AEROSOL pH IN HO CHI MINH CITY, VIET NAM

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ABSTRACT

Aerosol pH is an important parameter that affects air quality, and the health of aquatic and terrestrial ecosystems. However, the lack of such data was reported in Ho Chi Minh City (HCMC), Vietnam. In this study, we estimated the aerosol pH in fine particulate matter (PM2.5) collected in HCMC, Vietnam using the thermodynamic equilibrium models (E-AIM Extended Aerosol Inorganics Model and ISORROPIA-II), and the phase partitioning of ammonia. Aerosol pHs estimated by different methods were 1.7 – 2.9. Good correlations between the phase-partitioning approach and models in predicting the aerosol pH were observed with R^2 from 0.77 to 0.89, suggesting that the assumption of equilibrium is valid at the HCMC site.

Keywords: aerosol pH, PM2.5, AIM, ISORROPIA, Ho Chi Minh City.

1. INTRODUCTION

Fine particulate matter with an aerodynamic diameter of equal or less 2.5 μm (called PM2.5) could be related to adverse human health, visibility reduction and formation of acid rain and climate change. The property of PM2.5 is usually acidic because of its main components often being ammonium (NH_4^+), sulfate (SO_4^{2-}) and nitrate (NO_3^-). Aerosol acidity is an important property because many heterogeneous atmospheric chemical processes are pH dependent; for instance, oxidation of SO_2 to sulfate aerosol, hydrolysis of N_2O_5 on the aerosol [1, 2], formation of nitrate and secondary organic aerosol [2, 3], and trace metal mobilization [4].

In atmospheric chemistry, aerosol acidity can be expressed in two forms. An absolute acidity is the atmospheric free acidity in unit of mol H^+ per m^3 representing for the overall abundance of acidity. A relative acidity is the aerosol pH of the aqueous particle indicating for the acidic nature of the aerosol droplet. The aerosol pH is function of the free acid concentration and liquid water content in aerosol. Direct pH measurement is a challenge due to very low liquid water content of aerosol. Therefore, thermodynamic methods are commonly used to estimate the aerosol pH. The precursor gas and aerosol compositions based on the field measurements as well as ambient temperature and relative humidity is used as inputs. Several thermodynamic equilibrium models have been developed in recent years, e.g., ISORROPIA [5, 6], and AIM [7].

The objective of this study is to estimate the aerosol pH of PM2.5 collected at the HCMC site using the thermodynamic models. In addition, the aerosol pH is further predicted by the ammonia phase partitioning method for confirming the gas-aerosol equilibrium achieved at this study sites.

2. EXPERIMENT

2.1. Sampling and analyses

Air sample was collected using the open-face filter pack system (hereafter referring as FP). The FP was positioned on the roof-top of the building (10 m) in Ho Chi Minh City during sampling period. NILU filter holder system was used consisted of a one-stage aluminum alloy impactor (NL–4–2.5A, Tokyo Dylec Corp., Japan.) for particle size separation at 2.5 µm and six successive stages of filters. Sampling time was 24 hrs, and the flow rate was set at 4 L/min. The order of filters in holder was as follows: donut (for large particle >2.5 µm), Teflon (for fine particle ≤ 2.5 µm), NaCl-treated (for HNO_3 gas), and two Na_2CO_3-treated (for HONO and SO_2 gas), and H_3PO_4-treated (for NH_3 gas) filters. The samples were stored at –4 °C until analysis.

Before analysis, the sampled filters were extracted with 15 ml deionized water (resistivity ≈ 18.2 MΩ cm) using ultrasonic-assisted dissolution for PM2.5 filter and mechanical agitation for chemical-treated filters. The extraction was done in 1 hour at room temperature. Then, the solution was analyzed using ion chromatography. The field blank and sample filters were treated as the same manner, and the field blank concentrations for the target species were subtracted from the sample measurements.

The ambient temperature, relative humidity (RH) and the mass concentration of PM2.5 were obtained from the air monitoring station nearby.

2.2. Aerosol pH prediction

In order to evaluate aerosol pH in HCMC, we adopted two approaches. The first approach is the aerosol pH was calculated by two thermodynamic models: ISORROPIA-II [5, 6] and Extended Aerosol Inorganic Model (E-AIM) [7, 8].Based on the FP measurements in this study, the total concentration of gas and aerosol compositions are available. Therefore, the models were run in the "forward mode" as suggested by Hennigan*et al.*[9]. For the current analysis, we run ISORROPIA model in the simple and full models. The ISORROPIA simple model (referred as ISORROPIA*) considers only the $H^+ – NH_4^+ – NO_3^- – SO_4^{2-} – H_2O$ system, whereas the ISORROPIA full model (referred as ISORROPIA-II) treats the $H^+ – NH_4^+ – Na^+ – K^+ – Mg^{2+} – Ca^{2+} – Cl^- – NO_3^- – SO_4^{2-} – H_2O$ system. For AIM model, we consider the AIM-II only which treats the $H^+ – NH_4^+ – NO_3^- – SO_4^{2-} – H_2O$ system because the daily average RH is low.

The second approach is the ammonia phase partitioning method. The aerosol pH predicted by this method was compared to those estimated by thermodynamic models above. The agreement in predicting aerosol pH between two approaches confirms the gas-aerosol equilibrium which is achieved at the study sites. A detail description of this method has been reported in previous studies [9, 10].

3. RESULT AND DISCUSSION

3.1. Gas and ionic composition

The average concentrations of Na^+, NH_4^+, K^+, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-} in PM2.5 are 7.59, 37.81, 9.19, 5.04, 1.78, 6.92 and 22.59 µg/m^3, respectively. The gas concentrations of NH_3,

HNO_2, HNO_3 and SO_2 are 20.08, 0.38, 0.37 and 2.21 ppb, respectively. The ratio of NH_4^+ to SO_4^{2-} is approximately 1.6, suggesting the existence of NH_4HSO_4 in PM2.5. The HSO_4^- species in PM2.5 would affect to the strength of aerosol pH as discussed more detail in the following section.

Although the sampling campaign was designed to collect the air sample in two distinct seasons, the concentrations of the measured species did not reflect the season variation. The PM2.5 and water soluble inorganic ions in PM2.5 are mostly comparable in both seasons. In previous result we have analyzed the variation of the PM2.5 concentrations for four years (2013-2017) based on the continuous measurement. We found that the PM2.5 concentration in rainy season was much lower than that in dry season (unpublished data). The reason is likely that the air samples in this study were collected in the day without rain events during the rainy season. Therefore, in this study we do not analyze the seasonal variation for aerosol pH.

The concentrations of PM2.5 and main inorganic compositions measured in HCMC are compared to other locations as shown in Table 1. In general, the PM2.5 concentration at the HCMC site is much lower than that in Shanghai (China) and Kanpur (India), comparable to The Po Valley (Italy) and higher than that in Paris (France). As the main contributors to aerosol pH, the sulfate, nitrate and ammonium levels are also compared to other sites (Table 1). The total mass of water soluble inorganic ions in PM2.5 contributes only 15 % the mass of PM2.5 in HCMC, comparing to approximately 30 % in other sites. The result implies that other components (i.e. organic carbon, elemental carbon and trace metals) would be significant contributors to PM2.5 in HCMC, and they should be considered in the future studies.

Table 1. Comparisons of PM2.5 compositions with the previous studies, μg/m^3.

Location	PM2.5	WSII	SO_4^{2-}	NO_3^-	NH_4^+	References
HCMC	23.00 ± 6.78	4.08 ± 1.22	2.17 ± 0.80	0.43 ± 0.14	0.68 ± 0.96	This study
Paris, France	14.8 ± 9.6	6.94	2.0 ± 1.6	2.9 ± 3.7	1.4 ± 1.6	[11]
The Po Valley, Italy						[2]
Spring	36.8 ± 31.3	11.1 ± 12.6	2.4 ± 1.8	6.4 ± 8.3	2.4 ± 2.8	
Summer	14.5 ± 4.8	4.1 ± 2.2	2.7 ± 1.6	0.5 ± 0.5	1.0 ± 0.6	
Autumn	29.6 ± 16.2	9.6 ± 8.1	4.3 ± 3.2	2.9 ± 4.5	2.4 ± 2.0	
Winter	50.6 ± 21.4	13.1 ± 7.0	3.8 ± 2.6	6.1 ± 3.9	3.3 ± 1.6	
Shanghai, China	47.0	25.4	10.2	9.2	6.0	[12]
Shanghai, China	94.6	20.4	10.4	6.2	3.8	[13]
Kanpur, India	154	37.4	21.0	6.6	9.8	[14]

Notes: NA is not available. WSII denotes water soluble inorganic ion.

3.2. pH prediction

Aerosol acidity associated with the adverse human health effects and ecosystem degradation is widely observed in the atmosphere. The acidic aerosol enhances the condensation nuclei process which contributes to the formation of the clouds and droplets. Consequently, they impact on the visibility reduction and climate change. In addition, the acidic surface of the atmospheric aerosol enhances the reactions in the formation of secondary organic aerosol. Aerosol acidity mainly depends on the presence of the strong acid content including sulfuric and nitric acids. They can be expressed in two forms including aerosol pH and proton loading. The

major difference between those is that aerosol pH is the H^+ concentration per liquid water content in aerosol while proton loading is the H^+ concentration per unit volume of air (i.e. mol H^+ per m^3 air). The use of each form in describing chemical process in the atmosphere should be carefully because the proton loading used as a surrogate for pH is sometimes not correlation to aerosol pH. In this study, we firstly report the aerosol pH of PM2.5 collected in HCMC.

At first, to valid the models in estimating the aerosol pH, the predicted NH_3 concentrations by the models are compared to the measured NH_3 concentrations. As shown in Fig. 1, good agreements are observed demonstrating that the modeled results accurately represent the aerosol state. Therefore, the predicted pHs by the thermodynamic models are reasonable.

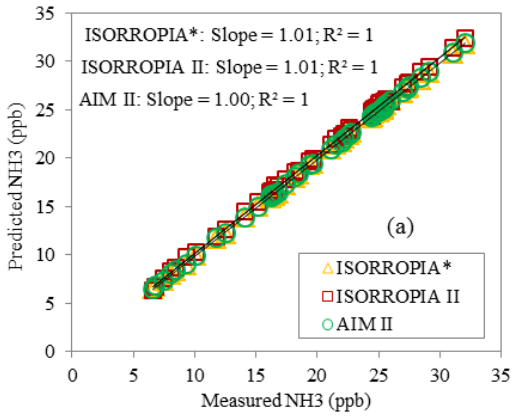

Figure 1. Evaluation of the thermodynamic model. The predicted NH_3 concentrations are compared to the measured NH_3.

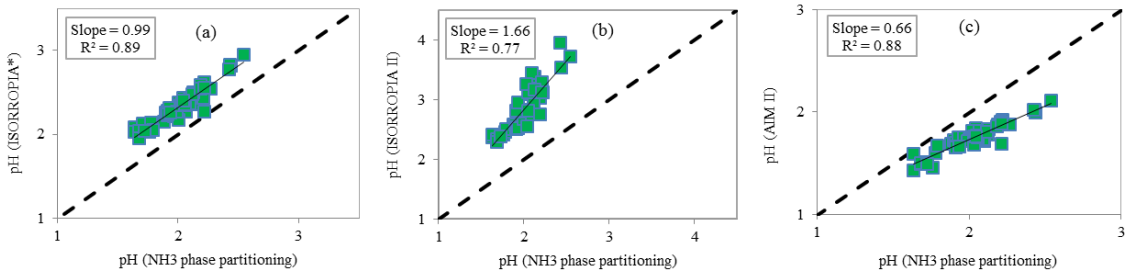

Figure 2. Comparison of predicted pH of PM2.5 estimated by various models and by the NH_3 phase-partitioning.

Table 2. Comparison of aerosol pH between in this study and in previous studies.

Model \ Site	Urban - HCMC (This study)	Beijing [1]	Shanghai [1]	The Po Valley [2]
ISORROPIA*	2.3 ± 0.2 (1.9 – 2.9)[a]			
ISORROPIA II	2.8 ± 0.4 (2.3 – 4.0)			
AIM	1.7 ± 0.1 (1.4 – 2.1)	−0.52 ± 0.62	−0.77 ± 0.67	2.3 ± 0.5
NH_3 phase partitioning	2.0 ± 0.2 (1.6 – 2.5)			

[a]Mean ± SD (Min – Max).

In this study, aerosol pH is calculated by two approaches including the thermodynamic models and the NH_3 phase partitioning. In the model approach, the gas-aerosol equilibrium is

enabled. As a result, the aerosol pH predicted by two methods would be well agreement. Fig. 2 shows the comparison of predicted pH estimated by the NH_3 phase partitioning method and by various models. A close agreement with square correlation coefficient (R^2) from 0.77 to 0.89 is observed, suggesting that the assumption of the NH_3/NH_4^+ equilibrium achieved at the study site is reasonable.

Table 2 summarizes the aerosol pH at the HCMC sites and shows a comparison to other locations. The aerosol pHs estimated by ISORROPIA*, AIM-II, NH3 phase partitioning and ISORROPIA II are 2.3 ± 0.2, 1.7 ± 0.1, 2.0 ± 0.2 and 2.8 ± 0.4, respectively. In the presence of crustal components (i.e. Na^+, Ca^{2+}), the aerosol pH predicted by ISORROPIA II model is slightly high approximately 0.5 pH unit as compared to the absence of those components. This result highlights the contribution of the crustal species in neutralizing the aerosol pH of PM2.5. Three methods (i.e. ISORROPIA*, AIM II and NH_3 phase partitioning) estimating the aerosol pH are mostly comparable.

In comparison to other locations in the world, the aerosol pH observed at the HCMC site is comparable to that observed in The Po Valley (Italy) [2]. However, as shown in Table 2, the pH at this study site is much lower than those reported in the Chinese cities [1]. Beijing and Shanghai are well-known as the most polluted cities in the world.

4. CONCLUSION

In this study, we firstly report the aerosol pH in PM2.5 based on the data which was collected at the HCMC site by using the filter pack method. The aerosol pH is a parameter of interest for the atmospheric implication of aerosols but is difficult to measure directly. To calculate the aerosol pH we apply two approaches including the thermodynamic equilibrium model (i.e. ISORROPIA and AIM) and the NH_3 phase partitioning method. At first, the predicted NH3 by models is compared to the measured NH_3. The close agreement validates the model predictions of the aerosol pH. In addition, the aerosol pH estimated by models agrees well with that estimated by the NH3 phase partitioning, demonstrating that the assumption of the NH3/NH4+ equilibrium is valid at the study site. During the study period, the aerosol is highly acidic. For instance, aerosol pH estimated by AIM II model varies from 1.4 to 2.1. The very low pH in PM2.5 observed in HCMC implicates the adverse human health effects when residents expose to acidic aerosols.

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