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Characterization of Atmospheric PM_{2.5} Inorganic Aerosols Using the Semi-Continuous PPWD-PILS-IC System and the ISORROPIA-II

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Abstract: A semi-continuous monitoring system, a parallel plate wet denuder and particle into liquid sampler coupled with ion chromatography (PPWD-PILS-IC), was used to measure the hourly precursor gases and water-soluble inorganic ions in ambient particles smaller than 2.5 µm in diameter (PM_{2.5}) for investigating the thermodynamic equilibrium of aerosols using the ISORROPIA-II thermodynamic equilibrium model. The 24-h average PPWD-PILS-IC data showed very good agreement with the daily data of the manual 5 L/min porous-metal denuder sampler with R² ranging from 0.88 to 0.98 for inorganic ions (NH₄⁺, Na⁺, K⁺, NO₃[−], SO₄^{2−}, and Cl[−]) and 0.89 to 0.98 for precursor gases (NH₃, HNO₃, HONO, and SO₂) and slopes ranging from 0.94 to 1.17 for ions and 0.87 to 0.95 for gases, respectively. In addition, the predicted ISORROPIA-II results were in good agreement with the hourly observed data of the PPWD-PILS-IC system for SO₄^{2−} (R² = 0.99 and slope = 1.0) and NH₃ (R² = 0.97 and slope = 1.02). The correlation of the predicted results and observed data was further improved for NH₄⁺ and NO₃[−] with the slope increasing from 0.90 to 0.96 and 0.95 to 1.09, respectively when the HNO₂ and NO₂[−] were included in the total nitrate concentration (TN = [NO₃[−]] + [HNO₃] + [HONO] + [NO₂[−]]). The predicted HNO₃ data were comparable to the sum of the observed [HNO₃] and [HONO] indicating that HONO played an important role in the thermodynamic equilibrium of ambient PM_{2.5} aerosols but has not been considered in the ISORROPIA-II thermodynamic equilibrium model.

Keywords: PPWD; PILS; PDS; ISORROPIA-II; precursor gas; water-soluble inorganic ion

1. Introduction

Particles smaller than 2.5 µm in diameter (PM_{2.5}) exposure has been confirmed to be associated with total mortality, cardiovascular and respiratory mortalities, lung cancer, influenza, etc. [1] due to its chronic adverse human health effects [2]. Some previous studies [3,4] have revealed that PM_{2.5} constituents such as sulfate, nitrate, and ammonium were responsible for these effects. Sulfate (SO₄^{2−}), nitrate (NO₃[−]), and ammonium (NH₄⁺) are the major water-soluble inorganic (WSI) species, which represent very large fractions in PM_{2.5} depending on source emissions, human activities, chemical reactions, and meteorological conditions [5]. For example, SO₄^{2−}, NO₃[−], and NH₄⁺ ions accounted for 39% to 63% on the episode days and from 14.5% to 39% on the non-episode days in Taiwan [6]. These WSI species influence the hygroscopic nature, acidity properties, optical properties, and lifetime of PM_{2.5} [7,8] in which SO₄^{2−}, NO₃[−], and NH₄⁺ ions are the secondary species mainly formed from the chemical reactions of precursor gases (NH₃, HNO₃, and H₂SO₄) and nucleation and

condensation processes [9]. For instance, up to 80% of NO_3^- and NH_4^+ in $\text{PM}_{2.5}$ can be formed from precursor gases in the South Coast Air Basin in the USA [10].

Generally, NH_3 prefers to react homogeneously with H_2SO_4 to form $(\text{NH}_4)_2\text{SO}_4$ first, and then the excess NH_3 reacts with HNO_3 to form NH_4NO_3 when the molar ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ is greater than two [11,12]. Therefore, the total molar concentration of SO_4^{2-} and NO_3^- shows a good correlation ($R^2 > 0.9$) with that of NH_4^+ [12]. The formation of sulfate and nitrate particles is also affected by environmental factors including temperature (T), relative humidity (RH) [12], wind speed [13], and pressure [11]. As compared with $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 is more unstable at high temperature and low relative humidity conditions [5] due to the reversible phase equilibrium with HNO_3 and NH_3 . The NO_3^- concentration can also be increased by the uptake of HNO_3 on particles at high RH and low T conditions [13,14]. In addition, NO_3^- (p) along with HONO can also be generated by the hydrolysis of NO_2 on the particle surface with the NH_3 promotion [15,16]. The additional HONO source also contributes to the formation of NO_3^- (p) due to the enhanced oxidation of hydroxyl radical (OH) with NO_2 to produce more HNO_3 [17]. In addition, $\text{HNO}_{3(g)}/\text{NO}_3^-$ (p) can be photolyzed to form HONO under moderate to low NO_2 conditions [18,19].

To determine the chemical composition of $\text{PM}_{2.5}$ aerosols by measuring the mass concentrations of precursor gases and particles simultaneously, a system consisting of a manual filter sampler and a denuder (i.e., annular denuder, coiled denuder, and honeycomb denuder) is usually used [20] since manual filter samplers show good measurement accuracy [21]. The samples are, then, extracted and mass concentrations are quantified using ion chromatography (IC). However, manual filter samplers have negative artifacts due to the semi-volatile nature of NH_4^+ and NO_3^- [22] resulting in underestimation [23,24]. A porous-metal denuder sampler (PDS) [25], which uses acidic/basic coated porous metal discs to capture the basic/acidic precursor gases combined with a Teflon filter to collect particles and back-up filters to collect the semi-volatile materials evaporated from collected particles, can be used for determining the accurate mass concentrations of gases and particles simultaneously without evaporation loss [26]. Nevertheless, this method can be time-consuming and labor-intensive and is not fast enough to characterize the rapid evolution of atmospheric particles.

Currently, there are some hourly monitoring systems for water-soluble ions in $\text{PM}_{2.5}$ including the wet-annular denuder and steam-jet aerosol collector (WAD/SJAC) [27], the monitor for aerosols and gases in ambient air (MARGA) [28], the gas particle ion chromatography system (GPIC) [29], the ambient ion monitor ion chromatograph (AIM-IC) [30], and the parallel plate wet denuder and particle into liquid sampler (PPWD/PILS) [31]. Some previous studies have shown that the WAD/SJAC measured NH_4^+ and SO_4^{2-} ion concentration incorrectly at high mass loading conditions [27], the MARGA biased low HNO_3 and NH_3 gas concentrations as compared with those measured by the denuder/filter pack method [32], the GPIC overestimated NH_3 and SO_2 mass concentrations and underestimated HNO_3 concentration as compared with the manual denuder sampler [33], and the AIM-IC overestimated SO_4^{2-} ion concentration [34] and underestimated 11% $\text{NH}_{3(g)}$, 19% $\text{SO}_{2(g)}$ and 12% $\text{HNO}_{3(g)}$ [35]. In comparison, the PPWD/PILS consisting of PPWD [36,37] and PILS [38,39] and coupled with the IC (i.e., PPWD-PILS-IC) developed by our group [31] showed good agreement with the PDS for precursor gases (slope 0.92–0.94) and $\text{PM}_{2.5}$ ion species as well (slope 0.75–0.97 and R^2 : 0.77–0.94). In addition, the PPWD-PILS-IC system has low MDLs (method detection limit) which are less than $0.01 \mu\text{g}/\text{m}^3$ for Na^+ , Ca^{2+} , NO_2^- , and SO_4^{2-} and $0.02 \mu\text{g}/\text{m}^3$ for NH_4^+ , NO_3^- , and Cl^- , respectively. However, the performance of the PPWD-PILS-IC needs to be studied further to improve the linear regression parameters for gases (R^2 0.76–0.83) and NH_4^+ ion (slope 0.84 and R^2 0.89).

The equilibrium partitioning of the WSI species in different phases (particle (p), aqueous (aq), and gas (g) phases) at different T and RH conditions is complex and nonlinear, which needs the support of some thermodynamic equilibrium models to simulate the physical and thermodynamic processes. To meet these needs, many thermodynamic equilibrium models have been developed including AIM2 [40], SCAPE2 [41], EQUISOLV II [42], ISORROPIA/ISORROPIA-II [43,44], GFEMN [45], EQSAM2 [46], HETV [47], MESA [48], and UHAERO [49]. Among these methods, the ISORROPIA-II

was used extensively since it includes the crustal elements (K^+ , Ca^{2+} , Mg^{2+} , and Na^+), can simulate the thermodynamic equilibrium of particles in the stable state or metastable state, and can be used to solve the forward problem or the reverse problem in which particle-phase species can be used to determine the partial pressure of the gas phase species under the equilibrium condition [47]. Additionally, the ISORROPIA-II thermodynamic equilibrium model has been proven to be an order of magnitude faster than the SCAPE2 [44]. Previous studies have shown that the ISORROPIA-II thermodynamic equilibrium model predicted accurately for NH_3 but had biases for NH_4^+ , NO_3^- , and HNO_3 as compared with the observations due to the uptake of HNO_3 on coarse particles [44,50,51] or the evaporation properties of NH_4NO_3 salt [52]. Therefore, this model should be studied further to improve its partitioning capability.

In this study, the hourly concentrations of precursor gases (NH_3 , HNO_3 , SO_2 , and $HONO$) and WSI ions (NH_4^+ , Na^+ , K^+ , SO_4^{2-} , NO_3^- , and Cl^-) in $PM_{2.5}$ were measured by the PPWD-PILS-IC monitoring system and the 24-h average data were averaged from the hourly concentrations and compared to the daily average data of the manual 5 L/min PDS (daily data no. (N) = 30). Then, the hourly data (N = 720) were input to the ISORROPIA-II thermodynamic equilibrium model to study the thermodynamic equilibrium of ambient $PM_{2.5}$ WSI aerosols.

2. Experimental Method

2.1. Five Liters Per Minute PDS Design and Laboratory Test

In this study, the 5 L/min PDS was scaled up from the original 2 L/min PDS developed by our group [25,26] to increase the collected mass. The new thinner and larger porous metal discs could be cleaned easily to minimize the background influence. As shown in Figure 1, the 5 L/min PDS, henceforth referred to as PDS, consisted of a 2.5 μm cutpoint cyclone to remove particles larger than 2.5 μm , two coated porous metal discs with a diameter of 37 mm, a thickness of 2.5 mm, and a pore diameter of 100 μm (P/N1000, Mott Inc., Farmington, CT) to capture precursor gases, 47 mm Teflon filter to collect non-volatile species in $PM_{2.5}$, and two back-up filters (47 mm nylon filter and 47 mm acid-coated quartz filter) to collect acidic and basic semi-volatile species, respectively. The first and second porous metal discs were coated with sodium carbonate/glycerin (1% w/v) and citric acid (1% w/v) to collect acid gases (HNO_2 , HNO_3 , and H_2SO_4) and basic gas (NH_3), respectively. The inner wall of the PDS was coated with Teflon material to avoid gas adsorption and minimize the loss of acidic/basic gases. The mass concentration of each WSI species is the sum of those on Teflon filter and back-up filters.

Figure 1. Schematic diagram of the 5 L/min porous-metal denuder sampler (PDS).

The preparation of the porous metal discs and filters is shown in detail in Section S1 in the Supplementary Information (SI) and described briefly here. The porous metal discs were cleaned 4–5 times with deionized (DI) water under the vacuum condition and ultrasonicated for 15–30 min before every coating and sampling process to eliminate the background effect. After cleaning, the background concentrations of the cleaned porous metal discs were 0.002, 0.008, 0.035, and 0.005 ppbv for NH_3 , HCl , HNO_2 , HNO_3 , and SO_2^- , respectively. After sampling, the porous metals were extracted with H_2O_2 solution (15 mL and 5 mM) under the vacuum condition and ultrasonicated for 30 min, and the filters were extracted with DI water for 60 min before the extracted samples were analyzed by IC to determine mass concentrations.

The PDS was tested for the particle penetration curve of the cyclone and the particle loss in the laboratory first, before the field test. Two porous metal discs and three filter holders were removed for testing the penetration curve of the cyclone, and then the cyclone and the three filter holders were removed for testing the particle loss of the porous metal discs. Figure 2 shows the experimental setup of the cyclone penetration curve and the PDS particle loss tests with the method shown in the previous studies [53,54]. A vibrating orifice aerosol generator (VOAG, TSI Model 3450, USA) was used to generate monodisperse NaCl particles ranging from 1.20 to 5.05 μm and an aerodynamic particle sizer (APS, model 3321, TSI Incorporated, St. Paul, MN, USA) was used to measure the upstream and downstream particle concentrations. The collection efficiency (%) and the particle loss (%) of each particle size are calculated as the difference of the upstream and downstream concentrations divided by the upstream concentration times 100%.

Figure 2. Experimental setup of the penetration curve and particle loss test of the 5 L/min PDS.

A spreadsheet was used to perform the numerical integration of the cyclone penetration curve and the particle loss curve with the three idealized ambient distributions to estimate the collected $\text{PM}_{2.5}$ and particle loss mass concentrations [53]. The percentage of the total particle loss is the ratio of the estimated mass concentration of particle loss and collected $\text{PM}_{2.5}$ times 100%.

2.2. Field Comparison Test

The field comparison test of the PPWD-PILS-IC system and the PDS was conducted at the 6th floor of the building of the Institute of Environmental Engineering, National Chiao Tung University (NCTU), Hsinchu City, Taiwan from 1 October 2018 to 15 April 2019. The sampling site is about 1 km away from a heavy-traffic road which is the major particle source at this site [55]. Thirty daily samples were collected by the PDS and 720 hourly monitoring data were obtained by the PPWD-PILS-IC system, respectively. The hourly data of the monitoring system was converted to the 24-h average data for comparison with the PDS data. The PPWD-PILS-IC monitoring system was presented in detail in Li et al. [31] and is described briefly below. A 16.7 L/min EPA PM_{10} inlet [54] and a $\text{PM}_{2.5}$ VSCC inlet (very sharp cut cyclone) were used to remove particles larger than 2.5 μm in aerodynamic diameter. Sample air was drawn through the PPWD at 12.3 L/min to capture water-soluble precursor

gases [36,37] first, before being introduced into the PILS to collect WSI ions [38]. The samples from the PPWD and the PILS were stored temporarily in syringes, and then injected in the IC in sequence for determining hourly mass concentrations of water-soluble gases and ions. The PDS sampling system was set up side-by-side with the PPWD-PILS-IC system, in which the flow rate was controlled at 5 L/min by a mass flow controller. The cyclone is covered by a rain cap and its inner wall is coated with silicone grease to eliminate the particle bounce effect.

To examine the ion balance measured by the monitoring system and the sampler, the anion and cation equivalents are calculated from the mass concentrations of WSI ions (i.e., [ion]) as:

$$\text{Anion equivalent (A)} = [\text{F}^-]/19 + [\text{Cl}^-]/35.5 + [\text{NO}_3^-]/62 + [\text{NO}_2^-]/46 + [\text{SO}_4^{2-}]/48 \quad (1)$$

$$\text{Cation equivalent (C)} = [\text{Na}^+]/23 + [\text{NH}_4^+]/18 + [\text{K}^+]/39.1 + [\text{Mg}^{2+}]/12 + [\text{Ca}^{2+}]/20 \quad (2)$$

To evaluate the performance of the monitoring system as compared to the PDS, the normalized mean bias (NMB, %) and the normalized mean difference (NMD, $\mu\text{g}/\text{m}^3$) for the PPWD-PILS-IC data are calculated as:

$$\text{NMB}(\%) = \frac{\sum_{i=1}^N \frac{C_1 - C_2}{C_2}}{N} \times 100\% \quad (3)$$

$$\text{NMD}(\mu\text{g}/\text{m}^3) = \frac{\sum_{i=1}^N C_1 - C_2}{N} \quad (4)$$

where C_1 ($\mu\text{g}/\text{m}^3$) and C_2 ($\mu\text{g}/\text{m}^3$) are the mass concentrations of the PPWD-PILS-IC and the PDS for different WSI ions and gases, respectively. N is the total number of daily samples ($N = 30$).

2.3. ISORROPIA-II Thermodynamic Equilibrium Model

To predict the equilibrium partitioning of WSI gases and species in $\text{PM}_{2.5}$, the ISORROPIA-II thermodynamic equilibrium model ($\text{NH}_4^+ - \text{Na}^+ - \text{K}^+ - \text{Mg}^{2+} - \text{Ca}^{2+} - \text{Cl}^- - \text{NO}_3^- - \text{SO}_4^{2-} - \text{H}_2\text{O}$ system) was used [44]. The forward mode (or closed system) and stable state were applied, in which the total concentrations of nitrate ($\text{TN} = [\text{HNO}_3] + [\text{NO}_3^-]$), ammonium ($\text{TA} = [\text{NH}_3] + [\text{NH}_4^+]$), other ion concentrations, temperature, and relative humidity were used as the input parameters. In this study, the TN input parameter was also revised as $\text{TN} = [\text{HNO}_3] + [\text{NO}_3^-] + [\text{HONO}] + [\text{NO}_2^-]$ to evaluate the effect of HONO on the nitrate ($\text{HNO}_3/\text{NO}_3^-$) system and ammonium ($\text{NH}_3/\text{NH}_4^+$) system. To evaluate the performance of the ISORROPIA-II thermodynamic equilibrium model, the NMB and the NMD are calculated using Equations (3) and (4), in which C_1 and C_2 are the mass concentrations of the ISORROPIA-II thermodynamic equilibrium model and the PPWD-PILS-IC for different WSI ions and gases, respectively with $N = 720$.

3. Results and Discussion

3.1. Laboratory Test Results of the 5 L/min PDS

Figure 3 shows the particle penetration curve of the cyclone (Figure 3a) and the particle loss curve of the PDS (Figure 3b). The cutpoint diameter ($D_{\text{pa}50}$) of the cyclone is $2.45 \mu\text{m}$, which meets the U.S. EPA criteria for $\text{PM}_{2.5}$ inlets ($D_{\text{pa}50} = 2.5 \pm 0.2 \mu\text{m}$) and is similar to that of the VSCC ($D_{\text{pa}50} = 2.52 \pm 0.02 \mu\text{m}$) [56]. The sharpness of the particle penetration curve is 1.27, which is less sharp than that of the VSCC (sharpness = 1.16) but still meets the requirements of 1.2 ± 0.1 regulated in China and European countries [57]. It indicates that the PDS cyclone is applicable as a $\text{PM}_{2.5}$ classifier. In addition, the particle loss of the PDS casing is very small, which is less than 2% for particles smaller than $4.0 \mu\text{m}$, whereas the particle loss of the two porous metal discs is from 1.9% to 67.5% with particles ranging from 1.2 to $5.0 \mu\text{m}$, that is, the porous metal discs can cause a large particle loss for coarse particles while the loss for fine particles is smaller than 14%. Moreover, the total $\text{PM}_{2.5}$ loss is 2.8, 2.2%, and 3.7% based on the three idealized fine, typical, and coarse ambient particle size distributions,

respectively with the average particle loss of only $2.9 \pm 0.8\%$ [58]. It means that the $PM_{2.5}$ loss of the porous metal disc is acceptable and would not affect the sampling accuracy of the PDS.

Figure 3. (a) Penetration curve and (b) particle loss of the 5 L/min PDS.

3.2. Field Comparison Test Results of PPWD-PILS-IC and PDS

Table 1 shows the average mass concentration and the mass percentage of each WSI species over the total mass concentration of the WSI species measured by the PDS. Among these WSI species, the mass concentrations of NH_4^+ , NO_3^- , and SO_4^{2-} account for 25.52%, 20.41%, and 38.94%, respectively with the mass concentrations ranging from 0.61 to $5.87 \mu g/m^3$, from 0.95 to $6.64 \mu g/m^3$, and from 1.08 to $8.27 \mu g/m^3$, respectively. The other WSI species' mass concentrations represent just less than 6.0% in $PM_{2.5}$ with the average mass concentrations lower than $1.0 \mu g/m^3$. It implies that SO_4^{2-} is the most dominant ion in $PM_{2.5}$ followed by NH_4^+ and NO_3^- , while Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Cl^- are the minor contributors to $PM_{2.5}$, at the NCTU site. The equivalent ratio of anions and cations (A/C ratio) of $PM_{2.5}$ WSI species collected by the PDS is 0.92 ± 0.20 , which falls within the range of acceptable ion balance of 0.85–1.15 [59] indicated that all the WSI ions in $PM_{2.5}$ were measured accurately.

Table 1. Mass concentration and percent mass of the particles smaller than $2.5 \mu m$ in diameter ($PM_{2.5}$) water-soluble inorganic species measured by the PDS.

NCTU	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	Total	A/C
Mass conc. ($\mu g/m^3$)	0.35 $\pm$ 0.19	3.22 $\pm$ 1.38	0.20 $\pm$ 0.07	0.07 $\pm$ 0.02	0.04 $\pm$ 0.02	0.31 $\pm$ 0.15	0.72 $\pm$ 0.33	0.22 $\pm$ 0.33	2.58 $\pm$ 1.60	4.02 $\pm$ 1.87	12.63 $\pm$ 1.71	0.92 $\pm$ 0.2
Percentage (%)	2.74	25.52	1.57	0.58	0.32	2.47	5.71	1.75	20.41	38.94	100	

The field comparison results of the PPWD-PILS-IC with the PDS for some major WSI species (Na^+ , K^+ , NH_4^+ , Cl^- , NO_3^- , and SO_4^{2-}) are shown in Figure 4. It is found that the linear regression slopes and coefficient (R^2) of the determination range from 0.99 to 1.17 and from 0.88 to 0.98, respectively, which are better than those (slope 0.75–0.97 and R^2 0.77–0.94) in Li et al. [31]. For K^+ , Na^+ , and NH_4^+ , the improvement is even more obvious with higher R^2 of 0.89, 0.92, and 0.93, respectively ($R^2 = 0.77$, 0.77, and 0.89, respectively in the previous study) implying good stability of the monitoring system and the manual sampler. The slopes of all WSI species are close to 1.0 with the NMBs (NMDs) of the PPWD-PILS-IC less than $\pm 10\%$ ($< \pm 0.2 \mu g/m^3$) except for NH_4^+ (NMB = -13.95% and NMD = $-0.36 \mu g/m^3$). This implies that the evaporation loss of NH_4^+ is similar to that found in previous studies [31,60].

Figure 4. Correlation plot of the parallel plate wet denuder and particle into liquid sampler coupled with ion chromatography (PPWD-PILS-IC) and the PDS for the water-soluble inorganic species in $PM_{2.5}$. (a) Na^+ ; (b) K^+ ; (c) NH_4^+ ; (d) Cl^- ; (e) NO_3^- ; and (f) SO_4^{2-} .

The field comparison results of the PPWD-PILS-IC with the PDS for the precursor gases (NH_3 , SO_2 , HNO_3 , and HONO) are shown in Figure 5. The average volume concentrations of NH_3 , SO_2 , HNO_3 , and HONO are 4.37 ± 2.40 , 0.79 ± 0.38 , 0.27 ± 0.18 , and 0.73 ± 0.26 ppbv, respectively. The results show very good agreement between the PPWD-PILS-IC data and the PDS data with the slope and R^2 varying from 0.87 to 0.95 and from 0.89 to 0.98, respectively and the NMBs (MNDs) less than $\pm 10\%$ (<0.1 ppbv). It is also found that the agreement between two methods for these precursor gases is improved as compared with that in the previous study. In this study, the PDS with a higher flow rate (5 L/min) and easy-to-clean discs are the key to the improvement. Now, the discs can be cleaned thoroughly with low blank values (<0.008 ppbv). In summary, the PPWD-PILS-IC system is validated with the current 5 L/min PDS for measuring hourly precursor gases and WSI species in $\text{PM}_{2.5}$ with great confidence.

Figure 5. Correlation plot of the PPWD-PILS-IC and the PDS for the precursor gases. (a) NH_3 ; (b) SO_2 ; (c) HNO_3 ; and (d) HONO .

3.3. ISORROPIA-II Thermodynamic Equilibrium Model Predictions Versus PPWD-PILS-IC Observations

The hourly data of the PPWD-PILS-IC ($N = 720$) was used in the ISORROPIA-II thermodynamic equilibrium model to study the gas-particle partitioning in $\text{PM}_{2.5}$. As shown in Figure 6, the observed

hourly data have a good ion balance with an A/C ratio of 1.10 ± 0.18 and R^2 of 0.94 and a strong relationship between $2[\text{SO}_4^{2-}] + [\text{NO}_3^-]$ and $[\text{NH}_4^+]$ with the slope of 0.87 and R^2 of 0.92. It indicates that the NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ salts are dominant at this sampling site and the observed anion and cation data are balanced.

Figure 6. Plot of (a) anion equivalent versus anion equivalent and (b) $2[\text{SO}_4^{2-}] + [\text{NO}_3^-]$ versus $[\text{NH}_4^+]$ measured by PPWD-PILS-IC ($N = 720$).

Figure 7 shows the linear correlation of the ISORROPIA-II results (i.e., predicted results) and the PPWD-PILS-IC data (i.e., observed data) for $\text{NH}_4^+(\text{p})$, $\text{SO}_4^{2-}(\text{p})$, $\text{NO}_3^-(\text{p})$, $\text{Cl}^-(\text{p})$, $\text{NH}_3(\text{g})$, and $\text{HNO}_3(\text{g})$ with the input parameters of T , RH , $[\text{SO}_4^{2-}]_{(\text{p})}$, $\text{TN} = [\text{HNO}_3]_{(\text{g})} + [\text{NO}_3^-]_{(\text{p})}$, $\text{TA} = [\text{NH}_3]_{(\text{g})} + [\text{NH}_4^+]_{(\text{p})}$, $\text{TC} = [\text{HCl}]_{(\text{g})} + [\text{Cl}^-]_{(\text{p})}$, $[\text{Na}^+]_{(\text{p})}$, $[\text{Mg}^{2+}]_{(\text{p})}$, $[\text{K}^+]_{(\text{p})}$, and $[\text{Ca}^{2+}]_{(\text{p})}$. The results show that the predicted SO_4^{2-} and NH_3 correlate very well with the observed data with the slopes close to 1.0 and R^2 higher than 0.97, whereas the predicted NH_4^+ and NO_3^- are also in good agreement with the observed data ($R^2 > 0.9$). However, the ISORROPIA-II thermodynamic equilibrium model underestimates NH_4^+ and NO_3^- with the NMBs (NMDs) of -27.57% ($-0.56 \mu\text{g}/\text{m}^3$) and -47.60% ($-1.06 \mu\text{g}/\text{m}^3$), respectively. We observed that lower concentrations and more scattered data for NO_3^- resulted in a greater negative NMB value, which was also found in the previous study [61]. Assuming that $2[\text{SO}_4^{2-}]$ fully balances with $[\text{NH}_4^+]$ in the model, since NH_3 is much preferred to react with H_2SO_4 to form SO_4^{2-} salts and $2[\text{SO}_4^{2-}] + [\text{NO}_3^-]$ shows the good correlation with $[\text{NH}_4^+]$, the slight under-prediction of NH_4^+ should be due to the under-prediction of NO_3^- . In comparison, the predicted values of Cl^- are comparable with the observations (slope = 0.74) but data are scattered at low concentrations ($648/720$ data $< 1 \mu\text{g}/\text{m}^3$) resulting in a moderate correlation with R^2 of 0.49. The distributions of the WSI ions at this sampling site were tested for five days from July 2016 to January 2018 using the NCTU micro-orifice cascade impactor (NMCI) [62,63]. The results, shown in Figure S1 in SI, indicated that Cl^- was mainly formed in coarse particles ($\text{PM}_{10-2.5}$) which were not measured in this study, resulting in the underestimation of the model for Cl^- and the overestimation for HCl (Figure S2 in SI). Since the sampling site is in the urban area and far from the coastal line ($>12 \text{ km}$), Cl^- existing in coarse particles could be formed from the heterogeneous reactions of HCl with the magnesium- and calcium-containing coarse particles [64] from the road dust source, resulting in low observed HCl and over-predicted HCl concentrations.

Figure 7. Correlation plot of the predicted results of ISORROPIA-II thermodynamic equilibrium model and the observed data of the PPWD-PILS-IC for (a) NH_4^+ ; (b) SO_4^{2-} ; (c) NO_3^- ; (d) Cl^- ; (e) NH_3 ; and (f) HNO_3 when $\text{TN} = [\text{HNO}_3] + [\text{NO}_3^-]$.

The poorest correlation between the predictions and observations is of HNO_3 , as shown in Figure 7f, which is also found in many previous studies [50,51,61]. It is revealed that the predicted HNO_3 is very sensitive to the error of NO_3^- prediction as predicted $[\text{HNO}_3] = \text{TN} - \text{predicted} [\text{NO}_3^-]$ [44]. As compared with other species, the NO_3^- variability is found to be sensitive to the change of the T and RH, since the deliquescence RH of the NO_3^- salts varies with the T variation. Figure S3 shows that the NO_3^- concentration increases with the decreasing T and the increasing RH depending on the total concentration of the WSI species. In addition, unlike SO_4^{2-} and NH_4^+ which are only dominant in fine particles ($\text{PM}_{2.5}$) and fewer in coarse particles (Figure S2), NO_3^- is present in both coarse and fine particles, as shown in Figure S2, which contributes to the error prediction for NO_3^- and HNO_3 . A similar result was also found in the previous study [50]. This is because SO_4^{2-} and NH_4^+ are mainly formed from the homogeneous reactions of precursor gases, whereas NO_3^- formation in fine particles is from the homogeneous reactions of HNO_3 , and NO_3^- formation in coarse particles is from the heterogeneous reactions of HNO_3 with crustal coarse particles (i.e., Ca^{2+} and Mg^{2+}) [12,61]. The coarse particle NO_3^- formation process results in low observed HNO_3 and over-predicted HNO_3 concentrations because the concentrations of Na^+ , Mg^{2+} , Ca^{2+} , and NO_3^- in the coarse mode are not included in the model. It can be seen that Mg^{2+} , Ca^{2+} , and Na^+ are dominant in coarse particles since the source of coarse particles at this sampling site is road dust. However, the K^+ distribution is complicated since it exists in both fine and coarse particles. The source of K^+ in the fine and coarse modes could be associated with the burning activities from the nearby temple and the road dust from the heavy-traffic road, respectively [65].

As found in many previous studies, the main formation pathway of HONO is related closely to the formation of NO_3^- in fine particles [66], which is not included in the model resulting in the underestimation of the predicted NO_3^- . In the humid and NH_3 -rich environment, HONO and HNO_3 can be generated from the heterogeneous reaction on particle surfaces, and then HNO_3 can be converted to NO_3^- in humid conditions (Equation (5)) [15,16] as:

Therefore, the formation of $\text{NO}_3^- (\text{p})$ is not only from the homogeneous reactions of HNO_3 with NH_3 and the uptake of HNO_3 on the particle surfaces but also the formation of the HONO by reactions shown above. As shown in Figure 8, the observed NO_3^- shows a better correlation with the observed HONO during the nighttime (from 6 p.m. to 6 a.m.) with R^2 of 0.41, while a poorer correlation is found during the daytime (from 7 a.m. to 5 p.m.) in the NH_3 -rich environment ($3.90 \pm 3.02 \mu\text{g}/\text{m}^3$). This result is because HONO is easily consumed in the daytime (up to 80% reduction) by photolysis (Equation (6)) [66,67] as:

Additionally, the heterogeneous formation of HONO on the wet particle surfaces can also be associated with the formation of NH_4^+ with the presence of NH_3 and SO_2 as follows [68]:

The relationship of the predicted/observed HNO_3 , the observed HONO, the predicted/observed NO_3^- , the T, and the RH, during 24 h, is shown in Figure 9 which presents the average data of each hour of HNO_3 , HONO, NO_3^- , T, and RH obtained in this study and NO_2 , NO, and O_3 obtained from the nearest Taiwan Environmental Protection Administration (TW EPA) station [69] during the sampling period. The predicted HNO_3 is much higher than the observed HNO_3 , especially during the daytime when the RH is low and the T is high. In contrast, the predicted/observed NO_3^- is high during the nighttime and low during the daytime, which is similar to the HONO variation. It indicates that the predicted HNO_3 determined in the model is just based on the thermodynamic equilibrium with NO_3^- at the given T and RH. It is observed that the HONO concentration is high during the nighttime

due to the hydrolysis formation at high NO_2 concentration and high RH and low during the daytime due to the photolysis reaction represented by the peak of O_3 . It is also seen that the concentration of HONO is quite close to that of the predicted HNO_3 during the nighttime, suggesting that there could be the heterogeneous conversion of HNO_3 on particle/ground surfaces under high NO concentrations as shown in Equation (8) below [66,70] as:

It is noted that HNO_3 could also be converted to HONO during the daytime due to the photolysis of surface-adsorbed HNO_3/NO_3 , as shown in Equation (9) below [18,19]. Therefore, the difference between the prediction and the observation for HNO_3 could be due to these conversion mechanisms which are not included in the ISORROPIA-II thermodynamic equilibrium model.

As shown in Figure 9, the diurnal trends of NO, NO_3^- , and HONO are found to be related to the variation of the particle source. NO, NO_3^- , and HONO show the peak concentrations at 6–8 a.m., the decrease in the early afternoon and the increase at 5–7 p.m., which is associated with the variation of the traffic flow rate (i.e., the total number of vehicle per hour) [55,71]. During the rush hours in the morning (6–9 a.m.), a high NO concentration is released from vehicles with a high flow rate leading to the formation of NO_3^- due to the homogeneous/heterogeneous reactions of HNO_3 resulting in the peak of NO and NO_3^- at 6 a.m. and HONO is formed from the reactions shown in Equations (8) and (9) resulting in a peak concentration at 8 a.m. During the noontime with a low traffic flow rate and a low relative humidity condition, NO, NO_3 , and HONO are decreased. During the rush hours in the evening (5–8 p.m.) with a high traffic flow rate, NO is increased again leading to an increase in NO_3^- and HONO.

Figure 10 shows the comparison of the ISORROPIA-II predictions with the observation data for NH_4^+ (p), NO_3^- (p), NH_3 (g), and HNO_3 (g), when TN input parameter was changed to $\text{TN} = [\text{HNO}_2]_{\text{(g)}} + [\text{HNO}_3]_{\text{(g)}} + [\text{NO}_2^-]_{\text{(p)}} + [\text{NO}_3^-]_{\text{(p)}}$. It is found that the predicted NH_3 still correlates well with the observation, whereas correlation slopes for NH_4^+ and NO_3^- are increased to 0.96 and 1.09, respectively, indicating that the prediction by the ISORROPIA-II equilibrium model for NH_4^+ and NO_3^- is improved. In addition, the NMBs (NMDs) of the NH_3 , NH_4^+ , and NO_3^- are decreased from 26.37% (+0.52 $\mu\text{g}/\text{m}^3$) to 18.49% (+0.31 $\mu\text{g}/\text{m}^3$), from −27.57% (−0.56 $\mu\text{g}/\text{m}^3$) to −16.87% (−0.33 $\mu\text{g}/\text{m}^3$), and from −47.60% (−1.06 $\mu\text{g}/\text{m}^3$) to −14.94% (−0.27 $\mu\text{g}/\text{m}^3$), respectively. It suggests that the hydrolysis formation of HONO contributes greatly to the formation of NH_4NO_3 salt and the equilibrium partitioning of the ammonium and nitrate aerosols. It can be seen that the sum of $[\text{NO}_3^-]$ and $[\text{NO}_2^-]$ is very close to $[\text{NO}_3^-]$ which implies that no salts are formed from NO_2^- ions. The underestimation and variabilities of the predicted NO_3^- at low concentrations (<5 $\mu\text{g}/\text{m}^3$) were found, which led to the overestimation and variabilities of the predicted HNO_3 (Figure 10d), similar to what was found in previous results (Figure 7f) with the NMB of +579% and the NMD of +1.09 $\mu\text{g}/\text{m}^3$. The comparable correlations between the predicted $[\text{HNO}_3]$ and the sum of observed $[\text{HNO}_3]$ and $[\text{HONO}]$ are found with the NMB and the NMD of +129% and +0.89 $\mu\text{g}/\text{m}^3$, respectively. Since HNO_3 is the terminal species in the ambient atmosphere, its measured concentrations could be very low (<1.0 $\mu\text{g}/\text{m}^3$) because of the photolysis of surface-adsorbed $\text{HNO}_3/\text{NO}_3^-$ to form HONO [18,19] or heterogeneous conversion of HNO_3 on particle/ground surfaces under high NO concentrations [66,70]. Therefore, the overestimation for the predicted HNO_3 by the ISORROPIA-II thermodynamic equilibrium model as compared with the observed HNO_3 and the better correlation between the predicted HNO_3 with the sum of the observed HNO_3 and HONO effectively explains the important conversion process of the HNO_3 to HONO in the ambient atmosphere. In the future, a quantitative study of these dynamic processes is needed to improve the model prediction capabilities of the ISORROPIA-II thermodynamic equilibrium model.

Figure 8. Correlation plot of HONO and NO_3^- .

Figure 9. Average data of each hour of the predicted/observed HNO_3 , the observed HONO, the predicted/observed NO_3^- , the temperature, the relative humidity, NO_2 , NO , and O_3 .

Figure 10. Correlation plot of the predicted results of the ISORROPIA-II thermodynamic equilibrium model and the observed data of the PPWD-PILS-IC for (a) NH_3 ; (b) NH_4^+ ; (c) NO_3^- and $\text{NO}_3^- + \text{NO}_2^-$; and (d) HNO_3 and $\text{HNO}_3 + \text{HONO}_2$ when $\text{TN} = [\text{HNO}_3] + [\text{NO}_3^-] + [\text{HONO}] + [\text{NO}_2^-]$.

4. Conclusions

This study conducted field comparison tests of the PPWD-PILS-IC monitoring system and the manual 5 L/min porous-metal denuder sampler for precursor gases (NH_3 , HNO_3 , HNO_2 , and SO_2) and water-soluble inorganic ions (Mg^{2+} , Ca^{2+} , Na^+ , K^+ , NH_4^+ , NO_3^- , SO_4^{2-} , Cl^- , NO_2^- , and F^-) in $\text{PM}_{2.5}$ to evaluate the sampling performance of the PPWD-PILS-IC system. Among these WSI species, SO_4^{2-} , NH_4^+ , and NO_3^- are the major species accounting for 38.94%, 25.52%, and 20.41% of the total mass concentration of the WSI species, respectively. The 24-h average PPWD-PILS-IC data agreed well with the daily PDS data, with the slope and R^2 ranging from 0.99 to 1.17 and from 0.88 to 0.98, respectively, and the NMBs were less than 10%, except for NH_4^+ (NMB = −13.95%), due to the evaporation loss effect of the PILS. Moreover, the correlation of the monitoring system data and the manual sampler data was improved, especially for precursor gases and K^+ , Na^+ , and NH_4^+ ions as compared with those in the previous study which used 2 L/min PDS as the reference. The 5 L/min

PDS showed good performance with small particle loss in the porous metal discs and low background interferences. In addition, the ISORROPIA-II thermodynamic equilibrium model was used to study the partitioning of the WSI species in PM_{2.5} aerosols. The predicted results correlated well with the observed data of the PPWD-PILS-IC system for SO₄^{2−} (slope = 1.0 and R² = 0.99) and NH₃ (slope = 1.02 and R² = 0.97), when TN = [HNO₃] + [NO₃[−]]. When TN was the sum of [HNO₃], [NO₃[−]], [HONO], and [NO₂[−]], the correlation for NH₄⁺ and NO₃[−] was improved with less under-prediction (slope = 0.96 for NH₄⁺ and 1.09 for NO₃[−]). This implied that the hydrolysis formation of HONO on particle surfaces contributed to the formation of NH₄NO₃ salt. The predicted HNO₃ is comparable to the sum of the observed [HNO₃] and [HONO] indicating that the HNO₃ could be converted to HONO due to the heterogeneous conversion and the photolysis reaction.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4433/11/8/820/s1>, Figure S1: The size distribution of the water-soluble inorganic ions (NH₄⁺, Na⁺, Ca₂⁺, Mg₂⁺, NO₃^{2−}, SO₄^{2−} and Cl[−]) sampled by NCTU micro-orifice cascade impactor (NMCI) at National Chiao Tung University (NCTU) site from July 2016 to January 2018., Figure S2: Comparison of the prediction and the observation for HCl, Figure S3: Correlation of NO₃[−] and water-soluble inorganic ions at different temperature (T) and relative humidity (RH) ranges.

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References

1. Miller, L.; Xu, X. Ambient PM_{2.5} human health effects—Findings in china and research directions. *Atmosphere* **2018**, *9*, 424. [CrossRef]
2. Braggio, J.T.; Hall, E.S.; Weber, S.A.; Huff, A.K. Contribution of satellite-derived aerosol optical depth PM_{2.5} bayesian concentration surfaces to respiratory-cardiovascular chronic disease hospitalizations in Baltimore, Maryland. *Atmosphere* **2020**, *11*, 209. [CrossRef]
3. Lin, H.; Tao, J.; Du, Y.; Liu, T.; Qian, Z.; Tian, L.; Di, Q.; Rutherford, S.; Guo, L.; Zeng, W.; et al. Particle size and chemical constituents of ambient particulate pollution associated with cardiovascular mortality in Guangzhou, China. *Environ. Pollut.* **2016**, *208*, 758–766. [CrossRef]
4. Hwang, S.L.; Lin, Y.C.; Lin, C.M.; Hsiao, K.Y. Effects of fine particulate matter and its constituents on emergency room visits for asthma in southern Taiwan during 2008–2010: A population-based study. *Environ. Sci. Pollut. Res. Int.* **2017**, *24*, 15012–15021. [CrossRef]
5. Guo, W.; Long, C.; Zhang, Z.; Zheng, N.; Xiao, H.; Xiao, H. Seasonal control of water-soluble inorganic ions in PM_{2.5} from nanning, a subtropical monsoon climate city in southwestern China. *Atmosphere* **2019**, *11*, 5. [CrossRef]
6. Tsai, J.H.; Lin, J.H.; Yao, Y.C.; Chiang, H.L. Size distribution and water soluble ions of ambient particulate matter on episode and non-episode days in southern Taiwan. *Aerosol. Air Qual. Res.* **2012**, *12*, 263–274. [CrossRef]
7. Cao, Z.; Zhou, X.; Ma, Y.; Wang, L.; Wu, R.; Chen, B.; Wang, W. The concentrations, formations, relationships and modeling of sulfate, nitrate and ammonium (SNA) aerosols over China. *Aerosol. Air Qual. Res.* **2017**, *17*, 84–97. [CrossRef]
8. Ramli, N.A.; Md Yusof, N.F.F.; Shith, S.; Suroto, A. Chemical and biological compositions associated with ambient respirable particulate matter: A review. *Water Air Soil Pollut.* **2020**, *231*. [CrossRef]
9. Chen, Y.; Xie, S.D.; Luo, B.; Zhai, C. Characteristics and sources of water-soluble ions in PM_{2.5} in the sichuan basin, China. *Atmosphere* **2019**, *10*, 78. [CrossRef]
10. Ying, Q.; Kleeman, M.J. Source contributions to the regional distribution of secondary particulate matter in California. *Atmos. Environ.* **2006**, *40*, 736–752. [CrossRef]
11. Seinfeld, J.H.; Pandis, S.N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*; John Wiley & Sons: Hoboken, NJ, USA, 2016.

12. Tsai, J.H.; Tsai, S.M.; Wang, W.C.; Chiang, H.L. Water-soluble ionic species of coarse and fine particulate matter and gas precursor characteristics at urban and rural sites of central Taiwan. *Environ. Sci. Pollut. Res. Int.* **2016**, *23*, 16722–16737. [[CrossRef](#)] [[PubMed](#)]
13. Lim, Y.; Seo, J.; Kim, J.Y.; Kim, Y.P.; Jin, H.C. Local formation of sulfates contributes to the urban haze with regional transport origin. *Environ. Res. Lett.* **2020**. [[CrossRef](#)]
14. Voutsas, D.; Samara, C.; Manoli, E.; Lazarou, D.; Tzoumaka, P. Ionic composition of PM_{2.5} at urban sites of northern Greece: Secondary inorganic aerosol formation. *Environ. Sci. Pollut. Res. Int.* **2014**, *21*, 4995–5006. [[CrossRef](#)] [[PubMed](#)]
15. Cui, L.; Li, R.; Zhang, Y.; Meng, Y.; Fu, H.; Chen, J. An observational study of nitrous acid (HONO) in Shanghai, China: The aerosol impact on HONO formation during the haze episodes. *Sci. Total Environ.* **2018**, *630*, 1057–1070. [[CrossRef](#)]
16. Xu, W.; Kuang, Y.; Zhao, C.; Tao, J.; Zhao, G.; Bian, Y.; Yang, W.; Yu, Y.; Shen, C.; Liang, L.; et al. NH₃-promoted hydrolysis of NO₂ induces explosive growth in HONO. *Atmos. Chem. Phys.* **2019**, *19*, 10557–10570. [[CrossRef](#)]
17. Qu, Y.; Chen, Y.; Liu, X.; Zhang, J.; Guo, Y.; An, J. Seasonal effects of additional HONO sources and the heterogeneous reactions of N₂O₅ on nitrate in the North China Plain. *Sci. Total Environ.* **2019**, *690*, 97–107. [[CrossRef](#)]
18. Ye, C.; Zhang, N.; Gao, H.; Zhou, X. Photolysis of particulate nitrate as a source of HONO and NO_x. *Environ. Sci. Technol.* **2017**, *51*, 6849–6856. [[CrossRef](#)]
19. Tsai, C.; Spolaor, M.; Colosimo, S.F.; Pikelnaya, O.; Cheung, R.; Williams, E.; Gilman, J.B.; Lerner, B.M.; Zamora, R.J.; Warneke, C.; et al. Nitrous acid formation in a snow-free wintertime polluted rural area. *Atmos. Chem. Phys.* **2018**, *18*, 1977–1996. [[CrossRef](#)]
20. Wei, L.; Duan, J.; Tan, J.; Ma, Y.; He, K.; Wang, S.; Huang, X.; Zhang, Y. Gas-to-particle conversion of atmospheric ammonia and sampling artifacts of ammonium in spring of Beijing. *Sci. China Earth Sci.* **2014**, *58*, 345–355. [[CrossRef](#)]
21. Le, T.C.; Shukla, K.K.; Chen, Y.T.; Chang, S.C.; Lin, T.Y.; Li, Z.; Pui, D.Y.H.; Tsai, C.J. On the concentration differences between PM_{2.5} FEM monitors and FRM samplers. *Atmos. Environ.* **2020**, *222*, 117138. [[CrossRef](#)]
22. Liu, C.N.; Lin, S.F.; Tsai, C.J.; Wu, Y.C.; Chen, C.F. Theoretical model for the evaporation loss of PM_{2.5} during filter sampling. *Atmos. Environ.* **2015**, *109*, 79–86. [[CrossRef](#)]
23. Liu, C.N.; Awasthi, A.; Hung, Y.H.; Gugamsetty, B.; Tsai, C.J.; Wu, Y.C.; Chen, C.F. Differences in 24-h average PM_{2.5} concentrations between the beta attenuation monitor (BAM) and the dichotomous sampler (Dichot). *Atmos. Environ.* **2013**, *75*, 341–347. [[CrossRef](#)]
24. Liu, C.N.; Lin, S.F.; Awasthi, A.; Tsai, C.J.; Wu, Y.C.; Chen, C.F. Sampling and conditioning artifacts of PM_{2.5} in filter-based samplers. *Atmos. Environ.* **2014**, *85*, 48–53. [[CrossRef](#)]
25. Tsai, C.J.; Huang, C.H.; Wang, S.H.; Shih, T.S. Design and testing of a personal porous-metal denuder. *Aerosol. Sci. Technol.* **2001**, *35*, 611–616. [[CrossRef](#)]
26. Tsai, C.J.; Huang, C.H.; Lin, Y.C.; Shih, T.S.; Shih, B.H. Field test of a porous-metal denuder sampler. *Aerosol. Sci. Technol.* **2003**, *37*, 967–974. [[CrossRef](#)]
27. Trebs, I.; Meixner, F.; Slanina, J.; Otjes, R.; Jongejan, P.; Andreae, M. Real-time measurements of ammonia, acidic trace gases and water-soluble inorganic aerosol species at a rural site in the Amazon Basin. *Atmos. Chem. Phys.* **2004**, *4*, 967–987. [[CrossRef](#)]
28. ten Brink, H.; Otjes, R.; Jongejan, P.; Slanina, S. An instrument for semi-continuous monitoring of the size-distribution of nitrate, ammonium, sulphate and chloride in aerosol. *Atmos. Environ.* **2007**, *41*, 2768–2779. [[CrossRef](#)]
29. Godri, K.; Evans, G.; Slowik, J.; Knox, A.; Abbatt, J.; Brook, J.; Dann, T.; Dabek-Zlotorzynska, E. Evaluation and application of a semi-continuous chemical characterization system for water soluble inorganic PM_{2.5} and associated precursor gases. *Atmos. Meas. Tech.* **2009**, *2*, 65–80. [[CrossRef](#)]
30. Nie, W.; Wang, T.; Gao, X.; Pathak, R.K.; Wang, X.; Gao, R.; Zhang, Q.; Yang, L.; Wang, W. Comparison among filter-based, impactor-based and continuous techniques for measuring atmospheric fine sulfate and nitrate. *Atmos. Environ.* **2010**, *44*, 4396–4403. [[CrossRef](#)]
31. Li, Z.; Liu, Y.; Lin, Y.; Gautam, S.; Kuo, H.C.; Tsai, C.J.; Yeh, H.; Huang, W.; Li, S.W.; Wu, G.J. Development of an automated system (PPWD/PILS) for studying PM_{2.5} water-soluble ions and precursor gases: Field measurements in two cities, Taiwan. *Aerosol. Air Qual. Res.* **2017**, *17*, 426–443. [[CrossRef](#)]

32. Rumsey, I.; Cowen, K.; Walker, J.; Kelly, T.; Hanft, E.; Mishoe, K.; Rogers, C.; Proost, R.; Beachley, G.; Lear, G. An assessment of the performance of the monitor for AeRosols and Gases in ambient air (MARGA): A semi-continuous method for soluble compounds. *Atmos. Chem. Phys.* **2014**, *14*, 5639–5658. [\[CrossRef\]](#)
33. Yao, X.; Shairsingh, K.; Lam, P.H.; Evans, G.J. Underestimation of sulfate concentration in PM_{2.5} using a semi-continuous particle instrument based on ion chromatography. *J. Environ. Monit.* **2009**, *11*, 1292–1297. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Wu, W.S.; Wang, T. On the performance of a semi-continuous PM_{2.5} sulphate and nitrate instrument under high loadings of particulate and sulphur dioxide. *Atmos. Environ.* **2007**, *41*, 5442–5451. [\[CrossRef\]](#)
35. Markovic, M.Z.; VandenBoer, T.C.; Murphy, J.G. Characterization and optimization of an online system for the simultaneous measurement of atmospheric water-soluble constituents in the gas and particle phases. *J. Environ. Monit.* **2012**, *14*, 1872–1884. [\[CrossRef\]](#)
36. Ku, Y.P.; Yang, C.; Lin, G.Y.; Tsai, C.J. An online parallel-plate wet denuder system for monitoring acetic acid gas. *Aerosol. Air Qual. Res.* **2010**, *10*, 479–488. [\[CrossRef\]](#)
37. Tsai, C.J.; Lin, G.Y.; Chen, S.C. A parallel plate wet denuder for acidic gas measurement. *AIChE* **2008**, *54*, 2198–2205. [\[CrossRef\]](#)
38. Weber, R.J.; Orsini, D.; Daun, Y.; Lee, Y.N.; Klotz, P.J.; Brechtel, F. A particle-into-liquid collector for rapid measurement of aerosol bulk chemical composition. *Aerosol. Sci. Technol.* **2001**, *35*, 718–727. [\[CrossRef\]](#)
39. Weber, R.; Orsini, D.; Duan, Y.; Baumann, K.; Kiang, C.; Chameides, W.; Lee, Y.; Brechtel, F.; Klotz, P.; Jongejan, P. Intercomparison of near real time monitors of PM_{2.5} nitrate and sulfate at the US environmental protection agency atlanta supersite. *J. Geophys. Res.* **2003**, *108*, 1984–2012. [\[CrossRef\]](#)
40. Clegg, S.L.; Pitzer, K.S. Thermodynamics of multicomponent, miscible, ionic solutions: Generalized equations for symmetrical electrolytes. *J. Phys. Chem.* **1992**, *96*, 3513–3520. [\[CrossRef\]](#)
41. Kim, Y.P.; Seinfeld, J.H.; Saxena, P. Atmospheric gas-aerosol equilibrium I. Thermodynamic model. *Aerosol. Sci. Technol.* **1993**, *19*, 157–181. [\[CrossRef\]](#)
42. Jacobson, M.Z.; Tabazadeh, A.; Turco, R.P. Simulating equilibrium within aerosols and nonequilibrium between gases and aerosols. *J. Geophys. Res.* **1996**, *101*, 9079–9091. [\[CrossRef\]](#)
43. Nenes, A.; Pandis, S.N.; Pilinis, C. ISORROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols. *Aquat. Geochem.* **1998**, *4*, 123–152. [\[CrossRef\]](#)
44. Fountoukis, C.; Nenes, A. ISORROPIA II: A computationally efficient thermodynamic equilibrium model for K^+ - Ca^{2+} - Mg^{2+} - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O aerosols. *Atmos. Chem. Phys.* **2007**, *7*, 4639–4659. [\[CrossRef\]](#)
45. Ansari, A.S.; Pandis, S.N. An analysis of four models predicting the partitioning of semivolatile inorganic aerosol components. *Aerosol. Sci. Technol.* **1999**, *31*, 129–153. [\[CrossRef\]](#)
46. Metzger, S.; Dentener, F.; Pandis, S.; Lelieveld, J. Gas/aerosol partitioning: 1. A computationally efficient model. *J. Geophys. Res.* **2002**, *107*, 1611–1624. [\[CrossRef\]](#)
47. Makar, P.; Bouchet, V.; Nenes, A. Inorganic chemistry calculations using HETV—A vectorized solver for the SO_4^{2-} - NO_3^- - NH_4^+ system based on the ISORROPIA algorithms. *Atmos. Environ.* **2003**, *37*, 2279–2294. [\[CrossRef\]](#)
48. Zaveri, R.A.; Easter, R.C.; Peters, L.K. A computationally efficient multicomponent equilibrium solver for aerosols (MESA). *J. Geophys. Res.* **2005**, *110*, D24203. [\[CrossRef\]](#)
49. Amundson, N.; Caboussat, A.; He, J.; Martynenko, A.; Savarin, V.; Seinfeld, J.; Yoo, K. A new inorganic atmospheric aerosol phase equilibrium model (UHAERO). *Atmos. Chem. Phys.* **2006**, *6*, 975–992. [\[CrossRef\]](#)
50. Sudheer, A.; Rengarajan, R. Time-resolved inorganic chemical composition of fine aerosol and associated precursor gases over an urban environment in western India: Gas-aerosol equilibrium characteristics. *Atmos. Environ.* **2015**, *109*, 217–227. [\[CrossRef\]](#)
51. Fountoukis, C.; Nenes, A.; Sullivan, A.; Weber, R.; Reken, T.V.; Fischer, M.; Matias, E.; Moya, M.; Farmer, D.; Cohen, R.C. Thermodynamic characterization of Mexico city aerosol during MILAGRO 2006. *Atmos. Chem. Phys.* **2009**, *9*, 2141–2156. [\[CrossRef\]](#)
52. Guo, H.; Liu, J.; Froyd, K.D.; Roberts, J.M.; Veres, P.R.; Hayes, P.L.; Jimenez, J.L.; Nenes, A.; Weber, R.J. Fine particle pH and gas–particle phase partitioning of inorganic species in Pasadena, California, during the 2010 CalNex campaign. *Atmos. Chem. Phys.* **2017**, *17*, 5703–5719. [\[CrossRef\]](#)
53. Le, T.C.; Tsai, C.J. Novel non-bouncing PM_{2.5} impactor modified from well impactor ninety-six. *Aerosol. Sci. Technol.* **2017**, *51*, 1287–1295. [\[CrossRef\]](#)

54. Le, T.C.; Shukla, K.K.; Sung, J.C.; Li, Z.; Yeh, H.; Huang, W.; Tsai, C.J. Sampling efficiency of low-volume PM₁₀ inlets with different impaction substrates. *Aerosol. Sci. Technol.* **2019**, *53*, 295–308. [CrossRef]
55. Chen, S.C.; Tsai, C.J.; Huang, C.Y.; Chen, H.D.; Chen, S.J.; Lin, C.C.; Tsai, J.H.; Chou, C.C.K.; Lung, S.C.C.; Huang, W.R. Chemical mass closure and chemical characteristics of ambient ultrafine particles and other PM fractions. *Aerosol. Sci. Technol.* **2010**, *44*, 713–723. [CrossRef]
56. Le, T.C.; Fu, C.X.; Sung, C.J.; Li, Z.Y.; Pui, D.Y.H.; Tsai, C.J. The performance of the PM_{2.5} VSCC and oil-Wetted M-WINS in long-Term field sampling studies. *Atmos. Environ.* **2020**. [CrossRef]
57. Le, T.C.; Tsai, C.J. Inertial impaction technique for the classification of particulate matters and nanoparticles: A review. *KONA Powder Part J.* **2020**. [CrossRef]
58. U.S. EPA. *Quality Assurance Guidance Document 2.12, Monitoring PM_{2.5} in Ambient Air Using Designated Reference or Class. I. Equivalent Methods*; Environmental Protection Agency: Research Triangle Park (RTP), NC, USA, 1998.
59. Sanusi, A.; Wortham, H.; Millet, M.; Mirabel, P. Chemical composition of rainwater in eastern France. *Atmos. Environ.* **1996**, *30*, 59–71. [CrossRef]
60. Sorooshian, A.; Brechtel, F.J.; Ma, Y.; Weber, R.J.; Corless, A.; Flagan, R.C.; Seinfeld, J.H. Modeling and characterization of a particle-into-liquid sampler (PILS). *Aerosol. Sci. Technol.* **2006**, *40*, 396–409. [CrossRef]
61. Huy, D.H.; Thanh, L.T.; Hien, T.T.; Takenaka, N. Comparative study on water-soluble inorganic ions in PM_{2.5} from two distinct climate regions and air quality. *J. Environ. Sci.* **2020**, *88*, 349–360. [CrossRef]
62. Liu, C.N.; Awasthi, A.; Hung, Y.H.; Tsai, C.J. Collection efficiency and interstage loss of nanoparticles in micro-orifice-based cascade impactors. *Atmos. Environ.* **2013**, *69*, 325–333. [CrossRef]
63. Chien, C.L.; Tien, C.Y.; Liu, C.N.; Ye, H.; Huang, W.; Tsai, C.J. Design and testing of the NCTU Micro-Orifice Cascade Impactor (NMCI) for the measurement of nanoparticle size distributions. *Aerosol. Sci. Technol.* **2015**, *49*, 1009–1018. [CrossRef]
64. Tobo, Y.; Zhang, D.; Nakata, N.; Yamada, M.; Ogata, H.; Hara, K.; Iwasaka, Y. Hygroscopic mineral dust particles as influenced by chlorine chemistry in the marine atmosphere. *Geophys. Res. Lett.* **2009**, *36*. [CrossRef]
65. Masri, S.; Kang, C.M.; Koutrakis, P. Composition and sources of fine and coarse particles collected during 2002–2010 in Boston, MA. *J. Air Waste Manag. Assoc.* **2015**, *65*, 287–297. [CrossRef] [PubMed]
66. Gall, E.T.; Griffin, R.J.; Steiner, A.L.; Dibb, J.; Scheuer, E.; Gong, L.; Rutter, A.P.; Cevik, B.K.; Kim, S.; Lefer, B.; et al. Evaluation of nitrous acid sources and sinks in urban outflow. *Atmos. Environ.* **2016**, *127*, 272–282. [CrossRef]
67. Gil, J.; Kim, J.; Lee, M.; Lee, G.; Lee, D.; Jung, J.; An, J.; Hong, J.; Cho, S.; Lee, J.; et al. The role of HONO in O₃ formation and insight into its formation mechanism during the KORUS-AQ Campaign. *Atmos. Chem. Phys.* **2020**. [CrossRef]
68. Ge, S.; Wang, G.; Zhang, S.; Li, D.; Xie, Y.; Wu, C.; Yuan, Q.; Chen, J.; Zhang, H. Abundant NH₃ in China enhances atmospheric HONO production by promoting the heterogeneous reaction of SO₂ with NO₂. *Environ. Sci. Technol.* **2019**, *53*, 14339–14347. [CrossRef]
69. TWEPA. Taiwan Air Quality Index. Available online: <https://airtw.epa.gov.tw/ENG/default.aspx> (accessed on 30 June 2020).
70. Kleffmann, J.; Wiesen, P. Heterogeneous conversion of NO₂ and NO on HNO₃ treated soot surfaces: Atmospheric implications. *Atmos. Chem. Phys.* **2005**, *5*, 77–83. [CrossRef]
71. Chen, S.C.; Tsai, C.J.; Chou, C.C.K.; Roam, G.D.; Cheng, S.S.; Wang, Y.N. Ultrafine particles at three different sampling locations in Taiwan. *Atmos. Environ.* **2010**, *44*, 533–540. [CrossRef]