Insights to the formation of secondary inorganic $PM_{2.5}$: Current knowledge and future needs

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Abstract: As a criteria pollutant, fine particulate matter (fine PM, i.e. $PM_{2.5}$) adversely affects public health and environment, contributes to visibility degradation and regional haze. Atmospheric fine PM includes primary and secondary $PM_{2.5}$. While the primary $PM_{2.5}$ is from direct emissions, the secondary $PM_{2.5}$ is formed in the atmosphere through photochemical reaction, condensation and other atmospheric processes. Although it is well known that ammonia (NH_3) may react with acidic gas species to form secondary inorganic $PM_{2.5}$ ($iPM_{2.5}$) as ammonium salts, limited research has been done to quantify the impacts of NH_3 emissions of animal feeding operations (AFOs) on the dynamics of such chemical reactions and gas-particle phases partitioning. This paper is to provide comprehensive review of existing research on AFO PM chemical speciation and on the formation of secondary $iPM_{2.5}$ as impacted by AFO air emissions. Research gaps and future studies in characterizing AFO PM and assessing impacts of AFO air emissions on atmospheric PM are discussed.

Keywords: environmental pollution, particulate matter, inorganic $PM_{2.5}$, animal feeding operations, ammonia, formation of secondary $PM_{2.5}$

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1 Introduction

Fine particulate matter (PM) refers to liquid and/or solid particles that are suspended in the air with aerodynamic equivalent disarmer (AED) smaller than or equal to 2.5 μm (i.e. $PM_{2.5}$). Studies indicate that $PM_{2.5}$ may cause serious environmental and health problems[1-7]. Exposure to $PM_{2.5}$ has been linked to a variety of lung and heart diseases that may lead to cardiovascular and respiratory mortality and premature death[1-6]. It was estimated that a 10 μg/m^3 increase in 2-day averaged $PM_{2.5}$ mass concentration may cause a 0.74% increase in non-accidental deaths[6]. In addition to the adverse health effects, $PM_{2.5}$ may also cause ambient air quality reduction and visibility impairment[8-9]. In atmosphere, particles with sizes in range of the light wavelength are more efficient to scatter and absorb the lights, causing atmospheric visibility degradation. Therefore, fine PM is a major contributor to regional haze and smog problems[8-10].

Based upon its physical and chemical properties as well as the formation mechanism, atmospheric PM may be classified as (1) fine *vs.* coarse PM; (2) organic *vs.* inorganic PM; (3) primary *vs.* secondary PM. The primary PM is emitted directly to the atmosphere whereas the secondary PM is formed in the atmosphere through photochemical reaction, condensation and other atmospheric processes[10-11]. Both primary and secondary PM may be organic and/or inorganic in nature. While most primary PM is coarse PM (AED>2.5 μm), secondary PM is fine in size (AED≤2.5 μm, i.e. $PM_{2.5}$).

On average, inorganic $PM_{2.5}$ ($iPM_{2.5}$) makes up about half of total atmospheric $PM_{2.5}$ in the United States[12-17],

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and 20%-30% of total $PM_{2.5}$ mass in urban environments in China[18-21]. Very litter $iPM_{2.5}$ is primary[22] and most of atmospheric $iPM_{2.5}$ is secondary, formed through acid/base neutralization processes, in which base NH_3 reacts with acidic gases, e.g., SO_2 and/or nitrogen oxides (NO_x) to form aerosols in $(NH_4)_2SO_4$ or NH_4HSO_4 or NH_4NO_3. In these ammonium salts formation processes, partitioning of gas-particle phases (NH_3-NH_4^+) is highly dependent on the temperature, relative humidity (RH), and availabilities of the precursor gases (i.e. NH_3, SO_x, NO_x)[11,22]. Therefore, control of atmospheric $PM_{2.5}$ requires systematical understanding of $iPM_{2.5}$ formation and the role of its precursor gas emissions.

As the most abundant base gas in atmosphere, NH_3 plays a very critical role in the formation of secondary $iPM_{2.5}$. Although it remains to be further validated, Pinder and Adams[22] suggested that control of NH_3 emissions may be used as a cost-effective supplementary strategy to reduce atmospheric $iPM_{2.5}$. Sources of atmospheric NH_3 include animal feeding operations (AFOs) (e.g. livestock, etc.), fertilizer application, fuel combustion, industrial processes, and others. As illustrated in Figure 1, AFOs is the largest source, responsible for approximate 80% of total NH_3 emissions in the U.S. Impact of AFO NH_3 emissions on the formation of atmospheric $iPM_{2.5}$ cannot be overlooked.

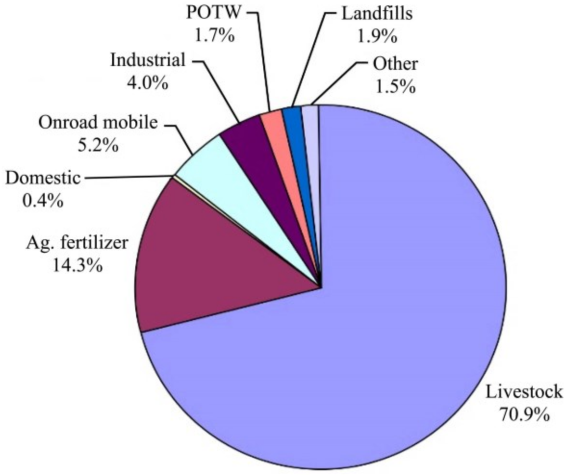


Figure 1 Contributions of various NH_3 emission sources to the U.S. National Emission Inventory (NEI)[23] (POTW: publicly owned treatment works)

Animal feeding operation facilities may emit large amount of gaseous pollutants (NH_3, H_2S, VOCs, and odor) and PM (TSP, PM_{10}, and $PM_{2.5}$)[24-26], they have been considered significant sources of atmospheric air pollutants[27]. In particular, PM emitted from AFO facilities may be classified as primary and secondary PM based upon its formation mechanism. It has been reported that PM in AFO houses is mainly primary, coarse and organic in nature[28-34]. In addition to direct emissions of PM, gaseous pollutants emitted from AFO facilities may be important precursors of secondary PM (organic and inorganic), which may represent a significant fraction of $PM_{2.5}$[31,32, 35-38].

Although the contributions of AFO air emissions to atmospheric $PM_{2.5}$ have not been experimentally quantified and impact of AFO precursor gas emissions on the formation of secondary $PM_{2.5}$ is not well understood, AFOs have been perceived to be important contributors to atmospheric $PM_{2.5}$[7]. This review paper aims to provide an overview of existing research on $PM_{2.5}$ chemical speciation and the formation of secondary $iPM_{2.5}$ as impacted by the NH_3 emissions from AFOs, the most important contributor to the atmospheric NH_3. Research gaps and future studies in characterizing AFO PM and assessing impacts of AFO air emissions on atmospheric PM are discussed.

2 $PM_{2.5}$ chemical compositions

Fundamental understanding of $PM_{2.5}$ source apportionment and formation of secondary $PM_{2.5}$ requires knowledge of $PM_{2.5}$ chemical compositions. In atmosphere, different areas and regions have different source types, climatology and geography; therefore, different concentrations and chemical/physical characteristics of ambient $PM_{2.5}$. Consequently, wide spatial and temporal variations in $PM_{2.5}$ concentrations and characteristics exist. In chemical characterization, $PM_{2.5}$ mainly consists of inorganic constituents (e.g. NH_4^+, SO_4^{2-}, NO_3^-, Na^+, K^+, Cl^-, etc.), carbon species (i.e. organic carbon (OC), element carbon (EC)), and trace elements (geological materials e.g., Al, Si, Ca, Ti, Fe, etc.). The ionic species of $PM_{2.5}$ link to various chemical reactions that lead to formation of secondary inorganic $PM_{2.5}$[39].

2.1 Ambient $PM_{2.5}$ chemical speciation monitoring networks in the U.S.

Chemical speciation provides characterization of ions, carbon species, and trace elements of PM. The approaches used in $PM_{2.5}$ chemical speciation include both field sampling and laboratory analysis. The full set of ambient $PM_{2.5}$ chemical speciation analysis includes examination of ions (NH_4^+, SO_4^{2-}, NO_3^-, Na^+, K^+, Cl^-), organic and elemental carbons (OC/EC), and trace elements (Na-Pb)[40,41]. In the U.S., three major chemical speciation networks provide complementary data on $PM_{2.5}$ chemical compositions to support PM source identification, implementation plan development, and health effects research. These three networks include the Interagency Monitoring of Protected Visual Environments (IMPROVE), the Clean Air Status and Trends Network (CASTNET), and the National Chemical Speciation Network (CSN). The IMPROVE network was established in 1988 to monitor mass concentrations and chemical compositions of $PM_{2.5}$ in the National Parks and other visibility protected rural areas for assessment of visibility degradation[42]. Data from IMPROVE have been used to calculate Haze Index in support of the USEPA's Regional Haze Rule[8]. The CASTNET was established in 1991 to monitor concentrations and depositions of sulfur and nitrogen species (gas and particulate phases) as well as ozone concentrations[43]. Data from the CAETNET have been used to assess long term trends in atmospheric sulfur and nitrogen pollutant concentrations and their depositions and ecological effects in response to changes in air emissions. The CSN began in 1999 to monitor mass and chemical compositions of $PM_{2.5}$ at representative sites in urban areas in the U.S.[44]. $PM_{2.5}$ analytes of the CSN are similar to those of the IMPROVE, consisting of an array of ions, carbon species, and trace elements. Data from 54 National Air Monitoring Stations (NAMS) of the CSN have been used for assessment of trends and data from 250 of State and Local Air Monitoring Stations (SLAMS) of the CSN provide information for developing effective State Implementation Plans (SIPs). Due to the different data use objectives, the target species of interest and analytical methods are different at these three speciation programs (networks). Table 1 provides a brief summary of the measurement parameters by the three networks[45].

Although these monitoring networks offer high quality PM chemical speciation datasets for air quality and public health studies, there is a lack of representation of agricultural operation areas to assess ambient $iPM_{2.5}$ as impacted by AFO NH_3 emissions, which account for majority of the nation's NH_3 emissions.

Table 1 Summary of the parameters measured by the three chemical speciation networks

	IMPROVE	CASTNET[a]	CSN
Sampling inlet heads	PM_{10} head + SCC[b] $PM_{2.5}$ head	Open faced inlet	PM_{10} head + SCC[b] $PM_{2.5}$ head
Sampling flow rate	22.8 LPM	1.5 LPM	6.7 LPM
Teflon Filter	$PM_{2.5}$ mass, trace elements[c]	Mass of non-size- selective PM, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+}, Cl^-	$PM_{2.5}$ mass, trace elements[c]
Nylon Filter	$PM_{2.5}$ ions: SO_4^{2-}, NO_3^-, Na^+, K^+, Cl^-, NH_4^+ (calculated)	HNO_3, SO_2	$PM_{2.5}$ ions: SO_4^{2-}, NO_3^-, Na^+, K^+, Cl^-, NH_4^+
Quartz Filter	$PM_{2.5}$ OC/EC[d]	--	$PM_{2.5}$ OC/EC[d]

Note: [a] CASTNET also includes measurements of gas pollutants (e.g. NO/NO_y, SO_2, CO, O_3), and meteorological parameters[46].

[b] SCC: sharp cut cyclone.

[c] Up to 48 elements (sodium through lead) are determined by Energy dispersive x-ray fluorescence (XRF).

[d] OC/EC operationally defined by a thermal-optical analysis method.

2.2 Chemical compositions of AFO PM

Although knowledge about PM source profile and chemical compositions is essential for source identification and development of source-specific PM mitigation techniques, study of AFO PM source apportionment and chemical speciation is very much limited. Aarnink et al.[47] reported that PM in livestock buildings is mainly composed of primary PM with organic matter in nature. Chemical compositions of PM in animal houses varied with animal species, housing type, waste management systems (e.g. dry or wet systems, with or without bedding materials, house cleaning methods, etc.). According to Aarnink et al.[47], every kilogram inhalable PM in swine houses contained 920 g of dry matter, 149.5 g ash, 67 g N, 14.7 g P, 27.8 g K, 7.8 g Cl and 8.2 g Na, respectively; every kilogram inhalable PM in broiler houses contained 911 g of dry matter, 97.4 g ash, 169 g N, 6.4 g P, 40.3 g K, 4.2 g Cl and 3.2 g Na, respectively (illustrated in Figure 2). Cambra-Lopez et al.[29,30,48] used particle morphological and chemical speciation data to identify and quantify the contributions of various sources to primary $PM_{2.5}$ and PM_{coarse} (i.e., $PM_{10-2.5}$) in poultry and swine production houses. They discovered that feather and manure are two major sources of PM in poultry houses, skin and manure are major sources of PM in swine houses (Table 2). Contribution from feed to both fine and coarse PM was insignificant.

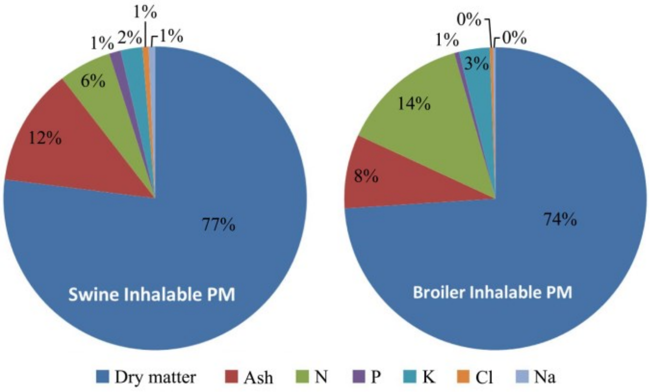


Figure 2 Compositions of inhalable PM in swine and broiler production houses[47]

Table 2 Relative percentage contributions (by mass) of source type to $PM_{2.5}$ and $PM_{10-2.5}$ in 21 animal production houses

House type	Source type[c]	$PM_{2.5}$	$PM_{10-2.5}$
Poultry[a]	feather	17%-68%	4%-49%
	manure	6%-77%	31%-96%
Swine[b]	skin	0-79%	0-71%
	manure	14%-95%	23%-92%

Note: [a] Poultry houses: 3 houses of broiler on bedding, 3 house of laying hens on floor, 3 houses of laying hens in aviary and 3 houses of turkey on bedding.
[b] Swine houses: 3 houses of piglets on slatted floor, 3 houses of growing-finishing pigs on partially slatted floor, 3 houses of dry and pregnant sows on slatted floor.
[c] Elements of N, Na, Mg, Al, Si, P, S, Cl, K and Ca presented in all sources and their relative concentrations were different among sources.

In a study of trace elements and soluble ions in $PM_{2.5}$ and PM_{10} emitted from 12 swine houses and 6 poultry houses in Midwest of U.S., Yang et al.[49] reported that 19 trace elements and 4 inorganic ions (Cl^-, NO_3^-, SO_4^{2-} and NH_4^+) were identified in PM samples taken from the animal production houses. Concentration of NH_4^+ in PM samples was less than 1% wt indicating insignificant formation of NH_4^+ containing secondary $PM_{2.5}$. In addition, significant differences in inorganic compositions were observed between PM_{10} and $PM_{2.5}$ collected from swine and turkey houses; seasonal variation of inorganic composition in PM_{10} was insignificant, but the seasonal variation of $PM_{2.5}$ inorganic composition was significant[49].

Elemental concentrations of PM_{10} and $PM_{2.5}$ were first investigated at a commercial dairy farm in Californian of U.S.[50] It was discovered that Si, Al, Mg, Fe, Ca, K, S and Cl accounted for 95.6% and 97.9% of the total elemental concentrations in $PM_{2.5}$ and PM_{10}, respectively. Significant differences in percentages of each element under dry and wet conditions were also observed. Different emission source types (e.g. drylot corrals, upwind freeway, etc.) and strength under dry and wet conditions were responsible for the variations of elemental concentrations and abundances of elemental compositions.

Chemical compositions of PM in animal houses (at source) and in the vicinity of the houses (in ambient) have seldom been studied simultaneously. In an investigation of $PM_{2.5}$ chemical speciation in an egg production house and at five ambient locations surrounding the production houses, Li et al.[32,36-38,51,52] reported that in the production house, NH_4^+, SO_4^{2-} and NO_3^- accounted for 10% of the $PM_{2.5}$ mass, but at ambient locations, NH_4^+, SO_4^{2-} and NO_3^- accounted for 36%-41% of the $PM_{2.5}$ mass. In house $PM_{2.5}$ had much higher concentrations of Ca, Cl, K, Mg, Na, P, S, Si and Zn than those of ambient $PM_{2.5}$ samples. All sampling locations (in-house and ambient stations) had very low concentrations of Ag, Al, As, Ba, Cd, Ce, Co, Cr, Cs, Cu, In, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, V and Zr. Different elemental composition distribution patterns were observed in $PM_{2.5}$ samples taken at the in-house station and the ambient stations (Figure 3). Majority components in $PM_{2.5}$ at this AFO site were organic. On average, OC accounted for above 50% of $PM_{2.5}$ mass at in-house and ambient stations; NH_4^+, SO_4^{2-} and NO_3^- accounted for about 40% of the total $PM_{2.5}$ mass in ambient locations and for only 12% of the total $PM_{2.5}$ mass in house.

3 Formation of secondary inorganic $PM_{2.5}$

3.1 Ammonia as a precursor to secondary inorganic $PM_{2.5}$

Major inorganic constituents of $iPM_{2.5}$ are NH_4NO_3, $(NH_4)_2SO_4$ and NH_4Cl[12-22]. These constitutes were formed through chemical reactions of NH_3 with acidic gases (e.g. SO_2 and NO_x)[11,53-55]. Figure 4a shows a depiction of the $iPM_{2.5}$ formation potential in response to the major precursor gases, and Figure 4b illustrates a simplified version of the chemical reaction processes to the formation of $iPM_{2.5}$.

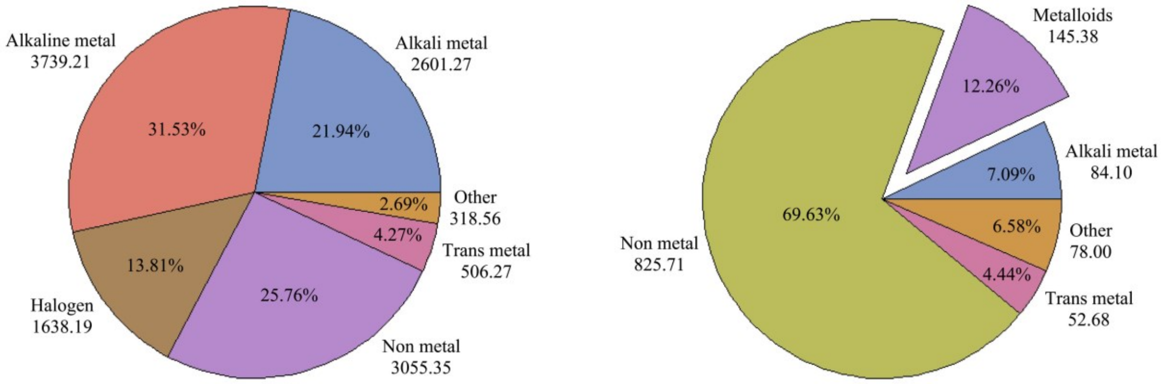


Figure 3 Elemental compositions of $PM_{2.5}$ in a production house (left) and at an ambient location in the vicinity of the egg production farm (right)[38]

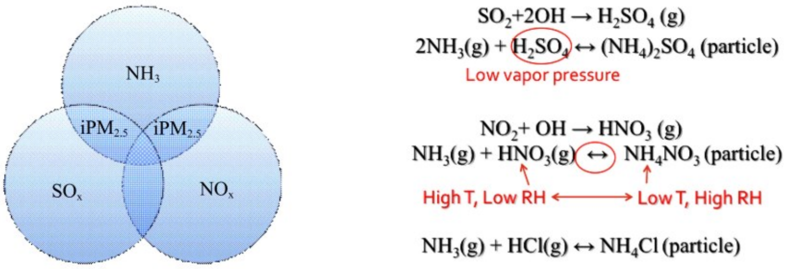


Figure 4 Thermodynamic equilibrium processes of the formation of the secondary $iPM_{2.5}$[11,55]

Due to the low vapor pressure of H_2SO_4, atmospheric NH_3 usually first reacts with H_2SO_4 to form $(NH_4)_2SO_4$. If more NH_3 is available, it then reacts with HNO_3 to form (NH_4NO_3)**[11]**. These chemical reactions are the most important equilibrium reactions for gas-particle phase partitioning that highly depend on NH_3 and acid concentrations, RH, and temperature[55,56]. The reverse reactions occur, especially for HNO_3 under high temperature and low RH such that the equilibrium is shifted to gas phase NH_3 and HNO_3; vice versa, when the temperature is low and RH is high, the equilibrium is shifted to particle phase of NH_4NO_3. Consequently, higher NH_4NO_3 fraction in winter aerosols is expected[13,57,58]. Contributions of inorganic constituents to total $PM_{2.5}$ mass demonstrated strong seasonally and geographically variations in response to changes of atmospheric meteorological and chemical conditions.

In addition to the formation of $(NH_4)_2SO_4$ and NH_4NO_3, NH_3 may also react with HCl to form NH_4Cl particle. Contribution of Cl^- to total inorganic $PM_{2.5}$ is usually minor[13].

3.2 Ammonia emission inventory and AFO Ammonia emissions

Due to its important impacts on the formation of secondary $iPM_{2.5}$ and on the ecosystems in general, AFO NH_3 emissions have been extensively studied[59-72]. Although considerable efforts have been made in developing NH_3 emission inventory that links atmospheric NH_3 to various emission sources[27,73], existing NH_3 emission inventories are considered highly uncertain in assessing significances of various source types. In the U.S., EPA's National Emission Inventory (NEI)[74] and CMU (Carnegie Mellon University) NH_3 emission inventory[75] are two major NH_3 emission inventory models that have been widely used in various air quality modeling and formation of secondary $iPM_{2.5}$ studies. According to EPA's NEI, emissions from AFOs account for approximate 80% of nation's NH_3 emissions (Figure 1). Significance of AFO NH_3 emissions cannot be overlooked in study of formation of $iPM_{2.5}$ on local and/or regional scales.

Ammonia has a short lifetime in the atmosphere[55,76,77]. Once emitted, NH_3 may be removed from atmosphere by dry and or wet depositions[78-81] Studies of transport of NH_3 and its reaction product NH_4^+ particulate suggest that NH_3 has a short rang dispersion due to its fast dry deposition, on the other hand, particulate NH_4^+ may transport in a long a range[56,79-88]. Asman and Sutton[56] reported that 10% of NH_3 emitted from 1 m height point source was dry deposited within

100 m from the source and 20% within 1 000 m from the source; at a given downwind distance, among the total deposition (NH_3 plus particulate NH_4^+): 44% NH_3 dry deposition, 6% NH_3 wet deposition, 14% NH_4^+ dry deposition and 36% NH_4^+ wet deposition. Ammonia dry deposition showed a high spatial variability due to spatial variations in emission sources, land uses and management practices[56,82-88]. Fast removal of NH_3 through dry and wet depositions may limit contribution of agricultural NH_3 emissions to the formation of secondary $iPM_{2.5}$ in the areas far away from agricultural intensive areas where significant SO_2 or NO_x may present in the air (e.g. urban environment).

3.3 Thermodynamic equilibrium modeling

As shown in Figure 4, a thermodynamic equilibrium exists between precursor gases and secondary NH_4^+ particulate of $iPM_{2.5}$. When NH_3 reacts with acidic gases, it is converted from gaseous phase to particulate phase that is called gas-particle partitioning. Two steps may involve in the gas-particle phase partitioning process. In the first step, NO_x and SO_2 can be transformed into HNO_3 and H_2SO_4 through oxidation processes. HNO_3 can be produced by heterogeneous hydrolysis of N_2O_5; hydroxyl radical (OH) can also oxidize NO_x into HNO_3[89]. SO_2 may be oxidized by oxidants like ozone and hydroxyl radical (OH) into H_2SO_4 gas or H_2SO_4 ions. In the second step, the three components, i.e., HNO_3, H_2SO_4, NH_3 may partition between gas and particle phases depending on temperature and relative humidity as well as molar concentrations of total sulfate, total nitrate and total ammonia. Nearly all of the H_2SO_4 gas can be neutralized and partition to the particle phase due to its low vapor pressure[90].

In gas-particle partitioning processes, NH_3 preferentially reacts with H_2SO_4 to form $(NH_4)_2SO_4$ and NH_4HSO_4, then remaining NH_3 can react with HNO_3 to form NH_4NO_3[89,91]. Sulfate salts and nitrate salts have different levels of thermal stability characteristics. While sulfate salts are thermally stable[92], NH_4NO_3 is not thermally stable enough such that it may decompose to HNO_3 and NH_3 when environmental conditions are under high temperature and low relative humidity that do not favor the particle phase partitioning. Potentials for the formation of sulfate salts and nitrate salts aerosols can be characterized using gas ratio (GR)[93]:

$$\mathrm{GR}=\frac{[\mathrm{TA}]-2[\mathrm{TS}]}{[\mathrm{TN}]}$$

where, [TA] is total amount of NH_3 and NH_4^+; [TS] is the total amount of SO_4^{2-}, HSO_4^- and H_2SO_4; [TN] is the total amount of NO_3^- and HNO_3.

In NH_3 poor regime, GR<0, this is insufficient NH_3 to neutralize all SO_4^{2-}; in moderate regime, 0<GR<1, there is sufficient NH_3 to neutralize SO_4^{2-} but not NO_3^- in NH-rich regime, GR>1, there is sufficient NH_3 to neutralize both SO_4^{2-} and NO_3^-. According to Wu et al.[94] in winter condition, NH_3 may not be fully neutralized by SO_4^{2-}, a more generic term $NH_3 + NO_3^-$ should be used to account for neutralization by NO_3^- such that an adjusted GR (AdjGR) should be used to examine $iPM_{2.5}$ sensitivity to NH_3 emission/ concentration.

$$\mathrm{AdjGR}=\frac{[\mathrm{NH_3}]+[\mathrm{NO_3^-}]}{[\mathrm{TN}]}$$

In addition to GR examination, the molar ratios of $(NH_4^+)_s/SO_4^{2-}$ (MR) were used to estimate neutralization of NH_3 associated with SO_4^{2-}[13,36,37,95].

$$\mathrm{MR}=\frac{[\mathrm{NH_4^+}]-[\mathrm{NO_3^-}]-[\mathrm{Cl^-}]}{[\mathrm{SO_4^{2-}}]}$$

where, $[NH_4^+]$, $[NO_3^-]$, $[Cl^-]$ and $[SO_4^{2-}]$ are measured molar concentrations of NH_4^+, NO_3, Cl^- and SO_4^{2-}, respectively. Formation of various $iPM_{2.5}$ constitutes would follow the pattern below[93]:

1) When MR<0.5, aerosol phase consist of H_2SO_4 and NH_4HSO_4;

2) When 0.5<MR<1.25, aerosol phase is dominant by NH_4HSO_4;

3) When MR=1.25, aerosol phase is dominant by $(NH_4)_3H(SO_4)_2$;

4) When MR=1.5, aerosol phase consists of $(NH_4)_3H(SO_4)_2$;

5) When MR>1.5, formation of $(NH_4)_2SO_4$;

6) When MR=2, complete neutralization of sulfate and predominance of $(NH_4)_2SO_4$.

Given the elevated concentration of NH_3 around AFO production facilities, the MR in AFO environments is expected to be 2. However, the observation by Li et al.[36,37] indicated that wind speed may affect transport of

NH_3 within the time scale of establishment of local gas-particle phase equilibrium such that low $(NH_4^+)_s/SO_4^{2-}$ molar ratios (<2) may occur indicating gas phase NH_3 was not in equilibrium with sulfate to form $(NH_4)_2SO_4$. Impact of wind speed, direction needs to be further investigated.

In study of gas-particle phase partitioning, a thermodynamic equilibrium model ISORROPIA-II was commonly used to examine response of $iPM_{2.5}$ to the change of precursor gas as well as to the changes of meteorological conditions[13,36,37,89,96]. The model inputs included simultaneously measured concentrations of NH_3, NO_x, SO_2, SO_4^{2-}, NO_3^-, Cl^-, $Ca^{+,}$ K^+, RH, T, and the model outputs included total aerosol NH_4^+, total aerosol NO_3^-, total aerosol SO_4^{2-}, total aerosol Cl^-, aerosol aqueous phase mass, aerosol solid phase mass. Simulation of $iPM_{2.5}$ responses to reductions in precursor concentrations and T/RH was also conducted to address dynamics of the formation of $iPM_{2.5}$[36, 37].

4 Contributions of AFO NH_3 emissions to the secondary $iPM_{2.5}$

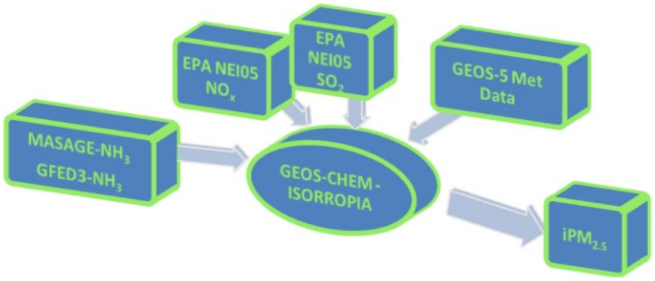
Although the fundamental knowledge about the formation of secondary NH_4^+ particulate is well established, the contributions of AFO air emissions to atmospheric secondary $iPM_{2.5}$ have not been well studied and experimentally quantified. Based upon the amount of NH_4^+ in sulfate and nitrate $PM_{2.5}$ from CASTNET and an assumption that the amount of NH_4^+ in sulfate and nitrate $PM_{2.5}$ emitted from AFOs is in the same fraction as that of the total NH_3 emissions attributable to AFOs, Hristov[97] conducted an hypothetic study to assess contribution of AFO NH_3 emissions to secondary $iPM_{2.5}$. It was discovered that $iPM_{2.5}$ formed from AFO NH_3 emissions contributed 5%-11% of total $PM_{2.5}$ mass across different regions in the U.S. and under different weather conditions. Under cold weather conditions, this contribution may reach as high as 20% in eastern U.S. For several reasons, research findings from this study are challenges and remain to be tested. First of all, chemical speciation data from CASTNET are not applicable to the AFO environment since the $PM_{2.5}$ samples were not taken from AFO environment. Secondly, there was lack of consideration of spatial and temporal variations in NH_3 emission inventory used in the study. Thirdly, there was lack of consideration of acidic gas availability in assessing the formation of secondary $iPM_{2.5}$. Last, but not least, there was lack of model validation in application of the hypothetic models to quantify the formation of $iPM_{2.5}$.

Walker et al.[13, 96] conducted several field monitoring studies coupled with statistic and ISORROPIA modeling to assess response atmospheric $iPM_{2.5}$ to precursor gas emissions at agricultural sites in southeastern U.S. where animal production and fertilizer are major sources of NH_3 emissions. It was revealed that NH_4^+, SO_4^{2-}, NO_3^- and Cl^- accounted for 22%, 53%, 24%, and 1% of total $iPM_{2.5}$ mass, respectively. Reductions of SO_2 and NO_x will lead to reduction of SO_4^{2-} and NO_3^- associated $iPM_{2.5}$ as well as total $PM_{2.5}$. Reducing SO_2 emissions is more effective in summer; whereas reducing NO_x and/or NH_3 emissions is more effective in winter time, which may lead to the greatest reduction of $iPM_{2.5}$. In agricultural areas where high NH_3 emissions are produced, NH_4^+ particulate formation is less likely to be limited by NH_3 availability, but more likely to be limited by availability of SO_2 and $NO_{x.}$ Response of $iPM_{2.5}$ to NH_3 concentrations/emissions is affected by the concentrations of acidic gas species, i.e. SO_2 and NO_x. When the acidic gas species are limited, significant reduction of NH_3 emissions/concentrations may not be effective in reducing $iPM_{2.5}$ concentrations.

In a recent field study by Li et al.[32,36,37,51], NH_3 concentrations and inorganic species of $PM_{2.5}$ in the vicinity of an AFO were simultaneously measured to investigate formation of secondary $iPM_{2.5}$. Response of NH_4^+ particulate to precursor gas concentrations and environmental parameters was modeled by ISORROPIA-II, using measured gas and particle concentrations as well as environmental parameters. It was discovered that $PM_{2.5}$ level responded nonlinearly to changes in NH_3 concentrations. While there was abundant NH_3 in the vicinity of this AFO facility, $PM_{2.5}$ concentration was relatively insensitive to changes in NH_3. The ISORROPIA results indicated that adding more NH_3 caused gas phase NH_3 to increase linearly but

NH_4^+ particulate leveled off as total NH_3 reached to a level greater than 10 $\mu g/m^3$. The model results also showed that NH_3 first reacted with H_2SO_4, then the remaining NH_3 would react with HCl and HNO_3, depending on the RH and temperature, therefore, the reduction of SO_4^{2-} had the most significant impact on the reduction of $PM_{2.5}$, and the abundant NH_3 in the system will react with H_2SO_4 to form $(NH_3)_2SO_4$. A reduction in NH_3 had limited impact on inorganic $PM_{2.5}$ at the research site due to limited concentrations of acidic gases.

Taking modeling approach, Paulot and Jacob[7] investigate the impact of NH_3 emissions from US food expert on atmospheric $PM_{2.5}$. Figure 5 illustrates the flow diagram of this modeling practice. It was reported that on average, the US food export increases $PM_{2.5}$ exposure by 0.36 $\mu g/m^3$. Due to lack of model validation, findings from this research remain to be tested and verified with observation data.



Note: MASAGE: model for agricultural NH_3 emission; GFED3: model for other anthropogenic sources NH_3 emissions; NEI05: national emission inventory for 2005; GEOS-5: NASA Goddard Earth Observation System for meteorological data

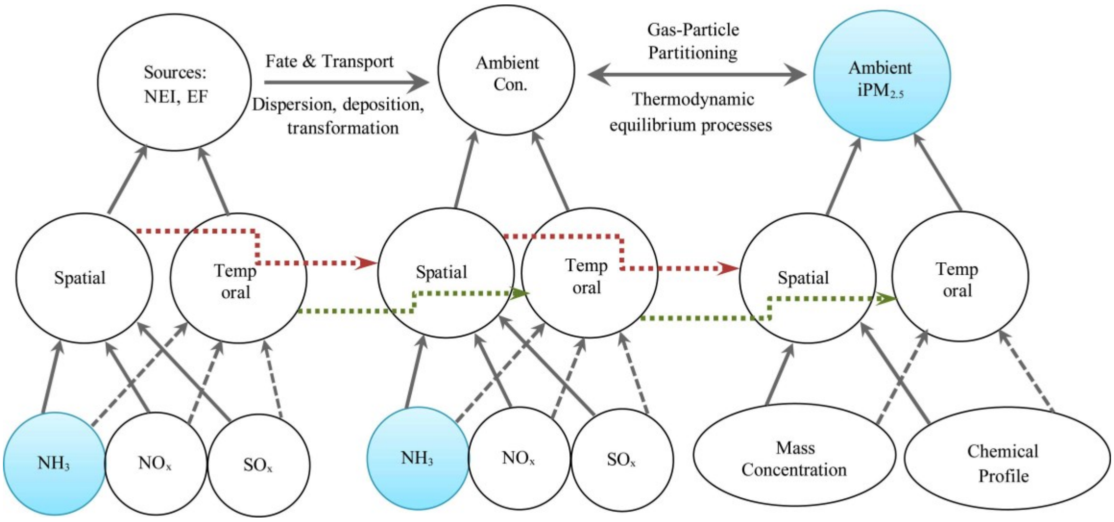
Figure 5 Modeling flow diagram for assessing the impact of NH_3 emissions from food export on $iPM_{2.5}$ by Paulot and Jacob[7]

While only limited research has been done on quantifying responses of the atmospheric secondary $iPM_{2.5}$ to AFO NH_3 emissions[13,32,36,37,51,52,79,94,96], impact of fate and transport of AFO NH_3 emissions on the formation of ambient $iPM_{2.5}$ is not truly understood. There is an urgent need for advanced understanding of fate and transport of AFO NH_3 emissions and how it would affect its potential for contributing to the formation of secondary $PM_{2.5}$ through experimental evaluations in the field and/or through simulation and validation of current atmospheric transport models and/or thermodynamic equilibrium aerosol model under the AFO environments[98].

5 Summary and recommendations

Animal feeding operations have been perceived to be important contributors to atmospheric $PM_{2.5}$. Although knowledge about PM chemical compositions is essential for source identification and development of source-specific PM mitigation techniques, chemical source profiles of AFO PM and chemical compositions of PM inside AFO facilities and in the surrounding areas of the facilities are unknown. Several ambient chemical speciation networks (e.g. IMPROVE, CASTNET, CSN) provide high quality PM chemical speciation datasets for air quality and public health studies, however, there is a lack of representation of intensive agricultural operation areas in networks to assess ambient $iPM_{2.5}$ as impacted by AFO NH_3 emissions that accounts for more than half of nation's NH_3 emissions.

Great challenge exists in assessing contributions of AFO NH_3 emissions to secondary $iPM_{2.5}$ due to lack of temporal and spatial monitoring data of atmospheric SO_2, NO_x and NH_3 concentrations in agricultural production areas where most NH_3 emissions are generated. Moreover, lack of holistic understanding of the pathway from NH_3 emissions to atmospheric $iPM_{2.5}$ (Figure 6) also limits our understanding of impact of NH_3 emissions on the formation of secondary $iPM_{2.5}$ at regional scale. Research gaps remain in systematic understanding of (1) NH_3 spatial and temporal variations of precursor gas emissions (i.e. NH_3, NO_x, SO_x); (2) deposition and transport of NH_3, NO_x, SO_x as impacted by emission source characteristics, land uses and management practices; (3) Dynamics of gas-particle phases (NH_3/NH_4^+) partitioning in response to the spatial and temporal variations of atmospheric NH_3, NO_x, SO_x concentrations as well as meteorological conditions. It is likely that fast removal of NH_3 through dry and wet deposition may limit agricultural NH_3 emission contribution to the formation of secondary $iPM_{2.5}$ in the area far away from emission sources where significant SO_2 or NO_x may present in the air. Further investigation is needed to advance our understanding of ambient secondary $iPM_{2.5}$ as impacted by agricultural NH_3 emissions and various ammonia mitigation strategies.



Note: NEI: National Emission Inventory, EF: Emission Factor.

Figure 6 Holistic pathways to the formation of atmospheric $iPM_{2.5}$

Based upon this comprehensive literature review of previous research on $iPM_{2.5}$ formation as impacted by AFO air emissions, following research needs are identified:

- Continued improvement of AFO NH_3 emission inventory;
- Simultaneous measurements of precursor gases (e.g. NH_3, NO_x, SO_2, etc.), $PM_{2.5}$ chemical compositions, and meteorological conditions in intensive AFO production areas to assess formation of secondary $iPM_{2.5}$ as impacted by AFO NH_3 emissions, and atmospheric chemical and meteorological conditions;
- Experimental based assessment of NH_3 and ammonium (NH_4^+) particulate dry deposition rates and velocities as impacted by AFO NH_3 emissions, distance from emission source, land usage, and meteorological conditions;
- Experimental identification of chemical compositions of AFO PM, both inside the AFO production facilities and in the vicinity of the those facilities;
- Development of experimental-based models describing NH_3/NH_4 deposition and formation of $iPM_{2.5}$ as a function of house emission rates, distance from the sources, ambient meteorological (e.g. T, RH, wind speed/direction), and chemical (e.g. SO_2, NO_x, etc.) conditions;
- Experimental validation of atmospheric transport models (e.g. CMAQ, etc.) for modelling NH_3 deposition in intensive AFO areas;
- Experimental validation of atmospheric transport models (e.g. CMAQ, etc.) and thermodynamic equilibrium aerosol models (e.g., ISORROPIA) for modelling gas-particle phase partitioning of secondary $iPM_{2.5}$ in AFO environments;
- Experimental based identification of key factors that affect precursor gas concentrations, and formation of secondary $iPM_{2.5}$ in AFO environments;
- Assessment of impact of management practices and mitigation strategies on NH_3 emissions, fate and transport of the emissions, and formation of secondary $iPM_{2.5}$.

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