Development of an Automated System (PPWD/PILS) for Studying PM$_{2.5}$ Water-Soluble Ions and Precursor Gases: Field Measurements in Two Cities, Taiwan

Ziyi Li$^{1}$, Yingshu Liu$^{1}$, Yujie Lin$^{2}$, Sneha Gautam$^{3}$, Hui-Chuan Kuo$^{2}$, Chuen-Jinn Tsai$^{2,*}$, Huajun Yeh$^{3}$, Wei Huang$^{3}$, Shih-Wei Li$^{4}$, Guo-Jei Wu$^{4}$

$^{1}$ School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China
$^{2}$ Institute of Environmental Engineering, National Chiao Tung University, Hsinchu 300, Taiwan
$^{3}$ Focused Photonics (Hangzhou), Inc., Zhejiang 310052, China
$^{4}$ Environmental Analysis Laboratory, Environmental Protection Administration, Jongli 320, Taiwan

ABSTRACT

An automated system consisting of a particle-into-liquid sampler (PILS) and a parallel plate wet denuder (PPWD) coupled with an ion chromatography was used for simultaneous measurement of ambient water-soluble ions in PM$_{2.5}$ and precursor gases. The performance of the PPWD/PILS was validated by comparing it with the PDS (porous metal denuder sampler) for precursor gases (NH$_3$, HONO, HNO$_3$, and SO$_2$) and PM$_{2.5}$ ionic species (NH$_4^+$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, Cl$^-$ and K$^+$) measured in Taipei and Hsinchu Cities of Taiwan. Good correlations were demonstrated with linear regression slopes ranging from 0.92 to 1.04 and 0.84 to 0.97 as well as $R^2$ ranging from 0.76 to 0.83 and 0.89 to 0.94, for precursor gases and PM$_{2.5}$ ions, respectively. The accuracy of the current system for precursor gases outperforms the other commercial systems. Field continuous data showed that NH$_3$ was the most abundant precursor gas with the diurnal pattern peaking at low nocturnal boundary heights and during rush hours with local traffic emissions in Taipei, and with the pattern peaking only at mid-day associated with regional sources in Hsinchu. A reverse diurnal pattern for HONO in Taipei reflected the daytime photolysis and its nocturnal heterogeneous reaction, while its concentration was relatively constant at very low level in Hsinchu. SO$_4^{2-}$, NH$_4^+$ and NO$_3^-$ exhibited very similar diurnal patterns with the mean concentrations of 4.56 ± 3.14, 1.55 ± 1.16 and 0.52 ± 0.5 µg m$^{-3}$ in Taipei, and 7.95 ± 5.52, 2.41 ± 1.95 and 0.96 ± 1.10 µg m$^{-3}$ in Hsinchu, respectively. Correspondingly high concentrations of major ions to precursor gases were associated with the photochemical secondary aerosol formations and heavy traffic in Taipei. Based on an ammonia-rich atmosphere and high SOR values, (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ were inferred to be the dominant inorganic salts in PM$_{2.5}$ at both sites, which were also verified by the ion balance analysis.

Keywords: PM$_{2.5}$; Automated measurement system PPWD/PILS; Inorganic ions; Precursor gases; Seasonal variation; Diurnal variation.

INTRODUCTION

Fine particulate matter (PM$_{2.5}$, particles with aerodynamic diameters less than 2.5 µm) in the atmosphere are known to be associated with adverse effects on health, visibility reduction and climate change (Seinfeld and Pandis, 2006; Pope et al., 2009; Gautam et al., 2016; Patra et al., 2016). Water-soluble ions often constitute a significant fraction of PM$_{2.5}$ mass (Lin et al., 2009; Chen and Tsai, 2010) and play an important role in hydroscopic nature and acidity of aerosol (Ocskay et al., 2006; Chan and Yao2008). Major water-soluble ions such as ammonium (NH$_4^+$), nitrate (NO$_3^-$) and sulfate (SO$_4^{2-}$), are secondary in nature and are formed by physical processes (e.g., nucleation and condensation) and chemical reactions among precursor gases such as ammonia (NH$_3$(g)), nitric acid (HNO$_3$(g)) and sulfuric acid (H$_2$SO$_4$(g)). In Taiwan, air pollution episodes caused by PM$_{2.5}$ are often related to water-soluble ions. Hsu et al. (2008) took 26 samples of PM$_{2.5}$ at Daliao and Tzouying sites and showed ionic species accounted for 45–53% of PM$_{2.5}$ mass, in which NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ were predominant. Lin et al. (2002) investigated PM$_{2.5}$ compositions in Kaohsiung City and established that SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ were the major ionic species, accounting for 42.2% of the PM$_{2.5}$ mass and
90% of the total water-soluble ions. Lung et al. (2002) indicated that total ionic species accounted for 46.4% and 44.6% of PM$_{2.5}$ mass on dust events and non-dust-event days, respectively in Taipei. Recently, at a remote site in southern Taiwan, the concentrations of main inorganic salts, SO$_4^{2–}$, NH$_4^+$, Na$^+$, NO$_3^–$, and Cl$^–$, were also found to be high accounting for 48.8 $\pm$ 27.4% of the PM$_{2.5}$ (Tsai et al., 2015). Secondary aerosols (SO$_4^{2–}$, NH$_4^+$ and NO$_3^–$) contributed approximately 50% and 60% of PM$_{2.5}$ mass in spring and winter respectively; but were responsible about 40% by mass in summer at Tainan, Taiwan (Lu et al., 2016). Particulate organic matter (OM) contributed the most (18–40% by mass in summer at Tainan, Taiwan (Lu et al., 2016). Iberian Peninsula was mainly composed of organic matter and ammonium sulfate, while EC and nitrate were minor components (Galindo et al., 2016).

To fully characterize the formation and diurnal behavior of PM$_{2.5}$ in the atmosphere, it is important to monitor the concentrations of PM$_{2.5}$ water-soluble species in parallel with associated precursor gases. Traditional monitoring methods based on filter collection followed by sample extraction and ion chromatography (IC) analysis typically take several hours to one day and can’t provide good time resolution. In addition, except for elements, filter sampling suffers from both negative artifacts caused by the loss of semi-volatile material (SVM) during sampling and conditioning (Tsai et al., 1997; Tsai and Perng, 1998; Tsai et al., 2000; Chen et al., 2010a; b; Liu et al., 2014) and positive artifacts due to the absorption of gaseous organic carbon (OC) or inorganic gases (NH$_3$, HNO$_3$, HCl and SO$_2$) by sampling media or collected particles (Cheng and Tsai, 1997; Zhu and Tsai, 2012; Liu et al., 2014). Several denuders have been developed to absorb these interference gases prior to filter sampling, such as the annular denuder (Possanzini et al., 1983; Tsai and Perng, 1998), coiled denuder (Pui et al., 1990), honeycomb denuder (Koutrakis et al., 1993), and porous-metal denuder (PDS) (Huang et al., 2001; Tsai et al., 2001a, b, 2003). But these manual sampling methods, it is inevitably labor-intensive and easily contaminated during subsequent extraction of the filter by an aqueous extractant, and analysis by IC. These shortcomings of filter sampling and analysis have highlighted the need for automated semi-continuous instruments capable of measuring particles and its precursor gases in the atmosphere.

Some semi-continuous instruments with IC have been developed, including the particle-into-liquid sampler (PILS) (Weber et al., 2001); the wet-annular denuder/steam-jet aerosol collector (WAD/SJAC) (Trebs et al., 2004) and its commercialized version, the Monitor for AeRosols and GAses in ambient air (MARGA) (ten Brink et al., 2007; Makkonen et al., 2012); the Gas-Particle Ion Chromatography system (GPIC, Dionex Corporation, USA; Godri et al., 2009) and its modified design, the Ambient Ion Monitor-Ion Chromatograph (AIM-IC; URG Corporation, USA; Nie et al., 2010) consisting of a parallel plate wet denuder (PPWD) and a particle supersaturation chamber (PSSC). However, sampling bias of these monitors was found in performance tests conducted by several research groups. For GPIC, Yao et al. (2009) showed over- prediction by the GPIC for NH$_3$ and SO$_2$ measurements and under-prediction for HNO$_3$ as compared to the 24-h average data of the denuder. In an evaluation of AIM-IC (AIM 9000B), Wu and Wang (2007) found that at high SO$_2$(g) mixing ratios, the measurements were biased high for sulfate due to the inability of the denuder to remove SO$_2$(g) adequately from ambient air. Markovic et al. (2012) pointed out that the online AIM-IC measurements of NH$_3$(g), SO$_2$(g), and HNO$_3$(g) are biased low by 11%, 19%, and 12% respectively. The correction factors of 1.12, 1.23, and 1.14, respectively, should be applied to ambient measurements to account for the biases. Trebs et al. (2004) found that the online WAD/SJAC sampler was biased low for ammonium and sulfate compared to offline filters when mass loadings were high. Rumsey et al. (2014) showed that in comparison to the denuder/filter pack, MARGA performed well for SO$_2$, SO$_4^{2–}$ and NH$_4^+$ but did not meet the linear regression slope goals of 0.8 to 1.2 for HNO$_3$ and NH$_3$.

A newly designed PILS (Weber et al., 2001) employed with a modified particle size magnifier (Okuyama et al., 1984) has been proven to be a powerful tool for online measurement by continuously collecting ambient particles into a small flow of purified water. The PILS mainly consists of a steam generation system for producing and injecting steam, a condensation chamber for growing particles into collectable droplets, a single jet inertial impactor for collecting the enlarged particles onto a quartz plate, and a peristaltic pump for handling the liquid in the system. The PILS has lower limits of detection (LOD) than those of the SIAC (Khlystov et al., 1995). The LODs of NH$_4^+$, NO$_3^–$, SO$_4^{2–}$ and Cl$^–$ for the PILS are 0.05, 0.10, 0.18 and 0.10 µg m$^{-3}$, respectively, whereas the corresponding LODs for the SIAC are 0.08, 0.40, 0.64 and 0.48 µg m$^{-3}$, respectively. Weber et al. (2003) showed the PILS agreed with other semi-continuous techniques well and was in agreement with filter measurements of nonvolatile species. However, the two serial annular denuders installed before the PILS only trap interfering gases but without chemical analysis. So far, the combination of a wet denuder and the PILS for simultaneous measurements of gases and particles has not been reported yet.

In this work, a parallel plate wet denuder (PPWD) and a PILS (Model 4001, BMI Inc.) coupled with an IC (850 professional IC, Metrohm AG, Switzerland) were used to measure ambient water-soluble species in PM$_{2.5}$ and its precursor gases simultaneously at an hourly resolution. Precursor gases are collected by the PPWD first. PM$_{2.5}$ water-soluble species are then collected by the PILS. For the present PPWD, sand-blasted (a microscaled surface roughness) glass plates coated with TiO$_2$ nanoparticles (P25, Degussa, Germany) were used as the collection plates to improve the wettability of the active surfaces for excellent...
capture of acidic and basic gases (Tsai et al., 2008; Ku et al., 2010). The water contact angle was measured to be as small as $4 \pm 3.58^\circ$ and the water film was found very uniform for long-term operation. A more detailed description of this semi-continuous monitoring system is provided in Section 2.2.

The objective of the study is to present the field validation results of the PPWD/PILS system. Based on semi-continuous monitoring data in Taipei city and Hsinchu city of Taiwan, insight into the behavior of PM$_{2.5}$ a diurnal variations of water-soluble compositions were discussed.

**EXPERIMENTAL METHOD**

**Sampling Sites and Strategy**

Field measurement of particle and its precursor gases were carried out at three different sites of Taiwan i.e., Zhongshan (4th July–22nd July 2014), Zhudong (23rd September, 2014–23rd October 2014) and NCTU (9th March–30th March 2014). A total 1440 samples such as 410, 694, 336 samples for Zhongshan, Zhudong and NCTU, respectively were collected. Measurements of precursor gases and PM$_{2.5}$ ion species by collocated PPWD/PILS and manual PDS were first conducted. In March, 2014, the sampling site was located on the second floor of a teaching building of National Chiao-Tung University (NCTU) campus in Hsinchu City, Taiwan, about 1 km away from a heavy-traffic road, where inorganic species dominates as found in our previous work (Liu et al., 2013). In May, 2014, the sampling site was located at Zhongshan Monitoring Station (25°03’N, 121°31’E) in Taipei, the capital city of Taiwan and a megacity with a population of about 2.7 million. The Zhongshan station is situated on the fourth floor of a junior high school and its Google map is shown in Fig. 1. The main pollutant could originate from the No. 1 National Highway on the North and several East-to-West parallel arteries on the South.

To investigate the characteristics of ionic compositions and precursor gases of PM$_{2.5}$ based on the measurements by the PPWD/PILS, two continuous field tests were carried out at Zhongshan Air Monitoring Station from July 4th–22nd, 2014, and at Zhudong Air Monitoring Station (24°44’N, 121°05’E) from September 23rd to October 23rd, 2014, respectively. The latter station is situated on the fourth floor of a primary school in Zhudong town with a population of about 96,000. The station is on the southern side of the Touqian River and is sandwiched by two mountain terrains with natural surrounding as shown in Fig. 1. The main pollutant could originate from the local emission sources alone the southeast-northwest valley as well as the traffic of the No. 3 National Highway about 7 km away on the Northwest and the No. 68 Provincial Highway 400 m away on the Northeast.

**PPWD/PILS System**

The schematic diagram of the PPWD/PILS system is presented in Fig. 2. The system mainly consists of four parts: (a) the gas collection unit (PPWD) – for the collection of water-soluble gases into aqueous samples; (b) the particle collection unit (PILS) – for the collection of water-soluble PM$_{2.5}$ into aqueous samples; (c) the sample unit (syringe pump) – for simultaneous storage of collected samples and sequential injection into the IC; (d) the sample analysis unit – for the analysis of anionic and cationic chemical species collected in aqueous solution. To operate the system at 12.3 L min$^{-1}$, the gap between the two parallel plates, $h$, of the present PPWD was decreased to 2 mm from 4 mm the original version which runs at 5 L min$^{-1}$ (Tsai et al., 2008) to remain high gas collection efficiencies by keeping the dimensionless parameter $\mu$ the same according to the Gormley and Kennedy theory (Hinds, 1999). All gas tubing and valves of PPWD were made of Teflon to prevent the interaction between the gases and the tube and the fittings. (Tsai et al., 2008).

Ambient sample air is first drawn through the inlet tube at 16.7 L min$^{-1}$. A very sharp cut cyclone (VSCC, BGI Inc., Waltham, Massachusetts) with 2.5 µm cut-point is installed at the inlet of the PPWD. The sample flow is then branched into a bypass flow of 4.4 L min$^{-1}$ and another flow of 12.3 L min$^{-1}$ to be introduced into the PPWD-PILS system. As the air flow passes through the PPWD, water-soluble gases are adsorbed by the water film. After that, the denuded aerosol flow enters the PILS in which droplets collected on the impaction plate are washed off continuously with a constant water flow spiked with internal standards for both cation and anion (LiBr, 50 ppb) at 0.10 mL min$^{-1}$.

The control sequence of syringe pumps for sampling and injecting gaseous and particulate samples are presented in Fig. 3. Each 1-h period consists of 55 min sampling process and 5 min injecting process for both gases and particles. During the sampling process, liquid streams containing dissolved gases (G1) from the PPWD and particles (P1) from the PILS are simultaneously drawn into Syringe-1-1 and Syringe-1-2 (20 mL), respectively. Subsequently during injecting process, G1 is injected into the IC for composition analysis while P1 is injected into Syringe-2 for temporary storage (injection speed: 4 mL min$^{-1}$). After that, Syringe-1-1 and Syringe-1-2 are shifted to draw the liquid sample streams again for the next 55-min sampling of gases (G2) and particles (P2), during which the IC analysis of previous G1 (25 min) and P1 (30 min including 5-min injection from Syringe-2) will be completed. In this way, semi-continuous hourly monitoring of gaseous and particulate compounds can be achieved.

**PDS**

The PDS (Tsai et al., 2001a) was chosen for manual filter sampling and it was deployed simultaneously with PPWD/PILS system. Ambient air was sampled by at a flow rate of 2 L min$^{-1}$ through an inlet cyclone with the cutoff size of 2.5 µm and then through two denuder discs and a filter pack. Each sample was collected for 24 hours. Two porous-metal discs (diameter: 2.54 cm; pore size: 100 µm; thickness: 0.317 cm; P/N1000, Mott Inc., Farmington, CT) were used in series. The first disc was coated with sodium carbonate/glycerin to collect acid gases (i.e., SO$_2$ and HNO$_3$), and the second was coated with citric acid to collect basic gases (i.e., NH$_3$). The denuders were followed by a Teflon filter for collecting particles, then a nylon filter
Fig. 1. Locations and sampling sites of Zhongshan, Zhudong and NCTU.
for collecting chloride and nitrate, finally a citric (500 µL, 1%) coated glass fiber filter for collecting ammonium. After sampling, the porous-metal discs were extracted with 15 mL H₂O₂ solution (5 mM) under a vacuum and ultrasonic condition for 30 min. The Teflon, nylon and glass fiber filters were extracted with 30 mL distilled deionized water for 60 min. All of these extracted samples were analyzed by the IC.

**IC Systems**
An IC system (Metrohm 850 Professional IC) was connected with the PPWD/PILS system, PM₂.₅ water-soluble ions (SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺) and gaseous SO₂ and NH₃ were hourly determined. Similarly, another IC system (Metrohm 883 Basic IC plus) was used to analysis PDS, 24-hr average concentrations of the same ions, acidic and basic gases. In both IC, the anion eluent was a mixture of sodium carbonate and Sodium hydrogen carbonate solution (3.2 mM + 1.0 mM) with flow rate 0.8 mL min⁻¹ and the flow path consisted of a guard column (METROSEP A SUPP, 4/5 S-Guard), analytical column (METROSEP A SUPP, 5 250/4.0 mm) and a suppressor.
(MSM). The cation eluent was a mixture of Nitric acid and dipicolinic acid (1.7 mM + 0.7 mM), with flow rate 1.2 mL min⁻¹ (Metrohm 850 Professional IC) and 0.9 mL min⁻¹ (Metrohm 883 Basic IC plus) and the flow path consisted of a guard column (METROSEP C 4 S-Guard), analytical column (METROSEP C 4 250/4.0). With the Metrohm 850 Professional IC, the loop sizes were 1000 µL for anion and 1300 µL for cation. With the Metrohm 883 Basic IC plus, the sample loop sizes were 500 µL for both. Five out of ten concentrations (1–100 ppb) of standard solutions were selected for calibration, the R² of calibration curve should be above 0.995.

Sampling and Analytical Quality Assurance (QA) / Quality Control (QC)

The IC was calibrated offline by injecting mixed standards of anions (F⁻, Cl⁻, Br⁻, NO₃⁻, SO₄²⁻) and cations (Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) into corresponding concentrators. Within the concentration range of the each ambient sample, the standard solution was divided into different standard concentrations, 0.5, 1, 3, 5, 10, 40, 80 and 100 ppb, to establish a standard calibration baseline for ion estimations. The eluent for anion analysis system was an aqueous solution of 3.2 mM Na₂CO₃ and 1.0 mM NaHCO₃ at a flow rate of 0.8 mL min⁻¹, and for cation analysis system was a solution of 1.7 mM HNO₃ and 0.7 mM dipicolinic acid at a flow rate of 1.2 mL min⁻¹. The suppressor was regenerated using 50 mM H₂SO₄ solution.

The method detection limit (MDL) of the PPWD/PILS was estimated as the threefold standard deviation (3σ) of standard samples (n = 7) spiked with standard solutions of a smallest possible concentration (2 ppb). Field blanks of the instrument for gases and particles were checked by running the automated system without introducing the air flow, which would be subtracted from the measured results. MDL and blank values of the each investigated ion for the PPWD/PILS were listed in Table 1.

RESULTS AND DISCUSSION

Comparison of PPWD/PILS with PDS

To evaluate PPWD/PILS measurement of precursor gases, comparisons with 24-h PDS denuder sampling results were conducted. PPWD data were averaged over 24-h in parallel with the denuder measurement. Fig. 4 shows the regression plots for NH₃, HONO, HNO₃ and SO₂ online data with the PDS data. Good correlations between the two methods were found, with the slopes of zero-intercept fitting lines close to 1.0 (ranging from 0.92 to 1.04), and R² ranging from 0.76 to 0.83.
Table 1. Summary of PPWD/PILS MDL and blank values for individual ionic species.

<table>
<thead>
<tr>
<th></th>
<th>Na⁺</th>
<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>NO₂⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDL Gas (ppbv)</td>
<td>0.0060</td>
<td>0.0160</td>
<td>0.0041</td>
<td>0.0197</td>
<td>0.0073</td>
<td>0.0144</td>
<td>0.0058</td>
<td>0.0022</td>
</tr>
<tr>
<td>Particle (µg m⁻³)</td>
<td>0.0074</td>
<td>0.0155</td>
<td>0.0089</td>
<td>0.0202</td>
<td>0.0140</td>
<td>0.0058</td>
<td>0.0195</td>
<td>0.0094</td>
</tr>
<tr>
<td>Blank values PPWD (ppbv)</td>
<td>0.012</td>
<td>0.509</td>
<td>0.016</td>
<td>0.000</td>
<td>0.604</td>
<td>0.000</td>
<td>0.138</td>
<td>0.242</td>
</tr>
<tr>
<td>PILS (µg m⁻³)</td>
<td>ND</td>
<td>0.055</td>
<td>ND</td>
<td>ND</td>
<td>0.157</td>
<td>ND</td>
<td>0.144</td>
<td>0.254</td>
</tr>
</tbody>
</table>

Fig. 4. Comparisons of 24-h average concentrations measured by the PPWD/PILS and PDS.

Excellent gas adsorption condition at the PPWD water film (Tsai et al., 2008) suggested high gas collection efficiency with a very good accuracy for NH₃ and SO₂ in comparison to the manual denuder data. The regression analysis with a slope less than 1.0 for HNO₃ was likely attributed to the low concentrations approaching the detection limit and potential losses occurred along the inlet tubing wall for its “sticky” nature. For HONO, a slope smaller than 1.0 was likely due to the artifact aqueous formation of HONO from dissolved NO₂ and SO₂ at wetted denuder walls (Spindler et al., 2003).

Similarly, concentrations of PM₂.₅ ions from PPWD/PILS were also averaged to a 24-h basis for comparisons with the PDS data, as shown in Fig. 5. For NH₄⁺, NO₃⁻ and SO₄²⁻, excellent correlations were observed from two data sets, with the slopes ranging from 0.84 to 0.97, R² ranging from 0.89 to 0.94. The slope for NH₄⁺, 0.84, is less than 1.0, which is consistent with the value of 0.88 obtained in the previous study (Sorooshian et al., 2006) due to the evaporation loss of ammonium species in the PILS. With less gaseous interferences, the online measurement system performs particularly well for these three major ions. Results for Na⁺, Cl⁻ and K⁺ measured by two techniques also agreed well, with the slopes of 0.75, 0.95 and 0.84, and R² of 0.77, 0.83 and 0.77, respectively. Underestimation of Na⁺, Cl⁻ and K⁺ might be associated with their low concentrations approaching the MDLs of PILS and diffusion loss in the inlet tubing (Drewnick et al., 2003; Orsini et al., 2003).

A summary of linear regression coefficients (with and without intercept being forced to zero) of the PPWD/PILS vs. the PDS results are provided in Table 2. It shows that the current PPWD/PILS system outperforms the MARGA (Rumsey et al., 2014) for either especially gaseous NH₃ and HNO₃, or particulate nitrate in terms of slopes and R².

Continuous Hourly Monitoring Data

Meteorological Conditions

The meteorological conditions considered in the two measurement campaigns include rain fall (RF), temperature (T), relative humidity (RH), wind speed (WS) and wind direction (WD). Figs. 6(a) and 6(b) present the temporal variations of the meteorological parameters during measurements at Zhongshan monitoring station (July 4–22,
Fig. 5. Comparisons of 24-h average concentrations measured by the PPWD/PILS vs. concentrations measured with the PDS.

2014) and Zhudong monitoring station (September 23–October 23, 2014), respectively. In Zhongshan, T, RH, WS and WD varied very much before July 16. After that a shift in the wind direction to southeast (WD between 90 and 120°) resulted in less variation in T and RH for the next few days except July 19th when the WD became random again. For the period in Zhudong, the weather appeared more stable and regular. The wind was either dominated by the northeasterly monsoon (WD ~50°) primarily from October 4th to 12th with varied speeds (WS from 1 to 8 m s⁻¹) or by the southeasterly wind (WD ~140°) with more constant WS range of 1–3 m s⁻¹. The values of T and RH showed regular trends except for the very high RH and gentle varying T due to a rain event (rain fall up to 5.5 mm) during October 11th to 13th as well as a corresponding wind direction shift. It is worth mentioning that for each day WS tended to reach a minimum between midnight and dawn, indicating a reduced boundary layer height during this period, while the increase in WS after sunrise indicated that the turbulent mixing of boundary layer became more intensive (Hu et al., 2008).

Precursor Gases

The 24-h concentration of precursor gases (i.e., NH₃, HONO, HNO₃ and SO₂) at sampling sites are presented in Fig. 7. The mean concentrations for the both measurements follow the order of: NH₃ > SO₂ > HONO > HNO₃. It should be noted that HNO₃ contributed a little to the nitrate gas-phase compounds at the both stations with non-obvious diurnal variations and very low concentration values, some of which were below the MDL. Generally, the concentrations of the investigated gases except HNO₃ could reach relatively high levels before the rain events on July 14th (Zhongshan) and on October 11th (Zhudong), but decreased rapidly and stayed low for at least one day after the rains. In addition to the rain-scavenging effects, the pollutant concentrations were impacted very much by the wind direction. For example after July 16, all gaseous concentrations (as well as particulate pollutants shown in Fig. 9) decreased when the WD was shifted to the east (except July 19) and the influence of Northern No. 1 national highway traffic on Zhongshan station disappeared (Fig. 1(b)). In comparison to Zhongshan, more regular variations for precursor gases can be found in the Zhudong, especially within the first half of October (4th–12th) when northeasterly monsoon predominated and gaseous concentrations except NH₃ became lower. These can be attributed to the less influence of anthropogenic sources in Zhudong. The natural winds blowing from the mountain areas, although the dense residential houses near the station would contribute to NH₃ emissions. In the following, more detailed analysis (diurnal cycles averaged) of each gas are presented in Zhongshan and Zhudong (Fig. 8). The diurnal data for precursor gases in the Zhongshan from July 16th to 22nd and in Zhudong from October 4th to 12th are also plotted for references in Figs. S1(a) and S1(b), respectively in Supplementary Material.

(a) NH₃. The average NH₃ concentration measured by the PPWD/PILS was 6.20 ± 2.98 ppb in Zhongshan, higher than Zhudong (2.69 ± 1.59 ppb). As indicated in Fig. 8(a),
the NH₃ diurnal trend during the test in Zhongshan exhibited a less pronounced variation and peaked at 04:00 and 20:00. These two peaks were mainly due to the accumulation of pollutants within the low nocturnal boundary layer and the emissions from vehicles and other anthropogenic sources, respectively. Similar bimodal diurnal pattern was also observed by Li et al. (2006). In contrast, during the test in Zhudong, NH₃ exhibited a diurnal trend more likely associated with a more regional nature, in which the concentration was raised to a peak at midday and then lowered to a valley at midnight as shown in Fig. 8(b). Good correlations of NH₃ concentrations with T were ascribed to the evaporation of ammonium nitrate particles into NH₃ at warm T around midday and dissolution of NH₃ into humid aerosols at high RH during nighttime. Rapid growth of NH₃ concentration between 07:00–09:00 was related to the increasing boundary layer after sunrise.

(b) HONO. Concentration trend of HONO was more pronounced with higher mean value in Zhongshan (1.56 ± 0.84 ppb) than in Zhudong (0.51 ± 0.14 ppb). During Zhongshan test, nighttime HONO concentrations were generally higher than the daytime data, with a clear maximum concentration at 20:00–0:00 and a minimum at 12:00–14:00. These can be explained by the major reaction in the formation of HONO through heterogeneous reaction: NO + OH + M → HONO + M (Kleffmann et al., 2003), and in the dissociation of HONO by solar radiation: HONO + hν → OH + NO (Harrison et al., 1996). Effect of dissociation overwhelmed that of the formation in the daytime and the process was reversed at nighttime, and the gap between the two effects was widened in summer with longer sunlight and higher temperature. Atmospheric HONO concentration also depended on NOx (Kurtenbach et al., 2001) originated from biomass burning. Therefore, the HONO trend was flat at very low levels in Zhudong station which is located in a suburban area with less human activities.

(c) SO₂. Diurnal variation of SO₂ showed a pronounced pattern similar to that of NH₃, in Zhongshan measurement with the mean concentration of 1.47 ± 0.96 ppb. Fossil fuel burning and vehicle emissions nearby the site could be significant sources of SO₂ and hence, peaks at rush hour (20:00) resulted from traffic activities and subsequent lower concentrations could be found at nighttime. The average SO₂ concentration measured by the PPWD/PILS system was only 0.17 ± 0.14 ppb with a flat diurnal variation in Zhudong. In addition to the scarce anthropogenic sources at this station, the low volatility of particulate SO₄²⁻ could be another reason for the small difference in SO₂ concentration between day and night, corresponding to a weak correlation with solar radiation and temperature.

PM₂.₅ Ionic Species
Observation of PM₂.₅ species provides insight into aerosol interactions with the gas phase, which can be strongly dependent on the ambient meteorological condition (Chang et al., 2007) and precursor gas (Ansari and Pandis, 1998). Figs. 9(a) and 9(b) shows the concentration trends for PM₂.₅ (data provided by monitoring stations) along with the fraction of the secondary inorganic aerosol (SIA, being the

<table>
<thead>
<tr>
<th>Table 2. Linear regression coefficients (with and without intercept being forced to zero) for the PPWD/PILS 24-h averaged data in the comparison to the corresponding PDS results for major inorganic species at NCTU and Zhongshan monitoring station sites.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PPWD/PILS</strong></td>
</tr>
<tr>
<td>NH₃</td>
</tr>
<tr>
<td>HNO₃</td>
</tr>
<tr>
<td>SO₂</td>
</tr>
<tr>
<td>NH₄⁺</td>
</tr>
<tr>
<td>NO₃⁻</td>
</tr>
<tr>
<td>SO₄²⁻</td>
</tr>
</tbody>
</table>

*MARPD: median absolute relative percent difference. **MU1: MARGA Unit 1; MU2: MARGA Unit 2.
Fig. 6. Temporal variations of the meteorological parameters during measurement at (a) Zhongshan station and (b) Zhudong station.
Fig. 7. Hourly concentrations of gases: (a) Zhongshan station, and (b) Zhudong station.
concentrations for PM$_{2.5}$ species were observed before measurements. As seen from Fig. 9(a), at Zhongshan, higher played key roles in some concentration drops during the likely attributed to the rain-scavenging (July 15$^{th}$) effect as observed since October 4$^{th}$ when northeasterly monsoon at Zhudong, low concentrations of the major ions were temporarily changed, and were soon brought back to low concentrations increased on July 19 when wind direction and southern major east-to-west local roads. The ion reduced the influences of northern No. 1 National Highway as well as southeast winds associated with clean air which correlated with the aggregate primary emissions from traffic, the biggest contributor -- the secondary organic aerosol (SOA) which arrived with the transport of relatively clean air from the northern mountainous area. It is noteworthy that around October 6$^{th}$, the concentrations peaked for a while, likely due to a homebound rush from a local festival. After the raining episode (October 9$^{th}$–12$^{th}$) and the shift of wind (October 13$^{th}$) from southeast along the Touqian River, the ion concentrations increased and peaked to high values. These high concentrations could be related to the formations of the ammonium nitrate and ammonium sulfate being favored at lower T and higher RH, and to the changes in atmospheric transport by alternatively shifting winds which destabilized the boundary layer allowing regional emissions to mix to greater heights than normal (Lee et al., 2008).

The diurnal variations of major ions over Zhongshan and Zhudong measurement periods are shown in Figs. 10(a) and 10(b), and will be discussed in detail in the following paragraphs. To see the special stages when wind effects predominated, diurnal data for Zhongshan from July 16$^{th}$ to 22$^{nd}$ and for Zhudong from October 4$^{th}$ to 12$^{th}$ were plotted in Figs. S2(a) and S2(b), respectively in Supplementary Material. Diurnal variations of precursor gases (NH$_3$, HONO and SO$_2$) measured with the PPWD/PILS, and T and RH at (a) Zhongshan station (July 4–22), and (b) Zhudong station (September 23–October 23).
Fig. 9. Hourly concentrations of PM$_{2.5}$ and its major ions (NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$) measured with PPWD/PILS at (a) Zhongshan station (July 4–22), (b) Zhudong station (September 23–October 23).
Ion Balance calculations are frequently used to validate the equivalence of cations and anions obtained by the following equations:

\[ C = \frac{\text{Na}^+}{23} + \frac{\text{NH}_4^+}{18} + \frac{\text{K}^+}{39} + 2 \times \frac{\text{Mg}^{2+}}{24} + 2 \times \frac{\text{Ca}^{2+}}{40} \]  
\[ A = \frac{\text{F}^-}{19} + \frac{\text{Cl}^-}{35.5} + \frac{\text{NO}_3^-}{62} + 2 \times \frac{\text{SO}_4^{2-}}{96} \]  

A plot of the total positive charges against negative charges is given in Fig. 11(a). In Zhongshan measurement, slope close to 1 (0.97) with \( R^2 = 0.97 \) reasonably represents an ion balance for ambient sampling species. As evidenced by the plot of \([\text{NH}_4^+] \) versus \(2[\text{SO}_4^{2-}] + [\text{NO}_3^-] \) are shown in Fig. 11(b), good correlation \( (R^2 = 0.95) \) result with slope of 0.88 indicated that the most \( \text{NH}_4^+ \) was in the forms of ammonium sulfate and ammonium nitrate, while the levels of ammonia could be insufficient to fully neutralize the sulfate and nitrate during the summer. In Zhudong, larger deviations from 1:1 line than in Zhongshan for both plots are observed. Some unmeasured ammonium cations in organic species or soil-derived species (Shon et al., 2012) could be responsible for the deficit in \( \text{NH}_4^+ \) (Fig. 11(b)). In addition, excess \( \text{NO}_3^- \) emissions originating from the highway 200 m northeast of the site would be another reason. The corresponding data for the ion balance in Zhongshan from July 16th to 22nd and in Zhudong from October 4th to 12th are presented in Fig. S3 of the Supplementary Material.

CONCLUSION

This study presents the development, validation and field application of an automated instrument for simultaneous measurements of water-soluble \( \text{PM}_{2.5} \) ions and their precursor gases. With the combining use of the PPWD and the PILS coupled with IC, the instrument enables the collection of gas and particle at hourly temporal resolution. Its performance was validated by the comparison with the parallel manual denuder/filter-pack (PDS) method for 24-h average data. Good agreements between two techniques was found from the linear regression results for precursor gases (\( \text{NH}_3 \), 

---

**Fig. 10.** Diurnal variations of \( \text{PM}_{2.5} \) major ions measured by the PPWD/PILS system, T and RH at sampling sites.
HONO, HNO₃ and SO₂ and PM₂.₅ major ions (NH₄⁺, NO₃⁻ and SO₄²⁻) with slopes ranging from 0.92 to 1.04 and 0.84 to 0.97 as well as R² ranging from 0.76 to 0.83 and 0.89 to 0.94, respectively. Comparisons for Na⁺, Cl⁻ and K⁺ yielded relatively lower slopes (0.75–0.95) and R² (0.77–0.83) likely due to low concentrations approaching the MDLs and inevitable diffusion losses.

Continuous measurement campaigns based on the PPWD/PILS were conducted at Zhongshan station (Taipei City) and Zhudong station (Hsinchu City). High measurement time resolution enables us to look at how concentrations of major precursor gases (NH₃, HONO and SO₂) and particulate compounds (NH₄⁺, NO₃⁻ and SO₄²⁻) changed with meteorological and anthropogenic conditions. In July Zhongshan measurement period, various anthropogenic activities and fugitive meteorological conditions resulted in: (1) higher concentrations of precursor gases; (2) less ion fraction in PM₂.₅; (3) less regular diurnal trend for each species, as compared to the measurement in Zhudong where a relatively stable meteorology could be found with limited anthropogenic sources. Deeper insights into the formation of major gas and particle species were also discussed by depicting diurnal patterns for averaged over both measurement periods.

NH₃ was observed to be the most abundant precursor gas and present similar diurnal variation to SO₂, in which for Zhongshan, peaks before sunrise and after sunset respectively reflected the accumulation of pollutants in a low nocturnal boundary layer height and heavy traffic during evening rush hours, and for Zhudong, a peak at midday and a valley at night exhibited a diurnal trend more associated with natural reasons. On the contrary, HONO in Zhongshan showed lower concentration during daytime and higher concentration at night, indicating daytime photolysis and nocturnal heterogeneous reaction of HONO. In Zhudong, the trend of HONO was flat at very low levels due to the less human activities.

For major PM₂.₅ ions, SO₄²⁻, NH₄⁺ and NO₃⁻ showed similar diurnal patterns with the mean concentrations of 4.56 ± 3.14, 1.55 ± 1.16 and 0.52 ± 0.5 μg m⁻³ at Zhongshan period, and of 7.95 ± 5.52, 2.41 ± 1.95 and 0.96 ± 1.10 μg m⁻³ at Zhudong, respectively. The very low level of particulate NO₃⁻ accompanied with scarce HNO₃ were consistent with other reported data likewise in the northwest coastal cities of Taiwan. Higher concentrations of SO₄²⁻ and NH₄⁺ were associated with, in Zhongshan, the photochemical secondary aerosol formations during summer time and the traffic activities, and in Zhudong, the changes in atmospheric transport and destabilized the boundary layer caused by alternatively shifted winds allowing regional emissions to mix. High values of SOR obtained in this study suggested the secondary formation of SO₄²⁻ from SO₂, and (NH₄)₂SO₄ was inferred to be the dominant inorganic salt in PM₂.₅. This was also confirmed by strong relationship between [NH₄⁺] and 2[SO₄²⁻] + [NO₃⁻] for all measurement data.

ACKNOWLEDGEMENT

The financial support of the Natural Science Foundation of China (Grant 51478038) and the Taiwan Environmental Protection Agency (EPA-103-1602-02-09 and EPA-104-1602-02-08) is gratefully acknowledged.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

REFERENCES


Chen, S.C., Tsai, C.J., Huang, C.Y., Chen, H.D., Chen, S.J.,


Lin, J.J. (2002). Characterization of the major chemical species in PM$_{2.5}$ in the Kaohsiung City, Taiwan. Atmos. Environ. 36: 1911–1920.


Received for review, October 12, 2016
Revised, November 18, 2016
Accepted, November 19, 2016