# A preliminary review of gas-to-particle conversion monitoring and modelling efforts in the USA

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**Abstract:** Ammonia and inorganic acid gases emitted from livestock and poultry operations, manure treatment, handling and application can affect air quality by the formation of secondary fine particles. The process of gas-to-particle conversion (GTPC) of relatively short-lived gaseous ammonia to more persistent fine particles can affect local and regional air quality far away from the agricultural sources. This study focused on understanding the phenomenon and related problems of the GTPC process between ammonia, acid gases and fine particles in the atmosphere. We discuss the knowledge of PM measurement technologies with their uncertainties and introduce the most recent aerosol models available developed to simulate the equilibrium partitioning of inorganic compounds between the gas and aerosol phases. We discuss the development and evaluate progress on ambient PM research using 3D air quality models and demonstrate the importance of the GTPC process concerning the contribution of ammonia on fine PM formation in agricultural areas.

**Keywords:** aerosol; aerosol models; ammonia; fine particle (PM<sub>2.5</sub>); gas-to-particle conversion; GTPC; nitric acid; particulate matter (PM); sulphuric acid.

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#### 1 Introduction

Since the mid-1970s, atmospheric particulate matter (PM) has been considered a major air pollutant because of its adverse health effects, visibility impairment, radiative forcing effects on climate and aesthetic property damage (Gray et al., 1986; Heintzenberg, 1990; Meng et al., 1995; US EPA, 2004a,b,c; Warneck, 2000). In particular, evaluation of adverse human health effects has been one of main priorities in PM research programmes administered by the US EPA (US EPA, 2004c). By 1996, the epidemiological research associated with human health problems and air quality issues led to the promulgation of PM National Ambient Air Quality Standards (NAAQS) in 1997 that included new standards for  $PM_{2.5}$  (particulate matter with the size equal or smaller than 2.5  $\mu m$  in aerodynamic diameter) 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).

Since 1998, the US EPA has initiated a Particulate Matter Research Program to identify the relationships between PM and human health, to develop the predictive and evaluative tools to determine the compliance of NAAQS, and to develop needed

mitigation strategies (US EPA, 2004b,c). Modelling is the integral part of this programme. The 3D air quality models have been considered 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, regulatory assessment, as well as scientific studies conducted by academic and research institutions. In order to characterise its performance and to improve the capability of air quality models, the evaluation process is crucial to these air quality models if they are to be used for regulatory purposes (US EPA, 2004a). However, the main challenges remain, relating to the accuracy of PM measurements (both mass and species composition) and the aerial pollutant emission inventory, and to sufficient organic chemistry information for the simulation of semi-volatilce organic compounds (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.

Most 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  $\mu$ m). 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, the secondary PM formation rate could depend on numerous factors including: precursor concentrations, reactive gaseous concentrations, such as ozone, hydroxyl radical, nitrate radical, peroxy radicals and hydrogen peroxide, organic carbon, and atmospheric conditions, such as temperature and relative humidity. The common components of atmospheric particles, such as inorganic aerosol salts including sulphate, nitrate, and ammonium, insoluble materials, organics, crustal material, and water, reach the particulate phase by several different pathways (Figure 1). Although numerous chemical species have been identified in secondary aerosols, the most prevalent species are sulphate, 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 in determining the mass of atmospheric PM (Figure 2). Ammonia and acid gases in the atmosphere are known as major inorganic atmospheric aerosol precursor sources and control the composition of PM in the atmosphere through the GTPC process. Atmospheric reduced nitrogen ammonia  $(NH_{2})$  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 PM2.5 (Meng et al., 1995), thus resulting in longer resident time of ammonium  $(NH_{4}^{+})$  species in the atmosphere. Thus, the spatial scale of NH<sub>3</sub> and NH<sub>4</sub> 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 an air quality model 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 1 Routes of incorporation of chemical species into atmospheric PM (Meng et al., 1995)

Figure 2 Chemical coupling between the atmospheric gases, particles and droplet phases (Meng et al., 1995)



The objectives of this study are to develop a manuscript to explain diverse steps in understanding the phenomenon and related issues regarding the GTPC process between ammonia, acid gases and fine particles in the atmosphere. It provides information on most current technologies applied to a national monitoring network of PM<sub>2.5</sub> in the United States, and indicates the uncertainties involved in ambient particulate matter (PM) measurements. It presents a comparison between the most recent aerosol models available developed to simulate the equilibrium partitioning of inorganic compounds between the gas and aerosol phases, and discusses development and evaluation progress on ambient PM research using 3D air quality models. Finally, we discuss the importance of the GTPC process regarding the contribution of ammonia to fine PM formation in agricultural areas.

#### 2 Chemistry of atmospheric particulate matter

#### 2.1 Ammonia

Interest in atmospheric reduced nitrogen species ammonia  $(NH_3)$  and ammonium  $(NH_4)$ has increased in recent years and environmental pollutants considered due to their role as sources of fixed nitrogen to soil and plants and the credential role in GTPC forming atmospheric PM25 (Baek and Aneja, 2004a,b; Baek et al., 2004; Roelle, 2002; US EPA, 2004a,b; 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 NH<sub>3</sub> (Aneja et al., 2000; Battye et al., 1994, 2003; Heber et al., 2001; Koziel et al., 2004b; Pain et al., 1998; Van Der Hoek, 1998; Warneck, 2000). A major source of ammonia gas has been contributed by livestock – approximately 73% of total ammonia emissions ( $\approx$  45 Tg-N/year) (US EPA, 2003). In the US, approximately 44% of total ammonia nitrogen (NH<sub>3</sub>-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<sub>3</sub> as a contributor to the total atmospheric nitrogen deposition is governed in part by the GTPC rate of NH<sub>3</sub> to NH<sup>+</sup><sub>4</sub>. Ammonia has a short lifetime, approximately 0.5 to five days or less, (Aneja et al., 2000) due to the rapid GTPC of NH<sub>3</sub> to NH<sup>+</sup><sub>4</sub> 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 five to ten days, will be transported longer distances downwind from its sources. Determining PM2 5 source contributions is complicated due to the fact that often half or more of the  $PM_{25}$  mass is composed of secondarily formed species through GTPC.

#### 2.2 Acid gases (precursors)

Atmospheric acid gases (H2SO4, HNO3, and HCl) have been identified as major contributors to the acidification of soil, and precipitation, and are also associated with adverse health effects, mainly respiratory diseases (US EPA, 2004a,b; Warneck, 2000). Sulphuric acid  $(H_2SO_4)$ , and nitric acid  $(HNO_3)$ , the two major acidic gases in the atmosphere, come from the oxidation of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>, and NO<sub>x</sub> to HNO<sub>3</sub>. These acid gases are neutralised in the atmosphere by NH<sub>3</sub>, the principal gaseous alkaline specie. Thus, NH<sub>3</sub> not only plays a role in determining the acidification and eutrophication of ecosystems but also neutralises 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 odourous 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., 1995) (Figures 1 and 2).

Atmospheric gas phase oxidation of SO<sub>2</sub> takes place both by gas phase reaction and by aqueous phase reaction. The atmospheric oxidation of  $SO_2$  occurs largely by a sequence of reactions initiated by the reaction of OH<sup>•</sup> with SO<sub>2</sub>. H<sub>2</sub>SO<sub>4</sub> vapour rapidly transfers to the particulate phase by nucleation or condensation on the pre-existing particle surface. Gas-phase organic and  $NO_x$  chemistry is driven by the hydroxyl (OH<sup>•</sup>) 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.  $CH_3C(O)OONO_2$ . 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 the reaction of peroxylacetyl radicals  $CH_3C(O)OO^-$  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 the 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 NH4NO3 formations. Aqueous phase  $HNO_3$  formation of  $NO_2$  contributes a major part to the formation of  $HNO_3(aq)$  compared to aqueous phase oxidation reaction, because  $HNO_3$  exists as gas phases in the atmosphere when the RH is less than 98% (Figure 2).

#### 2.3 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, aluminium, silicon, magnesium and iron, are generally found in the coarse particles. Secondary PM is mainly formed through two major particle formation processes in the atmosphere. One process is the nucleation process by low vapour pressure gases:

- directly emitted
- formed by chemical reactions in the atmosphere.

The second process is the condensation of low vapour pressure gases on the surface of existing particles (Figure 2). Fine particles ( $PM_{2.5}$ ) include both the accumulation (0.1  $\mu m \le D_p \le 1 \sim 3 \mu m$ ) and nuclei ( $\le 0.1 \mu m$ ) modes (US EPA, 2004a). An aerosol may be defined as a suspended solid and/or liquid phase particles in the atmosphere including all vapour or gas phase components.

Nucleation processes in the atmosphere may involve the organic compound,  $NH_3$ , water and sulphuric acid ( $H_2SO_4$ ) generated by the homogenous heteromolecular nucleation of  $H_2SO_4$  vapour from the gas phase oxidation of  $SO_2^{\bullet}$  and  $OH^{\bullet}$  radicals in the atmosphere. As  $H_2SO_4$  is formed, it can either nucleate to form new particles or it can condense on existing accumulation particles. Sulphuric acid forms atmospheric aerosol salts, such as ammonium bisulfate ( $NH_4HSO_4$ ) and ammonium sulfate ( $(NH_4)_2SO_4$ ) with  $NH_3$  (Figures 1 and 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.

#### 2.4 Formation of secondary PM

Most secondary PM undergoes thermodynamic equilibrium chemical reactions called the GTPC process. The GTPC process tends to reside in the accumulation mode PM range (typically 0.1 to 2.5  $\mu$ m). 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, the secondary PM formation rate could depend on numerous factors including:

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

The common components of atmospheric particles, such as inorganic aerosol salts including sulphate, 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 sulphate, nitrate, ammonium and water. Heintzenberg (1990) and Gray et al. (1986) indicated that inorganic aerosol salts comprise 25–65% of the dry total of fine aerosol mass and, together with water, make up 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 in determining the mass of atmospheric PM. Ammonia and acid gases in the atmosphere are known as major inorganic atmospheric aerosol precursor sources and control the composition of PM in the atmosphere through the GTPC process.

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<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, and HCl) and forms atmospheric ammonium aerosol salts, such as ammonium sulphate ( $[NH_4]_2SO_4$ ), ammonium bisulphate ( $NH_4HSO_4$ ), 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 vapour in the atmosphere (Figure 2). There are two different types of chemical reactions with regard to the fine particle formation in the atmosphere, i.e. heterogeneous and homogeneous reactions, respectively. Homogeneous chemical reaction involves forming a condensable species, such as the oxidation of sulphur dioxide to sulphuric acid. Condensable species can either nucleate to form a new particle (nucleation), or can condense onto the surface of an existing particle (condensation) (US EPA, 2004a; Warneck, 2000). 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<sub>3</sub>) (s) particle to produce calcium nitrate CaNO<sub>3</sub> (s), is one type of heterogeneous reaction. Aqueous-phase chemical reactions, such as the oxidation of the dissolved sulphur dioxide (SO<sub>2</sub>) (g) to sulphate (SO<sup> $\frac{1}{4}$ </sup>) (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 particles in the atmosphere mainly depends on the existence of sulphuric acid (H<sub>3</sub>SO<sub>4</sub>) formed from the atmospheric oxidation of sulphur dioxide. Atmospheric nitrate is also essentially secondary due to oxides of nitrogen reacting in the atmosphere to form nitric acid vapour, which in turn, may react with ammonia gas to form particulate ammonium nitrate. However, when gas phase SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>/acidic particles coexist with NH<sub>4</sub>NO<sub>3</sub> 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 depend strongly on the concentrations of their gaseous species, such as ammonia and acidic gases, and the interactions between these precursors and preexisting particles. However, relatively small amounts of particulate sulphate, nitrate and chloride species in coarse particles originate from the SO<sub>2</sub>, HNO<sub>3</sub> 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). The low vapour pressure of sulphuric 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 vapour in the atmosphere, sulphuric 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  $SO^{-2}_{4}$  (Pacyna and Benson, 1996).

In general, ammonia, nitric acid and sulphuric acid are highly soluble inorganic species in the atmosphere and they are efficiently removed by wet deposition or rain out, and/or by a neutralisation process. An increase of RH results in an increase in the growth in the liquid water content of PM, thereby increasing the absorption capacity of aerosol with regard to gaseous sulphuric and nitric acids. Ammonium bisulphate and ammonium sulphate 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, sulphuric acids, nitric acids, and water vapour in the atmosphere (Cadle et al., 1982; Lee et al., 1993). The gas-to-particle conversion process can determine the resident time (lifetime) of ammonia and ammonium in the atmosphere. The spatial scale of NH<sub>3</sub> 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<sub>3</sub> to NH<sup>+</sup><sub>4</sub> and relatively high dry deposition velocity to the surfaces near its source. However, ammonium primarily formed by the GTPC process has a longer lifetime, approximately five to ten 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<sub>2</sub> emissions from agriculture.

Table 1 lists most of the identified equilibrium chemical reactions known to be occurring in the atmosphere. These reactions are currently used in several thermodynamic equilibrium models, such as EQUIL and KEQUIL (Bassett and Seinfeld, 1983; 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.

Table 1	List of equilibrium	chemical reactions	in the atmosphere	(Zhang et al., 2000)
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	Equilibrium chemical reactions		Equilibrium chemical reactions
1	$H_2O_{(l)} \leftrightarrow H^+_{(aq)} + OH^{(aq)}$	27	$\mathrm{KCl}_{(s)} \leftrightarrow \mathrm{K}^{+}_{(aq)} + \mathrm{Cl}^{-}_{(aq)}$
2	$H_2SO_{4(aq)} \leftrightarrow H^+_{(aq)} + HSO^{4(aq)}$	28	$K_2SO_{4(s)} \leftrightarrow 2K^+_{(aq)} + SO2^{-4}_{(aq)}$
3	$HSO_{4(aq)} \leftrightarrow H_{(aq)} + SO^{2}_{4(aq)}$	29	$\text{KHSO}_{4(s)} \leftrightarrow \text{K}^{+}_{(aq)} + \text{HSO}^{-}_{4(aq)}$
4	$NH_{3(g)} \leftrightarrow NH_{3(aq)}$	30	$\text{KNO}_{3(S)} \leftrightarrow \text{K}^+_{(aq)} + \text{NO}^{3(aq)}$
5	$NH_{3(aq)}+H_2O_{(aq)}\leftrightarrow NH_{4(aq)}+OH_{(aq)}$	31	$CaCl_{2(s)} \leftrightarrow Ca^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$
6	$\mathrm{NH}_{3(g)}^{+}\mathrm{H}^{+}_{(aq)} \leftrightarrow \mathrm{NH}^{+}_{4(aq)}$	32	$CaSO_{4} \cdot 2H_{2}O_{(s)} \cdot Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)} + 2H_{2}O_{(l)}$
7	$\mathrm{NHO}_{3(g)} \leftrightarrow \mathrm{H}^{+}_{(aq)} + \mathrm{NO}^{-}_{3(aq)}$	33	$Ca(NO_3)2_{(s)} \leftrightarrow Ca^{2+}_{(aq)} + 2NO^{-}_{3(aq)}$
8	$\operatorname{HCl}_{(g)} \leftrightarrow \operatorname{H}^{+}_{(aq)} + \operatorname{Cl}^{-}_{(aq)}$	34	$MgCl_{2(s)} \leftrightarrow Mg^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$
9	$NaCl_{(s)} \leftrightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$	35	$MgSO_{4(s)} \leftrightarrow MG^{2+}_{(aq)} + SO^{2-}_{4(aq)}$
10	$NH_4SO_{4(s)} \leftrightarrow NH_{4(aq)}^+HSO_{4(aq)}^-$	36	$Mg(NO_3)_{2(s)} \leftrightarrow Mg^{2+}_{(aq)} + 2NO^{-}_{3(aq)}$
11	$(NH_4)_2SO_{4(s)} \leftrightarrow 2NH_{4(aq)}^+ SO_{4(aq)}^-$	37	$CO_{2(g)} \leftrightarrow CO_{2(aq)}$
12	$Na_2SO_{4(s)} \leftrightarrow 2Na_{4(aq)}^+ + SO^{2}_{4(aq)}$	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	$HCO_{3(aq)} \leftrightarrow CO^{2}_{3(aq)} + H^{+}_{(aq)}$
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	$Na_2CO_{3(s)} \leftrightarrow 2Na^+_{(aq)} + CO^2_{3(aq)}$
16	$NH_{3(g)}+HCl_{(g)} \leftrightarrow NH^{+}_{4(aq)}+Cl^{-}_{(aq)}$	42	$NaHCO_{3(s)} \leftrightarrow Na^{+}_{(aq)} + HCO^{-}_{2(aq)}$
17	$NH_4Cl_{(s)} \leftrightarrow NH_{3(g)} + HCl_{(g)}$	43	$K_2CO_{3(s)} \leftrightarrow 2K^+_{(aq)} + CO^{2-}_{3(aq)}$
18	$NH_4Cl_{(s)} \leftrightarrow NH^+_{4(aq)} + Cl^{(aq)}$	44	$\text{KHCO}_{3(s)} \leftrightarrow \text{K}^+_{(aq)} + \text{HCO}^{2(aq)}$
19	$NaCl_{(s)}+HNO_{3(g)} \leftrightarrow NaNO_{3(s)}+HCl_{(g)}$	45	$CaCO_{3(s)} \leftrightarrow Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$
20	$NaNO_{3(s)} \leftrightarrow Na^{+}_{(aq)} + NO^{-}_{3(aq)}$	46	$MgCO_{3(s)} \leftrightarrow Mg^{2+}_{(aq)} + CO^{2-}_{3(aq)}$
21	$NaHSO_{4(s)} \leftrightarrow Na^{+}_{(aq)} + HSO^{-}_{4(aq)}$	47	$NH_2COONH_{4(s)} \leftrightarrow NH_2CO^{-}_{2(aq)} + H^{+}_{(aq)}$
22	$(\mathrm{NH}_{4})_{3}\mathrm{H}(\mathrm{SO}_{4})_{2(s)} \leftrightarrow 3\mathrm{NH}^{+}_{4(aq)}$ + $\mathrm{HSO}^{-}_{4(aq)} + \mathrm{SO}^{2-}_{4(aq)}$	48	$Na_{2}SO_{4}(NH_{4})_{2}SO_{4}\cdot 4H_{2(S)} \leftrightarrow 2Na^{+}_{(aq)} + 2SO^{2-}_{4(aq)} + H^{+}_{4(aq)} + H^{-}_{2}O_{(l)}$
23	$Na_{3}H(SO_{4})_{2(s)} \leftrightarrow 3Na^{+}_{(aq)} + HSO^{-}_{4(aq)}$ $+SO^{2-}_{4(aq)} + 2NO^{-}_{3(aq)}$	49	$NaH_{3}(SO_{4})_{2} \cdot H_{2}O_{(s)} \leftrightarrow Na^{+}_{(aq)} + 2HSO^{2-}_{4(aq)} + H_{2}O_{(l)}$
24	$(\mathrm{NH}_{4})_{2}\mathrm{SO}_{4}\cdot\mathrm{2NH}_{4}\mathrm{NO}_{3(g)}\leftrightarrow 4\mathrm{NH}^{+}_{4(aq)} \\ +\mathrm{SO}^{2-}_{4(aq)}+2\mathrm{NO}^{-}_{3(aq)}$	50	$\begin{array}{l} \text{NaHSO}_4 \cdot \text{H}_2\text{O}_{(g)} \leftrightarrow \text{Na}^+_{(aq)} + \text{HSO}^2_{{4(aq)}} \\ + \text{H}_2\text{O}_{(l)} \end{array}$
25	$(\mathrm{NH}_{4})_{2}\mathrm{SO}_{4}\cdot\mathrm{3NH}_{4}\mathrm{NO}_{3(g)}\leftrightarrow\mathrm{5NH}^{+}_{4(aq)}$ $+\mathrm{SO}^{2}_{-4(aq)}+2\mathrm{NO}^{-}_{3(aq)}$	51	$\begin{array}{l} \mathrm{Na_2SO_4} \cdot 10\mathrm{H_2O}_{(g)} \leftrightarrow 2\mathrm{Na^+}_{(aq)} + \mathrm{SO^2}_{-4(aq)} \\ + 10\mathrm{H_2O}_{(l)} \end{array}$
26	$\begin{array}{l} \mathrm{NH}_{4}\mathrm{HSO}_{4}\mathrm{\cdot}\mathrm{NH}_{4}\mathrm{NO}_{3(g)} {\leftrightarrow} 2\mathrm{NH}^{+}_{4(aq)} \\ +\mathrm{HSO}^{-}_{4(aq)} +\mathrm{NO}^{-}_{3(aq)} \end{array}$	52	$\begin{array}{l} \mathrm{Na_2SO_4\cdot NaNO_3\cdot H_2O_{(5)}} \leftrightarrow 3\mathrm{Na^+}_{(aq)} \\ +\mathrm{SO^2}_{{4(aq)}} +\mathrm{NO^-}_{3(aq)} +\mathrm{H_2O_{(l)}} \end{array}$

Note: 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.

#### **3** PM measurements

Since the US EPA promulgated new NAAQS for  $PM_{2.5}$  in 1997, it has initiated a comprehensive national research programme with the coordinated efforts of intramural and US EPA-funded extramural investigators, partners and other federal organisations.

The goal of this PM research programme is to identify the relationships between PM and human health, and develop the predictive and evaluative tools to determine compliance of the NAAQS standard and the required 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 application. We also discuss new techniques that attempt to improve the problems and uncertainties of current techniques.

The US EPA's FRMs for PM<sub>10</sub> and PM<sub>2.5</sub> determine mass gravimetrically. A number of gravimetrical samplers have been designed as a PM<sub>10</sub> reference sampler. The Tapered Element Oscillating Microbalance (TEOM) is one of most widely used samplers due to its continuous real-time measurement capability. The PM<sub>2.5</sub> FRM sampler consists of a PM<sub>10</sub> inlet, a PM<sub>2.5</sub> impactor and a 47-mm PTFE (polytetrafluoroethylene) filter with a 99% collection efficiency and 24-hour sampling duration. In particular, for FRM PM25 mass measurement, FRM specifies the sampler design and the strict sample handling and analysis. The sample filters are equilibrated for 24 hours at a temperature between 20 and 23°C and at an RH between 30 and 40% to reduce all particle-bound water (PBW) and to stabilise the filter plus sample weight. As a part of National Monitoring Network (NMN) programme, the PM25 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<sub>10</sub> and  $PM_{25}$  concentrations and chemical speciation monitoring across the country for the purpose of compliance with air quality standards and trends.



Figure 3 Map of STN and IMPROVE monitoring network in US in 2003 (US EPA, 2003)

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 US The  $PM_{2.5}$  STN is a network of the mass-based FRM network and 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 programme, the STN quantifies mass concentrations and  $PM_{2.5}$  constituents, including numerous trace elements, ions (sulphate, nitrate, sodium, potassium and 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 exactly the same aerosol monitoring protocol.

#### 3.1 Uncertainties in PM measurement

The US FRM for  $PM_{2.5}$  and  $PM_{10}$  provide relatively precise (± 10%) methods for determining the gravimetric mass concentrations (US EPA, 2004a). However, there are several uncertainties related to the mass concentration and composition of PM. The general filtration-based mass measurements for RFM increase significant evaporative losses of particulate nitrate and a variety of SVOCs that could exist in the atmosphere in a dynamic equilibrium state between the gas phase and the aerosol phase (Babich et al., 2000; Kim et al., 1995) (Figure 4). Ammonium nitrate, SVOCs, and PBW are the major uncertainties and they pose challenges in atmospheric PM measurements. Those uncertainties are strongly dependent on ambient temperature, RH and particle composition (McInnes et al., 1996; Ohta and Okita, 1990). Loss of ammonium nitrate and SVOCs could have a positive or a negative effect on atmospheric PM mass concentrations. A positive sampling effect could occur when ambient RH is high. It leads to a higher PBW of PM and absorbs the gas-phase components on the surface of PM. The effect on the accuracy of atmospheric PM measurements from these volatilisation losses is more significant for PM<sub>2.5</sub> than for PM<sub>10</sub> because most of the nitrate and a portion of SVOC, is formed by equilibrium chemical reactions in the atmosphere. Herring and Cass (1999) also found that the amount of nitrate on a PTFE filter was 28% lower on the total PM2.5 mass concentration than that on a nylon filter due to the loss of ammonium nitrate ( $NH_4NO_3$ ) (Babich et al., 2000; Herring and Cass, 1999; US EPA, 2004a; Zhang and McMurray, 1992).



Figure 4 Schematic showing major non-volatile and semi-volatile organic components of PM<sub>2.5</sub> (US EPA, 2004a)

Semivolatile components subject to evaporation during or after sampling

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 (NH<sub>4</sub>NO<sub>3</sub>) or semi-volatile organic PM

### 3.2 Sampling of ammonia, acid gases, and fine particle $(PM_{2,5})$

Sampling and subsequent quantification of ammonia, acid gases and fine particles can be achieved simultaneously with denuder sampling systems and ion chromatography-based analysers. The denuder system consists of three major parts: a cyclone separator removes alkaline coarse particles (defined as greater than 2.5 µm aerodynamic diameter), and thereby prevents the neutralisation of acid gases, two diffusion denuders in series, coated with sodium carbonate and citric acid for the collection of NH<sub>3</sub> and acid gases, respectively. Finally, a filter pack containing a PTFE and a nylon filter for the 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 the filter-based PM measurement method and could be applied to the measurement 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 still 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 volatilisation (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 the accurate measurement of nitrate and SVOC components in atmospheric  $PM_{2.5}$  (Gundel and Lane, 1999; Herring and Cass, 1999; Tsai and Huang, 1995; Zhang and McMurray, 1992). Current continuous

atmospheric PM mass measurement is conducted by a TEOM monitor, which is normally operated at 50°C in order to remove all PBW in atmospheric  $PM_{2.5}$  and  $PM_{10}$ . It causes the volatilisation (loss) of ammonium nitrate and SVOC due to a 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 (1999) compared the mass concentrations from a TEOM monitor, average of 24-hour RFM PM25 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 PM25 and RAMS. Koutrakis et al. (1996) developed a Continuous Ambient Mass Monitor (CAMM) by monitoring the increase in the pressure drop on the membrane filter used for particle sampling. The beta-gauge monitoring technique has been used effectively to measure the mass of equilibrated PM collected on PTFE filter with time intervals in 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 5 shows all continuous PM<sub>2.5</sub> mass monitoring locations for RAMS (TEOM), CAMM, Beta-gauge monitoring techniques in the United States in 2001.



Figure 5 All PM<sub>2.5</sub> continuous monitoring sites by type of monitor in 2001 (US EPA, 2003)

Source: http://www.epa.gov/ttn/amtic/files/ambient/monitorstrat/maps2.pdf

## 4 Thermodynamic equilibrium aerosol models

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, 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)
- EQUISOLV II (Jacobson, 1997a,b, 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 a thermodynamic equilibrium state.

Bassett and Seinfeld (1983) developed EQUIL in order to calculate the inorganic aerosol composition in a system of  $NH_4^+SO^2_4-NO_3^-H_2O$ . The same authors introduced the upgraded version (KEQUIL) later (1984), to account for the dependence of the partial vapour pressure on the sphericity of the particle surface. The sphericity of the 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 vapour pressure above a curved surface compared to the vapour pressure above a flat surface.

MARS-A (Saxena et al., 1986) was developed by US 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 3D air quality model. However, there are two major deficiencies of the MARS-A model:

- its use of thermodynamic properties, such as equilibrium constant, activity coefficients, at only 298.15 K
- its failure to consider the major components in aerosol composition, such as sodium (Na<sup>+</sup>) and chloride (Cl<sup>-</sup>) species.

Zhang et al., (2000) indicated that these three models, EQUIL, KEQUIL, and MARS-A, could not be applicable for near coast area modelling studies due to lack of  $Na^+$  and  $Cl^-$  in the system.

SEQUILIB model (Pilinis and Seinfeld, 1987) incorporated not only the Na<sup>+</sup> and Cl<sup>-</sup> 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 a similar algorithm to SEQUILIB, with an updated thermodynamic constant 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 chose the different approach to simulate the partitioning of chemical species between gas, aqueous and solid phases. AIM2 is a molar-fraction-based model, called the Pitzer method (Pitzer, 1991) that uses the 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 result in very comparable results under most particulate matter composition except for high gas concentrations with very low relative humidity (RH) conditions which other models could simulate unrealistic concentrations (Clegg et al., 1998).

An updated version of EQUISOLV, EQUISOLV II under H<sup>+</sup>-NH<sup>+</sup><sub>4</sub>-Na<sup>+</sup>-SO<sup>2</sup><sub>4</sub>-NO<sup>-</sup><sub>3</sub> Cl<sup>-</sup>-H<sub>2</sub>O-Ca<sup>2+</sup>-K<sup>+</sup>-Mg<sup>2+</sup> 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 greater than the Mass Flux Iteration (MFI), which is used to iterate each equilibrium equation to converge species concentrations (Jacobson, 1999; Zhang et al., 2000). EQUISOLV II uses, simultaneously, both AEI and MFI for the partitioning of chemical species between gas, aqueous and solid phases to improve computational efficiency over large numbers of spatial grid cells, and particle size bins for 3D air quality modelling.

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. A more detailed comparison between EQUISOLV II and ISORROPIA will be discussed below.

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 3D particulate matter modelling 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 modelling study in the coastal area and the urban/regional-scale modelling 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 3D eulerian atmospheric chemical transport models with many spatial grid cells to use the aerosol equilibrium models including particle size bins. Three-dimensional models capable of tracking aerosol dynamics, such as the GTPC process, particle formation and size distribution, have been combined to simulate the behaviour of organic and inorganic aerosols (US EPA, 2004a,b; Zhang et al., 2004). Large-scale 3D eulerian atmospheric chemical models have been combined with SEQUILIB (Lurmann et al., 1997; Pilinis and Seinfeld, 1987), MARS-A (Binkowski and Shankar, 1995), EQUISOLV (Jacobson, 1997a,b, 1999; Jacobson et al., 1996), SCAPE2 (Meng et al., 1995), and ISORROPIA (Nenes et al., 1998). Although limited comparisons among equilibrium models have been conducted (Kim et al., 1993b; Welxer and Seinfeld, 1991), no detailed evaluation based on observations of aerosol behaviour 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 behaviour prediction in atmosphere.

## 4.1 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 (Baek, 2002). Tables 2 and 3 summarise the major characteristics and equilibrium chemical treatments from both models. Both models incorporated the ZSR method (Robinson and Stokes, 1964; Zdanovskii, 1948), which considers the hysteresis effect simulating the metastable water presence below the deliquescence relative humidity (DRH) of an aerosol salt for estimating equilibrium water content within the PM composition. The temperature dependence of equilibrium constants and DRH is also considered in both models.

Characteristics		ISORROPIA	EQUISOLV II	
System		NH <sub>4</sub> -Na-SO <sub>4</sub> -NO <sub>3</sub> -Cl	NH <sub>4</sub> -Na-SO <sub>4</sub> -NO <sub>3</sub> -Cl-Ca-Mg K-CO <sub>3</sub>	
Chemical species phases	Gas	NH <sub>3</sub> , HNO <sub>3</sub> , HCl, H <sub>2</sub> O	NH <sub>3</sub> , HNO <sub>3</sub> , HCl, CO <sub>2</sub> , H <sub>2</sub> O	
	Liquid	$\begin{array}{l} {\rm NH^{+}_{4},Na^{+},H^{+},SO^{2}_{{4}},} \\ {\rm HSO^{-}_{4},NO^{-}_{3},OH^{-},H^{}_{2}O(l)} \end{array}$	ISORROPIA + Ca <sup>2+</sup> , K <sup>+</sup> , Mg <sup>2+</sup> , CO <sup>2-</sup> <sub>3</sub> , HCO <sub>3</sub> <sup>-</sup>	
	Solid	NH <sub>4</sub> HSO <sub>4</sub> , (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , (NH <sub>4</sub> ) <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> , NH <sub>4</sub> NO <sub>3</sub> , NH <sub>4</sub> Cl, NaCl, NaNO <sub>3</sub> , NaHSO <sub>4</sub> , Na <sub>2</sub> SO <sub>4</sub>	$\begin{split} & \text{ISORROPIA} + \text{KCl}, \text{K}_2\text{SO}_4, \\ & \text{KHSO}_4, \text{KNO}_3, \text{CaCl}_2, \text{CaSO}_4, \\ & \text{Ca(NO}_3)_2, \text{MgCl}_2, \text{MgSO}_4, \\ & \text{Mg(NO}_3)_2, \text{Na}_2\text{CO}_3, \text{NaHCO}_3, \\ & \text{K}_2\text{CO}_3, \text{KHCO}_3, \text{CaCO}_3, \text{MgCO}_3 \end{split}$	
Binary activity method		K-M method	Pitzer method	
Multi-component activity		Bromley method	Bromley method	
coefficient metho	d			
Water activity		ZSR	ZSR	
Kelvin effect		No	Yes	
Solution method		Iterative Bisection	Analytical Equilibrium Iteration (AEI) + Mass Flux Iteration (MFI)	
Reference		Nenes et al. (1998)	Jacobson (1999)	

 Table 2
 Major characteristics of ISORROPIA and EQUISOLV II

	Equilibrium chemical reactions	Constants	а	b $R$	SORROPIA	EQUISOLV II
E1	$\mathrm{H_2O}_{(aq)} \!$	$1.010 \times 10^{-14}$	- 22.52	26.92	•	•
E2	$H_2SO_{4(aq)} \leftrightarrow H^+_{(aq)} + HSO^{4(aq)}$	$1.0  imes 10^3$	Ι	Ι		•
E3	$HSO^{-4(aq)} \leftrightarrow H^{+}(aq) + SO^{2} - 4(aq)$	$1.015  imes 10^{2-}$	8.85	25.14	•	•
E4	$NH_{3(g)} \leftrightarrow NH_{3(aq)}$	5.764  imes 101	13.79	-5.393	•	
E5	$\mathrm{NH}_{3(aq)} + \mathrm{H}_{2}\mathrm{O}_{(aq)} \leftrightarrow \mathrm{NH}^{+}_{4(aq)} + \mathrm{OH}^{-}_{(aq)}$	$1.805  imes 10^{-5}$	-1.50	26.92	•	
E6	$\mathrm{NH}_4\mathrm{HSO}_{4(s)} \leftrightarrow \mathrm{NH}^+_{4(aq)} + \mathrm{HSO}^{(aq)}$	$2.55  imes 10^{2 a}$	-2.87	15.83	•	•
Ε7	$(\mathrm{NH}_4)_2\mathrm{SO}_{4(s)}\leftrightarrow 2\mathrm{NH}^+_{4(aq)}+\mathrm{SO}^2_{-4(aq)}$	$1.817 \times 10^{0  b}$	-2.65	38.57	•	•
E8	$(NH_4)_3H(SO_4)_{2(s)} \leftrightarrow 3NH^+_{4(aq)} + HSO^{4(aq)} + SO^2_{4(aq)}$	$4.0026 \times 10^{1} \mathrm{c}$	-5.19	54.40	•	•
E9	$HNO_{3(g)} \leftrightarrow H^+_{(aq)} + NO^{3(aq)}$	$2.511 \times 10^{6}$	29.17	16.83	•	•
E10	$\mathrm{NH}_4\mathrm{NO}_{3(s)} \leftrightarrow \mathrm{NH}_{3(g)} + \mathrm{HNO}_{3(g)}$	$5.746 \times 10^{-17} \mathrm{d}$	- 74.38	6.12	•	•
E11	$\mathrm{NH}_4\mathrm{NO}_{3(s)} \leftrightarrow \mathrm{NH}^+_{4(aq)} + \mathrm{NO}^{3(aq)}$	$1.4863 \times 10^{1}  \mathrm{e}$	-10.364	17.561		•
E12	$\mathrm{NH}_{3(g)} + \mathrm{NHO}_{3(g)} \leftrightarrow \mathrm{NH}^+_{4(aq)} + \mathrm{NO}^{3(aq)}$	$2.587  imes 10^{17}$	64.02	11.44		•
E13	$HCI_{(g)} \leftrightarrow H+_{(aq)}+CI^{-}_{(aq)}$	$1.971 \times 10^{6}$ f	30.20	19.91	•	•
E14	$\mathrm{NH}_4\mathrm{Cl}_{(\mathrm{s})} \leftrightarrow \mathrm{NH3}(g) + \mathrm{HCl}_{(g)}$	$1.086 \times 10^{-16}$ g	-71.00	2.40	•	•
E15	$\mathrm{NH}_4\mathrm{Cl}_{(s)} \leftrightarrow \mathrm{NH}^+_{4(aq)} + \mathrm{Cl}^{(aq)}$	$2.205 \times 10^{1 \ h}$	-5.95	16.91	•	•
E16	$\mathrm{NH}_{3(g)} + \mathrm{HCl}_{(g)} \leftrightarrow \mathrm{NH}^+_{4(aq)} + \mathrm{Cl}^{(aq)}$	$2.025  imes 10^{17}$	65.05	14.51		•
E17	NaHSO <sub>4(s)</sub> $\leftrightarrow$ Na <sup>+</sup> <sub>(aq)</sub> +HSO <sup>-</sup> <sub>4(aq)</sub>	$2.413 \times 10^{4  i}$	0.79	14.75	•	•
E18	$(\mathrm{Na})_2\mathrm{SO}_{4(s)} \leftrightarrow 2\mathrm{Na}^+_{(aq)} + \mathrm{SO}^{2}_{-4(aq)}$	$4.799 \times 10^{-1}$ j	0.98	39.75	•	•

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

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Jinnucu	,		
EQUISOLVII	• • •	ae liquid, and	
ISORROPIA	••	, the aqueous, th	
q	16.01 16.90 - 2.19	es in the gas, ssed as	ctively ctively vely vely ctively ively ively ively tively tively tively
а	- 8.22 - 1.56 5.63	ms of the specie e, To are exprei	SOLV II, respe SOLV II, respecti LV II, respecti SOLV II, respecti SOLV II, respect SOLV II, respect SOLV II, respect OLV II, respect OLV II, respect OLV II, respect OLV II, respect OLV II, respect
Constants	$\begin{array}{c} 1.1977 \times 10^{-1} \\ 3.7661 \times 10^{1k} \\ 4.008 \times 10^{0} \end{array}$	represent concentratio e reference temperatur	ind 1.77 × 10 <sup>2</sup> in EQUI and -197.36 in EQUISO and 54.40 in EQUISO 6, and 12.71 in EQUISI 6, and 6.12 in EQUISI 7, and 5.35 in EQUISI 7, and 16.92 in EQUISI 8, and 14.75 in EQUISI 8, and 14.75 in EQUISI 9, and 16.90 in EQUISI 9, and 16.90 in EQUISI
Equilibrium chemical reactions	E19 NaNO <sub>3(s)</sub> $\leftrightarrow$ Na <sup>+</sup> <sub>(aq)</sub> +NO <sup>-</sup> <sub>3(aq)</sub> E20 NaCl <sub>(s)</sub> $\leftrightarrow$ Na <sup>+</sup> <sub>(aq)</sub> +Cl <sup>-</sup> <sub>(aq)</sub> E21 NaCl <sub>(s)</sub> +HNO <sub>3(g)</sub> $\leftrightarrow$ NaNO <sub>3(s)</sub> +HCl <sub>(g)</sub>	Notes: The subscripts, <i>g</i> , <i>aq</i> , <i>l</i> , and <i>s</i> in the equilibrium reactions the solid phases, respectively. Equilibrium constants at the $K(T) = K_o \exp\left[-\frac{\Delta H^o(T_o)}{RT}\left(\frac{T_o}{T}-1\right) - \frac{\Delta C_o}{R}\left(1 + \ln\left(\frac{T_o}{T}\right) - \frac{T_o}{T}\right)\right]$	where $T_0 = 298.15$ K where $T_0 = 298.15$ K The values of K for E6 is 1.383 × 10 <sup>0</sup> in ISORROPIA, an The values of K, a, and b for E7 are 1.096 × 10 <sup>0</sup> , -2.45, The values of K, a, and b for E10 are 4.360 × 10 <sup>1</sup> , -7.19, The values of K, a, and b for E11 are 1.225 × 10 <sup>1</sup> , -10.33 The values of K, a, and b for E11 are 1.225 × 10 <sup>1</sup> , -10.33 The values of K, a, and b for E14 are 9.685 × 10 <sup>-17</sup> , -711, The values of K, a, and b for E14 are 9.685 × 10 <sup>-17</sup> , -0.191, The values of K, a, and b for E17 are 3.861 × 10 <sup>2</sup> , -1.191, The values of K, a, and b for E17 are 3.861 × 10 <sup>2</sup> , -1.191, The values of K, a, and b for E17 are 3.801 × 10 <sup>2</sup> , -0.191, The values of K, a, and b for E17 are 3.829 × 10 <sup>11</sup> , 0.098

 Table 3
 Equilibrium chemical reactions at 298.15 K used in ISORROPIA and EQUISOLV II (continued)

There are several major differences between these two models. First is the treatment of the chemical equilibrium reactions and the equilibrium constants (Table 2). EOUISOLV II uses the thermodynamic system of NH<sup>+</sup><sub>4</sub>-Na<sup>+</sup>-H<sup>+</sup>-SO<sup>2</sup><sub>-</sub><sub>4</sub>-HSO<sup>-</sup><sub>4</sub>-NO<sup>-</sup><sub>3</sub>-Cl<sup>-</sup>-OH<sup>-</sup>-H<sub>2</sub>O(l) Ca<sup>2+</sup>-K<sup>+</sup>-Mg<sup>2+</sup>-CO<sup>2-</sup><sub>3</sub>-HCO<sup>-</sup><sub>3</sub> and ISORROPIA does not include Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, CO<sup>2-</sup><sub>3</sub>,  $HCO_{3}^{-}$ . For the purpose of comparison,  $Ca^{2+}$ ,  $K^{+}$ ,  $Mg^{2+}$ ,  $CO_{3}^{-}$ ,  $HCO_{3}^{-}$  was not taken into account in EQUISOLV II. EQUISOLV II explicitly includes the dissociation of H<sub>2</sub>SO<sub>4</sub>(l) in the liquid phase (i.e.  $H_2SO_4(l) \leftrightarrow HSO_4^- + H^+$ ) and has the option for including the gas-liquid, the solid-liquid, and/or the solid-gas equilibrium of  $NH_4NO_3(s)$  and  $NH_4Cl(s)$ , such as E10, E11, E12, E14, E15, and E16 (Table 3). However, ISORROPIA does not treat the dissociation of  $H_2SO_4(l)$  in the solid-liquid and/or the gas-liquid equilibrium of  $NH_4NO_3(s)$  (E11 and E12) and  $NH_4Cl(s)$  (E16). Another difference lies in the equilibrium reaction of  $NH_3(g)$  with other species. ISORRPIA treats the dissociation of  $NH_3(g)$  with H<sub>2</sub>O in the aqueous phases (NH<sub>3</sub>(g) + H<sub>2</sub>O(l)  $\leftrightarrow$  NH<sup>+</sup><sub>4</sub> + OH<sup>-</sup>) (E5), and the gas-liquid equilibrium  $NH_3(aq)$  (E4). On the other hand, EQUISOLV II treats the reaction of  $NH_3(g)$ with  $HNO_3(g)$  in aqueous phases, such as  $NH_3(g) + HNO_3(g) \leftrightarrow NH_4^+ + NO_3^-$  (E15), and the reaction of NH<sub>3</sub>(g) with HCl(g) in aqueous phases, such as NH<sub>3</sub>(g) + HCl(g)  $\leftrightarrow$  NH<sup>4</sup><sub>4</sub> + Cl<sup>-</sup> (E12). Moreover, these two models show slightly different equilibrium constant values from E7, E8, E10, E11, E13-15, E17, E18, and E20 (Table 3).

Secondly, 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).

Thirdly, 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 converse 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 MFI and 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 a relatively higher computational efficiency for 3D air quality PM modelling.

Fourthly, each model conducts a different DRH treatment for each aerosol salt and mixture salts (Table 2). Nenes et al., (1998) indicated the importance of the DRH of each aerosol salt and mixed aerosol salts, which treat the transition between the aqueous and the 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 that the DRH of the mixture is a function of mixture composition. The minimum DRH is known as 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 can potentially affect the predicted role of aerosols, since the presence of water in the 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.

#### 5 Development and evaluation of air quality model

With the promulgation of the new PM<sub>2.5</sub> NAAQS, all designated non-attainment areas and surrounding regions may need to reduce emission of PM2.5 and their precursors to attain the NAAQS. Since 1998, the US EPA initiated the Particulate Matter Research Program to identify the relationships between PM and human health. This programme also develops the predictive and evaluative tools to determine compliance of NAAQS standard and the needed mitigation strategies. The 3D 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 both regulatory assessment as well as scientific studies conducted by research institutions. In order to characterise its performance and to improve the capability of air quality models, the evaluation process is crucial to these air quality models if they are to be used for regulatory purposes. By 2004, the EPA had accumulated the ambient PM25 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 3D 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) (Wexler and Seinfeld, 1991). For the regional scale models, there is the EPA's third generation air quality model, EPA's Model-3/Community Multiscale Air Quality (CMAQ) (US EPA, 2004a) and the Regional Particulate Model (RPM) (Binkowski and Shankar, 1995). The US EPA and the NOAA have recently teamed up to develop Air Quality Forecasting (AQF) capability and to implement a nationwide routine AQF programme with an initial target on PM using a complex chemical transport model (US EPA, 2004b). In 1998, US EPA released the initial version of the EPA's 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  $PM_{25}$ in the atmosphere. It is capable not only of characterising the atmospheric PM size distributions and the processes of condensation (new particle formation) and coagulation (particle growth) but also to simulate equilibrium aerosol species.

A thermodynamic equilibrium model, ISORROPIA, which is a computationally efficient and rigorous thermodynamic model has been incorporated into CMAQ model to simulate the thermodynamics of inorganic PM (US EPA, 2004b; Zhang et al., 2004). The results showed that both CMAQ models performed well in predicting sulphate but under-predicted ammonia, nitrates,  $PM_{2.5}$ ,  $PM_{10}$ , and organic carbon concentrations (US EPA, 2004a). US 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

Carnegie-Mellon University (CMU) bulk aqueous-phase chemistry into 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 model performance were well performed in sulphate, but under-predicted in secondary organic PM and nitrate concentrations. Both models stated the potential uncertainties could result from uncertainties in the emission inventory. It 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<sub>2.5</sub> and that can be used to improve human exposure estimates and forecasting to attain the NAAQS for PM<sub>2.5</sub>.

#### 6 Importance of fine particulate matter (PM, 5) in agricultural air quality

Atmospheric reduced nitrogen species ammonia (NH<sub>3</sub>) and ammonium (NH<sup>+</sup><sub>4</sub>) 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<sub>2.5</sub>. A major source of ammonia gas has been known as livestock approximately 73% of total ammonia emission ( $\approx$  45 Tg-N/year) (US EPA, 2003). In the US, approximately 44% of total ammonia nitrogen (NH<sub>3</sub>-N) emissions ( $\sim$  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<sub>3</sub>, as a contributor to the total atmospheric nitrogen deposition, is governed in part by the GTPC rate of NH<sub>3</sub> to NH<sup>+</sup><sub>4</sub>. Ammonia has a short lifetime, approximately 0.5 to five days or less, (Aneja, et al., 2000) due to the rapid GTPC of NH<sub>3</sub> to NH<sup>+</sup><sub>4</sub> 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<sup>+</sup><sub>4</sub>. Ammonium, which has a longer lifetime, approximately five to ten days, will be transported longer distances downwind from its sources.

Determining PM25 source contributions is complicated due to the fact that often half or more of the PM2.5 mass is composed of secondarily formed species through GTPC. In addition, the lifetime of PM2.5 could vary by several days, thus transporting it up to approximately 1500 miles away from its source to affect a region. It is theoretically feasible that a large source of  $NH_3$  (e.g. a 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 (US 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. US EPA (2003) analysed the contribution of PM<sub>2.5</sub> 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 PM2.5 in urban downwind locations. In general, this approach assumes that the PM2.5 at the rural sites is 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.

Figure 6 shows the local (urban) and regional (rural) contributions to major urban chemical  $PM_{2.5}$  components, sulphates, ammonium, nitrate, total carbonaceous mass and crustal species (US EPA, 2004b). 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. It illustrates that most species of  $PM_{2.5}$  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; US EPA, 2003) (Figure 7). This result reflects the importance of  $PM_{2.5}$  from agricultural (rural) areas. It may be viewed as a first step in differentiating between regional and local sources that contribute to  $PM_{2.5}$  mass. More work is needed to estimate the contributions of regional background associated with urban areas using spatial analysis and/or an air quality model to identify and examine specific emission sources on finer time

**Figure 6** Comparison of atmospheric PM<sub>2.5</sub> chemical components, such as inorganic species (ammonium, sulfate and nitrate), total carbonaceous mass (TCM = k \* OC + EC), crustal species, between urban and rural area (US EPA, 2003)



Figure 7 Map of ammonia emission distribution in US in 1999. Shaded areas coincide with major dairy (CA), beef cattle (TX), swine (IA and NC), and poultry (e.g. TN, GA) producing areas



resolution to get to the next and more refined level of local/regional source contributions.

#### 7 Discussion

Several major discussions emerge from this preliminary review study:

- Ammonia and inorganic acid gases emitted from livestock and poultry operations, manure treatment, handling and application can affect air quality by the formation of secondary particulate in the fine, PM<sub>2.5</sub> range. This range of PM is a regulated air pollutant.
- In generation, the formation of secondary fine particulate matter is controlled by the availability of precursor gases in the atmosphere including SO<sub>x</sub>, NO<sub>x</sub>, chlorine, ammonia, water and other species.
- 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.
- Models for the formation of fine PM from substrates such as ammonia are available and have been used for air quality modelling 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 include:
  - simultaneous field measurements of ammonia and acid gases at typical livestock and poultry sources
  - development of emission factors for ammonia and acid gases

- incorporation of ammonia sources to local and regional air quality models
- modelling the fate of ammonia and acid gas emissions from livestock and poultry operations.

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