

GAS-TO-PARTICLE CONVERSION PROCESS BETWEEN AMMONIA, ACID GASES, AND FINE PARTICLES IN THE ATMOSPHERE

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SUMMARY

Ammonia emissions are associated with many agricultural operations including animal and poultry operations, waste and wastewater treatment operations, and fertilizer and manure land applications. The fate of ammonia released to atmosphere is affected by interaction with other gases, aerosols, and fine particles. These interactions affect the gas-to-particle conversion. This process alters ammonia concentrations downwind from agricultural operations. However, experimental research and modeling of the gas-to-particle conversion processes in ammonia-rich environments is generally limited. This paper summarizes the state-of-the-art knowledge related to gas-to-particle conversion of ammonia.

Ammonia and inorganic acid gases emitted from livestock and poultry operations and manure treatment, handling and application can affect air quality by formation of secondary particulate in the fine, PM_{2.5} range (a regulated air pollutant). The process of gas-to-particle conversion of relatively short-lived gaseous ammonia to more persistent fine particulate can affect local and regional air quality far away from the agricultural sources. Emissions of ammonia from livestock and poultry operations can potentially be detrimental to the air quality in non-compliance areas. Several models for the formation of fine PM from substrates such as ammonia are available and have been used for air quality modeling on a local and regional scale. These models can be adapted or modified to include emissions of ammonia and acid gases from livestock and poultry operations.

More research is needed to improve the knowledge related to the role of ammonia gas-to-particle conversion. These needs include: (1) simultaneous field measurements of ammonia and acid gases at typical livestock and poultry sources, (2) development of emission factors for ammonia and acid gases, (3) incorporation of ammonia from agricultural sources to local and regional air quality models, and (4) modeling the fate of ammonia and acid gases emissions from livestock and poultry operations.

HISTORICAL PERSPECTIVE

With promulgation of PM_{2.5} (particulate matter with the size equal or smaller than 2.5 μm in aerodynamic diameter) National Ambient Air Quality Standards (NAAQS) in 1997, many programs have been put in place to reduce levels of PM. These programs control either direct PM emission and/or the emissions that contribute to atmospheric PM formation. U.S. Environmental Protection Agency (EPA) (2003) reported that atmospheric PM_{2.5} concentrations have decreased 10% nationally since 1999. Generally, PM_{2.5} has decreased the most in regions with the highest concentrations—the Southeast (20%), southern California (16%), and the Industrial Midwest (9%). With the exception of the Northeast, the remaining regions posted modest declines in PM_{2.5} from 1999 to 2003. Overall, a variety of local and national programs have resulted in a 5% decrease in estimated direct emissions of PM_{2.5} over the past 5 years. In addition, programs that reduce the gaseous emissions of sulfur and nitrogen oxides (SO₂ and NO_x, respectively) and volatile organic compounds (VOCs) that can form particles in the atmosphere have yielded additional reductions.

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AEI	Analytical Equilibrium Iteration
AIRS	Aerometric Information Retrieval System
CAMM	Continuous Ambient Mass Monitor
CASTNet	Clean Air Status and Trends Network
CMAQ	Community Multi-scale Air Quality
DRH	Deliquescence Relative Humidity
EC	Elemental Carbon
FRM	Federal Reference Method
GTPC	Gas-To-Particle Conversion
IMPROVE	Interagency Monitoring of PROtected Visual Environments
MADRID	Model of Aerosol Dynamic, Reaction, Ionization, and Dissolution
MDRH	Mutual Deliquescence Relative Humidity
MFI	Mass-Flux Iteration
NAAQS	National Ambient Air Quality Standard
NH ₄ Cl	ammonium chloride
NH ₄ HSO	ammonium bisulfate
(NH ₄) ₂ SO ₄	ammonium sulfide
NH ₄ NO ₃	ammonium nitrate
NMN	National Monitoring Network
OC	Organic Carbon
PAN	peroxyacetyl nitrate (CH ₃ C(O)OONO ₂)
PBW	Particle-Bound Water
CH ₃ C(O)OO [•]	peroxylacetyl radical
PM	Particulate Matter
RAMS	Real-time total Ambient Mass Sampler
RH	Relative Humidity
SEARCH	South Eastern Aerosol Research and Characterization
STN	Speciated Trends Network
SVOC	Semi-Volatile Organic Compounds
TCM	Total Carbonaceous Mass (TCM = constant × OC + EC)
TEOM	Tapered Element Oscillating Microbalance
U.S. EPA	United States Environmental Protection Agency
UAM	Urban Airshed Model
VOC	Volatile Organic Compound

The national monitoring network program has been deployed since 1999 for a continuous real-time PM_{2.5} mass measurement (U.S. EPA, 2004a,b,c). This program uses several systems such as nationwide network Federal Reference Methods (FRM) and speciation monitors utilizing analytical methods for inorganic species, organic and elemental carbon, and crustal species (ammonium, silica, calcium, iron and titanium). However, there are several critical uncertainties related to mass concentration and composition of PM including losses due to volatilization of (1) ammonium nitrate, (2) semi-volatile organic compounds, and (3) removal of particle-bound water (PBW) which affects atmospheric PM_{2.5} mass and composition. Several new monitoring methods have been introduced to reduce the uncertainties of PM_{2.5} mass measurements (U.S. EPA, 2004a; Babich et al., 2000; Hering and Cass, 1999; Zhang and McMurray, 1992). One is a Real-time Total Ambient Mass Sampler (RAMS) which measures the total atmospheric PM mass including SVOCs. It utilizes a TEOM monitor in combination with a PTFE-coated filter for particles followed by a charcoal-impregnated filter for SVOCs evaporated from the particles. Wang (1996) developed a Continuous Ambient Mass Monitor (CAMM) that monitors the incremental increase of the pressure drop on membrane filter used for particle sampling. The beta-gauge monitoring technique has been used effectively to measure the mass of equilibrated PM collected on a PTFE filter with time intervals on the order of 1hr. However, PM measurements utilizing this technique can also be affected

by the same problems of PBW removal as other continuous real-time PM mass monitoring techniques.

As a part of nationwide monitoring network program, U.S. EPA has deployed a speciated trends network (STN) for PM_{2.5} mass monitoring and chemical speciation (U.S. EPA, 2004d). The PM_{2.5} STN was established in 1999 as a mass-based FRM network for the assessment of trends at representative urban areas across the U.S. The STN currently has a total of 54 monitoring sites. The STN has quantified PM_{2.5} mass concentrations and PM_{2.5} constituents, including numerous trace elements, ions (i.e., sulfate, nitrate, sodium, potassium, and ammonium), elemental carbon (EC) and organic carbon (OC). In 1987, the IMPROVE aerosol monitoring network was established originally for determining the types of pollutants and sources primarily responsible for visibility impairment (U.S. EPA, 2004d). The IMPROVE network has expanded from its original 20 monitoring sites to over 110 sites in 2003. In addition, there are currently over 50 supplemental sites in regionally representative rural areas that deploy the IMPROVE aerosol monitoring protocol (U.S. EPA, 2003).

Since 1998, U.S. EPA has initiated the Particulate Matter Research Program to identify the relationships between PM and human health, to develop the predictive and evaluative tools to determine compliance of NAAQS, and to develop needed mitigation strategies (U.S. EPA, 2004b,c). Modeling is the integral part of this program. The three dimensional air quality models have been known as the most reliable probing tools to simulate the chemical and physical processes of atmospheric PM. The simulations, which can be conducted on a myriad of spatial and temporal scales, support policies and regulatory assessment, as well as scientific studies conducted by academic and research institutions. In order to characterize the performance and to improve the capability of air quality models, an evaluation process is crucial to these air quality models if they are to be used for regulatory purpose (U.S. EPA, 2004a). However, the main challenges remain related to accurate PM measurements (both mass and composition) and aerial pollutant emission inventory, and to sufficient organic chemistry information for simulation of semi-VOCs (SVOCs) in the atmosphere. To address these limitations, the development and improvement of air quality models is necessary by comparing model simulation results with observational atmospheric PM data.

Agriculture is known as the major source of ammonia and other acid gas emissions (Aneja et al., 2000, 2001; Li et al., 1999). Fertilizer application, swine, beef cattle, dairy, sheep and poultry operations, manure treatment, manure storage, land applications, and manure composting emit considerable amounts of ammonia (U.S. EPA, 2003; Battye et al., 1994; Battye et al. 2003). Atmospheric reduced nitrogen ammonia (NH₃) has been considered as an environmental pollutant due to its role as a source of fixed nitrogen to soil and plants and the critical role in gas-to-particle conversions forming atmospheric PM_{2.5} (Meng et al., 1997), thus resulting in a longer resident time of ammonium (NH₄⁺) species in the atmosphere. Thus, the spatial scale of NH₃ and NH₄⁺ emissions from agricultural areas has the potential to determine local and regional PM_{2.5} source contributions to urban air pollution. To date, our knowledge related to the fate of ammonia and acid gases emissions from agriculture is limited. More work is needed to estimate the contributions of regional background associated with urban areas using spatial analysis and/or air quality models to identify and examine specific emission sources on a finer time resolution to get to the next and more refined level of local/regional source contributions.

Atmospheric Particulate Matter

Since the mid-1970s, atmospheric particulate matter (PM) has been considered as a major air pollutant because of its adverse health effects, visibility impairment, radiative forcing effects on climate, and aesthetic property damage (U.S. EPA, 2004a,b,c; Warneck, 2000; Meng et al., 1997; Gray et al., 1986; Heintzenberg, 1989). In particular, evaluation of adverse human health effects has been one of main priorities in PM research programs administered by the U.S. EPA (U.S. EPA, 2004c). By 1996, the epidemiological research associated with human health problems and air quality issues led to the promulgation of PM NAAQS in 1997 that included new standards for PM_{2.5} in the atmosphere. Particle size is not only one of the most critical parameters in determining the physical and chemical properties, effects, and fate of atmospheric PM but it also strongly influences optical properties (e.g., light scattering). Light scattering affects atmospheric visibility and radiative forcing balance on local, regional, and global scales of climate. The major effect of atmospheric PM on climate is a radiative forcing which controls the radiation balance through direct

and indirect mechanisms. Atmospheric PM can scatter and absorb both visible and infrared radiation in the atmosphere and affect the overall radiation budget resulting in a warming or cooling effect depending upon PM size, index of refraction, and distribution in the atmosphere (Willeke and Whitby, 1975).

Sources of Particulate Matter

Atmospheric PM originates from a variety of sources (both natural and anthropogenic) and has a range of chemical, physical and thermodynamic properties (Warneck, 2000). Primary particles emitted directly into the atmosphere are, in general, wind-blown dust, sea salt, road dust, mechanically generated particles and combustion-generated particles, e.g., fly ash and soot. Crustal species including calcium, aluminum, silicon, magnesium and iron are generally found in the coarse particles. Secondary particles are formed through two major particle formation processes in the atmosphere. One process is the nucleation process by low vapor pressure gases (1) directly emitted or (2) formed by chemical reactions in the atmosphere. The second process is the condensation of low vapor pressure gases on the surface of existing particles. Fine particles ($PM_{2.5}$) include both the accumulation ($0.1\mu\text{m} < D_p < 1\sim 3\mu\text{m}$) and nuclei ($< 0.1\mu\text{m}$) modes (U.S. EPA, 2004). An aerosol may be defined as a suspended solid and/or liquid phase particles in the atmosphere including all vapor or gas phase components.

Nucleation processes in the atmosphere may involve organic compound, NH_3 , water, and sulfuric acid (H_2SO_4) generated by the homogenous heteromolecular nucleation of H_2SO_4 vapor from the gas phase oxidation of $SO_2\cdot$ and $OH\cdot$ radicals in the atmosphere (Figure 1). As H_2SO_4 is formed, it can either nucleate to form new particles or it can condense on existing accumulation particles. Sulfuric acid forms atmospheric aerosol salts, such as ammonium bisulfate (NH_4HSO_4) and ammonium sulfate ($(NH_4)_2SO_4$) with NH_3 (Figure 2). Particles in the nuclei mode may be transferred into the accumulation mode by coagulation. However, accumulation mode particles do not ordinarily grow into the coarse mode, because concentrations are too low for coagulation to be effective. Nucleation leads to an increase in particle number as well as increase in particle mass. Condensation leads only to an increase of particle mass and surface area, but does not affect the total number of particles.

Formation of Secondary Particulate Matter

Most of secondary PM undergoes thermodynamic equilibrium chemical reactions called the *gas-to-particle conversion (GTPC)* process. The GTPC process tends to reside in the accumulation mode PM range (typically 0.1 to 2.5 μm). This fine PM range is the most critical with respect to human health, visibility, and detrimental ecosystem effects caused by acid dry/wet deposition. Due to complicated chemical reactions in the atmosphere, secondary PM formation rate could depend on numerous factors including:

1. precursor concentrations;
2. reactive gaseous concentrations, such as ozone, hydroxyl radical, nitrate radical, peroxy radicals and hydrogen peroxide, organic carbon; and
3. atmospheric conditions, such as temperature and relative humidity.

The common components of atmospheric particles, such as inorganic aerosol salts including sulfate, nitrate, and ammonium, insoluble materials, organics, crustal material, and water, reach particulate phase by several different pathways (Figure 1).

Although numerous chemical species have been identified in secondary aerosols, the most prevalent species are sulfate, nitrate, ammonium and water. Heintzenberg (1990) and Gray et al. (1986) indicated that inorganic aerosol salts comprise 25-65% of dry total fine aerosol mass and together with water consist of a significant portion of the total aerosol mass (especially in high relative humidity environments). A portion of the organic aerosol is also attributed to secondary processes (Jacobson 1997a,b; Warneck, 2000). Aside from the direct emission of particles into the atmosphere, GTPC processes play an essential role determining the mass of atmospheric PM. Ammonia and acid gases in the atmosphere are known as major inorganic atmospheric aerosol precursor sources and control composition of PM in the atmosphere through GTPC process.

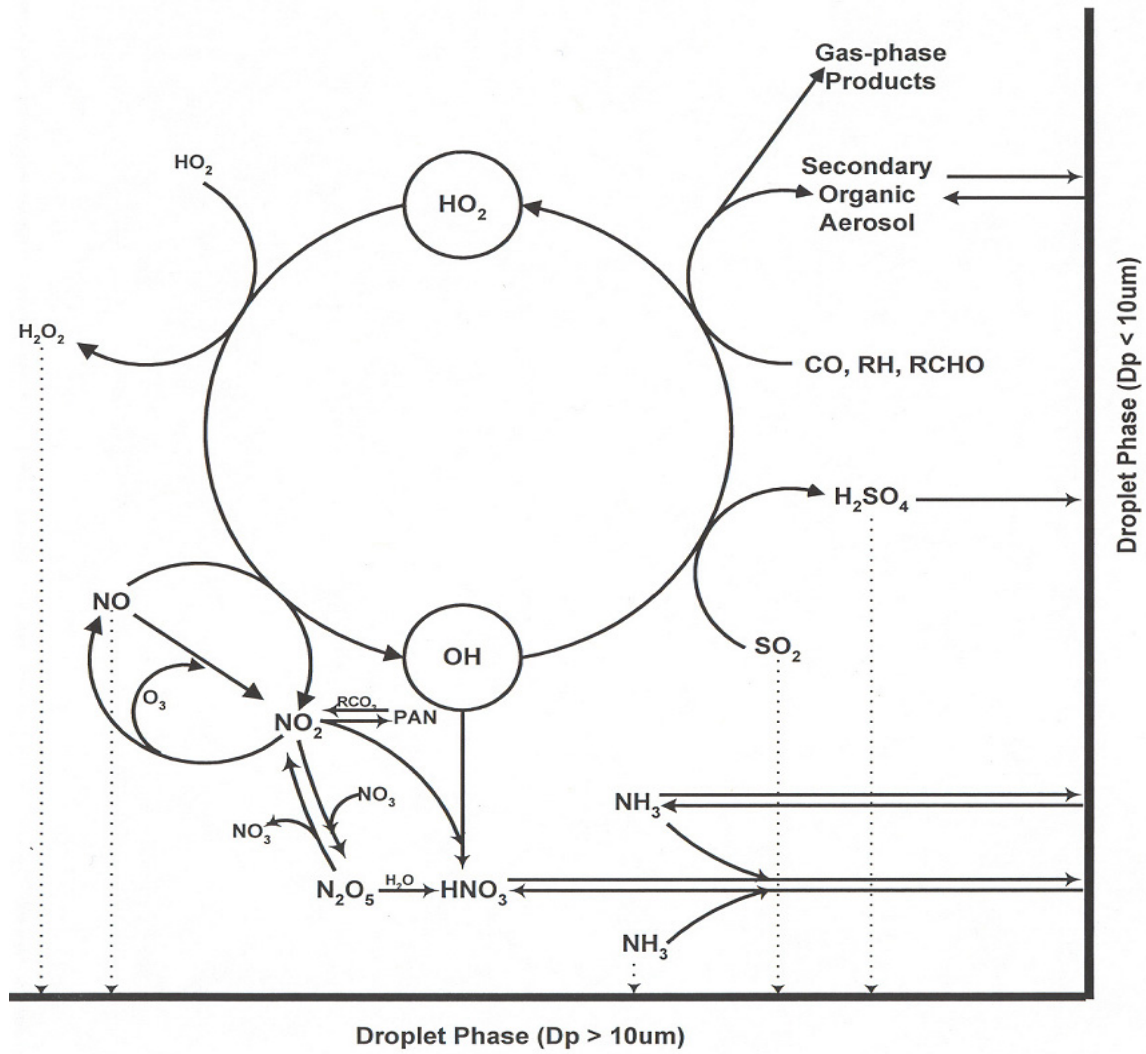


Figure 1. Chemical coupling between the atmospheric gases, particles, and droplet phases (Meng et al., 1997).

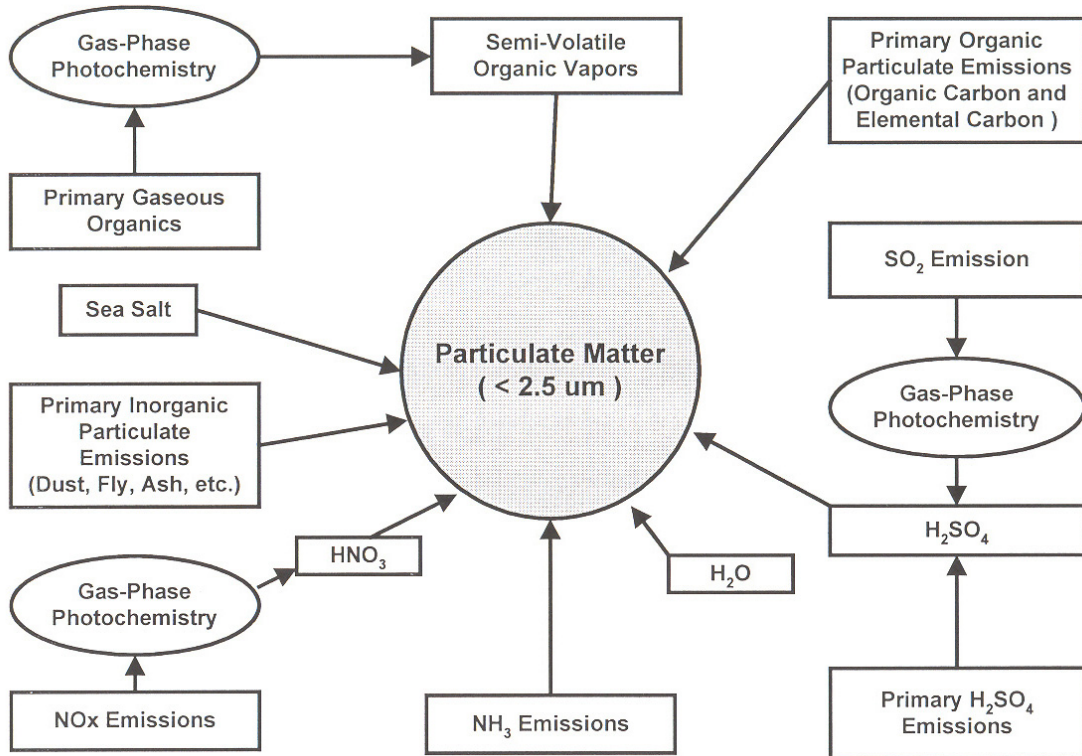


Figure 2. Routes of incorporation of chemical species into atmospheric PM (Meng et al., 1997).

The gas-to-particle conversion process in the atmosphere can be accomplished by condensation, which adds mass onto pre-existing aerosols, or by direct nucleation from gaseous precursors, forming aerosols (Baek and Aneja, 2004a,b; Baek et al., 2004; Warneck, 2000). Ammonia, a predominant alkaline component in the atmosphere, reacts with acid gases (H_2SO_4 , HNO_3 , and HCl) and forms atmospheric ammonium aerosol salts, such as ammonium sulfate ($[\text{NH}_4]_2\text{SO}_4$), ammonium bisulfate (NH_4HSO_4), ammonium nitrate (NH_4NO_3), and ammonium chloride (NH_4Cl). The ammonium salts can exist as solid particles or liquid droplets depending on the amount of water vapor in the atmosphere (Figures 1 and 2).

CHEMISTRY OF ATMOSPHERIC PARTICULATE MATTER

There are two different types of chemical reactions with regard to the fine particle formation in the atmosphere, heterogeneous and homogeneous reactions. Homogeneous chemical reactions involve forming a condensable species, such as the oxidation of sulfur dioxide to sulfuric acid. Condensable species can either nucleate to form a new particle (nucleation), or can condense onto the surface of an existing particle (condensation) (Warneck, 2000; U.S. EPA, 2004a). Another mechanism is a heterogeneous chemical reaction involving both gas and particle phase components. Transformation on the surface of particles, such as the uptake of HNO_3 (g) on the surface of calcium carbonate (CaCO_3) (s) particle to produce calcium nitrate CaNO_3 (s), is one type of heterogeneous reaction. Aqueous-phase chemical reactions, such as the oxidation of the dissolved sulfur dioxide (SO_2) (g) to sulfate (SO_4^-) (aq), provide an important mechanism for conversion of gas to particle. Heterogeneous reactions increase the particle mass by the addition of aerosol materials to existing particles.

The acidity of particle in the atmosphere mainly depends on existence of sulfuric acid (H_2SO_4) formed from atmospheric oxidation of sulfur dioxide. Atmospheric nitrate is also essentially secondary due to oxides of nitrogen reacting in the atmosphere to form nitric acid vapor, which in turn may react with ammonia gas to form particulate ammonium nitrate. However, when gas phase $\text{SO}_3/\text{H}_2\text{SO}_4/\text{acidic}$ particles coexists with NH_4NO_3 particles in the atmosphere, nitric acid will be released and substituted with H_2SO_4 to form acidic NH_4HSO_4 particles due to their higher volatilities. Thus, secondary particle formation can strongly depend on the concentrations of their gaseous species, such as ammonia and acidic gases, and the interactions between these precursors and pre-existing particles. However, relatively small amount of particulate sulfate, nitrate, and chloride species in coarse particle originate from the SO_2 , HNO_3 and HCl reactions with coarse PM instead of equilibrium chemical reactions. In the following section, the precursor formations and their linked relations of GTPC processes are discussed (Figure 2).

Acid Gases: Precursors

Atmospheric acid gases (H_2SO_4 , HNO_3 , and HCl) have been identified as not only major contributors to the acidification of soil and precipitation, but are also associated with adverse health effects, mainly respiratory diseases (EPA, 2004; Warneck, 2000). Sulfuric acid (H_2SO_4), and nitric acid (HNO_3), the two major acidic gases in the atmosphere, come from oxidation of SO_2 to H_2SO_4 , and NO_x to HNO_3 . These acid gases are neutralized in the atmosphere by NH_3 , the principal gaseous alkaline species. Thus, NH_3 not only plays a role in determining acidification and eutrophication of ecosystems but also neutralizes acidic species in the atmosphere. Other than chemical reactions between acid gases and ammonia, organic compounds (e.g., carboxyl acid, also known as fatty volatile acid, and major odorous gases associated with livestock operations) (Koziel et al., 2004a) are also involved in GTPC processes for fine particle formation (Baek and Aneja, 2004a,b; Meng et al., 1997) (Figures 1 and 2).

Atmospheric gas phase oxidation of SO_2 takes place both by gas phase reaction and by aqueous phase reaction. Atmospheric oxidation of SO_2 largely occurs by a sequence of reactions initiated by the reaction of OH^\bullet with SO_2 . H_2SO_4 vapor rapidly transfers to the particulate phase by nucleation or condensation on pre-existing particle surfaces. Gas-phase organic and NO_x chemistry is driven by the hydroxyl (OH^\bullet) radical produced by photochemical reactions during ozone formation (Bowman and Seinfeld, 1994). The major sinks of gas phase NO_x are the formation of HNO_3 and peroxyacetyl nitrate (PAN), i.e., $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$. The principal oxidation reaction of gas-phase production of nitrate is that of photochemically produced OH^\bullet radical with NO_2 to form HNO_3 .

Due to its reversible formation through reaction of peroxyacetyl radicals $\text{CH}_3\text{C}(\text{O})\text{OO}^\cdot$ and NO_2 , PAN could be a temporary NO_x reservoir for the formation of HNO_3 . Once formed, HNO_3 may be either removed by deposition or by formation of ammonium nitrate (NH_4NO_3) aerosol salt with ammonia (NH_3) in the particle. The concentrations of NH_3 could determine both the HNO_3 loss and the NH_4NO_3 formations. Aqueous phase HNO_3 formation depends on the uptake of N_2O_5 and NO_3 radicals in cloud water. However, gas phase oxidation of NO_2 contributes a major part to the formation of $\text{HNO}_3(aq)$ than the aqueous phase oxidation reaction, because HNO_3 exists as gas phases in the atmosphere when the RH is less than 98% (Figure 2).

The Gas-to-Particle Conversion Process

Gas-to-particle conversion can be accomplished by condensation, which adds mass to pre-existing aerosols, or by direct nucleation from the gas when aerosols are formed. Gas-to-particle conversion strongly depends on the concentration of acid gases and water vapor in the atmosphere. Table 1 lists most of the identified equilibrium chemical reactions known to be occurring in atmosphere. These reactions are currently used in several thermodynamic equilibrium models, such as EQUIL and KEQUIL (Bassett and Seinfeld, 198, 1984), MARS-A (Saxena et al., 1986), SEQUILIB (Pilinis and Seinfeld, 1987), SCAPE2 (Kim et al., 1993a,b, 1995; Meng et al., 1995), AIM2 (Clegg et al., 1992, 1998), ISORROPIA (Nenes et al., 1998), GFEMN (Ansari and Pandis, 1999), and EQUISOLV II (Jacobson, 1997a,b, 1999; Jacobson et al., 1996). These models simulate the equilibrium partitioning of inorganic and organic compounds between the gas and aerosol phases in the atmosphere. Each model has their own selection of equilibrium equations and equilibrium constants.

The low vapor pressure of sulfuric acid (H_2SO_4) allows it to condense easily on particle and droplet surfaces. Because the rate of condensation is dependent on the amount of water vapor in the atmosphere, sulfuric acid can hardly be found in the gas phase. However nitric acid is much more volatile than H_2SO_4 and is not likely to form particles by homogeneous or heteromolecular nucleation. Therefore, due to its volatility, particulate nitrate is believed to be lower in concentration than SO_4^{2-} (Seinfeld and Pandis, 1998; Pacyna et al., 1996).

In general, ammonia, nitric acid, and sulfuric acid are highly soluble inorganic species in the atmosphere and they are efficiently removed by wet deposition or rain out, and/or by the neutralization process. Increasing RH results in an increase of the growth in the liquid water content of PM, thereby increasing the absorbing capacity of aerosol with regard to gaseous sulfuric and nitric acids. Ammonium bisulfate and ammonium sulfate are effective condensation nuclei (Warneck, 2000), facilitating droplet formation. As a result of these mechanisms, the composition of aerosols in a local area is largely influenced by the concentration of ammonia, sulfuric acids, nitric acids, and water vapor in the atmosphere (Cadle, et al., 1982, and Lee, et al., 1993). Gas-to-particle conversion process can determine the resident time (lifetime) of ammonia and ammonium in the atmosphere. The spatial scale of NH_3 as a contributor to the total atmospheric nitrogen deposition is governed in part by the GTPC rate of NH_3 to NH_4^+ . Aneja et al. (2000) indicated that ammonia has a short lifetime due to the rapid conversion of NH_3 to NH_4^+ and relatively high dry deposition velocity to the surfaces near its source. However, ammonium primarily formed by GTPC process has a longer lifetime, approximately 5 to 10 days, and could be transported for longer distances downwind from its sources. This observation is critically important for the evaluation of the effects of NH_3 emissions from agriculture.

MEASUREMENTS OF PARTICULATE MATTER

Since the U.S. EPA promulgated new NAAQS for $\text{PM}_{2.5}$ in 1997, the U.S. EPA has initiated a comprehensive national research program with the coordinated efforts of intramural and U.S. EPA-funded extramural investigators, partners, and other federal organizations. The goal of this PM research program is to identify the relationships between PM and human health, and develop the predictive and evaluative tools to determine compliance of NAAQS standard and the needed mitigation strategies. Research related to observational reference methods and atmospheric simulation models that support regulatory needs are crucial to accomplish these goals. In this section, we discuss the current PM measurement reference methods with their advantages and their uncertainties in applications. We also discuss new techniques that attempt to improve problems and uncertainties of current techniques.

Table 1. List of equilibrium chemical reactions in the atmosphere (Zhang et al., 2000).^[a]

Equilibrium Chemical Reactions		Equilibrium Chemical Reactions	
1	$H_2O_{(l)} \leftrightarrow H_{(aq)}^+ + OH_{(aq)}^-$	27	$KCl_{(s)} \leftrightarrow K_{(aq)}^+ + Cl_{(aq)}^-$
2	$H_2SO_{4(aq)} \leftrightarrow H_{(aq)}^+ + HSO_{4(aq)}^-$	28	$K_2SO_{4(s)} \leftrightarrow 2K_{(aq)}^+ + SO_{4(aq)}^{2-}$
3	$HSO_{4(aq)}^- \leftrightarrow H_{(aq)}^+ + SO_{4(aq)}^{2-}$	29	$KHSO_{4(s)} \leftrightarrow K_{(aq)}^+ + HSO_{4(aq)}^-$
4	$NH_{3(g)} \leftrightarrow NH_{3(aq)}$	30	$KNO_{3(s)} \leftrightarrow K_{(aq)}^+ + NO_{3(aq)}^-$
5	$NH_{3(aq)} + H_2O_{(aq)} \leftrightarrow NH_{4(aq)}^+ + OH_{(aq)}^-$	31	$CaCl_{2(s)} \leftrightarrow Ca_{(aq)}^{2+} + 2Cl_{(aq)}^-$
6	$NH_{3(g)} + H_{(aq)}^+ \leftrightarrow NH_{4(aq)}^+$	32	$CaSO_4 \cdot 2H_2O_{(s)} \leftrightarrow Ca_{(aq)}^{2+} + SO_{4(aq)}^{2-} + 2H_2O_{(l)}$
7	$HNO_{3(g)} \leftrightarrow H_{(aq)}^+ + NO_{3(aq)}^-$	33	$Ca(NO_3)_{2(s)} \leftrightarrow Ca_{(aq)}^{2+} + 2NO_{3(aq)}^-$
8	$HCl_{(g)} \leftrightarrow H_{(aq)}^+ + Cl_{(aq)}^-$	34	$MgCl_{2(s)} \leftrightarrow Mg_{(aq)}^{2+} + 2Cl_{(aq)}^-$
9	$NaCl_{(s)} \leftrightarrow Na_{(aq)}^+ + Cl_{(aq)}^-$	35	$MgSO_{4(s)} \leftrightarrow Mg_{(aq)}^{2+} + SO_{4(aq)}^{2-}$
10	$NH_4HSO_{4(s)} \leftrightarrow NH_{4(aq)}^+ + HSO_{4(aq)}^-$	36	$Mg(NO_3)_{2(s)} \leftrightarrow Mg_{(aq)}^{2+} + 2NO_{3(aq)}^-$
11	$(NH_4)_2SO_{4(s)} \leftrightarrow 2NH_{4(aq)}^+ + SO_{4(aq)}^{2-}$	37	$CO_{2(g)} \leftrightarrow CO_{2(aq)}$
12	$Na_2SO_{4(s)} \leftrightarrow 2Na_{(aq)}^+ + SO_{4(aq)}^{2-}$	38	$CO_{2(aq)} + H_2O_{(l)} \leftrightarrow HCO_{3(aq)}^- + H_{(aq)}^+$
13	$NH_{3(g)} + HNO_{3(g)} \leftrightarrow NH_{4(aq)}^+ + NO_{3(aq)}^-$	39	$HCO_{3(aq)}^- \leftrightarrow CO_{3(aq)}^{2-} + H_{(aq)}^+$
14	$NH_4NO_{3(s)} \leftrightarrow NH_{3(g)} + HNO_{3(g)}$	40	$NH_{3(aq)} + HCO_{3(aq)}^- \leftrightarrow NH_2CO_{2(aq)}^- + H_2O_{(l)}$
15	$NH_4NO_{3(s)} \leftrightarrow NH_{4(aq)}^+ + NO_{3(aq)}^-$	41	$Na_2CO_{3(s)} \leftrightarrow 2Na_{(aq)}^+ + CO_{3(aq)}^{2-}$
16	$NH_{3(g)} + HCl_{(g)} \leftrightarrow NH_{4(aq)}^+ + Cl_{(aq)}^-$	42	$NaHCO_{3(s)} \leftrightarrow Na_{(aq)}^+ + HCO_{3(aq)}^-$
17	$NH_4Cl_{(s)} \leftrightarrow NH_{3(g)} + HCl_{(g)}$	43	$K_2CO_{3(s)} \leftrightarrow 2K_{(aq)}^+ + CO_{3(aq)}^{2-}$
18	$NH_4Cl_{(s)} \leftrightarrow NH_{4(aq)}^+ + Cl_{(aq)}^-$	44	$KHCO_{3(s)} \leftrightarrow K_{(aq)}^+ + HCO_{3(aq)}^-$
19	$NaCl_{(s)} + HNO_{3(g)} \leftrightarrow NaNO_{3(s)} + HCl_{(g)}$	45	$CaCO_{3(s)} \leftrightarrow Ca_{(aq)}^{2+} + CO_{3(aq)}^{2-}$
20	$NaNO_{3(s)} \leftrightarrow Na_{(aq)}^+ + NO_{3(aq)}^-$	46	$MgCO_{3(s)} \leftrightarrow Mg_{(aq)}^{2+} + CO_{3(aq)}^{2-}$
21	$NaHSO_{4(s)} \leftrightarrow Na_{(aq)}^+ + HSO_{4(aq)}^-$	47	$NH_2COONH_{4(s)} \leftrightarrow NH_2CO_{2(aq)}^- + H_{(aq)}^+$
22	$(NH_4)_3H(SO_4)_2_{(s)} \leftrightarrow 3NH_{4(aq)}^+ + HSO_{4(aq)}^- + SO_{4(aq)}^{2-}$	48	$Na_2SO_4(NH_4)_2SO_4 \cdot 4H_2O_{(s)} \leftrightarrow 2Na_{(aq)}^+ + 2SO_{4(aq)}^{2-} + 2NH_{4(aq)}^+ + 4H_2O_{(l)}$
23	$Na_3H(SO_4)_2_{(s)} \leftrightarrow 3Na_{(aq)}^+ + HSO_{4(aq)}^- + SO_{4(aq)}^{2-}$	49	$NaH_3(SO_4)_2 \cdot H_2O_{(s)} \leftrightarrow Na_{(aq)}^+ + 2HSO_{4(aq)}^{2-} + H_{(aq)}^+ + H_2O_{(l)}$
24	$(NH_4)_2SO_4 \cdot 2NH_4NO_{3(s)} \leftrightarrow 4NH_{4(aq)}^+ + SO_{4(aq)}^{2-} + 2NO_{3(aq)}^-$	50	$NaHSO_4 \cdot H_2O_{(s)} \leftrightarrow Na_{(aq)}^+ + HSO_{4(aq)}^{2-} + H_2O_{(l)}$
25	$(NH_4)_2SO_4 \cdot 3NH_4NO_{3(s)} \leftrightarrow 5NH_{4(aq)}^+ + SO_{4(aq)}^{2-} + 2NO_{3(aq)}^-$	51	$Na_2SO_4 \cdot 10H_2O_{(s)} \leftrightarrow 2Na_{(aq)}^+ + SO_{4(aq)}^{2-} + 10H_2O_{(l)}$
26	$NH_4HSO_4 \cdot NH_4NO_{3(s)} \leftrightarrow 2NH_{4(aq)}^+ + HSO_{4(aq)}^- + NO_{3(aq)}^-$	52	$Na_2SO_4 \cdot NaNO_3 \cdot H_2O_{(s)} \leftrightarrow 3Na_{(aq)}^+ + SO_{4(aq)}^{2-} + NO_{3(aq)}^- + H_2O_{(l)}$

^[a] The subscripts, *g*, *aq*, *l*, and *s* in the equilibrium reactions represent concentrations of the species in the gas, the aqueous, the liquid, and the solid phases, respectively.

The U.S. EPA's FRMs for PM₁₀ and PM_{2.5} determine mass gravimetrically. A number of gravimetric samplers have been designed as a PM₁₀ reference sampler. The Tapered Element Oscillating Microbalance (TEOM) is one of most widely used samplers due to continuous real-time measurement capability. The PM_{2.5} FRM sampler consists of a PM₁₀ inlet, a PM_{2.5} impactor, and a 47-mm PTFE filter with a 99% collection efficiency and 24-hour sampling duration. Especially, for FRM PM_{2.5} mass measurement, FRM specifies the sampler design and the strict sample handling and analysis. The sample filters are equilibrated for 24 hours at temperature between 20° and 23°C and at RH between 30 and 40% to reduce PBW and to stabilize the filter plus sample weight. As a part

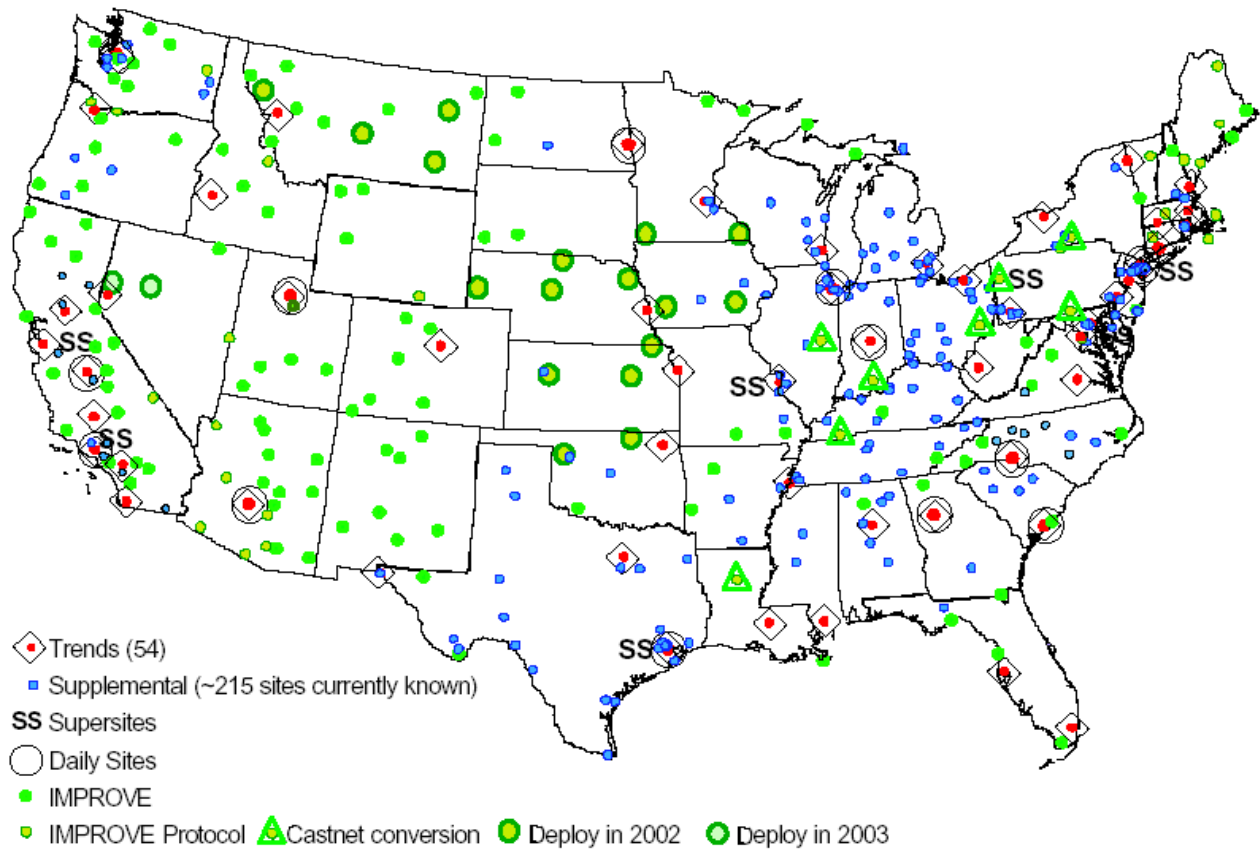


Figure 3. Map of STN and IMPROVE monitoring network in U.S in 2003 (U.S. EPA, 2003).

of National Monitoring Network (NMN) program, the $PM_{2.5}$ chemical Speciation Trends Network (STN) has been deployed. The STN consists of 54 national ambient monitoring stations (NAMS) and approximately 250 supplemental state and local air monitoring stations (Figure 3). In addition, over 110 Interagency Monitoring of PROtected Visual Environment (IMPROVE) locations and Aerometric Information Retrieval System (AIRS) have provided measurement of PM_{10} and $PM_{2.5}$ concentrations and chemical speciation monitoring across the country for the purpose of compliance with air quality standards and trends.

Ambient monitoring data from the $PM_{2.5}$ chemical STN and the IMPROVE aerosol monitoring network were the main sources of data used to assess the urban and rural $PM_{2.5}$ species concentrations across the U.S. The $PM_{2.5}$ STN is a network of the mass-based FRM network has been implemented in support of the $PM_{2.5}$ NAAQS. It provides nationally consistent speciated $PM_{2.5}$ data for the assessment of trends at representative urban areas across the country (Figure 3). As part of a routine monitoring program, the STN quantifies mass concentrations and $PM_{2.5}$ constituents, including numerous trace elements, ions (sulfate, nitrate, sodium, potassium, ammonium), elemental carbon (EC) and organic carbon (OC).

In 1987, the IMPROVE aerosol monitoring network was established among federal and state agencies to provide information for determining the types of pollutants and sources primarily responsible for visibility impairment. The IMPROVE network has expanded from its original 20 monitoring sites to over 110 sites in 2003 including previous CASTNet (Clean Air Status and Trends Network) sites. In addition, there are currently over 50 supplemental sites in regionally representative rural areas that deploy the exact same aerosol monitoring protocol.

Uncertainties in Particulate Matter Measurement

The U.S. FRM for $PM_{2.5}$ and PM_{10} provide relatively precise ($\pm 10\%$) methods for determining the gravimetric mass concentrations (U.S. EPA, 2004a). However, there are several uncertainties related to mass concentration and composition of PM. The general filtration-based mass measurements for RFM increases significant evaporative losses of particulate nitrate and a variety of SVOCs that could exist in the atmosphere in dynamic equilibrium state between gas phase and aerosol phase (Babich et al., 2000; Kim et al., 1995; Pankow, 1994). Ammonium nitrate, SVOCs, and PBW are the major uncertainties and they pose challenges in atmospheric PM measurements.

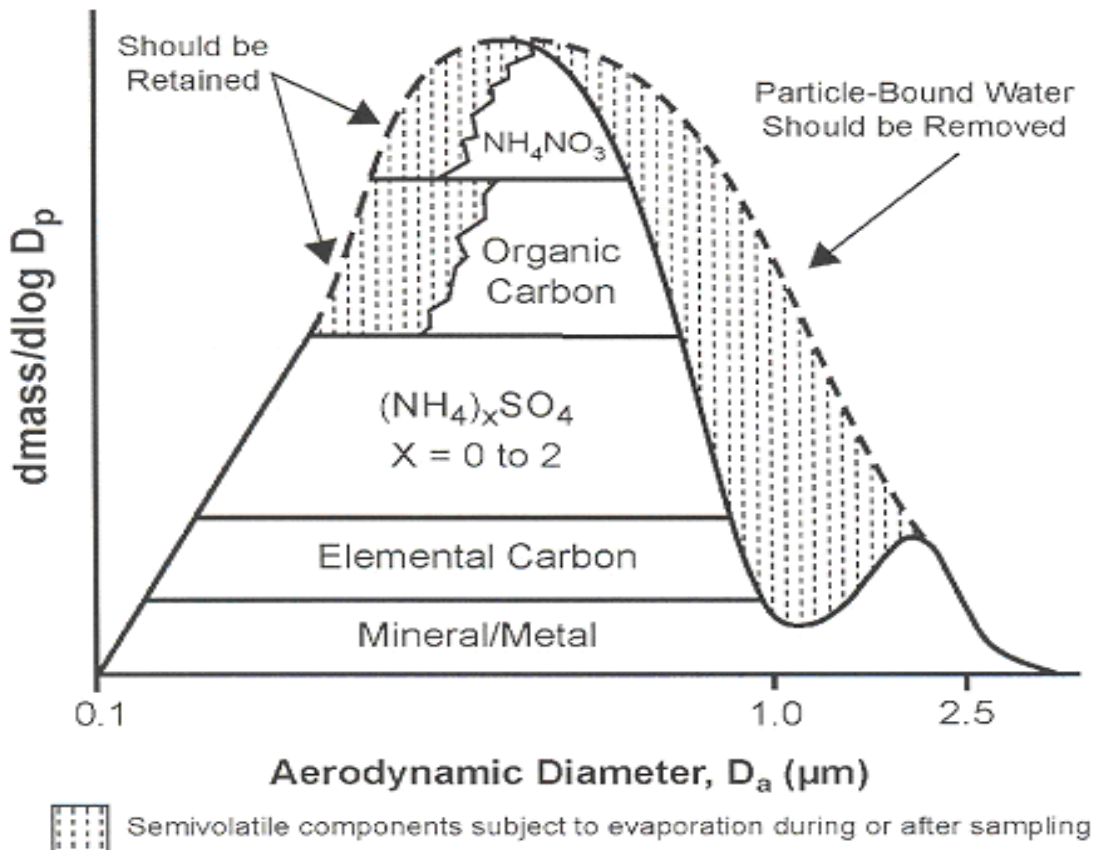


Figure 4. Schematic showing major non-volatile and semi-volatile organic components of PM_{2.5} (U.S. EPA, 2004a). Note: SVOCs are subject to partial-to-complete loss during equilibration or heating. The optimal techniques would be to remove all particle-bound water (PBW) but no ammonium nitrate (NH₄NO₃) or semi-volatile organic PM.

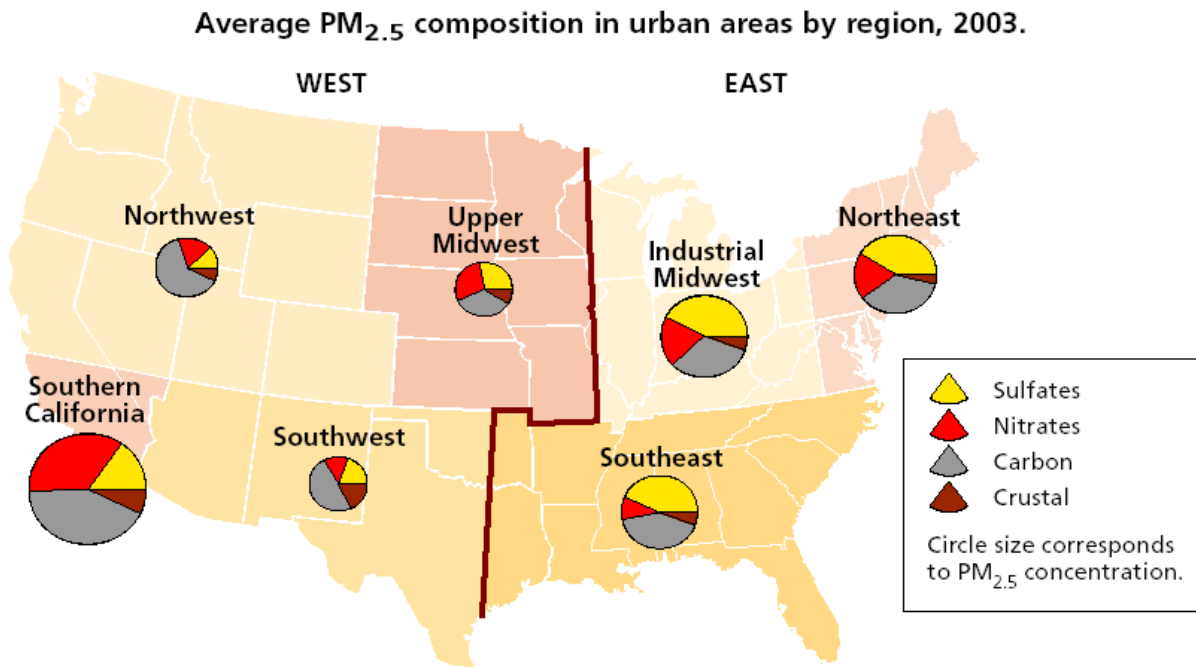


Figure 5. Average PM_{2.5} chemical composition in urban areas by region, 2003 (U.S. EPA, 2003). Note: In this report, the term “sulfates” refers to ammonium sulfate and “nitrates” refers to ammonium nitrate. “Carbon” refers to total carbonaceous mass, which is the sum of estimated organic carbon mass and elemental carbon. “Crustal” is estimated using the IMPROVE equation for fine soil at <http://vista.cira.colostate.edu/improve>.

Those uncertainties are strongly dependent on ambient temperature, RH, and particle composition (Lee et al., 1997; McInnes et al., 1996; Ohta et al., 1998).

Loss of ammonium nitrate and SVOCs could have positive or negative effect on atmospheric PM mass concentrations. A positive sampling effect could occur when ambient RH is high. It leads to higher PBW of PM and absorbs the gas-phase components on the surface on PM (Figure 4). The effect on the accuracy of atmospheric PM measurements from these volatilization losses is more significant for PM_{2.5} than for PM₁₀ because most of the nitrate and a portion of SVOC are formed by equilibrium chemical reactions in the atmosphere. The FRM PM_{2.5} measurement uncertainties could vary by geographical sampling location. U.S. EPA (2003) reported that the nitrate concentrations in PM composition in the western U.S. are higher than those in eastern United States and indicated that the PM_{2.5} mass concentration uncertainties could be higher than in the eastern U.S. (Figure 5). Hering and Cass (1999) also found that the amount of nitrate on a PTFE (polytetrafluoroethylene) filter was 28% lower on the total PM_{2.5} mass concentration than that on a nylon filter due to the loss of ammonium nitrate (NH₄NO₃) (U.S. EPA, 2004a; Babich et al., 2000; Hering and Cass, 1999; Zhang and McMurray, 1992).

Sampling of Ammonia, Acid Gases, and Fine Particles (PM_{2.5})

Sampling and subsequent quantification of ammonia, acid gases, and fine particles can be achieved simultaneously with denuder sampling systems and ion chromatography-based analyzers. The denuder system consists of three major parts: a cyclone separator which removes alkaline coarse particles (defined as greater than 2.5 μ m aerodynamic diameter) and thereby prevents neutralization of acid gases; two diffusion denuders in series, coated with sodium carbonate and citric acid for collection of NH₃, and acid gases, respectively; and finally, a filter pack containing a PTFE and a nylon filter for collection of fine particles. The loss of particulate nitrate could be determined by comparing nitrate collected on a PTFE filter to that collected on a nylon filter, which absorbs nitric acid as it evaporated from ammonium nitrate on a PTFE filter. The denuder system is an improvement over filter-based PM measurement methods and could be applied for measurements of aerosol phase organic compounds. This can be achieved by conducting air sampling with a quartz filter for measurement of organic compounds including semi-volatile and non-volatile elemental carbon (EC) and organic carbon (OC). However, there are still uncertainties related to possible association and interferences of organic gases on a quartz filter during sampling. There are not enough research studies and data to evaluate the extent of these uncertainties on organic compound measurements due to the interference of organic gas and volatilization (loss) of SVOCs on a quartz filter.

To date, there are only a few viable denuder systems capable of continuous measurements and analysis. The efficiency of the denuder system sampling strongly depends on increasing the residence time of the sampled aerosol in the denuder. There are many studies to determine the approximate residence time for accurate measurement of nitrate and SVOC components in atmospheric PM_{2.5} (Gundel and Lane, 1999; Hering and Cass, 1999; Tsai and Huang, 1995; Zhang and McMurry, 1992). Current continuous atmospheric PM mass measurement is conducted by a TEOM monitor, which is normally operated at 50°C in order to remove PBW in atmospheric PM_{2.5} and PM₁₀. It causes the volatilization (loss) of ammonium nitrate and SVOC due to the 50°C operation temperature. The TEOM is capable of measuring the mass of non-volatile PM instead of the total PM including SVOCs and ammonium nitrate (Rupprecht et al., 1995). The PBW removal process in TEOM causes the differences in atmospheric PM mass measurements.

There are several new monitoring systems available to overcome the PBW issues in a TEOM monitor. One is a Real-time Total Ambient Mass Sampler (RAMS), which measures the total atmospheric PM mass including SVOCs by using a TEOM monitor combining two filters. These are a PTFE filter for particles followed by a charcoal-impregnated filter for SVOCs evaporated from the particles. Eatough et al. (1999) compared the mass concentrations from a TEOM monitor, average of 24-hour RFM PM_{2.5} sampler, and real-time RAMS and indicated the significant losses of nitrate and SVOCs from a TEOM monitor during daytime compared to 24-hour average RFM PM_{2.5} and RAMS. Koutrakis et al. (1996) developed a Continuous Ambient Mass Monitor (Camm) by

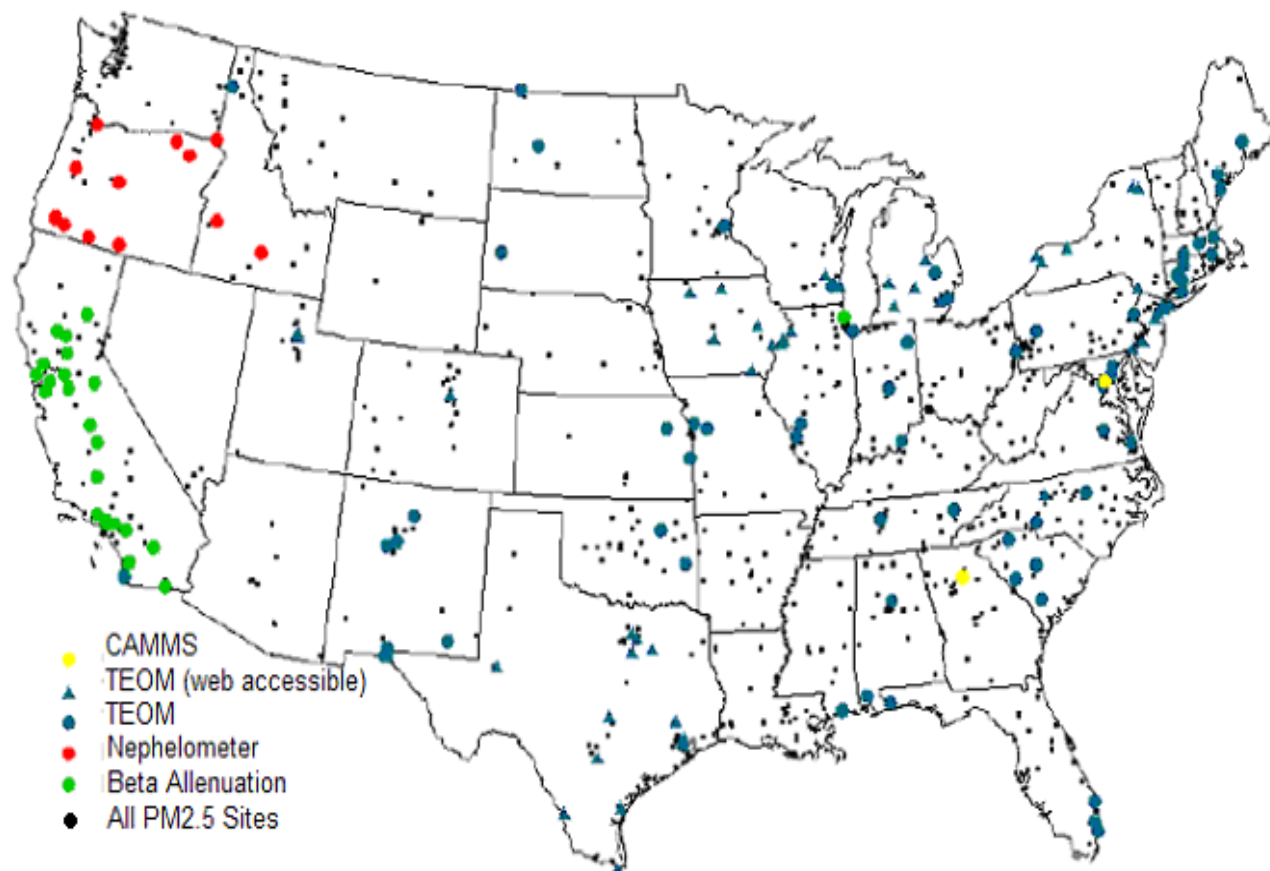


Figure 6. All PM_{2.5} continuous monitoring sites by type of monitor in 2001 (U.S. EPA, 2003).
(Source: <http://www.epa.gov/ttn/amtic/files/ambient/monitorstrat/maps2.pdf>.)

monitoring the increase of the pressure drop on membrane filter used for particle sampling. Beta-gauge monitoring technique has been used effectively to measure the mass of equilibrated PM collected on PTFE filter with time intervals on the order of an hour. However, this technique has the same problems of PBW removal as other continuous real-time PM mass monitoring techniques. Figure 6 presents all continuous PM_{2.5} mass monitoring locations for RAMS (TEOM), CAMM, and Beta-gauge monitoring techniques in the United States in 2001.

MODELS FOR GAS-TO-PARTICLE CONVERSION

Over the past two decades, several atmospheric aerosol models, called thermodynamic equilibrium models, have been developed to simulate the equilibrium partitioning of inorganic compounds between the gas and aerosol phases. These include:

- EQUIL and KEQUIL (Bassett and Seinfeld, 1983 and 1984),
- MARS-A (Saxena et al., 1986),
- SEQUILIB (Pilinis and Seinfeld, 1987),
- SCAPE2 (Kim et al., 1993a, 1993b, and 1995; Meng et al., 1995),
- AIM2 (Clegg et al., 1992 and 1998),
- ISORROPIA (Nenes et al., 1998),
- GFEMN (Ansari and Pandis, 1999), and
- EQUISOLV II (Jacobson, 1997a, 1997b, and 1999; Jacobson et al., 1996).

All these models assume that all internally mixed particles (i.e., uniform composition) of the same size range have the same chemical composition, and that gas and aqueous phases for the volatile compounds exist in thermodynamic equilibrium state.

Bassett and Seinfeld (1983) developed EQUIL in order to calculate the inorganic aerosol composition in a system of NH_4^+ - SO_4^{2-} - NO_3^- - H_2O . The same authors introduced the upgraded version (KEQUIL) later (1984), to account for dependence of the partial vapor pressure on the sphericity of the particle surface. The sphericity of particulate surface plays an important part in the so-called Kelvin effect (Bassett and Seinfeld, 1984) which could control the equilibrium composition. The

Kelvin effect is responsible for the increase of equilibrium vapor pressure above a curved surface compared to the vapor pressure above a flat surface.

MARS-A (Saxena et al., 1986) was developed by U.S. EPA for a system of NH_4^+ - SO_4^{2-} - NO_3^- - H_2O to reduce the computational calculation time while maintaining reasonable agreement with EQUIL and KEQUIL in order to incorporate into a three-dimensional (3-D) air quality model. However, there are two major deficiencies of the MARS-A model: (1) its use of thermodynamic properties, such as equilibrium constant, activity coefficients, at only 298.15 K and (2) its failure to consider the major components in aerosol composition, such as sodium (Na^+) and chloride (Cl^-) species. Zhang et al., (2000) indicated that these three models, EQUIL, KEQUIL, and MARS-A, could not be applicable for near-coast area modeling studies due to lack of Na^+ and Cl^- in the system.

The SEQUILIB model (Pilinis and Seinfeld, 1987) incorporated not only the Na^+ and Cl^- species, but also presented an algorithm for calculating the distribution of volatile species among particles of different sizes. Kim et al. (1993a,b) developed SCAPE2, which uses an algorithm similar to SEQUILIB, with updated thermodynamic constants and activity at various temperatures. This model is an improvement over MARS-A and KEQUIL. SCAPE2 also considers the pH effects on aerosol composition, temperature dependence of single-aerosol salt deliquescence points, and the soluble crustal ionic species such as Ca^{2+} , K^+ , and Mg^{2+} . The AIM2 model was developed under the same system as SEQUILIB but uses a different approach to simulate the partitioning of chemical species among gas, aqueous, and solid phases. AIM2 is a molar-fraction-based model, called the Pitzer method (Pitzer, 1991), that uses mole fraction scale instead of molar scale. All models presented in here are molar-based where all species concentrations, activity coefficients, and equilibrium constants are expressed on the molar scale. Both approaches simulate very comparable results under most particulate matter compositions except for high gas concentrations with very low relative humidity (RH) conditions, which in other models could simulate unrealistic concentrations (Clegg et al., 1998).

An updated version of EQUISOLV, EQUISOLV II under H^+ - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O - Ca^{2+} - K^+ - Mg^{2+} system uses a different numerical approach for solving equilibrium equations, called the Analytical Equilibrium Iteration (AEI). The AEI increases the computational calculation time about 13 to 48 times than the Mass-Flux Iteration (MFI), which is used to iterate each equilibrium equation to converge species concentrations (Jacobson, 1999 and Zhang et al., 2000). EQUISOLV II uses simultaneously both AEI and MFI for partitioning of chemical species between gas, aqueous, and solid phases to improve a computational efficiency over large numbers of spatial grid cells, and particle size bins for 3-D air quality modeling.

ISORROPIA, “equilibrium” in Greek, has been developed as a computationally efficient and rigorous thermodynamic model. One of the main components of the model is the implementation of mutual deliquescence relative humidity (MDRH) of multicomponent aerosol salts, which lowers the deliquescence relative humidity (DRH) point of the aerosol phase. This model uses a weighted average approach to approximate the aerosol composition in mutual deliquescence regions, instead of performing the full calculations. This approximation reduces the necessary computations and is expected to increase the solution time compared to EQUISOLV II. More detailed comparison between EQUISOLV II and ISORROPIA will be discussed later.

Ansari and Pandis (1999) compared four equilibrium models: GFEMN, ISORROPIA, SCAPE2, and SEQUILIB, and recommended ISORROPIA for use in large-scale aerosol transport models. Zhang et al. (2000) also reviewed the similarities and differences in simulation results predicted by five thermodynamic equilibrium modules, i.e., MARS-A, SEQUILIB, SCAPE2, AIM2, and EQUISOLV II. This comparison provided the recommendations with regard to the relative advantages of these models, and the applications in 3-D particulate matter modeling studies. Zhang et al. (2000) recommended that the EQUISOLV II could be applied to simulate particulate matter for any atmospheric PM composition conditions. Baek (2002) suggested that ISORROPIA appears to be the model for the large-scale modeling study in the coastal area and the urban/regional-scale modeling area where atmospheric PM could be in acidic condition not only due to the treatments of MDRH for the mixed aerosols, but also non-convergence numerical solution error under highly acidic condition.

High computational efficiency may allow 3-D eulerian atmospheric chemical transport models with many number of spatial grid cells to use of the aerosol equilibrium models including particle size bins. Three-D models capable of tracking aerosol dynamics, such as GTPC process, particle formation, and size distribution, have been combined to simulate the behavior of organic and inorganic aerosols (U.S. EPA, 2004a,b; Zhang et al., 2004). Large-scale 3-D eulerian atmospheric chemical models have been combined with SEQUILIB (Pilinis and Seinfeld, 1988; Lurmann et al., 1997), MARS-A (Binkowski and Shankar, 1995), EQUISOLV (Jacobson et al., 1996; Jacobson 1997a,b, and 1999), SCAPE2 (Meng et al., 1998), and ISORROPIA (Nenes et al., 1998). Although limited comparisons among equilibrium models have been conducted (Welxer and Seinfeld, 1991; Kim et al., 1993b), no detailed evaluation based on observations of aerosol behavior has been performed in part due to limited field data. Even though the equilibrium models mentioned may agree with each other within a 5-10% error in stand-alone mode, their simulation results may introduce errors in aerosol behavior prediction in atmosphere.

Comparison Of EQUISOLV II and ISORROPIA

Both ISORROPIA and EQUISOLV II include the most recent and detailed treatments of aerosol thermodynamics available in terms of the number of chemical species and reactions. Tables 2 and 3 summarize the major characteristics and equilibrium chemical treatments from both models. Both models incorporated the ZSR method (Zdanovskii, 1948; Robinson and Stokes, 1964), which considers the hysteresis effect simulating the metastable water presence below deliquescence relative humidity (DRH) of an aerosol salt for estimating equilibrium water content within PM composition. The temperature dependence of equilibrium constants and DRH is also considered into both models. However, EQUISOLV II has the option for the Kelvin effect, which affects the equilibrium composition with particle size due to the increase of the equilibrium vapor pressure above a curved particle surface compared to a flat surface. The Kelvin effect is only significant for fine particle less than 0.1 μm in diameter. The Kelvin effect was excluded in ISORROPIA. Thus, for the purpose of comprehensive and quantitative comparison analysis, it can be assumed that the Kelvin effect does not significantly influence this comparison.

Table 2. Major characteristics of ISORROPIA and EQUISOLV II.

Characteristics		ISORROPIA	EQUISOLV II
System		NH ₄ -Na-SO ₄ -NO ₃ -Cl	NH ₄ -Na -SO ₄ -NO ₃ -Cl-Ca-Mg K-CO ₃
Chemical Species Phases	Gas	NH ₃ , HNO ₃ , HCl, H ₂ O	NH ₃ , HNO ₃ , HCl, CO ₂ , H ₂ O
	Liquid	NH ₄ ⁺ , Na ⁺ , H ⁺ , SO ₄ ²⁻ , HSO ₄ ⁻ , NO ₃ ⁻ , OH ⁻ , H ₂ O(l)	ISORROPIA + Ca ²⁺ , K ⁺ , Mg ²⁺ , CO ₃ ²⁻ , HCO ₃ ⁻
	Solid	NH ₄ HSO ₄ , (NH ₄) ₂ SO ₄ , (NH ₄) ₃ (SO ₄) ₂ , NH ₄ NO ₃ , NH ₄ Cl, NaCl, NaNO ₃ , NaHSO ₄ , Na ₂ SO ₄	ISORROPIA + KCl, K ₂ SO ₄ , KHSO ₄ , KNO ₃ , CaCl ₂ , CaSO ₄ , Ca(NO ₃) ₂ , MgCl ₂ , MgSO ₄ , Mg(NO ₃) ₂ , Na ₂ CO ₃ , NaHCO ₃ , K ₂ CO ₃ , KHCO ₃ , CaCO ₃ , MgCO ₃
Binary Activity Method		K-M Method	Pitzer Method
Multi-Component Activity Coefficient Method		Bromley Method	Bromley Method
Water Activity		ZSR	ZSR
Kelvin Effect		No	Yes
Solution Method		Iterative Bisection	Analytical Equilibrium Iteration (AEI) + Mass Flux Iteration (MFI)
Reference		Nenes et al. (1999)	Jacobson (1999)

Table 3. Equilibrium chemical reactions at 298.15K used in ISORROPIA and EQUISOLV II.

	Equilibrium Chemical Reactions	Constants	ISORROPI EQUISOLV			
			a	b	A	II
E1	$H_2O_{(aq)} \leftrightarrow H^+_{(aq)} + OH^-_{(aq)}$	1.010×10^{-14}	-22.52	26.92	•	•
E2	$H_2SO_{4(aq)} \leftrightarrow H^+_{(aq)} + HSO^-_{4(aq)}$	1.0×10^3	—	—		•
E3	$HSO^-_{4(aq)} \leftrightarrow H^+_{(aq)} + SO^{2-}_{4(aq)}$	1.015×10^{-2}	8.85	25.14	•	•
E4	$NH_{3(g)} \leftrightarrow NH_{3(aq)}$	5.764×101	13.79	-5.393	•	
E5	$NH_{3(aq)} + H_2O_{(aq)} \leftrightarrow NH^+_{4(aq)} + OH^-_{(aq)}$	1.805×10^{-5}	-1.50	26.92	•	
E6	$NH_4HSO_{4(s)} \leftrightarrow NH^+_{4(aq)} + HSO^-_{4(aq)}$	2.55×10^2 ^a	-2.87	15.83	•	•
E7	$(NH_4)_2SO_{4(s)} \leftrightarrow 2NH^+_{4(aq)} + SO^{2-}_{4(aq)}$	1.817×10^0 ^b	-2.65	38.57	•	•
E8	$(NH_4)_3H(SO_4)_2(s) \leftrightarrow 3NH^+_{4(aq)} + HSO^-_{4(aq)} + SO^{2-}_{4(aq)}$	4.0026×10^1 ^c	-5.19	54.40	•	•
E9	$HNO_{3(g)} \leftrightarrow H^+_{(aq)} + NO^-_{3(aq)}$	2.511×10^6	29.17	16.83	•	•
E10	$NH_4NO_{3(s)} \leftrightarrow NH_{3(g)} + HNO_{3(g)}$	5.746×10^{-17} ^d	-74.38	6.12	•	•
E11	$NH_4NO_{3(s)} \leftrightarrow NH^+_{4(aq)} + NO^-_{3(aq)}$	1.4863×10^1 ^e	-10.364	$\frac{17.56}{1}$		•
E12	$NH_{3(g)} + HNO_{3(g)} \leftrightarrow NH^+_{4(aq)} + NO^-_{3(aq)}$	2.587×10^{17}	64.02	11.44		•
E13	$HCl_{(g)} \leftrightarrow H^+_{(aq)} + Cl^-_{(aq)}$	1.971×10^6 ^f	30.20	19.91	•	•
E14	$NH_4Cl_{(s)} \leftrightarrow NH_{3(g)} + HCl_{(g)}$	1.086×10^{-16} ^g	-71.00	2.40	•	•
E15	$NH_4Cl_{(s)} \leftrightarrow NH^+_{4(aq)} + Cl^-_{(aq)}$	2.205×10^{1h}	-5.95	16.91	•	•
E16	$NH_{3(g)} + HCl_{(g)} \leftrightarrow NH^+_{4(aq)} + Cl^-_{(aq)}$	2.025×10^{17}	65.05	14.51		•
E17	$NaHSO_{4(s)} \leftrightarrow Na^+_{(aq)} + HSO^-_{4(aq)}$	2.413×10^4 ⁱ	0.79	14.75	•	•
E18	$(Na)_2SO_{4(s)} \leftrightarrow 2Na^+_{(aq)} + SO^{2-}_{4(aq)}$	4.799×10^{-1j}	0.98	39.75	•	•
E19	$NaNO_{3(s)} \leftrightarrow Na^+_{(aq)} + NO^-_{3(aq)}$	1.1977×10^{-1}	-8.22	16.01	•	•
E20	$NaCl_{(s)} \leftrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$	3.7661×10^1 ^k	-1.56	16.90	•	•
E21	$NaCl_{(s)} + HNO_{3(g)} \leftrightarrow NaNO_{3(s)} + HCl_{(g)}$	4.008×10^0	5.63	-2.19		•

The subscripts *g*, *aq*, *l*, and *s* in the equilibrium reactions represent concentrations of the species in the gas, the aqueous, the liquid, and the solid phases, respectively.

Equilibrium constants at the reference temperature, T_o , are expressed as :

$$K(T) = K_o \exp \left[-\frac{\Delta H^o(T_o)}{RT_o} \left(\frac{T_o}{T} - 1 \right) - \frac{\Delta C_p^o}{R} \left(1 + \ln \left(\frac{T_o}{T} \right) - \frac{T_o}{T} \right) \right], \text{ where } T_o = 298.15 \text{ K.}$$

^a The value of K for E6 is 1.383×10^0 in ISORROPIA, and 1.77×10^2 in EQUISOLV II, respectively.

^b The values of K, a, and b for E7 are 1.096×10^0 , -2.45, and -197.36 in EQUISOLV II, respectively.

^c The values of K, a, and b for E8 are 1.368×10^1 , -5.19, and 54.40 in EQUISOLV II, respectively.

^d The values of K, a, and b for E10 are 4.360×10^{-17} , -74.31, and 6.12 in EQUISOLV II, respectively.

^e The values of K, a, and b for E11 are 1.225×10^1 , -10.36, and 12.71 in EQUISOLV II, respectively.

^f The values of K, a, and b for E13 are 2.043×10^6 , 30.20, and 65.35 in EQUISOLV II, respectively.

^g The values of K, a, and b for E14 are 9.685×10^{-17} , -71.17, and 2.40 in EQUISOLV II, respectively.

^h The values of K, a, and b for E15 are 1.738×10^1 , -6.13, and 16.92 in EQUISOLV II, respectively.

ⁱ The values of K, a, and b for E17 are 3.861×10^2 , -1.91, and 14.75 in EQUISOLV II, respectively.

^j The values of K, a, and b for E18 are 4.7915×10^{-1} , 0.98, and 39.50 in EQUISOLV II, respectively.

^k The values of K, a, and b for E20 are 3.829×10^1 , -1.61, and 16.90 in EQUISOLV II, respectively.

There are several major differences between these two models. First is the treatment of the chemical equilibrium reactions and the equilibrium constants (Table 2). EQUISOLV II uses the thermodynamic system of NH_4^+ - Na^+ - H^+ - SO_4^{2-} - HSO_4^- - NO_3^- - Cl^- - OH^- - $\text{H}_2\text{O}(l)$ - Ca^{2+} - K^+ - Mg^{2+} - CO_3^{2-} - HCO_3^- and ISORROPIA does not include Ca^{2+} , K^+ , Mg^{2+} , CO_3^{2-} , HCO_3^- . For the purpose of comparison, Ca^{2+} , K^+ , Mg^{2+} , CO_3^{2-} , HCO_3^- was not taken into account in EQUISOLV II. EQUISOLV II explicitly includes the dissociation of $\text{H}_2\text{SO}_4(l)$ in the liquid phase (i.e., $\text{H}_2\text{SO}_4(l) \leftrightarrow \text{HSO}_4^- + \text{H}^+$) and has the option for including the gas-liquid, the solid-liquid, and/or the solid-gas equilibrium of $\text{NH}_4\text{NO}_3(s)$ and $\text{NH}_4\text{Cl}(s)$, such as E10, E11, E12, E14, E15, and E16 (Table 3). However, ISORROPIA does not treat the dissociation of $\text{H}_2\text{SO}_4(l)$ in the solid-liquid and/or the gas-liquid equilibrium of $\text{NH}_4\text{NO}_3(s)$ (E11 and E12) and $\text{NH}_4\text{Cl}(s)$ (E16). Another difference lies in the equilibrium reaction of $\text{NH}_3(g)$ with other species. ISORROPIA treats the dissociation of $\text{NH}_3(g)$ with H_2O in the aqueous phases ($\text{NH}_3(g) + \text{H}_2\text{O}(l) \leftrightarrow \text{NH}_4^+ + \text{OH}^-$) (E5), and the gas-liquid equilibrium $\text{NH}_3(aq)$ (E4). On the other hand, EQUISOLV II treats the reaction of $\text{NH}_3(g)$ with $\text{HNO}_3(g)$ in aqueous phases, such as $\text{NH}_3(g) + \text{HNO}_3(g) \leftrightarrow \text{NH}_4^+ + \text{NO}_3^-$ (E15), and the reaction of $\text{NH}_3(g)$ with $\text{HCl}(g)$ in aqueous phases, such as $\text{NH}_3(g) + \text{HCl}(g) \leftrightarrow \text{NH}_4^+ + \text{Cl}^-$ (E12). Moreover, these two models show slightly different equilibrium constant values from E7, E8, E10, E11, E13-15, E17, E18, and E20 (Table 3).

Second, the two models use different methods to calculate the binary activity coefficient for accurate equilibrium concentration calculations. ISORROPIA uses the Kusik-Meissner (K-M) method (1978) to calculate binary activity coefficients. On the other hand, EQUISOLV II uses the empirically-based Pitzer method requiring more parameters for estimating binary activity coefficient than the K-M method. However, for multicomponent calculations, both models use same the Bromley method recommended by Kim et al. (1993b).

Third, different numerical solution methods for chemical equilibrium were used in each model. ISORROPIA conducts the iterative bisectional Newton method (Kim et al., 1993a,b, 1995). It requires an initial guess of species concentrations. This method can fast converge mass and charge for most chemical systems except for some chemical systems with highly concentrated aerosol under low RH condition. It may cause negative concentrations due to extensive iterations. On the other hand, EQUISOLV II simultaneously uses both Mass Flux Iteration (MFI) and the Analytical Equilibrium Iteration (AEI) (Jacobson, 1997a,b, 1999). Both solutions conserve mass and charge, but do not require an initial guess of species concentrations, and can converge thousands of equilibrium equations simultaneously without negative concentration defect. This allows both solutions with relatively higher computational efficiency for 3-D air quality PM modeling.

Fourth, each model conducts the different DRH treatment for each aerosol salt and mixture salts (Table 2). Nenes et al. (1998) indicated the importance of DRH of each aerosol salt, and mixed aerosol salts, which treat the transition between the aqueous and solid aerosol phases. Tang and Munkelwitz (1993) suggested that the DRH of a mixed aerosol salt is lower than the minimum DRH of each aerosol salt, and the DRH of the mixture is a function of mixture composition. The minimum DRH is known as Mutual Deliquescence Relative Humidity (MDRH). At the MDRH, the aqueous phase is saturated with respect to all the salts, and it is the only RH in which an aqueous solution can coexist with solid phase aerosol salts. However, MDRH could lead to errors on a dry aerosol prediction when the RH lies around a MDRH. This potentially can affect the predicted role of aerosols, since the presence of water in PM composition affects the partitioning of volatile species and particle size. Simulation results between EQUISOLV II (excluding MDRH effect) and ISORROPIA (including MDRH effect) could show significant differences on atmospheric PM component prediction, especially around MDRH.

DEVELOPMENT AND EVALUATION OF AIR QUALITY MODELS

With the promulgation of the new $\text{PM}_{2.5}$ NAAQS, all designated non-attainment areas and surrounding regions may need to reduce emission of $\text{PM}_{2.5}$ and their precursors to attain the NAAQS. Since 1998, the U.S. EPA initiated the Particulate Matter Research Program to identify the relationships between PM and human health. This program also develops the predictive and evaluative tools to determine compliance of NAAQS standards and the needed mitigation strategies. The three-dimensional air quality models have been known as the most reliable probing tools to simu-

late the chemical and physical processes of atmospheric PM. The simulations, which can be conducted on a myriad of spatial and temporal scales, support both regulatory assessment as well as scientific studies conducted by research institutions. In order to characterize its performance and to improve capability of air quality models, an evaluation process is crucial to these air quality models if they are to be used for regulatory purpose. By 2004, EPA had accumulated the ambient PM_{2.5} mass and speciated chemical components data from its various monitoring sites from IMPROVE, CASTNet, STN, and AIRS. The data from the largely rural IMPROVE network and urban STN are used for the purpose of evaluation and development of their simulation performances.

There are many studies with regard to the use of 3-D air quality models to simulate atmospheric PM in the multi-scales. As an example of urban-scale models, there are the Urban Airshed Model with Aerosol (UAM-AERO) (Lurmann et al., 1997) and the Urban Airshed Model with the Aerosol Inorganics Model (UAM-AIM) (Sun and Wexler, 1998a,b). For the regional scale models, there is the EPA's third generation air quality model, EPA's Model-3/Community Multiscale Air Quality (CMAQ) (EPA, 2004) and the Regional Particulate Model (RPM) (Binkowski and Shankar, 1995). The U.S. EPA and the NOAA have recently teamed up to develop Air Quality Forecasting (AQF) capability and to implement a nationwide routine AQF program with an initial target on PM using a complex chemical transport model (U.S. EPA, 2004b). In 1998, the U.S. EPA released the initial version of its third generation air quality model, EPA's Model-3/CMAQ, to simulate the chemical and physical processes for multi-pollutants and multi-scales. In 2002, the aerosol-capable version of the CMAQ model was released to simulate the PM_{2.5} in the atmosphere. It is capable not only of characterizing the atmospheric PM size distributions and the processes of condensation (new particle formation) and coagulation (particle growth), but also simulating equilibrium aerosol species.

A thermodynamic equilibrium model, ISORROPIA, which is a computationally efficient and rigorous thermodynamic model has been incorporated into the CMAQ model to simulate the thermodynamics of inorganic PM (U.S. EPA, 2004b; Zhang et al., 2004). The results of these simulations showed that both CMAQ models performed well in predicting sulfate but under-predicted ammonia, nitrates, PM_{2.5}, PM₁₀, and organic carbon concentrations (EPA, 2004). The U.S. EPA released the refined 2003 CMAQ model which has increased the speciated aerosol evaluation. Zhang et al. (2004) incorporated a new aerosol model, the Model of Aerosol Dynamic, Reaction, Ionization, and Dissolution (MADRID) and the Carnegie Mellon University (CMU) bulk aqueous-phase chemistry into the CMAQ model to simulate ozone and PM, called CMAQ-MADRID. For simulating inorganic PM, a CMAQ-MADRID also conducted an ISORROPIA thermodynamic equilibrium model. Both models performed well for sulfate, but had under-prediction in secondary organic PM and nitrate concentrations. Both models stated the potential uncertainties that could result from uncertainties in the emission inventory. This underscores the need for improved inventory estimates for ammonia and carbon to evaluate and improve the model.

In implementing national standards such as the PM NAAQS, these models will focus on comparing model simulation results against data observed from STN and IMPROVE. These developments and improvements on air quality models will provide the spatial variability of ambient pollutants including precursors and atmospheric PM_{2.5} and that can be used to improve human exposure estimates and forecasting to attain the NAAQS for PM_{2.5}.

IMPORTANCE OF FINE PARTICULATE MATTER (PM_{2.5}) IN AGRICULTURAL AIR QUALITY

Atmospheric reduced nitrogen species ammonia (NH₃) and ammonium (NH₄⁺) have been considered environmental pollutants due to their role as sources of fixed nitrogen to soil and plants and the credential role in GTPC forming atmospheric PM_{2.5} (Baek and Aneja, 2004a,b; Baek et al., 2004; Roelle, 2003; U.S. EPA, 2004; Warneck, 2000). Ammonia is the most prevalent and abundant alkaline gas component in the atmosphere, and is fundamental in determining precipitation acidity (Baek, 2002; Warneck, 2000). On a global scale, domestic animals have been shown to be the largest source of NH₃ (Aneja et al., 2000; Battye et al., 1994; Heber et al., 2001; Koziel et al., 2004b; Pain et al., 1998; Van Der Hoek, 1998; Warneck, 2000; Battye, 2003). The major source of ammonia gas has been known as livestock, approximately 73% of total ammonia emission (~45 Tg-N/year) (U.S. EPA, 2003). In the U.S., approximately 44% of total ammonia nitrogen (NH₃-N)

emissions (~5.3 Tg-N/year) are contributed by cattle, approximately 27% by poultry, and approximately 10% by swine, in 1994 (Battye et al., 1994).

The spatial scale of NH_3 as a contributor to the total atmospheric nitrogen deposition is governed in part by the GTPC rate of NH_3 to NH_4^+ . Ammonia has a short lifetime, approximately 0.5 to 5 days or less (Aneja et al., 2001), due to the rapid GTPC of NH_3 to NH_4^+ and relatively high dry deposition velocity to the surfaces near its source. Ammonia, which is not deposited or scavenged by rain, will undergo conversion to particulate NH_4^+ . Ammonium, which has a longer lifetime, approximately 5 to 10 days, will be transported longer distances downwind from its sources.

Determining $\text{PM}_{2.5}$ source contributions is complicated due to the fact that often half or more of the $\text{PM}_{2.5}$ mass is composed of secondarily formed species through GTPC. In addition, lifetime of $\text{PM}_{2.5}$ could vary on the order of several days, thus transporting it up to approximately 1,500 miles away from its source to affect a region.

Thus, it is theoretically feasible that a large source of NH_3 (e.g., large poultry, dairy, beef cattle operation) can affect air quality in a remote area. Local and regional contributions to the urban areas could be estimated by accounting for the differences between the average concentrations of urban and nearby rural monitoring sites (U.S. EPA, 2004b). The regional emissions could come from sources such as power plants, natural sources and urban pollution. They can be transported hundreds of miles. The U.S. EPA (2003) analyzed the contribution of $\text{PM}_{2.5}$ chemical speciation in urban and rural areas. The rural sites were paired to a nearby matched urban site to determine how the contribution of an urban site may affect specific chemical components of $\text{PM}_{2.5}$ in urban downwind locations. In general, this approach assumes that the $\text{PM}_{2.5}$ at the rural sites are generally representative of the upwind regional concentrations and is not significantly influenced by nearby emissions. It is also assumed that the regional sources (including upwind urban areas) have the same impact on the rural monitors and the particular urban monitoring locations.

In a recent PM fine study (Baek and Aneja, 2004) conducted in agricultural (ammonia-rich) eastern North Carolina, sulfate is the most conspicuous constituent of all aerosols considered in the study, except for the marine aerosol, whose mass is dominated by sodium chloride. The origin of sulfate over the North American continent is primarily gas-to-particle conversion of SO_2 . The S content of the Earth's crust is too low for soils to provide a significant source of sulfate. Moreover, the mass concentration of PM fine in agricultural eastern North Carolina (i.e., ammonia-rich) was found to be similar to those in urban locations.

Figure 7 shows the local (urban) and regional (rural) contributions to major urban chemical $\text{PM}_{2.5}$ components, sulfates, ammonium, nitrate, total carbonaceous mass, and crustal species (U.S. EPA, 2004). Although there is uncertainty in the measured mass and in other measurement protocols, it is clear that the local contributions of all species are smaller than regional sources except for Fresno, CA where it had more local contributions than regional transport. Figure 7 illustrates that most species of $\text{PM}_{2.5}$ in the East are converted from regional emissions and are transported long distances from their sources. Ammonium concentrations were consistent with this observation because those areas are the largest swine operation states (the highest NH_3 emission sources) in the United States (Battye et al., 1994; U.S. EPA, 2001) (Figure 8). This result reflects on the importance of $\text{PM}_{2.5}$ from agricultural (rural) areas. It may be viewed as a first step in differentiating between regional and local sources that contribute to $\text{PM}_{2.5}$ mass. More work is needed for estimating the contributions of regional background associated with urban areas using spatial analysis and/or air quality models to identify and examine specific emission sources on finer time resolution to get to the next and more refined level of local/regional source contributions.

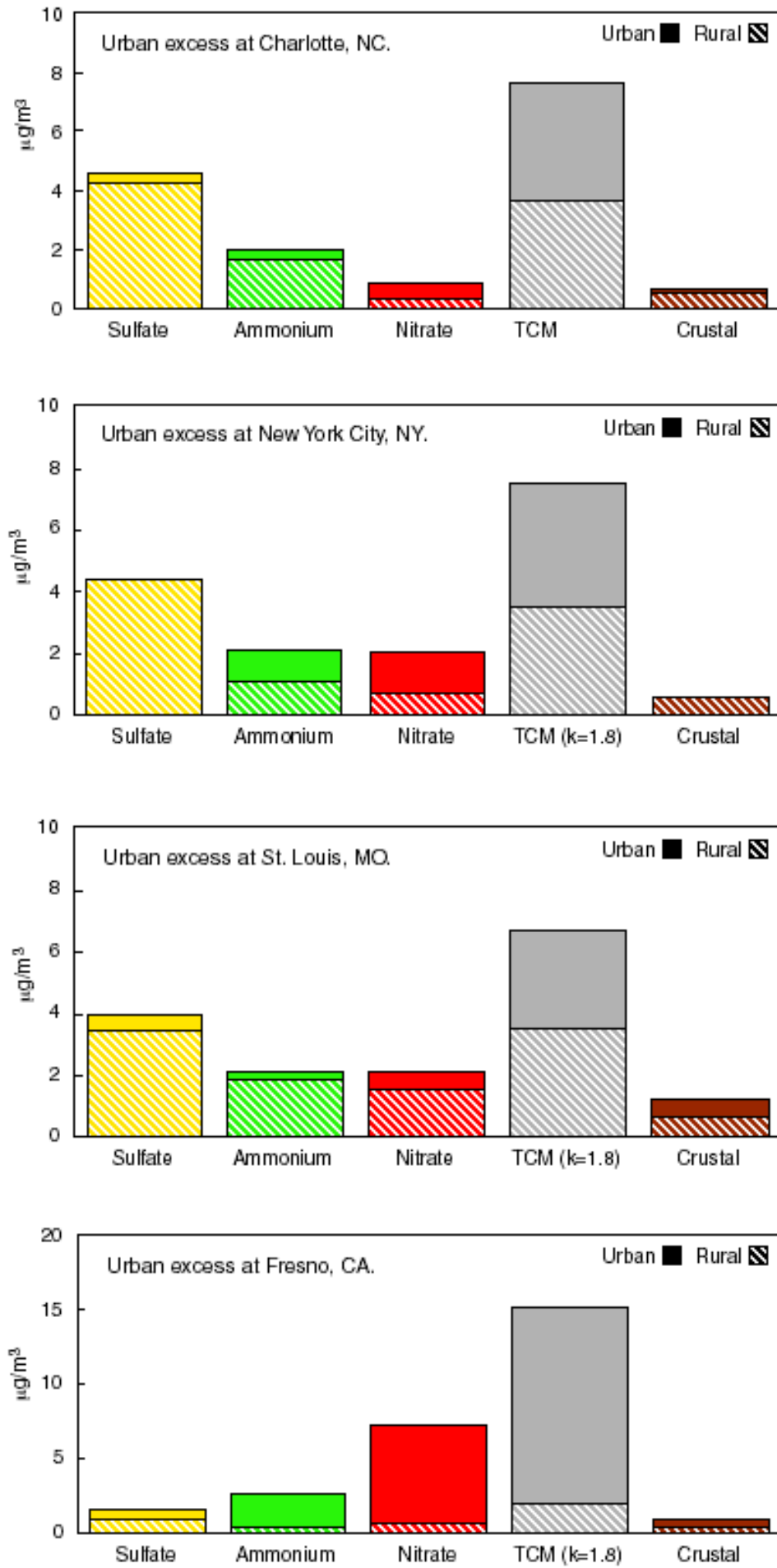


Figure 7. Comparison of atmospheric PM_{2.5} chemical components, such as inorganic species (ammonium, sulfate and nitrate), total carbonaceous mass (TCM=k*OC+EC), crustal species, between urban and rural area (U.S. EPA, 2003).

1999 Ammonia - Density

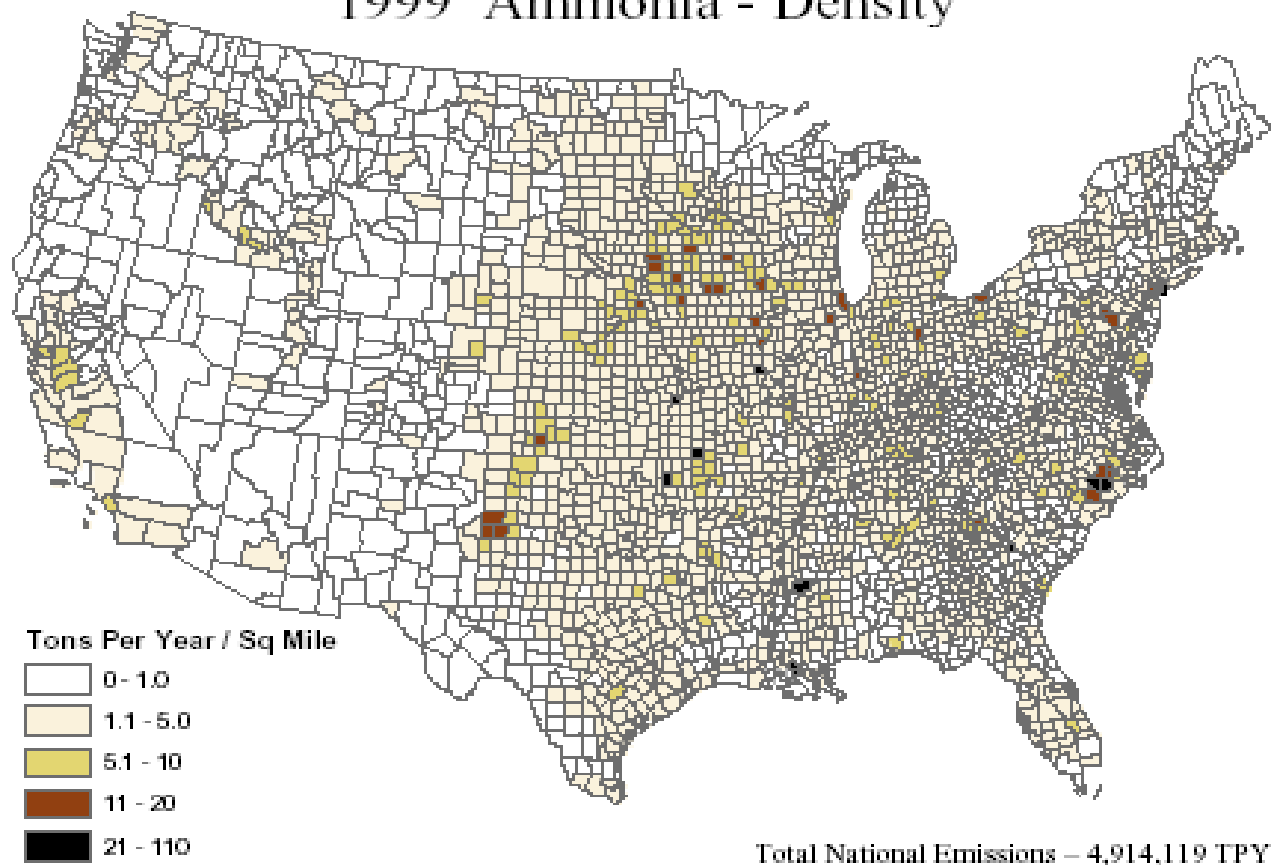


Figure 8. Map of ammonia emission distribution in U.S. in 1999. Shaded areas coincide with major dairy (CA), beef cattle (TX), swine (IA and NC), and poultry (e.g., TN, GA) producing areas.

CONCLUSIONS

Several major conclusions emerge from this white paper:

1. Ammonia and inorganic acid gases emitted from livestock and poultry operations and manure treatment, handling and application can affect air quality by formation of secondary particulate in the fine, $PM_{2.5}$ range. This range of PM is a regulated air pollutant.
2. In generation, the formation of secondary fine particulate matter is controlled by the availability of precursor gases in the atmosphere including SO_x , NO_x , chlorine, ammonia, water, and other species.
3. The process of gas-to-particle conversion of relatively short-lived gaseous ammonia to more persistent fine particulate can affect local and regional air quality far away from the sources.
4. Emissions of ammonia from livestock and poultry operations can potentially worsen the air quality in non-compliance areas.
5. Models for the formation of fine PM from substrates such as ammonia are available and have been used for air quality modeling on a local and regional scale. These models can be adapted or modified to include emissions of ammonia and acid gases from livestock and poultry operations.
6. More research is needed to improve the knowledge related to the role of ammonia gas-to-particle conversion. These include: (a) simultaneous field measurements of ammonia and acid gases at typical livestock and poultry sources, (b) development of emission factors for ammonia and acid gases, (c) incorporation of ammonia sources to local and regional air quality models, and (d) modeling the fate of ammonia and acid gases emissions from livestock and poultry operations.

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