Partitioning of NH$_3$-NH$_4^+$ in the Southeastern U.S.

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Abstract: The formation of inorganic fine particulate matter (i.e., PM$_{2.5}$) is controlled by the thermodynamic equilibrium partitioning of NH$_3$-NH$_4^+$. To develop effective control strategies of PM$_{2.5}$, we aim to understand the impacts of changes in different precursor gases on iPM$_{2.5}$ concentrations and partitioning of NH$_3$-NH$_4^+$. To understand partitioning of NH$_3$-NH$_4^+$ in the southeastern U.S., responses of iPM$_{2.5}$ to precursor gases in four seasons were investigated using field measurements of iPM$_{2.5}$, precursor gases, and meteorological conditions. The ISORROPIA II model was used to examine the effects of changes in total ammonia (gas + aerosol), total sulfuric acid (aerosol), and total nitric acid (gas + aerosol) on iPM$_{2.5}$ concentrations and partitioning of NH$_3$-NH$_4^+$. The results indicate that reduction in total H$_2$SO$_4$ is more effective than reduction in total HNO$_3$ and total NH$_3$ to reduce iPM$_{2.5}$ especially under NH$_3$-rich condition. The reduction in total H$_2$SO$_4$ may change partitioning of NH$_3$-NH$_4^+$ towards gas-phase and may also lead to an increase in NO$_3^-$ under NH$_3$-rich conditions, which does not necessarily lead to full neutralization of acidic gases (pH < 7). Thus, future reduction in iPM$_{2.5}$ may necessitate the coordinated reduction in both H$_2$SO$_4$ and HNO$_3$ in the southeastern U.S. It is also found that the response of iPM$_{2.5}$ to the change in total H$_2$SO$_4$ is more sensitive in summer than winter due to the dominance of SO$_4^{2-}$ salts in iPM$_{2.5}$ and the high temperature in summer. The NH$_3$ emissions from Animal Feeding Operations (AFOs) at an agricultural rural site (YRK) had great impacts on partitioning of NH$_3$-NH$_4^+$. The Multiple Linear Regression (MLR) model revealed a strong positive correlation between cation-NH$_4^+$ and anions-SO$_4^{2-}$ and NO$_3^-$ . This research provides an insight into iPM$_{2.5}$ formation mechanism for the advancement of PM$_{2.5}$ control and regulation in the southeastern U.S.

Keywords: inorganic PM$_{2.5}$; precursor gas; thermodynamic equilibrium modeling

1. Introduction

Particulate matter (PM) with aerodynamic diameter less than or equal to 2.5 $\mu$m (i.e., PM$_{2.5}$) causes adverse impacts on the environment and human health [1–5]. In general, PM$_{2.5}$ consists of inorganic ions, organic carbon (OC), elemental carbon (EC), various elements, and unclassified components [6–10]. Particulate matter can be classified as primary and secondary aerosol based on formation processes. Primary PM$_{2.5}$ is directly emitted from emission sources while secondary PM$_{2.5}$ is mainly formed through various chemical reactions and atmospheric processes [11–13]. The formation of the secondary inorganic PM$_{2.5}$ (iPM$_{2.5}$) is largely controlled by the chemical reactions between various precursor gases [14]. Ammonia (NH$_3$) neutralizes acidic species (e.g., nitric acid (HNO$_3$), sulfuric acid (H$_2$SO$_4$), and hydrochloric acid (HCl)) to form ammonium (NH$_4^+$) salts, and this dynamic process is called gas-particle partitioning of NH$_3$-NH$_4^+$ [15]. In the atmosphere, secondary iPM$_{2.5}$ mainly includes ammonium nitrate (NH$_4$NO$_3$), ammonium...
sulfate (\(\text{(NH}_4\text{)}_2\text{SO}_4\)), and ammonium chloride (NH\(_4\)Cl) and may account for a large portion of total PM\(_{2.5}\) \([16–21]\). Depending upon the availability of NH\(_3\), H\(_2\)SO\(_4\) may be partially or fully neutralized to form bisulfate (HSO\(_4^{2–}\)) or sulfate (SO\(_4^{2–}\)) salts and NH\(_3\) may also react with HNO\(_3\) to form NH\(_4\)NO\(_3\). As a semi-volatile compound, the formation of NH\(_4\)NO\(_3\) is also impacted by the ambient condition such as temperature (T) and relative humidity (RH); low T and high RH tend to favor the formation of NH\(_4\)NO\(_3\) \([22–24]\).

Studies on the formation of the iPM\(_{2.5}\) as impacted by the changes in the concentrations of precursor gases have been carried out through modeling approaches \([25–27]\). ISORROPIA II is a commonly used thermodynamic equilibrium model to simulate the dynamics of phase changes (e.g., gas, liquid, and solid) and interaction of different chemical species including NH\(_4^+\), nitrate (NO\(_3^{–}\)), SO\(_4^{2–}\), chloride (Cl\(^–\)), potassium (K\(^+\)), calcium (Ca\(^{2+}\)), magnesium (Mg\(^{2+}\)), and sodium (Na\(^+\)) in ambient air \([26,28]\). This model simulates the gas-particle partitioning phenomenon and impacts of T and RH on such partitioning \([29–32]\). The relationship of iPM\(_{2.5}\) and its precursor gases at an agricultural site located in eastern North Carolina (NC) was studied using field measurements and ISORROPIA model simulation \([33]\). The research examined the impacts of the 50% reduction in total NH\(_3\) (gas + aerosol), total HNO\(_3\) (gas + aerosol), and total H\(_2\)SO\(_4\) (aerosol) concentrations on the changes in iPM\(_{2.5}\) concentrations in winter and summer. It was found that the 50% reduction in total NH\(_3\) concentration may not lead to a significant reduction in iPM\(_{2.5}\) concentration. This may suggest that NH\(_3\) emissions from Animal Feeding Operations (AFOs) at agricultural sites led to elevated atmospheric NH\(_3\) concentration and NH\(_3\)-rich conditions dominated; thus, the change in iPM\(_{2.5}\) concentration was not sensitive to the change in NH\(_3\) concentrations. To understand the formation of iPM\(_{2.5}\) as impacted by AFOs NH\(_3\) emissions, the response of iPM\(_{2.5}\) to NH\(_3\) concentrations near an egg production farm in the southeastern U.S. was studied \([34]\). The NH\(_3\) concentrations and iPM\(_{2.5}\) chemical compositions measured at in-house and ambient locations were used as inputs in ISORROPIA II model to simulate the responses of iPM\(_{2.5}\) to the concentrations of precursor gases, T, and RH. It was confirmed that the most significant reduction in iPM\(_{2.5}\) could be achieved by the reduction in total H\(_2\)SO\(_4\) instead of total NH\(_3\). It was also suggested that in NH\(_3\)-rich areas, NH\(_3\) was in excess to neutralize the acidic gases and the formation of the iPM\(_{2.5}\) was limited by the availability of acidic gases \([34]\). The changes in the partitioning of NH\(_3\)-NH\(_4^+\) caused by the changes in precursor gases may vary under different ambient conditions in response to the unique atmospheric chemical conditions and local meteorology; thus, more efforts are needed to investigate the partitioning of NH\(_3\)-NH\(_4^+\) \([35–37]\).

The effects of changes in total H\(_2\)SO\(_4\) (aerosol), total NH\(_3\) (gas + aerosol), and total HNO\(_3\) (gas + aerosol) on iPM\(_{2.5}\) concentrations have been studied in the southeastern U.S. from 1998 to 2004 under the Southeastern Aerosol Research and Characterization (SEARCH) network. It was reported that the formation of NO\(_3^{–}\) was limited by the availability of NH\(_3\) in 1998–1999 \([38]\). Another study also indicated that the combination of the reductions in total H\(_2\)SO\(_4\) and total HNO\(_3\) was more effective to decrease iPM\(_{2.5}\) mass concentration in 1998–2001 \([39]\). Reduction in total H\(_2\)SO\(_4\) was more effective in decreasing iPM\(_{2.5}\) concentrations in 2004 \([40]\). Formation of iPM\(_{2.5}\) was limited by the availability of NH\(_3\) in rural-forest and coastal areas of the southeastern U.S. in 2004 \([41]\). While the above research provides fundamental understanding of secondary iPM\(_{2.5}\) formation, the implementations of new regulations \([42–44]\) led to the temporal changes in precursor gases emissions in the southeastern U.S.; thus, the responses of iPM\(_{2.5}\) concentrations and partitioning of NH\(_3\)-NH\(_4^+\) to the changes in total H\(_2\)SO\(_4\), total NH\(_3\), and total HNO\(_3\) may also change over time \([45]\). The objective of this research is to investigate the partitioning of NH\(_3\)-NH\(_4^+\) in urban and rural areas of the southeastern U.S. under different meteorological conditions using the latest field measurements of iPM\(_{2.5}\) and precursor gases. The research findings may provide further insights to develop effective PM\(_{2.5}\) control strategies.
2. Materials and Methods

2.1. Data Acquisition and Processing

This research utilized the 24 h particle-phase measurements and 1 h average gas-phase measurements from the SEARCH network [46] (Figure 1). For 24 h measurements, the chemical compositions of PM$_{2.5}$ were measured using filter-based Federal Reference Method (FRM), and 1 h average measurements were converted from 1 min or 5 min continuous measurements (Table S1); the detailed information about measurement techniques and detection limits can be found in SEARCH network literature [46]. The NH$_3$ gas concentration measurements were available at five sites named YRK, JST, CTR, BHM, and OLF in 2012–2016; thus, the responses of the partitioning of NH$_3$-NH$_4^+$ to the changes in precursor gases were investigated at these five sites. The dataset includes some NH$_3$ values that are either negative or below the detection limit. The negative values were excluded from data analysis, while the values below the detection limit were replaced with half of the detection limit [47,48].

![Geographical locations of the eight monitoring sites of the SEARCH network](image)

**Figure 1.** The geographical locations of the eight monitoring sites of the SEARCH network [46].

2.2. Investigation of the Partitioning of NH$_3$-NH$_4^+$

The partitioning of NH$_3$-NH$_4^+$ was investigated using ISORROPIA II [27]. The model performance evaluation was performed in another study; thus, it will not be further elaborated on. In this research, 10% to 90% reductions in total NH$_3$, total H$_2$SO$_4$, and total HNO$_3$ at the five sites in four seasons were used to investigate the responses of iPM$_{2.5}$ (NH$_4^+$ + NO$_3^-$ + SO$_4^{2-}$) to the changes in precursor gases in 2012–2016, spring and fall results are the transition case scenarios between summer and winter; thus, only summer and winter results are reported and discussed here. Moreover, only the gas-particle partitioning processes are considered, other processes such as emissions, dispersion, and dry and wet depositions are thus not included in this research.

The concentrations of iPM$_{2.5}$ and NH$_4^+$ under different total NH$_3$, total H$_2$SO$_4$, and total HNO$_3$ concentrations in four seasons were simulated using 24 h average data at the five sites. The gas-phase NH$_3$ molar fraction (NH$_3$/NH$_x$) in Equation (1) [49,50] was used to study the effects of changes in precursor gases on the partitioning of NH$_3$-NH$_4^+$.

$$\text{NH}_3/\text{NH}_x = [\text{NH}_3]/([\text{NH}_3] + [\text{NH}_4^+])$$

(1)

Gas ratio (GR) in Equation (2) [25,51] was calculated to study the effects of changes in precursor gases concentrations on the atmospheric chemical conditions, diurnal variation of iPM$_{2.5}$ and partitioning of NH$_3$-NH$_4^+$.

$$\text{GR} = ([\text{TA}] - 2 \times [\text{TS}])/[\text{TN}]$$

(2)

where [TA] is the sum of molar concentrations of NH$_3$ and ammonium (NH$_4^+$) (in the unit of µmol m$^{-3}$); [TS] is the sum of molar concentrations of SO$_4^{2-}$, bisulfate (HSO$_4^-$), and
H$_2$SO$_4$ (in the unit of $\mu$mol m$^{-3}$); and [TN] is the sum of molar concentrations of HNO$_3$ and nitrate (NO$_3^-$) (in the unit of $\mu$mol m$^{-3}$).

The pH [52] was calculated to study the acidity of the inorganic aerosol.

$$\text{pH} = -\log_{10} \frac{1000\gamma_{H^+} \cdot H^+_{\text{air}}}{W}$$

(3)

where $\gamma_{H^+}$ is the hydronium ion activity coefficient, which is set as unity; $H^+_{\text{air}}$ ($\mu$g m$^{-3}$) is the hydronium ion concentration in volume of air; and $W$ ($\mu$g m$^{-3}$) is particle water concentration associated with inorganic aerosol. Both $H^+_{\text{air}}$ and $W$ are from ISORROPIA II model output.

2.3. ISORROPIA II Model

The performance of ISORROPIA II for predicting inorganic aerosols in the southeastern U.S. was investigated in another research [53] and the ISORROPIA II model predicted the concentrations of various compositions of iPM$_{2.5}$ well.

For this study, the iPM$_{2.5}$ was assumed to be internally mixed, and the thermodynamic equilibrium was also assumed to be established instantaneously [29]. The ISORROPIA II allows the user to specify the problem type (forward or reverse) and thermodynamic state (stable or metastable). In this study, ISORROPIA II is set as forward type, which requires the concentrations of total NH$_3$ (gas + aerosol), total HNO$_3$ (gas + aerosol), and total H$_2$SO$_4$ (aerosol) as the model input. The metastable thermodynamic state was selected in this research [15,32].

2.4. Multiple Linear Regression Model

The multiple linear regression (MLR) model was constructed to examine the response of NH$_4^+$ to various factors. Step-wise model selection method based on the Bayesian information criterion (BIC) was used to select the best fitting model from Equation (4):

$$\text{NH}_4^+ = \beta_0 + \beta_1 \times x_i + \text{interaction terms} + \text{quadratic terms} + \epsilon_i$$

(4)

where $x_i$ are iPM$_{2.5}$ chemical components and gaseous pollutants including SO$_4^{2-}$, NO$_3^-$, Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$, Cl$^-$, NH$_3$, and HNO$_3$, ambient T, and RH. Interaction terms include up to two factors. All the gas- and particle-phase pollutants were converted in the unit of $\mu$g m$^{-3}$, T was in °C, RH was in %. The 24 h average Cl$^-$, K$^+$, Na$^+$, Mg$^{2+}$, Ca$^{2+}$, NH$_4^+$, SO$_4^{2-}$, and NO$_3^-$ data and 1 h average T, RH, NH$_3$, and HNO$_3$ data were available at the BHM site (2011–2016), CTR site (2012–2016), JST site (2010–2016), YRK site (2008–2016), OLF site (2013–2016), and OAK site (2010). The MLR model was built in two periods: 2008–2011 and 2012–2016. The best fitting MLR models vary in space and time and are only used to aid in the investigation of partitioning of NH$_3$-NH$_4^+$. 

3. Results and Discussion

3.1. Statistical Characterization of the Field Measurement Data

The statistical summaries of iPM$_{2.5}$ precursor gases, nonvolatile cations (NVCs), T and RH at six sites in two periods (2008–2011 and 2012–2016) are shown in Tables S2–S10. Tables S2–S10 reveal the seasonal variations of different precursor gases such as H$_2$SO$_4$, HNO$_3$, HCl, NH$_3$, and NVCs such as Na$^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$ as well as T and RH at the six sites of the SEARCH network. In general, T and RH were both lowest in winter and highest in summer (see the Supplementary Materials). The concentration of total H$_2$SO$_4$ was higher in summer than the other seasons at the six sites. The concentrations of total NH$_3$ and total HNO$_3$ did not exhibit a distinct seasonal pattern, which may be caused by spatial variation of emissions sources at the six sites of the southeastern U.S.

The concentrations of iPM$_{2.5}$ chemical compositions and precursor gases were also measured in different locations of the world. The aerosol composition measurements and source apportionment studies in a coastal city of eastern China during 2018–2019
indicated that inorganic aerosols accounted for a large portion of PM$_{2.5}$ mass concentration and local steel plant emissions were dominated by NH$_4$)$_2$SO$_4$ and ammonium bisulfate (NH$_4$HSO$_4$); in addition, the iPM$_{2.5}$ concentrations at the coastal city of China were much higher than that measured in the southeastern U.S. [54]. The inorganic composition of PM$_{2.5}$ and precursor gases were measured at Seoul and Deokjeok Island of South Korea in 2014, where the haze aerosols mainly consisted of inorganics (e.g., NH$_4^+$ salts); ISORROPIA II model simulations implicated that the addition of SO$_4^{2-}$ into the aerosols during the transport process increased the mass concentrations of NH$_4$NO$_3$, and another finding is that the concentrations of total NH$_3$, total HNO$_3$, and total H$_2$SO$_4$ were also higher than the measurement values in the southeastern U.S. during the same period of time [55]. Moreover, a newly developed method was used in Brno, Czech in 2018, to simultaneously measure the concentrations of gaseous NH$_3$ and aerosol NH$_4^+$ with a time resolution of 1 s; the measurement results indicated a seasonal variation for NH$_3$ and NH$_4^+$ with higher NH$_3$ concentrations in summer, and higher NH$_4^+$ concentrations in winter; the ratio of NH$_3$/NH$_4^+$ indicated the dominance of NH$_3$ and NH$_4^+$ in summer and winter, respectively [56]. The difference in local to regional emissions sources contributed to the spatial and temporal variations of iPM$_{2.5}$ and partitioning of NH$_3$-NH$_4^+$ across the world.

3.2. Seasonal Simulation of Partitioning of NH$_3$-NH$_4^+$

The responses of iPM$_{2.5}$, NH$_4^+$, and NH$_3$/NH$_x$ to the changes in total NH$_3$ and total HNO$_3$ in 2012–2016 are presented in Figure 2 and Figures S1–S4.
Atmosphere 2021, 1, 1681

0.266 µg m\(^{-3}\) in summer and winter of 2012–2016, the average total NH\(_3\) concentrations were reduced from 1.53 µg m\(^{-3}\) (0% reduction) to 0.153 µg m\(^{-3}\) (90% reduction) and from 2.66 µg m\(^{-3}\) (0% reduction) to 0.266 µg m\(^{-3}\) (90% reduction) in winter and summer, respectively; the average total HNO\(_3\) concentrations were reduced from 1.41 µg m\(^{-3}\) (0% reduction) to 0.141 µg m\(^{-3}\) (90% reduction) and from 1.11 µg m\(^{-3}\) (0% reduction) to 0.111 (90% reduction) in winter and summer, respectively.

As can be seen in Figures 2 and S1–S4, the formation of iPM\(_{2.5}\), NH\(_4^+\), and NH\(_3\)/NH\(_x\) were sensitive to the changes in total NH\(_3\) concentration when total NH\(_3\) concentration was reduced at least 20% or when total HNO\(_3\) concentration was not reduced in 2012–2016. Although the YRK, JST, BHM, and OLF sites were all under NH\(_3\)-rich condition, the pH analysis indicated that inorganic aerosols were still acidic (Table S11) instead of full neutralization. The reduction in total NH\(_3\) concentration could decrease the gas-phase NH\(_3\) concentration but could not decrease the formation of iPM\(_{2.5}\). When enough reduction in total NH\(_3\) was achieved or acidic gases (total H\(_2\)SO\(_4\) and total HNO\(_3\)) were in excess to react with NH\(_3\) gas, the subsequent reduction in total NH\(_3\) can lead to the decrease in iPM\(_{2.5}\).

The responses of iPM\(_{2.5}\), NH\(_4^+\), and NH\(_3\)/NH\(_x\) to the changes in total NH\(_3\) and total H\(_2\)SO\(_4\) are presented in Figures 3 and S5–S8.
As can be seen in Figures 3 and S5–S8, the formation of iPM$_{2.5}$ was very sensitive to the change in total H$_2$SO$_4$ concentration in summer and winter. The reduction in total H$_2$SO$_4$ can effectively decrease the concentration of iPM$_{2.5}$, and more NH$_3$ stayed in the gas-phase in this process. The responses of NH$_4^+$ to the change in total H$_2$SO$_4$ may exhibit two different regions. The less reduction in total NH$_3$ and the more reduction in total H$_2$SO$_4$ were achieved, the more sensitive the NH$_4^+$ responded to the change in total H$_2$SO$_4$. This can be explained that when NH$_3$ was not adequate to react with both HNO$_3$ and H$_2$SO$_4$, the reduction in H$_2$SO$_4$ may free some NH$_3$ associated with SO$_4^{2-}$, and the available NH$_3$ can react with HNO$_3$ to form NH$_4$NO$_3$, which lead to the decrease in SO$_4^{2-}$ salts and increase in NO$_3^-$ salts. Thus, NH$_4^+$ concentration may remain at approximately the same level. Furthermore, when greater than 80% reduction in total H$_2$SO$_4$ was achieved, the reduction in total H$_2$SO$_4$ may lead to the increase in iPM$_{2.5}$ at the JST (Figure S5), CTR (Figure S6), and OLF (Figure S8) sites in winter.

The formation of iPM$_{2.5}$ was more sensitive to the change in total H$_2$SO$_4$ in summer than in winter. This can be explained by the dominance of SO$_4^{2-}$ salts in iPM$_{2.5}$ in summer. The more intense summer solar radiation enhanced the transformation of SO$_2$ to SO$_4^{2-}$ [24]. Moreover, as the high T in summer did not facilitate the formation of NH$_4$NO$_3$, the decrease in SO$_4^{2-}$ salts caused by the reduction in total H$_2$SO$_4$ will not be offset by the increase in the NO$_3^-$ salts.

3.3. Diurnal Simulation of the Partitioning of NH$_3$-NH$_4^+$

In addition to the investigation of the partitioning of NH$_3$-NH$_4^+$ in four seasons, the partitioning of NH$_3$-NH$_4^+$ was also studied in different time of the day at the five sites in
2012–2016, the results of YRK site are shown in Figures 4–6, the results at the other sites are shown in Figures S9–S20.

Figure 4. Responses of iPM$_{2.5}$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, NH$_3$/NH$_x$, and GR to the reductions in TNH$_3$ at the YRK site in 2012–2016.

Figure 5. Responses of iPM$_{2.5}$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, NH$_3$/NH$_x$, and GR to the reductions in THNO$_3$ at the YRK site in 2012–2016.
Figures 4–6 indicate that the reduction in total NH3 and total HNO3 may not be effective in reducing the concentration of iPM2.5 unless more than a 60% reduction can be achieved. The reduction in total NH3 and total HNO3 can only lead to a decrease in NH4NO3, while the SO4^{2−} concentration remained at approximately the same level. The reduction in total NH3 concentration reduced both NH3/NHx and GR, and more NH3 partitioned towards particle-phase. The reduction in total HNO3 led to the increase in both NH3/NHx and GR, and more NH3 remained in the gas-phase. Overall, Figures 4–6 illustrate that the reductions in total NH3 and total HNO3 are ineffective for controlling iPM2.5 concentration.

Figure 6 shows that the reduction in total H2SO4 was more effective in reducing the concentrations of iPM2.5; however, the reduction in total H2SO4 may lead to the increase in NO3− concentration, especially at the CTR and OLF sites (Figures S14 and S20) (e.g., at 12:00 p.m., 80% total H2SO4 reduction at the CTR site (1.50→0.30 µg m^{−3}) resulted in the decrease in iPM2.5 (2.11→0.66 µg m^{−3}) and increase in NO3− (0.03→0.16 µg m^{−3})). The YRK, JST, and BHM sites were all in NH3-rich area, and the reduction in total H2SO4 may free some NH3 associated with H2SO4, however, the increase in gas-phase NH3 was not able to transform more HNO3 into particle-phase at NH3-rich sites (Figure 6, Figures S11 and S17). While at the CTR and OLF sites (Figures S14 and S20), the increase in gas-phase NH3 may change the partitioning of HNO3:NO3− toward particle-phase when the NH3 is not in excess to neutralize both HNO3 and H2SO4. The reduction in total H2SO4 can also increase both NH3/NHx and GR, which indicates that more NH3 stayed in the gas-phase rather than in the particle-phase in this process.

Reduction in total H2SO4 concentration may lead to a significant reduction in iPM2.5; thus, it was more effective than reducing total HNO3 and total NH3 concentrations to reduce iPM2.5 concentration. However, the reduction in total H2SO4 concentration may also increase the concentration NO3− at the CTR and OLF sites (Figures S14 and S20). Thus, the future reduction in iPM2.5 may necessitate the coordinated reduction in both H2SO4 and HNO3 in the southeastern U.S.
The YRK site was located in a rural area impacted by the NH\textsubscript{3} emissions from AFOs, while BHM and JST sites were located in the area impacted by industrial emission sources. The CTR site was located in a forest area and the OLF site was located in a suburban area. The spatial variation of the responses of the partitioning of NH\textsubscript{3}-NH\textsubscript{4}\textsuperscript{+} to the reductions in precursor gases implicated the important impact of AFOs NH\textsubscript{3} emissions. At the agricultural rural site—YRK site, the NH\textsubscript{3} emissions from AFOs led to elevated NH\textsubscript{3} concentration, which was in excess to neutralize acidic gases, and the formation of NH\textsubscript{4}NO\textsubscript{3} was not affected by the reduction in total H\textsubscript{2}SO\textsubscript{4} [36].

3.4. Multiple Linear Regression Model

The effects of the various predictor variables (e.g., SO\textsubscript{4}\textsuperscript{2−}, NO\textsubscript{3}−, NH\textsubscript{3}, etc.) on the response variable (NH\textsubscript{4}+) were estimated using regression analysis. The MLR models for the responses of NH\textsubscript{4}+ to various factors in two periods (2008–2011 and 2012–2016) at the six sites were shown in Tables 1, 2 and S12–S18.

Table 1. The summary of final MLR model coefficients at the YRK site from 2008 to 2011.

| Predictors   | Coefficients | SE  | t Value | Pr > |t|   |
|--------------|--------------|-----|---------|------|---|---|
| Intercept (β\textsubscript{0}) | 0.08 | 0.033 | 2.39 | 0.018 |
| SO\textsubscript{4}\textsuperscript{2−} (β\textsubscript{1}) | 0.33 | 0.009 | 37.11 | <2 × 10\textsuperscript{−16} |
| NO\textsubscript{3}− (β\textsubscript{2}) | 0.25 | 0.018 | 13.64 | <2 × 10\textsuperscript{−16} |
| (SO\textsubscript{4}\textsuperscript{2−}-3.27)\textsuperscript{2} (β\textsubscript{3}) | -0.008 | 0.001 | -5.74 | 4.5 × 10\textsuperscript{−8} |
| Mg\textsuperscript{2+} (β\textsubscript{4}) | -3.83 | 1.45 | -2.65 | 0.0089 |

Residual standard error: 0.1672 on 161 degrees of freedom. Multiple R-squared: 0.94. Adjusted R-squared: 0.94. F-statistic: 636.3 on 4 and 161 DF, p-value: <2.2 × 10\textsuperscript{−16}.

Table 2. The summary of final MLR model coefficients at the YRK site from 2012 to 2016.

| Predictors   | Coefficients | SE  | t value | Pr > |t|   |
|--------------|--------------|-----|---------|------|---|---|
| Intercept (β\textsubscript{0}) | 0.028 | 0.027 | 1.03 | 0.31 |
| SO\textsubscript{4}\textsuperscript{2−} (β\textsubscript{1}) | 0.38 | 0.013 | 29.58 | <2 × 10\textsuperscript{−16} |
| NO\textsubscript{3}− (β\textsubscript{2}) | 0.067 | 0.032 | 2.12 | 0.036 |
| (NO\textsubscript{3}−-0.41)\textsuperscript{2} (β\textsubscript{3}) | 0.155 | 0.028 | 5.62 | 1.23 × 10\textsuperscript{−7} |
| Na\textsuperscript{+} (β\textsubscript{4}) | -0.54 | 0.132 | -4.1 | 7.48 × 10\textsuperscript{−5} |
| K\textsuperscript{+} (β\textsubscript{5}) | -0.0025 | 0.00149 | -1.67 | 0.097 |
| (Na\textsuperscript{+}-0.04)\textsuperscript{2} (β\textsubscript{6}) | 0.71 | 0.29 | 2.43 | 0.0166 |
| HNO\textsubscript{2} (β\textsubscript{7}) | -0.045 | 0.027 | -1.66 | 0.0995 |
| K\textsuperscript{+} (β\textsubscript{8}) | 0.87 | 0.38 | 2.31 | 0.0226 |
| SO\textsubscript{4}\textsuperscript{2−}:T (β\textsubscript{9}) | -0.0029 | 0.000684 | -4.24 | 4.39 × 10\textsuperscript{−5} |
| T:HNO\textsubscript{2} (β\textsubscript{10}) | 0.0045 | 0.0014 | 3.25 | 0.00149 |

Residual standard error: 0.08419 on 122 degrees of freedom. Multiple R-squared: 0.97. Adjusted R-squared: 0.97. F-statistic: 443.7 on 10 and 122 DF, p-value: <2.2 × 10\textsuperscript{−16}.

In the linear regression analysis, the interaction terms may cause serious multicollinearity problem, which will provide redundant information [38]; thus, the model diagnostics may exclude the interaction terms when the variance inflation factor (VIF) for interaction term is greater than 10. The selection of predictor variables varied at different sites in different periods.

Both SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}− were included in the regression models at the six sites in two periods. The iPM\textsubscript{2.5} mainly consisted of NH\textsubscript{4}+ salts, most of the NH\textsubscript{4}+ cations were associated with SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}− anions. The coefficients for both SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}− were positive, which indicated the positive correlation between cation-NH\textsubscript{4}+ and anions-SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}−. The positive regression coefficients (0.29–0.38) for SO\textsubscript{4}\textsuperscript{2−} were greater than the coefficients for all the other predictor variables. The dominance of particle-phase SO\textsubscript{4}\textsuperscript{2−} salts led to the significant relationship between NH\textsubscript{4}+ and SO\textsubscript{4}\textsuperscript{2−}; the changes in SO\textsubscript{4}\textsuperscript{2−} can cause corresponding changes in NH\textsubscript{4}+. Some centered quadratic terms were included in the model as well, the quadratic terms indicated that the direction of the relationship...
between NH$_4^+$ and SO$_4^{2-}$, NO$_3^-$ may change as SO$_4^{2-}$ and NO$_3^-$ concentrations changed. The complex relationship between NH$_4^+$ and SO$_4^{2-}$, NO$_3^-$ may be caused by reactions between NH$_3$ and H$_2$SO$_4$, HNO$_3$, the dynamic changes in particle-phase SO$_4^{2-}$; NO$_3^-$ may also change the dynamic reactions of NH$_3$ and various acidic gases (e.g., the free NH$_3$ from the reduction in SO$_4^{2-}$ may react with HNO$_3$ to form NH$_4$NO$_3$).

As for the gas-phase NH$_3$, the BIC step-wise model selection method did not include NH$_3$ in the MLR model at the JST site in 2010–2011, at the YRK site in 2008–2011 and 2012–2016, and at the BHM site in 2012–2016. The exclusion of NH$_3$ indicated that NH$_3$ may not limit the formation of NH$_4^+$ salts at these three sites. Specifically, NH$_3$ was excluded from the regression model from 2008 to 2016 at the YRK site. The NH$_3$ emissions from AFOs contributed to the abundant NH$_3$ at the YRK site; thus, the NH$_3$-rich conditions dominated. While for the CTR site (Table S16) in 2012–2016, OAK site (Table S17) in 2010, and OLF site (Table S18) in 2013–2016, the NH$_3$ was included in the regression model and the coefficients were positive. Especially, at the OAK site, coefficient of NH$_3$ was 0.16, which was higher than the other sites. The positive coefficients suggested that the higher NH$_3$ led to increased formation of NH$_4^+$ salts at these sites.

As for the gas-phase HNO$_3$, it was included in the regression model at the YRK site in 2012–2016, and at the BHM site in 2011, and the regression coefficients for HNO$_3$ in these two models were negative. The semi-volatile characteristic of NH$_4$NO$_3$ may explain the negative coefficient. Under ambient conditions, such as high T and low RH, the NH$_4$NO$_3$ may decompose into gas-phase NH$_3$ and HNO$_3$, the increase in gas-phase HNO$_3$ leads to a decrease in NH$_4^+$. The interaction term—T:HNO$_3$ at the YRK site, may indicate the dependence of the formation of NH$_4$NO$_3$ on ambient conditions.

As for ambient meteorological conditions—T and RH, only T was included in the regression models at the JST site in 2012–2016 (Table S13), at the YRK site in 2012–2016 (Table 2), at the BHM site in 2011 (Table S14) and 2012–2016 (Table S15), and at the OAK site in 2010 (Table S17). The RH was excluded from all the regression models. The coefficients for T were all negative, which indicated that the increase in T led to the decrease in NH$_4^+$, but the coefficients for T were smaller compared to the coefficients for the other predictor variables. The smaller coefficient for T may indicate the relatively weak impact of T on the NH$_4^+$.

As for the NVCs and Cl$,^-$, although the concentrations were lower compared with the other gas- and particle-phase species, one of Mg$^{2+}$, Na$^+$, or Cl$^-$ was included in the regression models, this indicated that the NVCs and Cl$^-$ were important factors affecting the NH$_4^+$ concentration. The coefficients for Mg$^{2+}$ may exhibit some large values (e.g., −6.69 and −3.83), which indicated that there is a strong negative correlation between Mg$^{2+}$ and NH$_4^+$. However, ISORROPIA II model simulation implicated that the low concentration of Mg$^{2+}$ may not lead to a significant change in NH$_4^+$ concentration, which is against MLR model results.

4. Conclusions

In this research, the effects of changes in precursor gases on the formation of iPM$_{2.5}$ as well as the partitioning of NH$_3$-NH$_4^+$ were investigated using ISORROPIA II modeling approach with inputs of field measurements of gas-phase and particle-phase pollutants and meteorological data in the SEARCH network. The results indicated that the reduction in total H$_2$SO$_4$ was more effective to decrease the formation of iPM$_{2.5}$, especially under NH$_3$-rich conditions. In addition, the reduction in total H$_2$SO$_4$ may change the partitioning of NH$_3$-NH$_4^+$ towards gas-phase. Moreover, the reduction in total H$_2$SO$_4$ may lead to an increase in NO$_3^-$ when NH$_3$ was not in excess to neutralize the acidic gases. Thus, the future reduction in iPM$_{2.5}$ may necessitate the coordinated reduction in both H$_2$SO$_4$ and HNO$_3$ in the southeastern U.S. It was also discovered that the response of iPM$_{2.5}$ to the change in total H$_2$SO$_4$ was more sensitive in summer than winter. The dominance of SO$_4^{2-}$ salts in iPM$_{2.5}$ and high T in summer did not facilitate the formation of NH$_4$NO$_3$, the decrease in SO$_4^{2-}$ salts caused by the reduction in total H$_2$SO$_4$ will not be offset by the
Atmosphere 2021, 12, 1681

increase in the NO$_3^-$ salts. The significant NH$_3$ emissions from AFOs in the agricultural rural area had great impact on the partitioning of NH$_3$-NH$_4^+$, and the NH$_3$ emissions from the AFOs led to the elevated NH$_3$ concentration, which was in excess to neutralize acidic gases. The formation of NH$_4$NO$_3$ was not affected by the reduction in total H$_2$SO$_4$ in an agricultural rural area. The BIC stepwise model selection determined the MLR model to predict NH$_4^+$ at six sites, there was a strong positive correlation between cation-NH$_4^+$ and anions-SO$_4^{2-}$ and NO$_3^-$. The NH$_3$ was excluded from the regression model at the YRK site due to the abundant NH$_3$ emitted from AFOs, and the NVCs and Cl$^-$ were the significant impact factors affecting NH$_4^+$ concentrations.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/atmos12121681/s1, Table S1: Field measurements at the eight sites, Table S2: The statistics of different precursor gases of iPM$_{2.5}$ by season at the YRK site in 2008–2011, Table S3: The statistics of different precursor gases of iPM$_{2.5}$ by season at the YRK site in 2012–2016, Table S4: The statistics of different precursor gases of iPM$_{2.5}$ by season at the JST site in 2010–2011, Table S5: The statistics of different precursor gases of iPM$_{2.5}$ by season at the JST site in 2012–2016, Table S6: The statistics of different precursor gases of iPM$_{2.5}$ by season at the CTR site in 2012–2016, Table S7: The statistics of different precursor gases of iPM$_{2.5}$ by season at the BHM site in 2012-2016, Table S8: The statistics of different precursor gases of iPM$_{2.5}$ by season at the BHM site in 2013-2016, Table S9: The statistics of different precursor gases of iPM$_{2.5}$ by season at the OLFS site in 2011, Table S10: The statistics of different precursor gases of iPM$_{2.5}$ by season at the OLF site in 2013-2016, Table S11: The summary of aerosol pH at five sites in 2012 to 2016, Table S12: The summary of final MLR model coefficients at the JST site from 2010 to 2011, Table S13: The summary of final MLR model coefficients at the JST site from 2012 to 2016, Table S14: The summary of final MLR model coefficients at the BHM site in 2011, Table S15: The summary of final MLR model coefficients at the BHM site from 2012 to 2016, Table S16: The summary of final MLR model coefficients at the BHM site from 2012 to 2016, Table S17: The summary of final MLR model coefficients at the OAF site from 2013 to 2016, Figure S1: Responses of iPM$_{2.5}$, NH$_4^+$, and NH$_3$/NH$_4$ to the changes of TNH3 and THNO$_3$ at the JST site in summer and winter of 2012–2016, Figure S2: Responses of iPM$_{2.5}$, NH$_4^+$, and NH$_3$/NH$_4$ to the changes of TNH3 and THNO$_3$ at the CTR site in summer and winter of 2012–2016, Figure S3: Responses of iPM$_{2.5}$, NH$_4^+$, and NH$_3$/NH$_4$ to the changes of TNH3 and THNO$_3$ at the OLF site in summer and winter of 2013–2016, Figure S4: Responses of iPM$_{2.5}$, NH$_4^+$, and NH$_3$/NH$_4$ to the changes of TNH3 and THNO$_3$ at the BHM site in summer and winter of 2012–2016, Figure S5: Responses of iPM$_{2.5}$, NH$_4^+$, and NH$_3$/NH$_4$ to the changes of TNH3 and THNO$_3$ at the OLF site in summer and winter of 2013–2016, Figure S6: Responses of iPM$_{2.5}$, NH$_4^+$, and NH$_3$/NH$_4$ to the changes of TNH3 and TH$_2$SO$_4$ at the JST site in summer and winter of 2012–2016, Figure S7: Responses of iPM$_{2.5}$, NH$_4^+$, and NH$_3$/NH$_4$ to the changes of TNH3 and TH$_2$SO$_4$ at the CTR site in summer and winter of 2012–2016, Figure S8: Responses of iPM$_{2.5}$, NH$_4^+$, and NH$_3$/NH$_4$ to the changes of TNH3 and TH$_2$SO$_4$ at the BHM site in summer and winter of 2012–2016, Figure S9: Responses of iPM$_{2.5}$, NH$_4^+$, and NH$_3$/NH$_4$ to the changes of TNH3 and TH$_2$SO$_4$ at the BHM site in summer and winter of 2012–2016, Figure S10: Responses of iPM$_{2.5}$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, NH$_3$/NH$_4$, and GR to the reductions in TNH3 at the BHM site in 2012–2016, Figure S11: Responses of iPM$_{2.5}$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, NH$_3$/NH$_4$, and GR to the reductions in TNH3 at the BHM site in 2012–2016, Figure S12: Responses of iPM$_{2.5}$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, NH$_3$/NH$_4$, and GR to the reductions in TNH3 at the BHM site in 2012–2016, Figure S13: Responses of iPM$_{2.5}$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, NH$_3$/NH$_4$, and GR to the reductions in TNH3 at the CTR site in 2012–2016, Figure S14: Responses of iPM$_{2.5}$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, NH$_3$/NH$_4$, and GR to the reductions in TNH3 at the CTR site in 2012–2016, Figure S15: Responses of iPM$_{2.5}$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, NH$_3$/NH$_4$, and GR to the reductions in TNH3 at the JST site in 2012–2016, Figure S16: Responses of iPM$_{2.5}$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, NH$_3$/NH$_4$, and GR to the reductions in TNH3 at the JST site in 2012–2016, Figure S17: Responses of iPM$_{2.5}$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, NH$_3$/NH$_4$, and GR to the reductions in TNH3 at the JST site in 2012–2016, Figure S18: Responses of iPM$_{2.5}$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, NH$_3$/NH$_4$, and GR to the reductions in TNH3 at the JST site in 2012–2016, Figure S19: Responses of iPM$_{2.5}$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, NH$_3$/NH$_4$, and GR to the reductions in TNH3 at the JST site in 2012–2016, Figure S20: Responses of iPM$_{2.5}$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, NH$_3$/NH$_4$, and GR to the reductions in TNH3 at the JST site in 2012–2016.
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