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Responses of Secondary Inorganic $PM_{2.5}$ to Precursor Gases in an Ammonia Abundant Area in North Carolina

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ABSTRACT

Secondary inorganic fine particulate matter ($iPM_{2.5}$) constitutes a significant amount of the atmospheric $PM_{2.5}$. The formation of secondary $iPM_{2.5}$ is characterized by thermodynamic equilibrium gas-particle partitioning of gaseous ammonia (NH_3) and aerosol ammonium (NH_4^+). To develop effective strategies for controlling atmospheric $PM_{2.5}$, it is essential to understand the responses of secondary $iPM_{2.5}$ to different precursor gases. In southeastern North Carolina, the amount of NH_3 is in excess to fully neutralize acidic gases (i.e., NH_3-rich conditions). NH_3-rich conditions are mainly attributed to the significant NH_3 emissions in the region, especially from the large amounts of animal feeding operation (AFO). To gain a better understanding of the impact of NH_3 on the formation of secondary $iPM_{2.5}$ in this area, the responses of $iPM_{2.5}$ to precursor gases under different ambient conditions were investigated based upon three-year monitoring data of the chemical components in $iPM_{2.5}$, gaseous pollutants, and meteorological conditions. The gas ratio (GR) was used to assess the degree of neutralization via NH_3, and ISORROPIA II model simulation was used to examine the responses of $iPM_{2.5}$ to changes in the total NH_3, the total sulfuric acid (H_2SO_4), and the total nitric acid (HNO_3). It was discovered that under different ambient temperature and humidity conditions, the responses of $iPM_{2.5}$ to precursor gases vary. In general, $iPM_{2.5}$ responds nonlinearly to the total NH_3 but linearly to the total H_2SO_4 and the total HNO_3. In NH_3-rich regions, $iPM_{2.5}$ is not sensitive to changes in the total NH_3, but it is very sensitive to changes in the total H_2SO_4 and/or the total HNO_3. Reducing the total H_2SO_4, as opposed to the total HNO_3 or the total NH_3, leads to a significant reduction in $iPM_{2.5}$ and is thus a more effective strategy for decreasing the concentration of $iPM_{2.5}$. This research provides insight into controlling and regulating $PM_{2.5}$ in NH_3-rich regions.

Keywords: Ammonia; Inorganic $PM_{2.5}$; Thermodynamic equilibrium modeling; ISORROPIA II; Animal feeding operations.

INTRODUCTION

Particulate matter (PM) with an aerodynamic equivalent diameter less than or equal to 2.5 μm (i.e., $PM_{2.5}$) is one of the six criteria air pollutants regulated under National Ambient Air Quality Standards (NAAQS) (U.S. EPA, 2015a). Due to its adverse impacts on environment and human health, $PM_{2.5}$ has been an intensive research topic since 1987 (Donham *et al.*, 1995; Heederik *et al.*, 2007; Pope *et al.*, 2009; Pui *et al.*, 2014). Various chemical components contribute to $PM_{2.5}$ in different proportions, and the major chemical components of $PM_{2.5}$ include ammonium (NH_4^+), sulfate (SO_4^{2-}), nitrate (NO_3^-), organic carbon (OC), elemental carbon (EC), elements and other unknown components (Bell *et al.*, 2007). The secondary inorganic $PM_{2.5}$ ($iPM_{2.5}$) is formed through chemical reactions between basic and acidic gases (e.g., ammonia [NH_3], nitric acid [HNO_3] and sulfuric acid [H_2SO_4]) (Hinds, 1998; Seinfeld and Pandis, 2006). The $iPM_{2.5}$ mainly consists of NH_4^+ salts including ammonium nitrate (NH_4NO_3), ammonium sulfate ($(NH_4)_2SO_4$), ammonium bisulfate (NH_4HSO_4) and ammonium chloride (NH_4Cl) (Tanner *et al.*, 1979; Tolocka *et al.*, 2001; Walker *et al.*, 2004; Li *et al.*, 2012, 2014a).

Ammonia is the major alkaline gas that may react with acidic gases to form $iPM_{2.5}$ in ambient air, and this process is also called gas-particle partitioning of NH_3-NH_4^+. The neutralization degree of NH_3 can be characterized by gas ratio (GR), which is in Eq. (1) (Ansari and Pandis, 1998):

$$GR = \frac{[TA] - 2[TS]}{[TN]} \quad (1)$$

where TA is total available ammonia, including NH_3 and NH_4^+ (in the unit of μmole m^{-3}). TS is total sulfate including SO_4^{2-}, bisulfate (HSO_4^-) and H_2SO_4 (in the unit of μmole m^{-3}). TN is total available nitrate, including NO_3^-

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and HNO_3 (in the unit of μmole m^{-3}). When GR > 1, the total available ammonia exceeds the amount needed to fully neutralize both total sulfate and total available nitrate, and this is defined as NH_3-rich condition; under this condition, the changes of total available ammonia may not be a key factor to affect the concentration of $iPM_{2.5}$. When 0 < GR < 1, the amount of total available ammonia is adequate to fully neutralize total sulfate but not total available nitrate, and only NH_4NO_3 formation is limited by NH_3; under this condition, the decrease of NH_3 may lead to corresponding decrease of NH_4NO_3. When GR < 0, the amount of total available ammonia is not enough to fully neutralize either total sulfate or total available nitrate, and both $(NH_4)_2SO_4$ and NH_4HSO_4 are limited by NH_3 (Wang-Li, 2015).

Based on USEPA's National Emission Inventory (NEI), animal feeding operation (AFO) contributed to more than 70% of the total NH_3 emissions in the United States (U.S.) (U.S. EPA, 2015b). While the AFO NH_3 emissions present a great potential to the formation of secondary $iPM_{2.5}$ in some regions where a significant amount of AFO facilities are located, the dynamic contribution of such emissions to the ambient $iPM_{2.5}$ is not well understood spatially and temporally. To gain holistic understanding of atmospheric $PM_{2.5}$, it is essential to understand the dynamic responses of atmospheric $iPM_{2.5}$ to the AFO NH_3 emissions under different atmospheric conditions and geographical locations (Wang-Li, 2015).

To study the thermodynamic equilibrium processes of $iPM_{2.5}$ and its precursor gases, thermodynamic equilibrium model such as ISORROPIA was developed to simulate the gas-particle partitioning of NH_3-NH_4^+ (Nenes *et al.*, 1998, 1999). In ISORROPIA, the phase changes (e.g., gas, liquid, and solid) and interaction of different chemical species (NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, and Na^+) as well as the impacts of temperature (T) and relative humidity (RH) on partitioning of NH_3-NH_4^+ are simulated (Fountoukis and Nenes, 2007; Fountoukis *et al.*, 2009). In an application of ISORROPIA to assess the formation of $iPM_{2.5}$ at an agricultural site located in eastern North Carolina (NC), Walker *et al.* (2006) examined the change of $iPM_{2.5}$ concentration in response to the 50% reduction of total NH_3 (gas + aerosol), total HNO_3 (gas + aerosol) and total H_2SO_4 (aerosol) in winter and summer of 1999–2000. It was discovered that the 50% reduction of total NH_3 had the least impact on $iPM_{2.5}$ concentration as compared to the 50% reductions in total HNO_3 and H_2SO_4. This research suggested that at the agricultural sites with elevated atmospheric NH_3 concentration, the $iPM_{2.5}$ is more sensitive to acidic gases rather than NH_3. In another $iPM_{2.5}$ study, Goetz *et al.* (2012) investigated the effect of NH_3 emissions from swine production facilities on $iPM_{2.5}$ concentration at three locations in eastern NC. The $iPM_{2.5}$ chemical composition data obtained from air quality monitoring stations of NC Division of Air Quality and gaseous pollutant concentrations measured or cited from literature were used to conduct $iPM_{2.5}$ simulation using ISORROPIA under three T and RH conditions. The results indicated that the simulation results of $iPM_{2.5}$ by ISORROPIA agreed well with the observation. Furthermore, this research revealed that high precursor gas concentrations, low T, and high RH led to higher chance for secondary $iPM_{2.5}$ formation.

In order to gain advanced understanding of the formation of $iPM_{2.5}$ as impacted by AFO NH_3 emissions, Li *et al.* (2014b) investigated the formation of secondary $iPM_{2.5}$ in response to total NH_3 inside a production house and in the vicinity of an egg farm in the southeastern U.S. Onsite measurements of NH_3 concentrations and $PM_{2.5}$ chemical components at in-house and ambient locations were used to conduct ISORROPIA II simulation to predict gas-particle partitioning of NH_3-NH_4^+. Li *et al.* (2014b) confirmed that the most significant reduction of $iPM_{2.5}$ can be caused by the reduction of total H_2SO_4 instead of NH_3 and this is because the formation of $iPM_{2.5}$ is limited by the availability of acidic gases when NH_3 exceeds the amount needed to fully neutralize acid gases.

In addition to the local-scale simulation, ISORROPIA II has been embedded into chemical transport model (CTM) to study more complicated atmospheric gas-particle partitioning on regional and/or global scales. Paulot and Jacob (2014) estimated the contribution of agricultural NH_3 emissions to the ambient $PM_{2.5}$ in the U.S. using GEOS-Chem global CTM coupled with ISORROPIA II. This modeling practice reported that there is a 0.36 μg m^{-3} increase of ambient $PM_{2.5}$ concentration caused by NH_3 emissions associated with the U.S. food export activities.

As the research gap exists in quantifying the formation of secondary $iPM_{2.5}$ experimentally and/or through model simulation in AFO region, the objectives of this research were as follows: (1) investigation of the neutralization degree of NH_3; (2) examination of seasonal variation of $PM_{2.5}$ mass closure; and (3) study of the responses of secondary $iPM_{2.5}$ to the changes of total NH_3, total HNO_3, and total H_2SO_4 in an animal production area of NC under different meteorological conditions.

METHODS

Since NH_4^+, SO_4^{2-}, and NO_3^- account for the majority of atmospheric $iPM_{2.5}$ (Bell *et al.*, 2007), this research focuses on the responses of NH_4^+, SO_4^{2-}, and NO_3^- to the changes of total NH_3, total HNO_3 and total H_2SO_4 at a site where atmospheric NH_3 is abundant due to NH_3 emissions from AFO.

Research Site Selection and Data Collection

To achieve the research objective, the research site has to be in an area where a significant amount of AFO facilities are present. In addition, simultaneous measurements of gas-phase pollutants (e.g., NH_3 and HNO_3) and particle-phase ions (e.g., NH_4^+, SO_4^{2-}, and NO_3^-) are required input data to conduct ISORROPIA II simulation. Thus, the availability of the required measurement data is another criterion for the site selection. Based upon these two site selection criteria, a monitoring site (35.23146 N, 77.568792 W) in Lenoir County of NC was selected for this research. Fig. 1 shows this site marked on the AFO distribution map developed by Zhao and Wang-Li (2015). The majority of

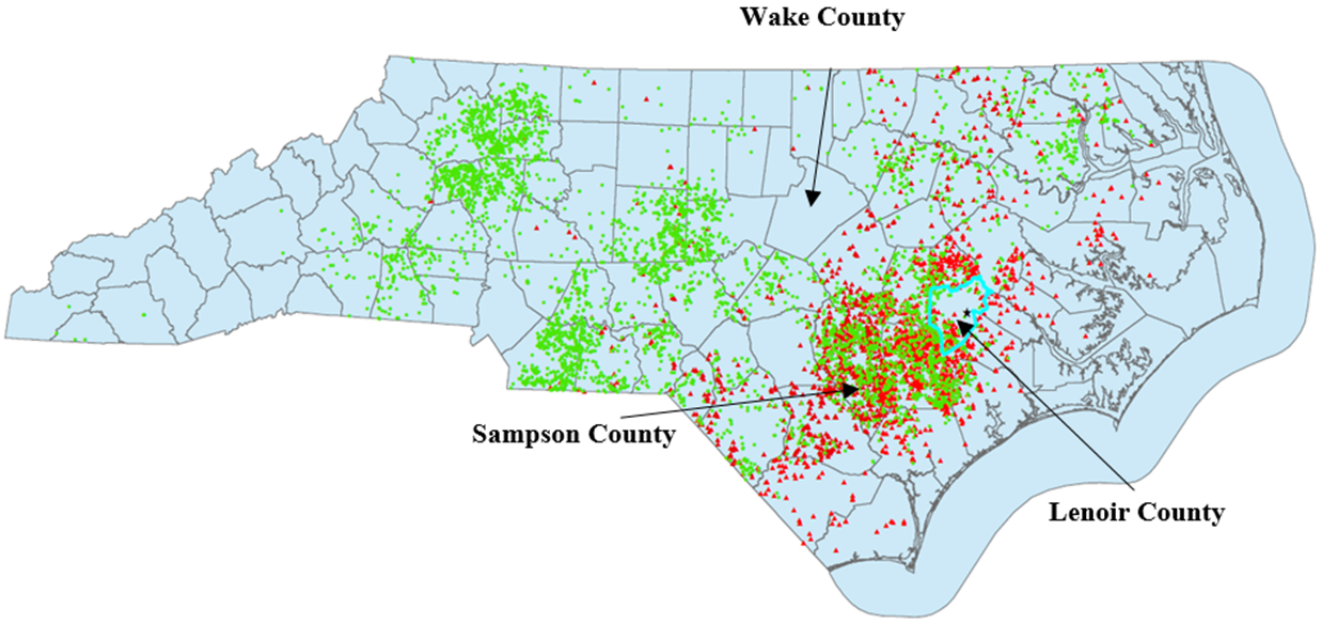

Fig. 1. Spatial distribution of poultry and swine farms across the entire NC (the black star: $iPM_{2.5}$ and NH_3 monitoring site; the red triangle: swine farms; the green solid circle: poultry farms).

the swine and poultry farms are in the south-central area of NC where the research site was also located.

At the selected site, 24-hr average measurements of $PM_{2.5}$ chemical components (e.g., NH_4^+, SO_4^{2-}, NO_3^-) and hourly measurements of NH_3, reactive oxides of nitrogen (NO_y), T and RH were taken in 2002–2004 and reported at the EPA's Air Quality System (AQS) website (https://aqs.epa.gov/api). The 24-hr $PM_{2.5}$ chemical composition data were measured every sixth day while the hourly NO_y concentrations, T, and RH were measured continuously for three years. To keep these data on the same time scale, hourly data on specific days when the $PM_{2.5}$ chemical composition data were taken were converted into 24-hr average data to match daily measurements of $PM_{2.5}$ chemical components. While the HNO_3 gas concentration is a required input for ISORROPIA II model, the HNO_3 gas measurements were not available. Thus, the NO_y concentration may be used to indirectly determine the HNO_3 gas concentration. In general, NO_y includes nitric oxide (NO), nitrous oxide (N_2O), HNO_3, peroxyacetyl nitrate (PAN), nitrous acid (HONO), nitrate radical (NO_3), dinitrogen pentoxide (N_2O_5), organic nitrates etc. In addition, NO, NO_2, HNO_3, and PAN are the major components of NO_y (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006). In atmosphere, HNO_3 is mainly formed through the oxidation of NO_2 following Eq. (2) in the daytime (Pun and Seigneur, 2001; Jacobson, 2005):

$$OH + NO_2 \rightarrow HNO_3 \quad (2)$$

where reaction (2) mainly happens in the daytime in which the photochemical reaction can provide adequate hydroxyl radical (OH).

To estimate the HNO_3 concentration through NO_y concentration, NO_2 concentration should be first determined. Luke *et al.* (2010) discovered that the fractional contribution of NO_2 in NO_y varied with the time of day. While no NO_2 measurement data were available in Lenoir County, there were simultaneous measurements of hourly NO_y and NO_2 concentrations in 2014 in Wake County, which is another county in southeastern NC (Fig. 1). The median NO_2/NO_y ratios for each of 24 hours in Wake County were used to estimate NO_2/NO_y ratios in Lenoir County. The fractional contributions of NO_2 to the total NO_y are set at different values in each of 24 hours based on the measurement data in Wake County, and this trend is consistent with the measurements performed by Luke *et al.* (2010).

In estimation of the HNO_3 concentrations, it was assumed that different percentages (0%, 0.5%, 1%, 5%, 10%, 25%, 50%, and 100%) of NO_2 might be converted to HNO_3 through Eq. (1). As for H_2SO_4, since it has very low vapor pressure, nearly all of the H_2SO_4 partition into the particle phase (Seinfeld and Pandis, 2006; Makar *et al.*, 2009).

Mass Closure Profile

The contribution of inorganic $PM_{2.5}$ to total $PM_{2.5}$ mass contribution was analyzed using mass closure profile of $PM_{2.5}$ chemical components. Major ions including $iPM_{2.5}$ anions/cations, up to 47 crustal elements, EC and OC as well as $PM_{2.5}$ mass concentration were simultaneously measured by MetOne SASS sampler. To develop a mass closure profile, $PM_{2.5}$ mass concentration measured by MetOne SASS Teflon was used to analyze the mass closure of $PM_{2.5}$ chemical components. When the sum of all the chemical component concentrations were greater than the measured $PM_{2.5}$ mass concentration, those data were excluded from mass closure analysis.

According to Dillner *et al.* (2012) and Weber *et al.* (2003), organic carbon matter (OCM) can be calculated using Eq. (3) to account for elements other than carbon:

$$OCM = 1.4 \times (OC_m - OC_b) \quad (3)$$

where OCM = organic carbon matter, OC_m = organic carbon measurement, and OC_b = field blank.

The contributions of various chemical components to $PM_{2.5}$ were calculated using Eq. (4):

$$P_i = (C_i/C_m) \times 100 \quad (4)$$

where P_i = percentage of the chemical component i in $PM_{2.5}$ mass concentration, C_i = concentration of chemical component i, and C_m = measured $PM_{2.5}$ mass concentration from MetOne SASS Teflon filter.

ISORROPIA II Settings

For this study, all the $iPM_{2.5}$ chemical components are assumed to be internally mixed, and the thermodynamic equilibrium is also assumed to be established very rapidly. The ISORROPIA II allows user to specify the problem type (forward or reverse) and thermodynamic state (stable or metastable); in this study, ISORROPIA II is set as forward + stable. As NH_3-NH_4^+-SO_4^{2-}-HNO_3-NO_3^- system is determined as the research focus, all the other species concentrations, including total sodium (Na^+), total hydrochloric acid (HCl), total calcium (Ca^{2+}), total potassium (K^+), and total magnesium (Mg^{2+}) are set as 0.

The examination of responses of $iPM_{2.5}$ to the total NH_3, total HNO_3, and total H_2SO_4 was based on the minimum, median and maximum concentrations of the input parameters measured in 2002–2004 using ISORROPIA II (Table 1).

Five T and RH conditions were used to test the responses of secondary $iPM_{2.5}$ to the changes of total NH_3, total H_2SO_4, and total HNO_3. These combinations include maximum T + minimum RH, minimum T + maximum RH, median T + median RH, maximum T + maximum RH, minimum T + median RH, of which, maximum T + maximum RH and minimum T + median RH represent the summer and winter conditions, respectively.

Statistical Analysis

All the data analyses, analysis of variance (ANOVA) test, paired *t*-test, and Tukey's Honest Significant Difference (HSD) test were performed using R.

RESULTS AND DISCUSSION

Statistical Characterization of the Field Measurements

Table 2 lists the summary of three-year measurements. Median NH_3 gas concentrations in winter and summer were 0.74 and 3.17 μg m^{-3}, respectively, and median NH_4^+ concentrations in winter and summer were 1.15 and 1.64 μg m^{-3}, respectively. Research performed by Walker *et al.* (2006) at a site in the neighboring county, Sampson County (Fig. 1), reported the median NH_3 gas concentrations of 2.60 and 6.18 μg m^{-3} in winter and summer, respectively, and median NH_4^+ aerosol concentrations of 1.90 and 1.69 μg m^{-3} in winter and summer, respectively. Comparatively, the NH_3 gas and NH_4^+ aerosol concentrations at the site in Sampson County were greater than the concentrations measured in this research. This can be justified by the difference of AFO distribution and density in these two counties shown in Fig. 1. The AFO density is much higher in Sampson County than in Lenoir County. In addition, minimum, median and maximum total H_2SO_4 concentrations of this site (0.59, 3.53 and 14.60) are comparable with those (0.58, 3.43 and 14.30) in Sampson County reported by Goetz *et al.* (2012).

Table 1. Inputs of the ISORROPIA II simulation.

Input variables	Minimum	Median	Maximum
Total NH_3	0.54	3.16	37.94
Total H_2SO_4	0.59	3.53	14.60
Total HNO_3	0.24	1.17	4.24
RH (%)	39	77	95
T (K)	271.95	292.05	305.95

Concentrations are expressed in μg m^{-3} as equivalent concentrations; total HNO_3 concentration is calculated based on 3.63% conversion percentage of NO_2 to HNO_3.

Responses of Total $iPM_{2.5}$ to Different Conversion Percentages of NO_2 to HNO_3

As it has been stated, 0%, 0.5%, 1%, 5%, 10%, 25%, 50% and 100% of NO_2 were assumed to be converted through Eq. (1) to HNO_3; in each case scenario, gas-phase HNO_3 and total HNO_3 concentrations were calculated based upon the different conversion ratios. The calculated total HNO_3 along with other model inputs (median values) were then used to simulate the formation of $iPM_{2.5}$ using ISORROPIA II. The predicted $iPM_{2.5}$ was compared with the measured $iPM_{2.5}$ concentrations under different NO_2-to-HNO_3 conversion percentages (Fig. 2).

Fig. 2 shows that as the percentage of NO_2 to HNO_3 conversion was increased from 0% to 100%, the ratio of predicted $iPM_{2.5}$ over measured $iPM_{2.5}$ was increased from 0.95 to 1.80, correspondingly. This can be explained that in Lenoir County, ambient NH_3 is abundant (GR > 1); while NH_3 preferentially reacted with H_2SO_4 to form $(NH_4)_2SO_4$ and ammonium bisulfate (NH_4HSO_4), excessive NH_3 could react with HNO_3 to form NH_4NO_3 (Tanner *et al.*, 1981; Yu *et al.*, 2005). When NH_3 concentration in the atmosphere exceeds the amount needed to fully neutralize both total HNO_3 and total H_2SO_4, more HNO_3 can favor the formation of NH_4NO_3, then increase the concentration of $iPM_{2.5}$.

When the conversion percentage of NO_2 to HNO_3 was set at 3.63%, the ratio of predicted $iPM_{2.5}$ over measured $iPM_{2.5}$ was close to 1, which may be indicative of a reasonable estimate of the conversion ratio. Moreover, Goetz *et al.* (2012) reported the minimum, median, and maximum concentrations of total HNO_3 were 0.26, 1.07, and 5.24 μg m^{-3}, respectively, in eastern NC in 2001–2004. The estimated minimum, median, and maximum total HNO_3 in this research were 0.24, 1.17, and 4.24 μg m^{-3}, respectively in 2002–2004. Thus, the estimation of the HNO_3 concentration generally agreed with the previous research.

Neutralization Degree of NH_3: GR

The neutralization degree of NH_3 was characterized by

Table 2. The statistics of concentrations of different gases and $PM_{2.5}$ chemical components by season.

Season		NH_3	HNO_3	NH_4^+	NO_3^-	SO_4^{2-}	$iPM_{2.5}$	TNH_3	$THNO_3$	TH_2SO_4	T (K)	RH (%)
Winter	N	28	28	28	28	28	28	28	28	28	28	28
	Mean	1.68	0.71	1.21	1.75	2.62	5.58	2.74	2.49	2.67	281.17	68.30
	SD	1.96	0.34	0.55	0.91	1.17	2.16	1.80	1.02	1.20	5.42	14.57
	Median	0.74	0.62	1.15	1.69	2.39	5.53	2.05	2.43	2.43	280.65	72.96
	Min	0.36	0.14	0.28	0.17	1.14	2.22	0.78	0.51	1.16	271.95	39.38
	Max	7.90	1.43	2.62	3.35	6.35	11.52	8.35	4.24	6.48	294.15	92.96
Spring	N	30	30	30	30	30	30	30	30	30	30	30
	Mean	4.47	0.32	1.42	0.82	4.00	6.25	5.73	1.16	4.08	290.90	75.08
	SD	4.23	0.13	0.77	0.45	1.73	2.82	4.30	0.49	1.76	5.42	11.09
	Median	3.12	0.30	1.48	0.66	4.14	6.25	4.41	1.09	4.23	290.50	76.37
	Min	0.36	0.12	0.01	0.26	0.58	0.85	0.69	0.46	0.59	279.65	45.46
	Max	15.29	0.60	3.19	1.78	7.39	11.86	18.12	2.17	7.54	300.45	94.71
Summer	N	30	30	30	30	30	30	30	30	30	30	30
	Mean	6.13	0.24	1.68	0.67	4.77	7.11	7.77	0.92	4.87	299.67	79.73
	SD	7.83	0.11	1.18	0.34	2.81	4.20	7.99	0.40	2.87	3.08	8.16
	Median	3.17	0.25	1.64	0.64	4.68	7.14	4.97	0.96	4.78	300.10	80.08
	Min	0.43	0.08	0.17	0.23	1.14	1.54	0.61	0.32	1.16	291.45	65.42
	Max	36.62	0.52	5.50	1.79	14.30	21.02	38.07	2.23	14.60	305.95	94.67
Fall	N	27	27	27	27	27	27	27	27	27	27	27
	Mean	2.97	0.52	1.67	0.93	4.42	7.02	4.49	1.47	4.51	293.18	79.37
	SD	6.99	0.39	1.38	0.70	3.21	4.95	6.68	0.90	3.27	5.93	8.46
	Median	1.10	0.46	1.30	0.58	3.40	5.41	2.50	1.11	3.47	293.85	80.75
	Min	0.35	0.06	0.07	0.18	0.66	0.94	0.54	0.24	0.67	280.95	62.58
	Max	36.96	1.87	6.61	2.76	14.30	23.67	36.52	3.67	14.60	301.85	95.00

All the concentration values are expressed in μg m^{-3}.
The concentration of HNO_3 is calculated based on the assumption that 3.63% of NO_2 was converted to HNO_3 through Eq. (1). $TNH_3 = NH_3 + NH_4^+$; $THNO_3 = HNO_3 + NO_3^-$; $TH_2SO_4 = H_2SO_4$; TNH_3, $THNO_3$, TH_2SO_4 are all expressed as the equivalent concentration; $iPM_{2.5}$ is the sum of NH_4^+, NO_3^- and SO_4^{2-}; T is temperature; RH is relative humidity.

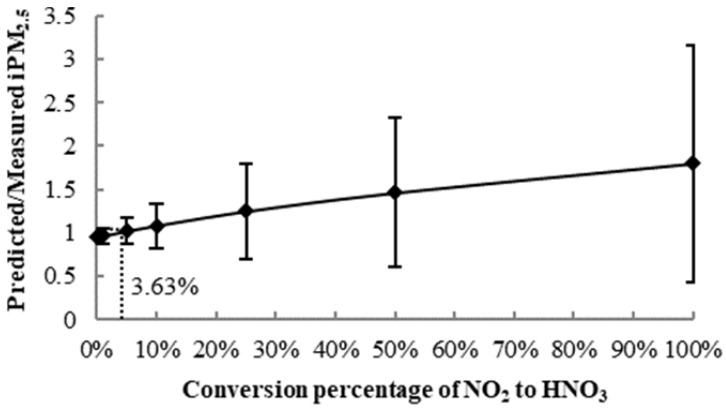

Fig. 2. The ratio of predicted $iPM_{2.5}$ concentration over measured $iPM_{2.5}$ concentration against conversion percentage of NO_2 to HNO_3.

GR. The ranges of GR in four seasons are listed in Table 3. This area was classified as the NH_3-rich area since the GR values were greater than 1 in most of the time. Specifically, in summer, 29 out of 30 data points were characterized as GR ≥ 1; even in winter, 23 out of 28 data points were GR > 1. In addition, the median GRs in four seasons were all larger than 1 with the highest GR-12.69 in summer. This observation indicated that the research site in Lenoir County was dominated by NH_3-rich condition such that there was a great potential for neutralizing acidic gases with excessive NH_3 in atmosphere.

Seasonal Variations of $PM_{2.5}$ Chemical Speciation

In Lenoir County, $PM_{2.5}$ mass concentration was measured in 2002–2004 using two methods, Federal Reference Method (FRM) and MetOne SASS chemical speciation sampler; both datasets came from gravimetric analysis. To check the data quality, the comparison between these two datasets were performed and the results are listed in Table 4.

As indicated by Table 4, the $PM_{2.5}$ mass concentration measurements from MetOne SASS sampler are significantly greater than the measurements from FRM method. The seasonal mass closure profile is shown in Fig. 3.

Table 3. Numbers in different GR ranges in four seasons of Lenoir County.

Season	Median GR	N	Numbers of GRs in different ranges			
			GR ≤ 1	1 < GR ≤ 3	3 < GR ≤ 10	GR > 10
Winter	1.93	28	5	14	7	2
Spring	10.30	30	2	9	4	15
Summer	12.69	30	1	2	9	18
Fall	4.35	27	2	10	12	3

Median GR is calculated based on the median total HNO_3, median total H_2SO_4 and median total NH_3 concentrations.
N is the total data point number in each season.

Table 4. Comparison of FRM vs. MetOne SASS measured $PM_{2.5}$ mass concentration.

Season	N	p-value	Mean ± SD (FRM vs. MetOne SASS)	
All (4 seasons)	160	7.59×10^{-6}	11.60 ± 5.77	12.72 ± 5.99
Winter	35	0.003	9.84 ± 3.33	11.01 ± 4.34
Spring	41	6.33×10^{-5}	11.15 ± 4.80	12.27 ± 5.07
Summer	46	0.19	13.77 ± 7.01	14.60 ± 6.95
Fall	38	0.01	11.09 ± 6.25	12.48 ± 6.55

Comparison is performed using paired *t*-test, 0.05 significance level.
FRM uses R&P Partisol Plus 2025 sequential air sampler with EPA Well Impact Ninety-Six (WINS) impactor.
MetOne SASS uses sharp cut cyclone (SCC) and Teflon filter.
N = number of samples.

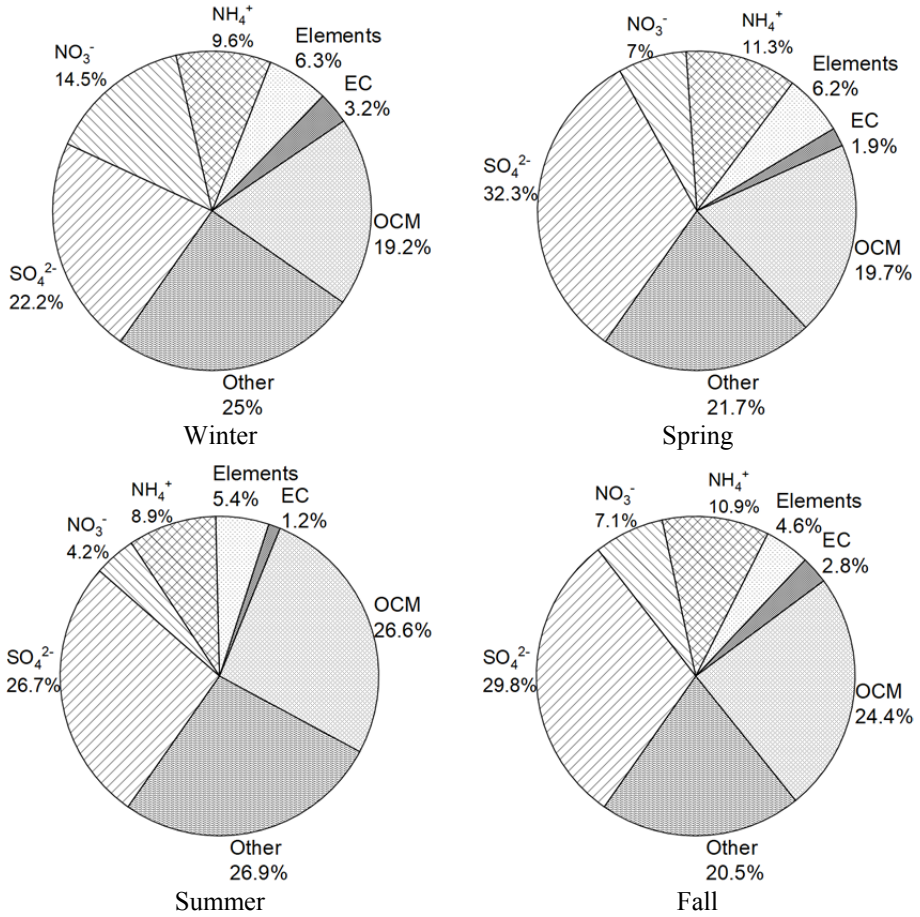

Fig. 3. $PM_{2.5}$ chemical speciation mass fractions in Lenoir County in four seasons.

As can be seen from Fig. 3, $iPM_{2.5}$ accounted for a large proportion of the total $PM_{2.5}$, and this fraction was highest in spring (51%) and lowest in summer (40%). For $iPM_{2.5}$ alone, three chemical species, SO_4^{2-}, NO_3^- and NH_4^+, also accounted for different fractions in four seasons. The results of Tukey's test were shown in Table 5.

As indicated by Table 5, the $PM_{2.5}$ concentration in summer was significantly higher than in winter; this can be explained by the seasonal variations of the major chemical components. The OCM and SO_4^{2-} together accounted for 41.4–54.2% of $PM_{2.5}$ mass concentration in four seasons; both species' concentrations were higher in summer than in winter. In addition, SO_4^{2-} was also the major component of $iPM_{2.5}$ and it accounted for 47.9–67.0% in the whole $iPM_{2.5}$. The NO_3^- concentration was significantly higher in winter than in summer. This may be due to semi-volatile characteristic of NH_4NO_3, according to Olszyna *et al.* (2005), SO_4^{2-} salts and NO_3^- salts own different levels of thermal stability, the NH_4NO_3 is not thermally stable so that it may decompose to gaseous HNO_3 and NH_3 when environmental conditions (high T and low RH) do not favor the particle phase. On the other hand, SO_4^{2-} salts are thermally stable compared with NO_3^- salts. In summer, the ambient conditions do not favor the formation of NH_4NO_3. However, the $(NH_4)_2SO_4$ can still form in summer; thus, SO_4^{2-} was the year-round major component of $iPM_{2.5}$ and this is consistent with the finding from Holt *et al.* (2015). However, as for NH_4^+, there is no significant difference between four seasons. The NH_3-rich conditions dominated in four seasons; NH_3 exceeded the amount needed to fully neutralize both HNO_3 and H_2SO_4. The NH_4^+ in the form of $(NH_4)_2SO_4$ was higher in summer than in winter and NH_4^+ in the form of NH_4NO_3 was higher in winter than in summer; thus, both seasonal variations offset the change of the NH_4^+ concentration in winter and summer.

Response of Secondary $iPM_{2.5}$ to Total NH_3

In this analysis, median total H_2SO_4 concentration and median total HNO_3 concentration were used under five T and RH case scenarios (Table 1) to simulate the $iPM_{2.5}$ formation with total NH_3 concentration ranging from 0.54 to 37.94 μg m^{-3}. The responses of $iPM_{2.5}$ to the change of total NH_3 are shown in Fig. 4. Under different conditions, the responses of $iPM_{2.5}$ to total NH_3 were different. The concentration of $iPM_{2.5}$ responded to the total NH_3 nonlinearly.

Under maximum T + minimum RH (305.95 K + 39%), the change of $iPM_{2.5}$ concentration is caused by the change of SO_4^{2-}, HSO_4^-, and NH_4^+. When the total NH_3 concentration is changed from 0.54 μg m^{-3} to 37.94 μg m^{-3}, the GR is also changed from –2.17 to 116.29; during this process, the response of $iPM_{2.5}$ to total NH_3 is changed from sensitive to insensitive. When GR ≤ 0, increasing total NH_3 concentration can increase the concentration of particle-phase SO_4^{2-} and NH_4^+ while at the same time decrease the concentration of HSO_4^-. This is because that when NH_3 gas is insufficient for fully neutralizing total H_2SO_4, both $(NH_4)_2SO_4$ and NH_4HSO_4 exist in the system and adding more NH_3 can react with the available H_2SO_4 and at the same time convert NH_4HSO_4 to $(NH_4)_2SO_4$. When GR > 0, NH_3 is adequate to fully neutralize total H_2SO_4, and there is excessive NH_3 in the system. In the whole

Table 5. Comparisons of different $PM_{2.5}$ chemical component concentrations by season.

Species	Season	N	Mean ± SD	Tukey Grouping
$PM_{2.5}$	Winter	35	11.01 ± 4.34	B
	Spring	41	12.27 ± 5.07	A/B
	Summer	46	14.60 ± 6.95	A
	Fall	38	12.77 ± 6.88	A/B
OCM	Winter	23	2.42 ± 1.93	B
	Spring	34	2.74 ± 2.18	B
	Summer	38	4.29 ± 2.89	A
	Fall	34	3.35 ± 2.12	A/B
EC	Winter	35	0.36 ± 0.18	A
	Spring	41	0.25 ± 0.25	A/B
	Summer	46	0.18 ± 0.10	B
	Fall	38	0.34 ± 0.37	A
SO_4^{2-}	Winter	35	2.81 ± 1.34	B
	Spring	41	4.09 ± 1.61	A/B
	Summer	46	4.60 ± 2.55	A
	Fall	38	2.98 ± 2.88	A/B
NO_3^-	Winter	35	1.97 ± 1.09	A
	Spring	41	0.94 ± 0.58	B
	Summer	46	0.66 ± 0.36	B
	Fall	38	1.02 ± 0.94	B
NH_4^+	Winter	35	1.33 ± 0.68	A
	Spring	41	1.51 ± 0.76	A
	Summer	46	1.62 ± 1.07	A
	Fall	38	1.52 ± 1.24	A

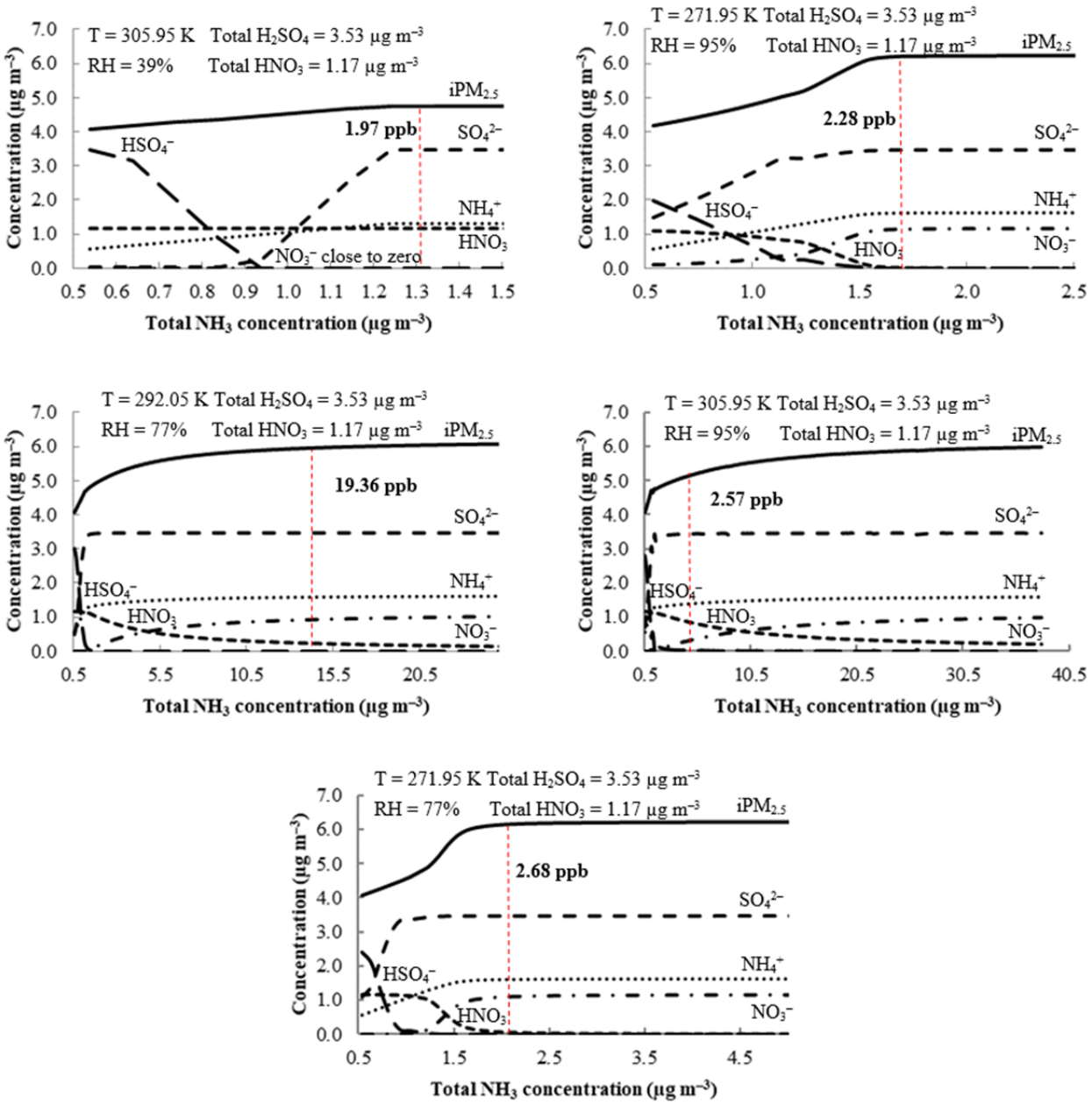

Fig. 4. Responses of different $iPM_{2.5}$ chemical components to total NH_3 concentration under five T and RH conditions.

process, NO_3^- aerosol is close to 0, and HNO_3 concentration remains the constant. This is because that high T and low RH do not favor the formation of semi-volatile compound NH_4NO_3; even when there is excessive NH_3 existing in the system, HNO_3 will not react with NH_3 to be converted to NO_3^-. Thus, in the end, increasing NH_3 will not change the concentration of any component in the system, and the response of $iPM_{2.5}$ to total NH_3 is insensitive.

Under minimum T + maximum RH (271.95 K + 95%), the change of $iPM_{2.5}$ concentration is caused by the changes of SO_4^{2-}, HSO_4^-, NH_4^+ and NO_3^-. When GR ≤ 1.63, increasing total NH_3 concentration can increase the concentration of SO_4^{2-}, NH_4^+ and NO_3^- while at the same time decrease the concentration of HSO_4^-. This is owing to the fact that low T and high RH can favor the formation of NH_4NO_3; when GR ≤ 0, adding more NH_3 can react with H_2SO_4 and at the same time convert NH_4HSO_4 to $(NH_4)_2SO_4$. When 0 < GR ≤ 1.63, the excessive NH_3 can react with HNO_3 to form NH_4NO_3 until all the HNO_3 is depleted. After GR > 1.63, adding more NH_3 will not change the concentration of $iPM_{2.5}$ significantly; this is due to lack of available acidic gases, which have been fully neutralized by NH_3 gas.

Under median T + median RH (292.05 K + 77%), changes in the $iPM_{2.5}$ chemical composition are similar to those under the condition of minimum T + maximum RH (271.95 K + 95%); the difference is the peak $iPM_{2.5}$ concentration value and the GR at which the system reaches the peak $iPM_{2.5}$ concentration. Fig. 4 shows that the difference in peak $iPM_{2.5}$ concentration is caused by the NO_3^- concentration.

Lower T and higher RH can favor the formation of NH_4NO_3; thus, the peak $iPM_{2.5}$ under median T + median RH is about 6.13 μg m^{-3}, which is less than the peak $iPM_{2.5}$ concentration (6.24 μg m^{-3}) under minimum T + maximum RH (271.95 K + 95%) and greater than the peak $iPM_{2.5}$ concentration (4.76 μg m^{-3}) under maximum T + minimum RH.

According to Table 2, at summertime, the ambient meteorology was characterized by high T + high RH; at wintertime, the ambient meteorology was characterized by low T + median RH. In order to capture the seasonal variation of $iPM_{2.5}$, these two combinations of T and RH are added to the analysis. As shown in Fig. 4, under maximum T + maximum RH (305.95 K + 95%), the change of $iPM_{2.5}$ concentration is similar to the condition of median T + median RH. The difference is the peak $iPM_{2.5}$ concentration; the peak $iPM_{2.5}$ concentration under maximum T + maximum RH is close to 6.00 μg m^{-3}, which is lower than the peak $iPM_{2.5}$ concentration, 6.13 μg m^{-3}, under median T + median RH. This is owing to the fact that higher T does not favor the formation of NH_4NO_3 and this case scenario can represent ambient condition in the summertime of this region. Under minimum T + median RH (271.95 K + 77%), the change of $iPM_{2.5}$ concentration is caused by the change of SO_4^{2-}, NH_4^+, NO_3^-, and HSO_4^-, and this trend is similar to the condition of minimum T + maximum RH; the difference is the threshold value of total NH_3 concentration that indicates the transition from sensitive to the insensitive region.

Upon the above analysis, the threshold values of total NH_3 concentration at which transition from sensitive to the insensitive happens are identified for all the case scenarios (Table 6). Greater than threshold values, the $iPM_{2.5}$ becomes insensitive to the change of total NH_3 concentration.

Table 6 shows that under condition of median T + median RH, the threshold values of total NH_3 concentration and GR are the largest. Under condition of minimum T + maximum RH, the threshold values of total NH_3 concentration and GR are the smallest. According to Table 3, the ambient condition is dominated by NH_3-rich condition; thus, under most of the cases, the response of $iPM_{2.5}$ to total NH_3 is insensitive. Thus, reducing total NH_3 concentration will not lead to significant decrease of $iPM_{2.5}$ concentration.

Response of Secondary $iPM_{2.5}$ to Total H_2SO_4

In this analysis, median total NH_3 concentration and median total HNO_3 concentration were used under five T and RH case scenarios (Table 1) to simulate the $iPM_{2.5}$ formation with total H_2SO_4 concentration changing from 0.59 to 14.60 μg m^{-3}. The results are shown in Fig. 5.

Fig. 5 shows that the response of $iPM_{2.5}$ to total H_2SO_4 is linear. Increasing total H_2SO_4 concentration can lead to the increase of $iPM_{2.5}$ concentration. Under maximum T + minimum RH (305.95 K + 39%), the change of $iPM_{2.5}$ concentration is caused by the change of SO_4^{2-}, HSO_4^-, and NH_4^+. As the formation of NH_4NO_3 is not favored under this condition, the concentration of NO_3^- is close to 0, and HNO_3 gas concentration remains the constant. While under the conditions of minimum T + maximum RH (271.95 K + 95%), median T + median RH (292.05 K + 77%), maximum T + maximum RH (305.95 K + 95%), and minimum T + median RH (271.95 K + 77%), the change of $iPM_{2.5}$ concentration is caused by the change of SO_4^{2-}, HSO_4^-, NH_4^+ and NO_3^-. With the increase of total H_2SO_4, NH_3 gas concentration is decreased due to the reaction with H_2SO_4, and during this process, H_2SO_4 also competes with HNO_3 to react with NH_3 to form $(NH_4)_2SO_4$ and NH_4HSO_4. When total H_2SO_4 concentration is greater than 9.0 μg m^{-3}, HSO_4^- begins to increase; this is because that if total NH_3 is not adequate to fully neutralize H_2SO_4, adding more H_2SO_4 can convert $(NH_4)_2SO_4$ to NH_4HSO_4.

In summary, the response of secondary $iPM_{2.5}$ to total H_2SO_4 concentration is linear. Adding more H_2SO_4 can increase $iPM_{2.5}$ concentration significantly; this is because of the excessive NH_3 existing in the system. When all the NH_3 gas is neutralized by H_2SO_4, SO_4^{2-} is converted to HSO_4^-; thus concentration of $iPM_{2.5}$ is increased. Response of secondary $iPM_{2.5}$ to total H_2SO_4 is not determined by NH_3-rich or NH_3-poor conditions in this research. This is because that in NH_3-NH_4^+-SO_4^{2-}-HNO_3-NO_3^- system, NH_3 gas preferentially reacts with H_2SO_4, and if total NH_3 is in excess of fully neutralizing H_2SO_4, excessive NH_3 can react with HNO_3. In this research, when there is excessive NH_3 existing in the system, adding more H_2SO_4 can directly increase the concentration of $(NH_4)_2SO_4$. After all the NH_3 is neutralized, $(NH_4)_2SO_4$ is then converted to NH_4HSO_4. In total, the $iPM_{2.5}$ concentration keeps increasing but with lower increasing rate (there are two stages in the Fig. 5, higher increase rate in the first stage and lower increase rate in the second stage).

Response of Secondary $iPM_{2.5}$ to Total HNO_3

In this analysis, median total NH_3 concentration and median total H_2SO_4 concentration were used under the five

Table 6. Threshold values of insensitive response of $iPM_{2.5}$ to total NH_3.

Ambient Conditions	Threshold total NH_3 concentration	Threshold GR value
Maximum T + minimum RH	1.34 μg m^{-3} (1.97 ppb)	0.37
Minimum T + maximum RH	1.74 μg m^{-3} (2.28 ppb)	1.63
Median T + median RH	13.74 μg m^{-3} (19.36 ppb)	39.64
Maximum T + maximum RH	1.74 μg m^{-3} (2.57 ppb)	1.63
Minimum T + median RH	2.04 μg m^{-3} (2.68 ppb)	2.58

When $d(iPM_{2.5})/d(\text{total } NH_3)$ is less than 0.2, the response of $iPM_{2.5}$ to total NH_3 is defined as insensitive.
Threshold GR value is calculated based on median total H_2SO_4 concentration and median total HNO_3 concentration, 3.53 and 1.17 μg m^{-3}, respectively.

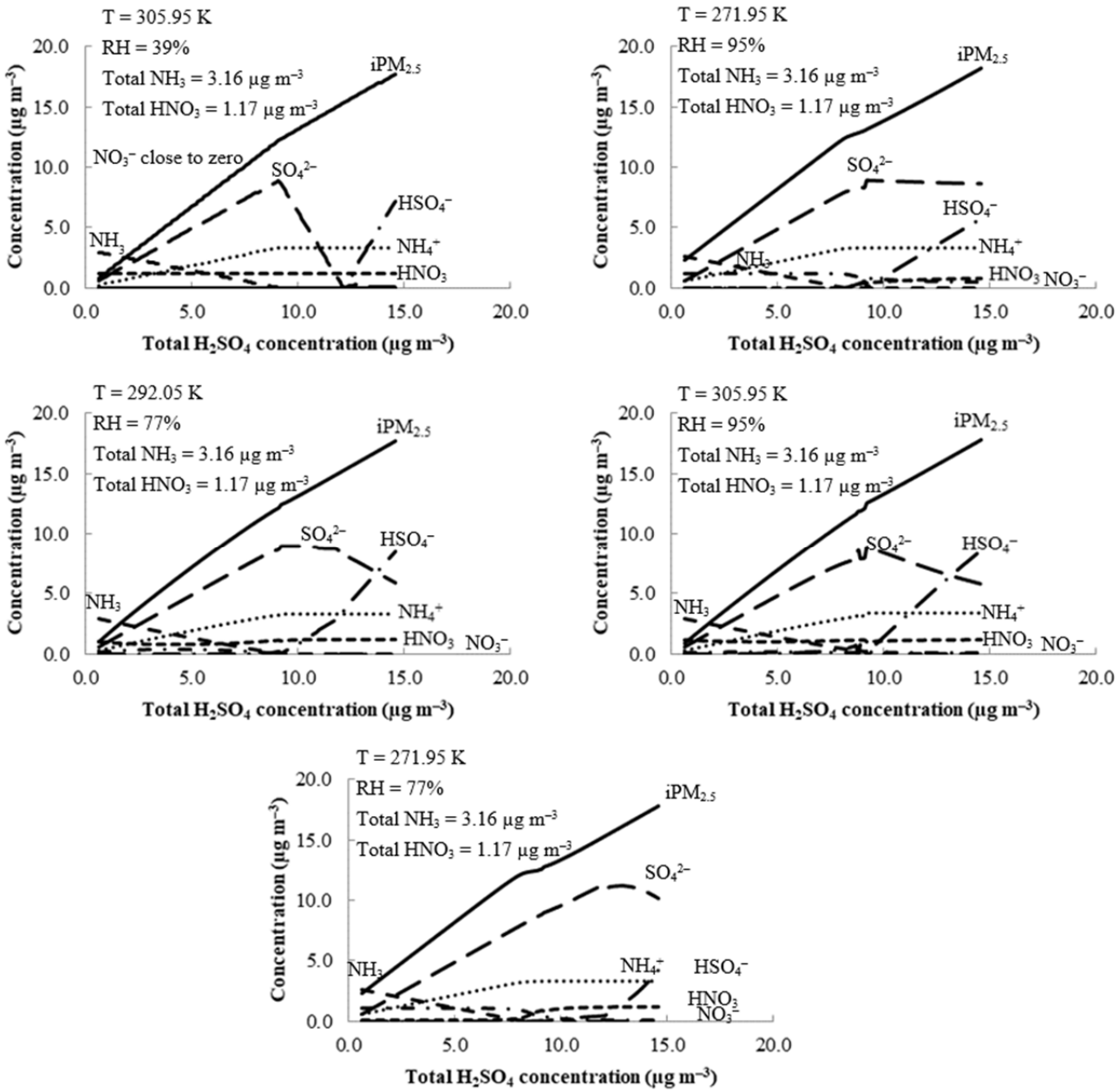

Fig. 5. Response of different $iPM_{2.5}$ chemical components to total H_2SO_4 concentration under five T and RH conditions.

T and RH case scenarios (Table 1) to simulate the $iPM_{2.5}$ formation with total HNO_3 concentration changing from 0.24 to 4.24 μg m^{-3}. The results are shown in Fig. 6.

Under maximum T + minimum RH (305.95 K + 39%), $iPM_{2.5}$ is insensitive to the change of total HNO_3. This is owing to the fact hat high T and low RH do not favor the formation of NH_4NO_3; even if there is excessive NH_3 gas in the system, it will not react with the added HNO_3 to form NH_4NO_3. Thus, all the other chemical components remain the constant and NO_3^- concentration is close to 0.

Under the conditions of minimum T + maximum RH (271.95 K + 95%), median T + median RH (292.05 K + 77%), maximum T + maximum RH (305.95 K + 95%), and minimum T + median RH (271.95 K + 77%), the changes of $iPM_{2.5}$ concentration is caused by the change of NH_4^+ and NO_3^-. This is because that under these four conditions, the formation of NH_4NO_3 is not limited by the ambient meteorology; thus, adding more HNO_3 can react with the available NH_3 to form NH_4NO_3, which leads to the increase of NO_3^- and NH_4^+ simultaneously. The SO_4^{2-} concentration remains the constant; this is due to the full neutralization of H_2SO_4 by NH_3.

In summary, the response of secondary $iPM_{2.5}$ to total HNO_3 is linear; adding more HNO_3 to the system can increase the $iPM_{2.5}$ concentration linearly due to the formation of NH_4NO_3. Under different ambient conditions, the increase rate of $iPM_{2.5}$ is different; lower T and higher RH favor the formation of NH_4NO_3 and lead to higher $iPM_{2.5}$ concentration.

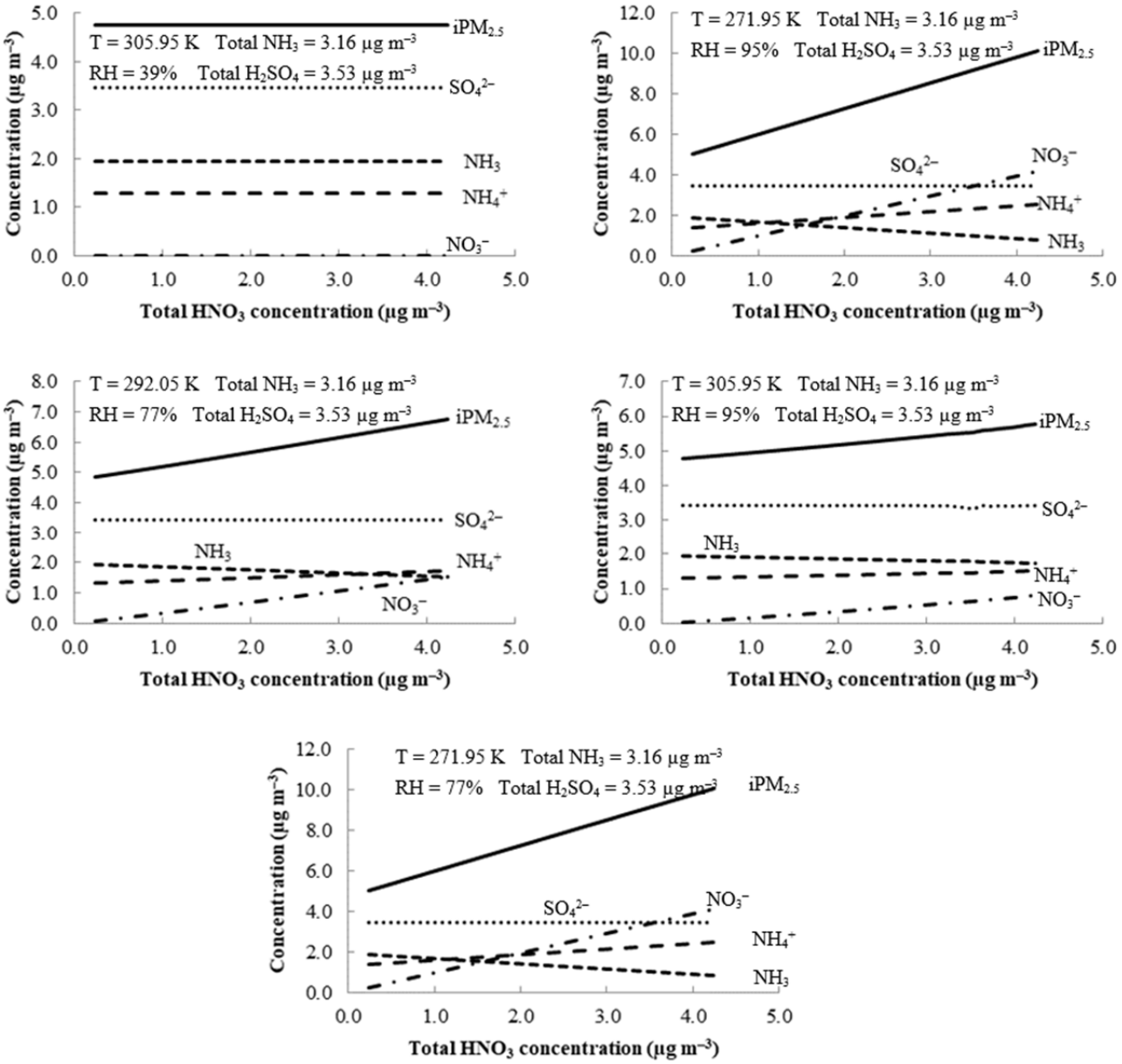

Fig. 6. Response of different $iPM_{2.5}$ chemical components to total HNO_3 concentration under five T and RH conditions.

Possible Mitigation Strategies for Ambient $iPM_{2.5}$ Reduction

Analysis of the $iPM_{2.5}$ responses to the precursor gases may lead to the development of the $iPM_{2.5}$ mitigation strategy. Under different ambient conditions, the responses of $iPM_{2.5}$ to total NH_3, total HNO_3, and total H_2SO_4 are different. In general, $iPM_{2.5}$ is more sensitive to the change of total H_2SO_4 concentration. The change of total NH_3 and total HNO_3 may also lead to the change of $iPM_{2.5}$ but may be limited by the neutralization degree of NH_3 and ambient conditions. In NH_3-rich condition, the change of total NH_3 concentration has the least impact on the $iPM_{2.5}$ concentration. Reducing total H_2SO_4 is more effective to decrease $iPM_{2.5}$ as compared to the reduction of total NH_3 and total HNO_3.

It needs to be noted that the two acidic gases used in ISORROPIA II, H_2SO_4 and HNO_3, are not directly emitted, but are transformed from the oxidation of nitrogen oxides (NO_x) and sulfuric dioxide (SO_2) in the atmosphere. Reducing the two acidic gases would require the reduction of their associated primary pollutants, NO_x and SO_2. Thus, in development of the total H_2SO_4 and HNO_4 concentration reduction strategies, strategies for SO_2 and nitrogen oxide (NO_x) emissions reduction should be taken.

CONCLUSIONS

In this research, the responses of $iPM_{2.5}$ to changes in the total NH_3, the total HNO_3, and the total H_2SO_4 were simulated by ISORROPIA II based upon three-year measurements of the chemical components in $iPM_{2.5}$ and gaseous pollutants as well as meteorological conditions. It was found that $iPM_{2.5}$ responds to precursor gases

differently under different T and RH conditions. In general, the response of $iPM_{2.5}$ to the total NH_3 is nonlinear, whereas its response to the total H_2SO_4 and the total HNO_3 is linear. In NH_3-rich regions, $iPM_{2.5}$ is insensitive to the total NH_3 but highly sensitive to the total H_2SO_4 and/or the total HNO_3. This research determined that the threshold values for the total NH_3 concentrations, below which the $iPM_{2.5}$ was insensitive to changes in the total NH_3, varied under different ambient conditions. Although dry and wet deposition and the nonlinear conversion of NO_x and SO_2 to HNO_3 and H_2SO_4 were not simulated with the thermodynamic model, inferences can still be drawn from our results about the dynamic changes in $iPM_{2.5}$ in response to changes in precursor gases, offering insight into controlling and regulating $iPM_{2.5}$ in NH_3-rich regions. These findings also illuminate the impact of AFO NH_3 emissions on the formation of secondary $iPM_{2.5}$, which may help to develop strategies for reducing ambient $PM_{2.5}$. Future studies may examine the quantitative contribution of AFO NH_3 emissions to forming $iPM_{2.5}$ using the Chemical Transport Model, thus further exploring the dynamic contribution of these emissions to the gas-particle partitioning of NH_3-NH_4^+.

ACKNOWLEDGMENTS

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SUPPLEMENTARY MATERIALS

The related raw data can found in the following link: https://drive.google.com/drive/folders/1m-QdMBd7T4eZ-AAmkzVIxcP5qG0eyJp8?usp=sharing.

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