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Characteristics of Atmospheric Aerosol and Acidic Gases from Urban and Forest Sites in Central Taiwan

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Abstract Measurements of atmospheric fine aerosols, acidic gases and ammonia were made at National Chung Hsing University (Urban) and Huisun forest area (Forest) sites in central Taiwan region during October (highest ozone month). Annular Denuder System (ADS) was used for sampling gaseous (nitrous acid, nitric acid, sulfur dioxide and ammonia) and fine aerosol species (ammonium, nitrate and sulfate). The results showed a significant diurnal variation in nitrous acid and nitric acid concentrations. Nitric acid was produced primarily during daytime in both sites. In the urban site, the average concentration of nitric acid during daytime was 5.8 times higher compared to nighttime while the average nitrous acid concentration during daytime was lower compared to nighttime, due to the photo-dissociation of nitrous acid. Sulfate, nitrate and ammonium were the major constituents of $PM_{2.5}$. Higher concentrations of nitrous acid, nitric acid, particulate nitrate and ammonium were recorded at urban site.

Keywords $PM_{2.5}$ · Acidic gases · Nitrate · Forest

Air pollution is a consequence of industrialization and urbanization and is known to cause serious human health hazards. Vehicular emissions, crustal materials, secondary aerosols, biomass burning, industrial emissions and marine spray are major pollution sources in urban areas of Taiwan (Chio et al. 2004). It is well evident from our previous studies that, dispersion of particulate matter in the atmosphere was mainly affected by anthropogenic emissions (Horng et al. 2007). In Taiwan, during PM_{10} episode days, dispersal of air pollutants was found to be affected by the lower wind speed, higher relative humidity and geographical characteristics (Tsai and Cheng 2004).

The composition of particles in air is complex and generally includes sulfates, nitrates and carbonaceous matters (Turpin et al. 1991; Cheng and Tsai 2000). Aerosols in atmosphere are formed by a complex chemical, physical, photochemical and oxidation reactions. The secondary particles usually contain sulfate, nitrate and ammonium generated by sulfur dioxide, nitrogen oxides, nitric acid and ammonia. It has been well documented that $PM_{2.5}$ (fine particle is defined as the particulate matter with aerodynamic diameters less than 2.5 μm) is a main fraction of PM_{10} in central Taiwan region (Chen and Mao 1999). Mortality and other epidemiological evidences were correlated directly to the presence of mass concentration of such fine particulates in the atmosphere (Pope et al. 1995). Hence, the present study was designed to investigate the concentration profile of acidic anions in fine particulate matter and acidic gases during daytime and nighttime at National Chung Hsing University (Urban) and Huisun forest area (Forest) sites in central Taiwan. The data generated from this study is anticipated to provide important details on characteristics and distribution of atmospheric particulate and acidic gases in central Taiwan region.

Materials and Methods

For characterizing the acidic gases and particulate matter in urban and forest sites of Taiwan, the Taichung city and Ren-Ai township were selected. Taichung is a commercial metropolitan with a population size over a million, while,

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the Ren-Ai township (Huisun forest area) is a forest area with a total population of 16,000. The urban area sampling site was National Chung Hsing University (NCHU) campus located to the south of Taichung city with traffic emissions and industries as major air pollution sources, while the forest area sampling site was Huisun forest area (HS), which is located 750 m above sea level and is surrounded by large trees. Aerosol samples were collected during 18th–31st of October 2002. During this period of year, a high level of ozone was recorded earlier by Cheng et al. (2001). Collection time was divided as daytime and nighttime (8:00 am. to 8:00 pm. and 8:00 pm. to 8:00 am).

Annular denuder system (ADS) was used to collect $PM_{2.5}$ and gaseous samples. The inlet of ADS contained Teflon coated aluminum cyclone with 10 L min^{-1} flow rate as to remove coarse particles (particulate matter with aerodynamic diameters large than 2.5 μm). The first denuder from the cyclone was coated with Na_2CO_3 (1% glycerol in methanol/water) to collect HNO_2, HNO_3, SO_2. The second denuder was coated with citric acid to collect NH_3. The particulate ($PM_{2.5}$, SO_4^{2-}, NO_3^-, NH_4^+, Na^+) samples were collected on the teflon filter. The nylon filter was used to collect any particulate nitrates that might have evaporated from the teflon.

After each sampling, first and the second denuder samples were extracted with 10 mL of ultra pure water. All the extracts were transferred to 20 mL glass tube and stored at 4°C until analyzed. The teflon and nylon filters were cut into pieces and placed in a vial containing 10 mL of ultra pure water, and sonicated for 90 min. Thus extracted solution was filtered through a 0.22 μm pore size mixed cellulose esters filter and stored in a refrigerator at 4°C until analyzed. All extracts and SO_4^{2-}, NO_3^-, NH_4^+, Na^+ concentrations were determined by Dionex ion chromatography (Dionex DX 100). A QA/QC program of method detection limit (MDL), precision and accuracy were conducted during experiment. The MDLs, was calculated as three times the standard deviation of blanks, as 0.07, 0.03, 0.05 and 0.03 μg m^{-3} for SO_4^{2-}, NO_3^-, NH_4^+ and Na^+, respectively. Precision of the chemical analysis were determined to be less than 10%. The averages fortified sample recoveries for all species appeared in the range of 100 ± 8%. Microsoft Excel 2003 and STATISTICA (Stat. Soft. Inc. 1998) were used for data calculation and statistical analysis. One way analysis of variation was used to assess the difference between urban and forest sites in particulate matter, acidic and basic gases concentration, and meteorological parameters.

Results and Discussion

The average $PM_{2.5}$ and concentration of other chemical species in urban and forest sites are presented in Table 1.

Table 1 Comparison of mean chemical composition of $PM_{2.5}$ aerosol, gaseous pollutants and other meteorological parameters in NCHU (urban) and HS (forest) sampling sites

Species	Urban (n = 24)	Forest (n = 18)	Urban/forest
$PM_{2.5}$	37.1 ± 18.3	26.7 ± 9.6	1.4*
NO_3^-	4.2 ± 2.6	1.5 ± 1.8	2.8*
SO_4^{2-} (μg m^{-3})	6.5 ± 3.6	6.9 ± 3.6	1.0
NH_4^+	3.8 ± 1.8	3.2 ± 1.5	1.2
Na^+	0.3 ± 0.2	0.1 ± 0.2	1.9*
NO_x (ppb)	39.8 ± 12	7.8 ± 1.4	5.1*
SO_2	2.6 ± 0.9	1.5 ± 0.4	1.7*
CO (ppm)	0.9 ± 0.2	0.5 ± 0.1	1.7*
Wind speed (ms^{-1})	1.8 ± 0.7	1.0 ± 0.3	1.7*
Wind direction	NNW	WNW	
	SSW	NW	
Temperature (°C)	25.1 ± 2.3	20.6 ± 1.6	1.2*
Relative humidity (%)	73.8 ± 7.6	85.9 ± 6.4	0.9*
Neutralization ratio	1.0 ± 0.1	1.1 ± 0.1	1.0

* Denote the ratio has statistical significance at $p < 0.05$

The average wind speed recorded in forest site (1 m s^{-1}) was comparatively lesser as the selected forest site was surrounded by mountains. Average daily temperatures in urban and forest sites were 25°C and 20°C, respectively. The relative humidity in urban and forest sites were respectively 74% and 86%.

Air samples of urban site showed higher $PM_{2.5}$ and nitrate concentrations. Figure 1 displays the $PM_{2.5}$ and nitrate concentrations, which is 1.4 times and 2.8 times higher than the forest site, respectively. The elevated $PM_{2.5}$ and nitrate particle concentrations recorded in urban site can be attributed to traffic emissions and other industrial activities. No significant difference was observed in sulfate concentrations between two sampling sites. Prevailing wind in forest site was from northwestern direction, favoring the transportation of pollutants from Taichung City.

The neutralization ratio (NR) method was employed to detect the presence of acidic aerosol concentrations in both the sampling sites. Presence of non-sea-salt sulfate (NSS–SO_4^{2-}) in aerosols was corrected by subtracting the amount of SO_4^{2-} in sea salt from that of SO_4^{-2} measured in the atmosphere (Tsai and Cheng 1999). The amount of marine sulphate was estimated from the SO_4^{2-}/Na^+ ratio for bulk seawater. The suspended aerosols Na^+ in the atmosphere was assumed to be derived only from sea salt particles (Colbeck and Harrison 1984). Hence, the other chemical species present in bulk seawater off the Taichung coast were measured (Tsai and Cheng 1999). NSS–SO_4^{2-} and NR are defined as SO_4^{2-} (in μg m^{-3})–0.231 × Na^+(in μg m^{-3}) and NH_4^+(in neqm^{-3}) / [NSS–SO_4^{2-} (in neqm^{-3}) + NO_3^-

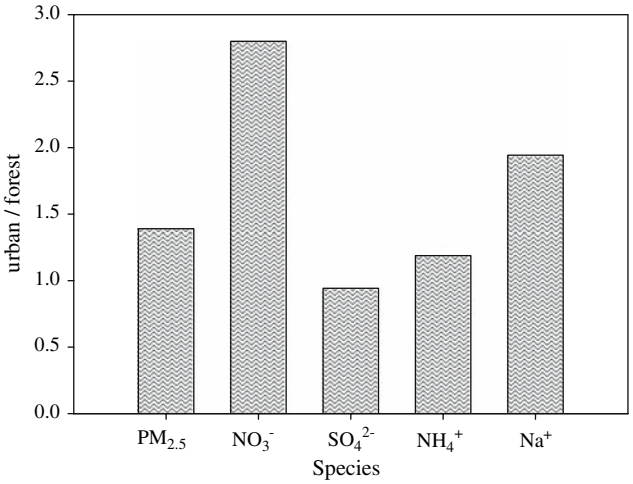

Fig. 1 The chemical composition of $PM_{2.5}$ aerosol, chemical species ratio in urban/forest sites

Table 2 Concentration and urban/forest ratios of HNO_3, HNO_2 and NH_3 (μg m^{-3}) during daytime, nighttime and full day

Periods	Species	Urban (n = 24)	Forest (n = 18)	Urban/forest
Full day	HNO_2	3.6 ± 2.4	0.3 ± 0.1	10.7*
	HNO_3	2.3 ± 2	0.7 ± 0.4	3.4*
	NH_3	6.2 ± 1.6	1.6 ± 0.6	3.9*
Daytime	HNO_2	2.3 ± 0.8	0.4 ± 0.1	6.0*
	HNO_3	3.5 ± 1.8	0.8 ± 0.3	4.3*
	NH_3	5.6 ± 0.8	1.9 ± 0.6	3.2*
Nighttime	HNO_2	5.6 ± 2.7	0.3 ± 0.2	19.4*
	HNO_3	0.6 ± 0.2	0.4 ± 0.3	1.4
	NH_3	7.0 ± 2.0	1.2 ± 0.4	5.3*

* Denote the ratio has statistical significance at $p < 0.05$

(in neqm^{-3})]. When the NR is close to a unit (one), it indicates the existence of ammonium sulfate and ammonium nitrate salts (Cheng and Tsai 2000). The NR ratio was neutral in both the sampling sites of our study. Hence, more sulfuric acid particles might have reacted with ammonia than nitric acid leading to increased sulfate particles.

The average concentrations of HNO_3, HNO_2 and NH_3 in two sampling sites are shown in Table 2. In the urban site, the average concentration of HNO_3 during daytime was 5.8 times higher than nighttime, while it was only two times higher in forest site. The HNO_3 concentration at both the sites was highest during day compared to nighttime. Generally, it is observed that HNO_3 concentration reaches maxima during daylight hours (Cobb and Braman 1995). Higher concentrations during daytime are favored by higher production NO_2, which reacts with hydroxyl radicals, high temperature and low relative humidity favoring the dissociation of ammonium and nitrate aerosols (Harrison and Allen 1990).

Mean concentration of HNO_2 during nighttime was 2.2 times higher than daytime in urban site. The lowest concentration of HNO_2 was recorded in forest site. Similar observations were also reported earlier, where concentrations HNO_2 were highest during nighttime in an urban location (Kitto and Harrison 1992). Hence, this particular event taking place only during nighttime might have been caused due to the absence of sunlight, which prevents the photolysis of HNO_2. The HNO_2 concentrations were highest during nighttime and lowest during daytime in the urban site.

Average concentrations of ammonia at urban and forest sites were 6.2 and 1.6 μg m^{-3}, respectively. The major sources of ammonia are local emissions and partly derived from agriculture and anthropogenic activities (Sakurai et al. 2003). Increase of ammonia concentration in urban site can be attributed to the anthropogenic activities. The forest site is located near to the mountainous region with no obvious emissions, and limited anthropogenic activities, hence showed relatively reduced ammonia oncentrations.

The relationship between precursor gases, particulate sulfate and nitrate are complex. Sulfate is usually formed from the precursor gas sulfur dioxide by a chain of chemical reactions while nitrates are formed from precursor gas nitrogen dioxide by a chemical reaction. The conversion ratios for nitrogen (F_n) and sulfur (F_s) can be used to estimate the differences between the oxidation process of nitrogen dioxide to nitrate and sulfur dioxide to sulfate respectively. The conversion ratio was defined as follows (Grosjean and Friedlander 1975; Kadowaki 1986; Khoder 2002):

$$\text{Sulfur conversion ratio}(\%) = \frac{SO_4^{2-}}{SO_2 + SO_4^{2-}}$$

$$\text{Sulfur nitrogen conversion ratio}(\%) = \frac{PNO_3^- + GNO_3^-}{NO_2 + PNO_3^- + GNO_3^-}$$

where the unit of SO_4^{2-} is the particulate sulfate concentration, as SO_2 μg m^{-3}; SO_2 is the gas phase SO_2 concentration, converted from ppm to μg m^{-3}; the unit of PNO_3^- is the particulate nitrate concentration, as NO_2 μg m^{-3}; GNO_3^- is the gaseous nitrate concentration, as NO_2 μg m^{-3}; NO_2 is the gas phase NO_2 concentration, converted from ppm to μg m^{-3}.

Sulfur conversion ratios (F_s) and nitrogen conversion ratios (F_n) were calculated based on the above equations (Tables 3). The mean sulfur conversion ratios (F_s) at urban and forest sites were 37% and 48%, respectively. Highest sulfur conversion ratio (F_s) was recorded in the forest site. It is assumed that, sulfate will be in the form of $(NH_4)_2SO_4$ in atmosphere or might have generated by the reaction

Table 3 Daily F_s and F_n ratios at urban and forest sites

Parameter	Urban		Forest	
	Range (n = 23)	Mean	Range (n = 15)	Mean
SO_2 (μg m^{-3})	3.7–13.3	6.8 ± 2.4	1.8–5.8	4.1 ± 1.2
PSO_4^{2-}	1.9–11.6	6.0 ± 2.7	2.1–11.7	6.0 ± 2.8
F_s (%)	20.3–57.4	36.6 ± 9.9	22.0–67.3	48.5 ± 13.9
NO_2 (μg m^{-3})	38.9–78.5	56 ± 10.3	7.5–16.4	11.3 ± 2.7
PNO_3^-	0.8–11.6	4.2 ± 2.6	0.1–3.8	1.3 ± 1.2
GNO_3^-	0.3–6.7	2.3 ± 2.0	0.2–1.5	0.8 ± 0.3
F_n (%)	2.5–13.8	7.5 ± 3.6	4.2–21.7	11.1 ± 5.6

between H_2SO_4, mist and gaseous NH_3. The sources of SO_2 particles are mainly fuel combustion, power plants and coal burning boilers. Atmospheric SO_2 was converted directly to H_2SO_4 after reacting with OH radical or H_2O_2. The SO_2 concentration at urban and forest sites were 2.6 and 1.5 ppb, respectively. In the urban site there was no complete transition to sulfate. Similarly, nitrogen conversion (F_n) values at urban and forest sites were 7% and 11%, respectively. The gaseous nitrate and particulate nitrate might have oxidized from NO_x. The source of atmospheric NO_x is usually from the mobile or stationary emissions. During daytime, the reaction between NO_2 and OH radical results in the formation of nitric acid while, N_2O_5 hydrolysis is an important source leading to the formation of nitric acid during the night (Russel et al. 1986). The particulate nitrate is generated by the reaction between nitric acid with ammonia. The average concentrations of NO_x at urban and forest site were 39.8 and 7.8, respectively indicating that the major portion of NO_x present in the urban site was not transformed to nitrate.

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References

Chen ML, Mao IF (1999) The $PM_{2.5}$ and PM_{10} particles in urban aerosol of Taiwan. Sci Total Environ 226:227–235

Cheng MT, Tsai YI (2000) Characterization of visibility and atmospheric aerosols in urban, suburban and remote areas. Sci Total Environ 263:101–114

Cheng WL, Pai JL, Tsuang BJ, Chen CL (2001) Synoptic patterns in relation to ozone concentrations in west-central Taiwan. Meteorol Atmos Phys 78:11–21

Chio CP, Cheng MT, Wang CF (2004) Source apportionment to PM_{10} in different air quality conditions for Taichung urban and costal areas, Taiwan. Atmos Environ 38:6893–6905

Cobb GP, Braman RS (1995) Relationships between nitrous acid and other nitrogen oxides in urban air. Chemosphere 31:2945–2957

Colbeck I, Harrison RM (1984) Ozone-secondary aerosol-visibility relationships in north-west England. Sci Total Environ 34:87–100

Grosjean D, Friendlander SK (1975) Gas-particulate distribution factors for organic and other pollutants in Los Angeles atmosphere. J Air Pollut Control Assoc 25:1038–1044

Harrision RM, Allen AG (1990) Measurements of atmospheric HNO_3, HCl, and associated species on a small network in eastern England. Atmos Environ 24:369–376

Horng CL, Cheng MT, Chiang WF (2007) Distribution of $PM_{2.5}$ and gaseous in central Taiwan during two Chinese festival periods. Environ Eng Sci 24:515–524

Kadowaki S (1986) On the nature of atmospheric oxidation processes of SO_2 to sulfate and of NO_2 to nitrate on the basis of diurnal variations of sulfate, nitrate, and other pollutants in an urban area. Environ Sci Technol 20:1249–1253

Khoder MI (2002) Atmospheric conversion of sulfur dioxide to particulate sulfate and nitrogen dioxide to particulate nitrate and gaseous nitric acid in an urban area. Chemosphere 49:675–684

Kitto AMN, Harrison RM (1992) Nitrous and nitric acid measurements at sites in southeast England. Atmos Environ 26A:235–241

Pope CA III, Dockery DW, Schwarts J (1995) Review of epidemiological evidence of health effects of particulate air pollution. Inhal Toxicol 17:1–18

Russel AG, Cass GR, Seinfeld JH (1986) On some aspects of nighttime atmospheric chemistry. Environ Sci Technol 20: 1167–1172

Sakurai T, Fujita S, Hayami H, Furuhashi (2003) A case study of high ammonia concentration in the nighttime by means of modeling analysis in the Kanto region Japan. Atmos Environ 37: 4461–4465

StatSoft, Inc (1998) Statistica for windows. StatSoft, Inc., 2300 East 14th street, Tulsa, OK 74104, USA

Tsai YI, Cheng MT (1999) Visibility and aerosol chemical compositions near the coastal area in central Taiwan. Sci Total Environ 231:37–51

Tsai YI, Cheng MT (2004) Characterization of chemical species in atmospheric aerosols in a metropolitan basin. Chemosphere 54:1171–1181

Turpin BJ, Huntzicker JJ, Larson SM, Cass GR (1991) Los Angeles summer midday particulate carbon: primary and secondary aerosol. Environ Sci Technol 25:1788–1793