stationary sources (TEPA, 2006). The
269 concentrations of gas and ionic species in particulate matter were generally similar, except for SO_4^{2-}
270 and NH_3, which were 30 and 300% higher in the current case, respectively. This may be attributed
271 mainly to the different emission sources and meteorological conditions in the two experimental areas.
272 The ionic species concentration in the Hong-Kong area was lower than that in our case, which may be
273 associated with long-range transport from mainland China and not with local emission over the
274 Hong-Kong area (Pathak et al., 2003). In addition to SO_2, the acid and base gas concentration in New
275 York (Bari et al., 2003a and 2003b) was also lower than in our study. New York is an urban area, so
276 pollution sources and meteorological characteristics are different from those in Daliao and Tzouying.
277 In New York, space heating was the major source of SO_2, and ammonia was emitted mainly from
278 livestock and ammonia-based chemical fertilizers.

279

3.2 Weather conditions

The detailed characteristics of the synoptic environment during the sampling period are summarized in **Table 3**. A high-pressure system was located over northern China during the first two days (22-23 Oct) of the experiment, while northeasterlies prevailed in the vicinity of Taiwan during that period. A sea breeze occurred over the Kaohsiung area during the day. Typhoon NOCK-TEN approached Taiwan on 24 Oct and landed on 25 Oct (**Figure 1**). Heavy precipitation occurred over northern Taiwan under the influence of Typhoon NOCK-TEN during the period of 24-26 Oct (low pressure is shown in **Figure 2a**), while no significant rainfall was observed in the Kaohsiung area. When Typhoon NOCK-TEN weakened and moved north, most of Taiwan was under a weak synoptic-control environment, since a high-pressure system seemed to be stationary over the Japan Sea during the period of 27-29 Oct. There was no precipitation during the period of 27-30 Oct in Taiwan. A significant sea breeze was observed in the Kaohsiung area during the day. A high-pressure system started to develop over Siberia on 31 Oct. The system enhanced and moved easterly during the subsequent few days. Taiwan was under the influence of this strong high-pressure system during the period of 31 Oct to 3 Nov. Cool, dry northeasterlies prevailed over northern Taiwan during the last few days of the experiment. The subsidence accompanied by the strong high-pressure system led to a clear, sunny sky over the Kaohsiung area.

The variations of temperature and relative humidity during the experiment are illustrated in **Figures 2b** and **c**. The diurnal variation of these two variables was obvious. During the day, the maximum temperature averaged below 30^{o}C around noon, and the lowest relative humidity was generally below 60% (except under the influence of Typhoon NOCK-TEN during the period of 24-26 Oct). At night, an increasing relative humidity trend can be observed, with the highest (over 75%) occurring just before sunrise.

The mixing height and atmospheric stabilities estimated by “Pasquill stability categories” are illustrated in **Figure 2e**. During the day, the mixing height was generally above 1000 m, while the atmospheric stabilities were categorized into “B” (moderately unstable) for most of the days. The

306 stabilities were categorized into “C” (slightly unstable) on 25 Oct, 30 Oct and 2 Nov, when the
307 weather was slightly cloudy and the average wind speed increased to 5 m s^{-1}. In contrast, the mixing
308 height averaged below 800 m during the night, and the atmospheric stabilities were all categorized as
309 “F” (extremely stable).

310 To show the distributions of wind speed and the frequency of the varying wind direction, a wind
311 rose analysis was carried out on the basis of observations at Kaohsiung station. **Figure 3a** indicates
312 that westerlies and northwesterlies prevailed over the Kaohsiung area during the day (i.e., 7 am-7 pm).
313 The westerly component implies a sea-breeze development over the coastal area. As shown, 57.4%
314 and 27.9% of the wind observations were within 1-4 m s^{-1} and 4-7 m s^{-1}, respectively. Alternatively,
315 the relatively weak northerlies and northeasterlies occurred during the period from 7 pm-7 am on the
316 following day (**Figure 3b**), while 82.7% of the wind observations were below 4 m s^{-1} at night.
317 Therefore, the atmosphere was relatively stable at night compared to the daytime, which was one of
318 the reasons for the high pollutant concentration at night.

319 3.2.1 Correlation of pollutant concentration and meteorological parameters

320 The correlation coefficients of the meteorological parameters and gaseous pollutant
321 concentration and particulate ions were determined by the Statistical Package for Social Sciences
322 (SPSS version 15.0) (Levesque, 2007). **Table 4** depicts the correlation between the major pollutant
323 concentrations and the meteorological parameters, i.e., wind speed (WS), mixing height (MH),
324 temperature (T), relative humidity (RH) and atmospheric stability (S). The atmospheric stability is
325 categorized into levels A-F corresponding to the values of 1-6. Although the atmospheric stability is
326 not a qualitative factor, the given number could be a method to determine the relationship between
327 atmospheric stability and other meteorological factors and air pollutants. The negative correlation
328 coefficients between $PM_{2.5}$ (as well as HNO_2, NH_3, Cl^-, NO_3^- and NH_4^+) at both stations, with WS,
329 MH and T corresponding to higher $PM_{2.5}$ concentration, occurred when WS, T and MH were lower.
330 The absolute values of the coefficient between $PM_{2.5}$ and WS (T) were higher than that between
331 $PM_{2.5}$ and MH, which implies that lower WS and T may lead to higher $PM_{2.5}$ concentration. Generally,

a more stable atmosphere and low MH was favorable for local pollutant accumulation; thus, there was a positive correlation between $PM_{2.5}$ concentration and S. Furthermore, higher RH was also a favorable condition for higher $PM_{2.5}$ concentration at night. The correlation between $PM_{2.5}$ and the meteorological parameters may apply to the species of HNO_2, NH_3, Cl^-, NO_3^- and NH_4^+ as well.

The relationship between HNO_3 concentration and meteorological parameters was almost opposite that of $PM_{2.5}$ (as well as HNO_2, NH_3, Cl^-, NO_3^- and NH_4^+). The positive correlation coefficients between HNO_3 and WS, MH and T indicated that higher HNO_3 concentration occurred when there was higher WS (**Figure 3** shows high WS during the day (**Figure 3(a)**), higher T (**Figure 2 (b)** shows high T during the day) and higher MH (**Figure 2e** shows high MH during the day) at the two stations. **Figure 2d** reveals high solar radiation during the day, ranging from 2.2-2.7 MJ/m^2. Solar radiation was low during the period of the tropical storm, especially in the daytime on 25 Oct. Alternatively, the relatively lower RH (**Figure 2c** shows low RH during the day than at night) and less stable environment (**Figure 2e** shows an unstable atmosphere during the day) might be favorable conditions for the higher HNO_3 occurrence reported in this study. The results show high HNO_3 formation during the day (**Table 1**). This may suggest that the high solar radiation could enhance the photochemical reaction, therefore the HNO_3 could be photolysis to be OH radical and NO_2.

In addition, T, MH, and RH affect the nitric acid concentration at the two stations; WS, MH and T were important factors for nitrous acid. For SO_2 the meteorological effects were a complex system (all of the meteorological factors affect the SO_2 concentration) during the sampling period. High WS was accompanied by low $PM_{2.5}$ concentration, and WS was the important factor for $PM_{2.5}$ concentration at the two stations. In addition, WS and T could be the more important meteorological factors affecting nitrate and ammonium content in $PM_{2.5}$.

3.2.2 Variation of pollutants concentration under the influence of typhoon and during the episode days

Figure 4 shows the concentration variations of major ionic species in $PM_{2.5}$ during the experiment. The concentration of $PM_{2.5}$ decreased from 53 to 16 $\mu g/m^3$, and the major ionic species, NO_3^-, SO_4^{2-}

and NH_4^+, all decreased significantly when the typhoon affected Taiwan during the period of 24-26 Oct. At the same time, the concentration of gaseous pollutants dropped off significantly as well. Although there was no significant heavy precipitation in the Kaohsiung area on those days (24-25 Oct), the heavy rainfall that accompanied the typhoon over northern Taiwan did improve the air quality noticeably and reduced the pollutant concentration. The heavy rainfall reduced the pollution transport from north to south at Daliao and Tzouying (southern Taiwan). The typhoon system led the precipitation from 24 to the night of 25 Oct, although the rain was not heavy and continuous in southern Taiwan. The scavenging effect could reduce the air pollution in southern Taiwan. Till the daytime of 26, the rain was stop in southern Taiwan, but the weather was still rainy in other area of Taiwan. After the typhoon system passed by, the pollutant concentration increased instantly and reached a peak within 12-24 hours. The concentrations of $PM_{2.5}$, NO_3^-, SO_4^{2-} and NH_4^+ increased 3.4 4.5, 3.2 and 4.8 times, respectively, at Daliao. At Tzouying, the concentrations of $PM_{2.5}$, NO_3^-, SO_4^{2-} and NH_4^+ increased 4, 4.8, 2.6 and 4.4 times, respectively. The pollutant concentration increase was mainly caused by local emission sources in the Kaohsiung area after the typhoon because, although the rainy weather was still over other parts of Taiwan at that point, it was not over the Kaohsiung area. Therefore, few air pollutants were transported from northern Taiwan to southern Taiwan. The Kaohsiung industrial metropolitan area is an ozone non-attainment region with a power plant, industries (petrochemical industry, iron and steel plant, etc.), and motor vehicles being the major sources. Therefore, the local combustion sources (i.e., coal and heavy oil consumption) are important to the source apportionment of fine particles. In addition, NO_2 concentration (**Figure 4**) was from 12-51 and 17-107 $\mu g/m^3$ for Daliao and Tzouying, respectively. Insignificant correlation observed NO_2 to HNO_3, and NO_3^- at both stations. HNO_3 revealed negative moderate correlation ($r=-0.6$) to NO_3^- at both stations that indicated the nitric acid could transfer into nitrate by chemical reaction in atmosphere.

Referring to the regulations of U.S. EPA, the definition of an air pollution episode day in this

study is when a daily $PM_{2.5}$ concentration has a value larger than 65 $\mu g/m^3$. Thus, there were 5 episode days in Daliao (22 Oct, 31 Oct and 1-3 Nov) and 2 episode days in Tzouying (2-3 Nov) during the experiment. From the analysis of weather conditions, Taiwan was influenced by a strong high-pressure system during the period of 31 Oct to 3 Nov. A strong subsidence accompanied the high-pressure system, which led to a relatively stable environment with clear skies and low wind speed over the Kaohsiung area.

Table 5 shows the pollutant concentration during the episode and non-episode days. For gaseous pollutants, an increase of 25-62%, 19% and 25-30% in HNO_3, HNO_2 and SO_2 was found on episode days, respectively. However, HCl was higher on non-episode days at both stations. Higher HCl concentration was observed on non-episode days than on episode days. This could be attributed to the reaction of HCl with NH_3, producing NH_4Cl (Seinfeld and Pandis, 1998; Chang and Allen, 2006), which can accumulate in fine particles. We measured high NH_3 concentration and low HCl in gas and high NH_4^+ and Cl^- in fine particulate matter during the episode days. The rich ammonia could promote the reaction of NH_4Cl in fine particles.

The concentration of NH_3 on episode days revealed a contrasting trend between the two stations. NH_3 was 1.5 times higher and 0.77 times lower than that on non-episode days in Daliao and Tzouying, respectively. A possible explanation for this may be the different emission sources that contributed to NH_3 concentration. Local agricultural and industrial processes play important roles in the accumulation of NH_3 in Daliao. Conversely, since Tzouying was located near the coastline, the pollutant transportation inland may make a relatively greater contribution to local NH_3. On episode days, $PM_{2.5}$ concentrations at both stations were 1.5-1.6 times higher than those on non-episode days. Major ionic species, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+ and K^+, at both stations had larger values on episode days (Table 5). Note that the differences of sulfate content in the $PM_{2.5}$ between episode and non-episode days at Tzouying (7 $\mu g/m^3$) were about twice that in Daliao (3.9 $\mu g/m^3$). This was the main reason for the higher $PM_{2.5}$ concentration in Tzouying during episode days. The emission from refinery plants around the sampling site and motor vehicles, together with photochemical reactions, may have led to higher sulfate content in $PM_{2.5}$ in Tzouying.

3.3 Relationship between gaseous pollutants and particulate ions

The correlation coefficient of gaseous pollutants and particulate ions was calculated by the software package SSPS (Levesque, 2007). Results indicated a high correlation ($0.9 > r > 0.7$) (Zhang et al., 2004) between HNO_2 and NO_3^- that indicated the phase transfer reactions in the atmosphere. NH_4^+, Cl^- and NO_3^- revealed high correlation which suggested the NH_4Cl and NH_4NO_3 could be the predominant components in $PM_{2.5}$ at Tzouying. In addition, the high correlation were determined between HNO^2 and NO_3^-, NH_3 and NH_4+, and NH_4^+, Cl^- and NO_3^- suggests phase transfer reactions. Therefore, NH_4Cl and NH_4NO_3 could be the predominant components of $PM_{2.5}$ at Daliao. Furthermore, the correlation coefficient of other gaseous pollutants and particulate ions was less than 0.8. For example, a low correlation coefficient of Na^+ vs. NO_3^- and Na^+ vs. Cl^- was measured at both stations. But moderate correlation coefficients of NH_4^+ vs. SO_4^{2-} (r=0.67 for Daliao and 0.69 for Tzouying) were found.

In addition, the SSPS-software (Levesque, 2007) was used for splitting the data set into a number of groups of observations conducted by cluster analysis, which are distinct in terms of typical group values of the variables, an approach that enables between-group variance to be maximized and within-group variance to be minimized. Applying correlation and cluster analysis to gaseous pollutants, ionic species in particulate matter, and meteorological parameters, three groups with a moderate correlation coefficient ($0.7 > r > 0.6$) were found in Daliao station. Group 1 included HNO_2, NH_3, and Cl^-; group 2 included NH_3, Cl^-, NO_3^-, and NH_4^+; and group 3 included $PM_{2.5}$, NO_3^-, SO_4^{2-} and NH_4^+. The group 1 indicated the chemical reaction in the atmosphere and group 2 indicated the transformation of gas to particle ($NH_{3(g)} \rightarrow NH_4^+{}_{(s)}$) and the potential of NH_4Cl and NH_4NO_3 in particulate constituents. The positive correlation in group 3 indicated that sulfate, nitrate and ammonium were the main ionic species in $PM_{2.5}$ (They also reflect the particulate mass fraction.). Based on the correlation species, cluster analysis a nd particulate mass portion, ammonium

compounds, i.e., ammonium nitrate, ammonium sulfate and ammonium chloride, were potential compounds in the particle mass, which indicates that their formation pathways were important reactions in the area.

HONO has been recognized as an important trace gas of troposphere where it rapidly undergoes photolysis by to release a significant amount of OH radicals and HONO could accumulate at night (Finlayson-Pitts et al., 2000). Some literatures proposed the reaction mechanism and explained the relation between HNO_2 and NO_3^- under high NH_3 condition (Zhang and Tao, 2010). The reaction is as follows:

$$2NO_{2(g)} + H_2O_{(g)} + NH_{3(g)} \rightarrow HONO_{(g)} + NH_4NO_{3(s)} \quad (1)$$

In addition, other heterogeneous reaction mechanism was proposed (Yu et al., 2009):

$$NO + HNO_{3\,(surface)} \rightarrow HONO + NO_2 \quad (2)$$

Therefore, the mechanisms could explain some of relationships between HNO_2 and NO_3^-.

Six groups of species with a higher correlation relationship were found in Tzouying.

Group 1 included HNO_3 and O_3 as well as the factor of temperature; group 2 included HNO_2, NH_3, $PM_{2.5}$, Cl^-, NO_3^-, NH_4^+, K^+, Ca^{2+}, NO_2, and NMHC; group 3 included NH_3, NO_3^-, and Cl^-; group 4 included $PM_{2.5}$, NO_3^-, SO_4^{2-} NH_4^+ and K^+; group 5 included Cl^-, NO_3^-, NH_4^+ and NMHC; and group 6 included NO_3^-, NH_4^+ K^+, and O_3. The species in group 1 implied a photochemical reaction of nitric acid and ozone, where the temperature was regarded as an indicator of the strength of sunshine. A relatively more complicated relationship occurred between the species categorized in group 2. A summary of the other groups indicated that ammonium nitrate, ammonium chloride, ammonium sulfate, ammonium bisulfate, potassium nitrate, and potassium sulfate were the important compounds in the particulate compositions. The main reactions could be the reaction of ammonia with hydrogen chloride to form ammonium chloride or with nitric acid to form ammonium nitrate and the reaction of ammonium with sulfate to form ammonium sulfate (Seinfeld and Pandis, 1998).

460 The daytime average humidity was 62% in Daliao and 65% in Tzouying. The average
461 nighttime humidity was 75% for Daliao and 72% for Tzouying. The deliquescence relative
462 humidity (DRH) values were 61.8, 52 and 40% for NH_4NO_3, $NaHSO_4$ and NH_4HSO_4, respectively,
463 which are all lower than ambient humidity. This implies that the species could be formed in the
464 particulate phase, but are easily dissociated under high relative humidity conditions. Conversely, the
465 DRH ranged from 74 to 84% for KCl, Na_2SO_4, NH_4Cl, $(NH_4)_2SO_4$, NaCl and $NaNO_3$. The DRH in
466 the latter case were higher than ambient humidity, which implies that these compounds could exist in
467 the particulate phase.

468 In the ammonia, nitric acid, sulfuric acid and water reaction system, with excess ammonia,
469 ammonia will react with nitrate and form NH_4NO_3. In contrast, in an insufficient NH_3 system, the
470 vapor pressure of NH_3 is low and cannot neutralize sulfate, so the sulfate will tend to drive the nitrate
471 to gas phase and the ammonium nitrate will be low or zero (Seinfeld and Pandis, 1998). During our
472 sampling period, 75% of the total days in Daliao displayed ammonia-rich conditions. The total
473 molar concentration of ammonia was high, over twice the total molar concentration of sulfate
474 (Seinfeld and Pandis, 1998), while only 54% of the total days in Tzouying were categorized as
475 ammonia-rich conditions. This finding was consistent with the fact that there was more ammonia
476 emission in Daliao based on the emission inventory over the Kaohsiung area. Therefore, ammonium
477 nitrate could be formed in the particulate phase in this sampling period, especially on episode days in
478 Daliao (high ammonia concentration in **Table 5**).

479

480 **4. Conclusions**

481 The results of composite pollutant concentration indicated that higher $PM_{2.5}$, HCl, NH_3, SO_2, Cl^-,
482 NO_3^-, SO_4^{2-} and NH_4^+ were found at Daliao than at Tzouying. This could be caused by the different
483 emission sources of the two stations and the fact that Daliao is far from the coastline. For particulate
484 compositions, sulfate, nitrate and ammonium were the major ionic species in $PM_{2.5}$. Higher $PM_{2.5}$, as
485 well as higher Cl^-, NO_3^- and NH_4^+, were found at night than during the day at both stations. In

addition, higher HNO_3 was found during the day, and the hydroxyl radical reaction may be potentially associated with this. In contrast, HNO_2 and NH_3 evidenced higher concentrations at night. This fact may be associated with HNO_2 being more easily photolyzed during the day, whereas the higher NH_3 may be attributed to the accumulation of NH_3 emission under the relatively stable atmosphere at night. During the sampling period, the synoptic weather environment was influenced by Typhoon NOCK-TEN, which produced heavy precipitation over northern Taiwan and led to a significant decrease in concentration for all pollutant species over Kaohsiung. However, the pollutant concentrations bounced back immediately (within 12-24 hours) after the typhoon moved away. Episode days generally occurred when there was a strong subsidence accompanied by a high-pressure system, which may lead to a more stable environment with lower wind speed and mixing height, resulting in higher $PM_{2.5}$, as well as HNO_2, NH_3, SO_4^{2-}, Cl^-, NO_3^-, NH_4^+ and K^+. Based on the high concentration of ammonia in the atmosphere, NH_4NO_3 could have formed in the air-basin during our sampling period. Although this study proposes some potential species (i.e., $(NH_4)_2SO_4$, $(NH_4)HSO_4$, and NH_4NO_3) in particulate chemical compositions, further work is needed to collect additional data and enable meaningful conclusions to be drawn regarding the reaction mechanisms.

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Figure and table Captions

Figures

Figure 1 Map of the sampling sites and typhoon track.

Figure 2 (a) Pressure (hPa) (b)Temperature (^{o}C), (c) relative humidity (%) (d) solar radiation (MJ/m^{2}) and (e) mixing height (m) during the period of 22 Oct – 3 Nov, 2004. The labels in (e) indicate the atmospheric stability in the respective time period.

Figure 3 Wind rose analysis for (a) daytime and (b) nighttime during the period of 22 Oct – 3 Nov, 2004.

Figure 4 Concentration variation of gaseous pollutants (μg/m^{3}), $PM_{2.5}$ (μg/m^{3}) and ionic species (μg/m^{3}) in $PM_{2.5}$ (bold line is Daliao and dash line is Tzouying)

Tables

Table 1 Composite gas and ionic species concentrations in $PM_{2.5}$

Table 2 Gas and ionic species concentrations in $PM_{2.5}$

Table 3 Summary of synoptic and mesoscale environments during the sampling period.

Table 4 Correlation relationship between gas and ionic species concentration and meteorological parameters

Table 5 Gas and ionic species concentrations during episode and non-episode days