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An Analysis of Four Models Predicting the Partitioning of Semivolatile Inorganic Aerosol Components

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ABSTRACT. A comparison is conducted between 4 atmospheric equilibrium models: GFEMN, ISORROPIA, SCAPE2, and SEQUILIB. While ISORROPIA, SCAPE2, and SEQUILIB simplify the problem at hand in an effort to reduce computational rigor, GFEMN does not employ many of the simplifying assumptions used in previous models, thus allowing it to accurately predict multistage aerosol behavior and deliquescence depression. We examine model performance for representative atmospheric environments over an extended composition, temperature, and RH domain and against observations in Southern California. The predictions of GFEMN, ISORROPIA, SCAPE2, and SEQUILIB are in general agreement, but the latter 3 do not adequately reproduce multistage deliquescence behavior for multicomponent systems. The most notable differences in model predictions occur for H^+ and aerosol water concentrations; discrepancies in predictions of aerosol nitrate and total dry inorganic PM concentrations are not as significant. The models predict different deliquescence relative humidities for multicomponent systems, but for ammonia poor environments, these discrepancies do not introduce differences in total dry inorganic PM predictions. Against measurements taken during the Southern California Air Quality Study (SCAQS), all models qualitatively reproduce but generally underpredict aerosol nitrate concentrations. Finally, based on its overall agreement with GFEMN and its computational efficiency, ISORROPIA appears to be the model of choice for use in large-scale aerosol transport models. In places where crustal material comprises a significant portion of total PM, SCAPE2 is an alternative.

INTRODUCTION

Over the past decade, several atmospheric aerosol models predicting the equilibrium partitioning of inorganic compounds between the gas and aerosol phases have been developed. These include EQUIL (Bassett and Seinfeld 1983), MARS (Saxena et al. 1986), SEQUILIB (Pilinis and Seinfeld 1987), AIM (Wexler and Seinfeld 1991), SCAPE (Kim et al. 1993a, 1993b), SCAPE2 (Kim and Seinfeld 1995; Meng et al. 1995b), EQUISOLV (Jacobson et al. 1996), and most recently ISORROPIA (Nenes et al. 1998a) and GFEMN (Ansari and Pandis

1999). These models have been used in a number of studies for the analysis of ambient measurements, as models in chemical transport measurements, and as tools for predicting aerosol behavior. For example, Watson et al. (1994a) and Kumar et al. (1998) used the thermodynamic calculations of SEQUILIB and SCAPE2, respectively, to determine emission control strategies most effective for reducing aerosol nitrate and ammonia concentrations in Phoenix, AZ and the San Joaquin Valley. SEQUILIB and SCAPE have also been used to estimate the water content of atmospheric aerosols (Pilinis et al. 1989; Meng et al. 1995). Ansari and Pandis (1998) applied GFEMN to investigate total inorganic PM response to changes in precursor concentrations. Furthermore, large-scale three-dimensional (3D) models capable of tracking aerosol dynamics rely on aerosol thermodynamic calculations of inorganic aerosol within their modeling framework. Such large-scale models have been combined with SEQUILIB (Pilinis and Seinfeld 1988; Lurmann et al. 1997), EQUISOLV (Jacobson et al. 1996; Jacobson 1997a, 1997b), SCAPE2 (Meng et al. 1998), and ISORROPIA (Nenes et al. 1998b) to simulate the dynamic behavior of inorganic and organic aerosol. Hence, accuracy and low convergence time are primary objectives in the development of thermodynamic equilibrium models for chemical transport models.

The aforementioned large-scale transport models have been used to simulate the pollutant concentrations during the Southern California Air Quality Study (SCAQS) conducted in 1987. Although each model has been evaluated against different episodes of the study, significant discrepancies in predictions have been reported (Lurmann et al. 1997; Meng et al. 1998) because each model was developed with a different modeling framework and with different equilibrium models and assumptions. However, at this stage it has yet to be determined if the differences in model predictions are a result of the different equilibrium models each uses in its framework. Although all equilibrium models rely on thermodynamic principles to predict inorganic aerosol behavior, their predictions of component concentrations may differ from one another. Therefore, based on the widespread application of equilibrium models, their examination and investigation of any resulting differences in predicting inorganic aerosol behavior is necessary. In addition, determining the most computationally suitable equilibrium model for use in applications such as 3D Eulerian urban airshed models is essential, as such large-scale models are computationally intensive.

Our objective is to closely examine the differences in selected aerosol equilibrium models over a broad temperature, RH, and composition domain. We investigate the differences in predictions of 4 atmospheric aerosol equilibrium models: SEQUILIB, SCAPE2, ISORROPIA, and GFEMN. SEQUILIB and SCAPE2 are two of the more widely used aerosol equilibrium models, and ISORROPIA has been shown to be an order of magnitude faster than SCAPE2 and SEQUILIB in determining inorganic aerosol behavior (Nenes et al. 1998a). GFEMN, as it uses adjusted thermodynamic parameters and the activity coefficient model of Clegg et al. (1998) allowing it to accurately predict multistage behavior and deliquescence depression of many aerosol systems, is included as a reference aerosol equilibrium model. Although EQUISOLV is another choice for an equilibrium model, we exclude it here as it is currently upgraded to EQUISOLV II. The predictions of EQUISOLV II will be compared to SCAPE2 and SEQUILIB in future work (Zhang et al. 1999).

In the following aerosol equilibrium model comparison, we examine aerosol nitrate, NH_4^+(aq), H^+, total dry inorganic particulate matter (PM), and aerosol water predictions for several model systems to closely examine model performance. We then extend the analysis to a broad temperature, RH, and composition domain to examine average model predictions and to determine the most computationally efficient model. Finally, we compare aerosol equilibrium model predictions against measurements taken at observation stations during SCAQS and attempt to explain any discrepancies.

MODEL FORMULATION

GFEMN, ISORROPIA, SCAPE2, and SEQUILIB have been developed to predict inorganic aerosol composition and state based on chemical thermodynamic principles. The theory of aerosol thermodynamics has been presented in detail elsewhere (Seinfeld and Pandis 1998; Denbigh 1981) and will therefore not be repeated here. Table 1 summarizes the major features of the 4 aerosol equilibrium models. GFEMN and SEQUILIB model the same species, yet ISORROPIA and SCAPE2 describe a larger system. ISORROPIA and SCAPE2 simulate the dissociation of H_2O into H^+ and OH^- and also the dissociation of NH_3(aq) into NH_4^+(aq). Furthermore, SCAPE2 incorporates the behavior of crustal species, Ca^{2+}, Mg^{2+}, and K^+. Crustal species can affect overall aerosol behavior in regions where there is a significant source of dust. However, all models exclude complex salt forms such as double salts, salt hydrates, and acid sodium salts in spite of their presence in the atmosphere (Harrison and Sturges 1984).

ISORROPIA, SCAPE2, and SEQUILIB treat the gas/aerosol system as a reactive one; an equilibrium expression involving an equilibrium constant (K_{eq}) is derived for each reaction. The resulting system of nonlinear algebraic equations, coupled with appropriate electroneutrality and mass conservation equations, is solved by Newton Raphson and bisection methods with the solution corresponding to a minimum of the Gibbs free energy. Ansari and Pandis (1999) showed, however, that an equation-oriented approach such as that used in SEQUILIB, SCAPE2, and ISORROPIA has difficulties in predicting deliquescence depression and multistage growth patterns commonly observed in multicomponent aerosol behavior.

To decrease computational rigor and thus convergence time, SEQUILIB, SCAPE2, and ISORROPIA divide the RH and composition domains into subdomains where only specific reactions are assumed to occur. For example, for an ammonia rich aerosol (total ammonia plus sodium to sulfate molar ratio is > 2), SEQUILIB assumes all particles are dry for $RH < 0.63$. In this case, no reactions including aqueous components are considered. GFEMN formulates the problem as a direct minimization of the Gibbs free energy where many sets of variables satisfy the constraints of the system, but only one case globally minimizes the Gibbs free energy corresponding to the stable equilibrium condition of the system. It relies on a global search of all possible scenarios satisfying the constraints of the system.

In formulating the equilibrium problem, 2 sets of thermodynamic data are needed. The first set, including $\Delta G_f^o, \Delta H_f^o$ and c_p, have been compiled for atmospheric species of interest by Wagman et al. (1968, 1982). The original SEQUILIB used the older data and SCAPE2 and ISORROPIA use the updated values to determine $K_{eq}(T)$. The major discrepancy in the 2 sets results in different $K_{eq}(T)$ for the formation of NH_4NO_3 (solid and aqueous) from gaseous

TABLE 1. Comparison of atmospheric equilibrium models

		SEQUILIB	SCAPE2	GFEMN	ISORROPIA
Components treated	Gas Phase	NH_3HNO_3, HCl, H_2O			
	Solid Phase	Na_2SO_4, $NaHSO_4$, NaCl, NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$	SEQUILIB +KCl, K_2SO_4, $KHSO_4$, KNO_3, $CaCl_2$, $CaSO_4$, $Ca(NO_3)_2$, $MgCl_2$, $MgSO_4$, $Mg(NO_3)_2$	same as SEQUILIB	
	Liquid Phase	H^+, NH_4^+, Na^+, NO_3^-, Cl^-, SO_4^{2-} HSO_4^-, H_2SO_4, H_2O	SEQUILIB +OH^-, NH_3, Ca^{2+}, Mg^{2+}, K^+	same as SEQUILIB	SEQUILIB + OH^-, NH_3
Thermodynamic Data[a]		Wagman et al. (1968)	Wagman et al. (1982)	adjusted	Wagman et al. (1982)
Solution method		Newton Raphson/bisection		global search of minima	bisection
Multicomponent Activity Coefficient Method		Bromley	Bromley, K–M, Pitzer	Clegg et al. (1997)	Bromley
Binary Activity Method		Pitzer	K–M	N/A	K–M
Temperature Dependence of DRH		no	yes		
Composition Dependence of DRH		no		yes	
Divided Composition Domain		yes		no	yes
Water activity		ZSR			

[a] K_{eq} for the formation of solid and liquid NH_4NO_3 was adjusted in SEQUILIB to match that of SCAPE2 and ISORROPIA.

NH_3 and HNO_3. However, the current version of SEQUILIB (v2.3) has "corrected" $K_{eq}(T)$ which agree with those of SCAPE2 and ISORROPIA for the formation of solid and liquid NH_4NO_3; the most recent version of SEQUILIB will be used in the subsequent analysis. GFEMN uses "adjusted" thermodynamic values to determine $\mu^o(T)$ in its minimization algorithm (Ansari and Pandis 1999) which allows it to accurately predict deliquescence of multicomponent inorganic aerosol.

The second set of data required in each of the models includes multicomponent and binary activity coefficients. For calculation of multicomponent activity coefficients, SEQUILIB and ISORROPIA incorporate the method by Bromley (1973) and SCAPE2 allows the choice of methods by Bromley (1973), Kusik and Meissner (1978), and Pitzer (1986). For calculation of binary activity coefficients, SCAPE2 and ISORROPIA use the method by Kusik and Meissner (1978) and SEQUILIB uses that of Pitzer (Pitzer and Mayorga 1973). Kim et al. (1993a, 1993b) compared the activity coefficient methods and concluded that the Kusik-Meissner method best reproduces bi-

nary activity experimental observations, yet for multicomponent activity coefficient methods, no definite conclusions could be drawn as limited experimental data is available for comparison. Clegg and Brimblecombe (1995) noted that for atmospheric applications, previous activity coefficient methods although computationally simple introduce errors in atmospheric aerosol modeling, especially at conditions close to saturation and at supersaturation. To minimize such error, GFEMN uses the model developed by Clegg et al. (1998) to calculate multicomponent activity coefficients. With this model there is no need for any external determination of binary activity coefficients. All activity coefficient methods, however, rely on parameterizations which result in less than perfect fits to experimental data. This may result in a loss of accuracy for some systems.

The deliquescence behavior of inorganic aerosol has been measured as a function of ambient temperature and aerosol composition (Tang et al. 1978; Tang and Munkelwitz 1993, 1994a). SCAPE2 and ISORROPIA use data from Wexler and Seinfeld (1991) to calculate the deliquescence relative humidity (DRH) as a function of temperature for single salts. ISORROPIA incorporates phase diagrams determined by Potukuchi and Wexler (1995a, 1995b) and a weighting system for wet and dry conditions to determine DRH and deliquescence behavior as a function of composition for many systems. These diagrams do not include all possible combinations of species of interest, and in such cases, ISORROPIA approximates DRH behavior based on other combinations of species. GFEMN implicitly calculates the temperature and composition dependence on the deliquescence behavior of aerosols through its direct minimization of the Gibbs free energy; it does not require any external data to determine such dependence. SCAPE2 and SEQUILIB make no attempt at predicting DRH as a function of composition and SEQUILIB also does not predict DRH(T).

Finally, all models use the ZSR relation in determining the water activity of the system. GFEMN, SCAPE2, and the current version of ISORROPIA (v1.1) use updated data (Chan et al. 1992; Tang and Munkelwitz 1994b), when applicable, for required binary water activities in the ZSR relation. It should be noted that at low RH where saturated solutions may be present or for cases where solute-solute interactions become significant (ternary and higher-order systems, acidic solutions), the potential error in using the ZSR relation for calculating the water activity may increase (Chan et al. 1992; Chan et al. 1997; Clegg et al. 1997).

MODEL PERFORMANCE FOR REPRESENTATIVE SYSTEMS

To determine the major differences in the predictions of the aerosol equilibrium models, several representative systems are examined corresponding to nonurban continental, remote continental, and marine atmospheric conditions. There are no clear concentration boundaries distinguishing one aerosol type against another, yet each type serves more as a qualitative classification. Concentrations "typical" of the aerosol types mentioned were based on work by Heitzenberg (1989). The predictions of GFEMN are included since its direct minimization approach, adjusted thermodynamic parameters, and use of the activity coefficient model of Clegg et al. (1998) allow it to better reproduce multicomponent aerosol behavior (Ansari and Pandis 1999). For the following simulations, it is assumed that the aerosol systems exhibit deliquescence as opposed to efflorescence behavior.

NonUrban Continental Aerosol

For nonurban continental aerosol, sulfates, nitrates, and ammonium salts make up the majority of fine inorganic PM. Sodium and chloride are not as abundant and will be set to low concentrations for the following simulations. For a nonurban continental aerosol, which is generally ammonia rich, the major components forming are NH_4NO_3 and $(NH_4)_2SO_4$; small amounts of Na_2SO_4 may also be present. Although no laboratory measurements for such a system are available, its behavior can be described qualitatively. NH_4NO_3 has a lower DRH (62%) than $(NH_4)_2SO_4$ (80%) and in a multicomponent mixture, deliquesces first at a RH lower than its DRH (Wexler and Seinfeld 1991). The deliquescence of NH_4NO_3 is accompanied by the gradual dissolution of $(NH_4)_2SO_4$ and by an increase in the nitrate and ammonia concentrations with increasing RH. As RH continues to increase, the particle absorbs more water and the remaining $(NH_4)_2SO_4$ deliquesces; the particle is completely aqueous. Figure 1 shows model predicted aerosol nitrate and aqueous aerosol sulfate concentrations as a function of RH for the nonurban continental aerosol. For low RH (< 0.50), the system consists of solid NH_4NO_3, Na_2SO_4, and $(NH_4)_2SO_4$; no water is present. In this region, as seen by the top panel in Figure 1, GFEMN predicts significantly higher concentrations of aerosol nitrate, whereas SCAPE2, SEQUILIB, and ISORROPIA predict similar amounts. The difference results from values of K_{eq} each model uses for the formation of solid NH_4NO_3 from gaseous NH_3 and HNO_3. SCAPE2, SEQUILIB, and ISORROPIA use values from Wagman et al. (1968, 1982), where $K_{eq} = 59$ ppb^2 at 298 K. GFEMN uses adjusted thermodynamic parameters which result in $K_{eq} = 45$ ppb^2 at 298 K. Although reported values of K_{eq} range from 30 to 59 ppb^2 (Stelson et

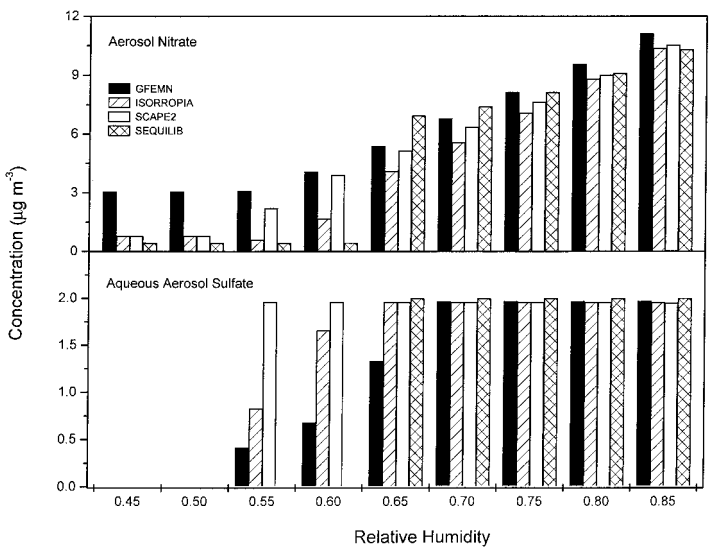


FIGURE 1. Predicted aerosol nitrate and aqueous aerosol sulfate concentrations as a function of RH for nonurban continental aerosol at 298.15 K. Model input: $NH_3^T = 8$ μg m^{-3}, $HNO_3^T = 15$ μg m^{-3}, $H_2SO_4 = 2$ μg m^{-3}, Na = 0.2 μg m^{-3}, HCl = 0.2 μg m^{-3}.

al. 1979; Stelson and Seinfeld 1982a, 1982b; Kim et al. 1993a; Mozurkewich 1993), that used by GFEMN is in agreement with the latest value reported by Mozurkewich (1993).

Over the RH range of 0.50–0.62, all models except SEQUILIB predict particle deliquescence as evident by the formation of aqueous aerosol sulfate and increasing aerosol nitrate. The nitrate predictions of SCAPE2 approach that of GFEMN, whereas ISORROPIA predicts less. SEQUILIB does not predict deliquescence until RH = 0.63 because it does not consider DRH depression observed for multicomponent aerosols. For RH > 0.63, all models predict similar nitrate concentrations. The relatively high initial aerosol nitrate prediction of SEQUILIB for RH > 0.63 is the result of the Pitzer binary activity coefficient method it uses which is not accurate at conditions close to saturation. ISORROPIA predicts slightly less nitrate until RH = 0.80, a result of the different convergence criteria within the subdomains it uses in determining aerosol behavior. The nitrate predictions of GFEMN are highest because of its use of adjusted thermodynamic parameters.

Figure 1 also shows the formation of aqueous aerosol sulfate, and as seen, GFEMN and ISORROPIA predict its expected gradual formation as $(NH_4)_2SO_4$ dissolves with increasing RH. ISORROPIA estimates the dissolution of solid species based on a weighting factor, c, of wet and dry states given by

$$c = \frac{RH - RH_{wet}}{MDRH - RH_{wet}}, \tag{1}$$

where $MDRH$ is the mutual deliquescence relative humidity for a given mixture and RH_{wet} is the DRH of the component with the lowest DRH. $MDRH$ for a multicomponent aerosol system is the minimum RH at which deliquescence occurs and is a function of composition. Potukuchi and Wexler (1995a, 1995b) have determined $MDRH$ for many multicomponent mixtures. Thus, if $RH < RH_{wet}$ and $MDRH < RH_{wet}$, (1) is used to define c, which in turn is used to calculate aerosol water and solid component concentrations based on

$$H_2O = (1 - c)^* H_2O_{wet}, \tag{2}$$

$$\phi = c\phi_{dry} + (1 - c)\phi_{wet}, \tag{3}$$

where ϕ is the concentration of a solid component and the subscripts "wet" and "dry" refer to wet and dry solutions, respectively. For the nonurban continental aerosol presented in Figure 1, where the solid components present are NH_4NO_3, $(NH_4)_2SO_4$, and Na_2SO_4, $MDRH = 0.50$, $RH_{wet} = 0.62$ (the DRH of NH_4NO_3), and at RH = 0.55, $c = 0.58$. Using Equation (3) to determine the concentration of solid $(NH_4)_2SO_4$ and Na_2SO_4, $\phi = 1.22$ and 0.36, respectively, which results in a total aqueous sulfate concentration of 0.83 $\mu g\ m^{-3}$ at RH = 0.55. Thus, ISORROPIA assumes a multicomponent particle is completely aqueous for $RH > RH_{wet}$. This assumption and the weighting system estimate in Equations (1)–(3) causes the discrepancy between GFEMN and ISORROPIA in predicting aqueous aerosol sulfate in Figure 1. It should be noted that as GFEMN uses a direct minimization of the Gibbs free energy and the activity coefficient model of Clegg et al. (1998), its prediction is probably more accurate than that of ISORROPIA. SEQUILIB and SCAPE2 do not predict such a smooth formation process, but instead predict a nearly instantaneous deliquescence of $(NH_4)_2SO_4$.

Small differences in aerosol water content for model predictions are evident for $0.50 < RH < 0.75$, as shown in Figure 2 for the nonurban continental aerosol. These differences are a direct result of the differing model predictions of aerosol nitrate and aqueous aerosol sulfate. For RH <

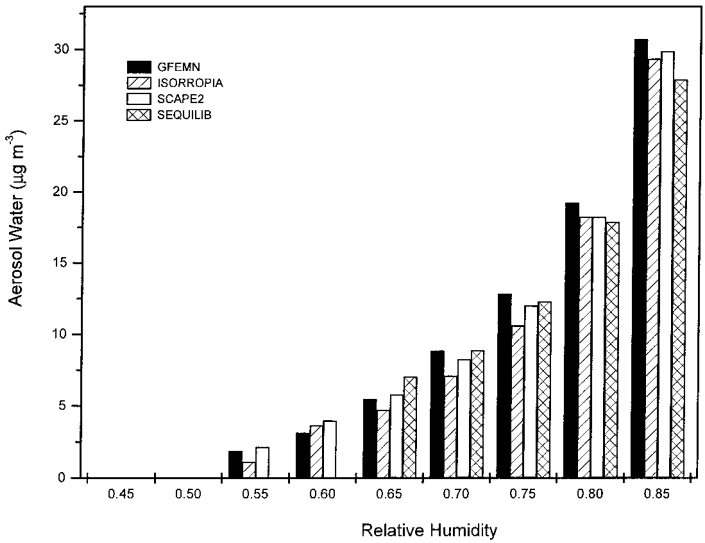


FIGURE 2. Predicted aerosol water concentration as a function of RH for the nonurban continental aerosol examined in Figure 1.

0.60, GFEMN and SCAPE2 predict similar aerosol water concentrations. ISORROPIA predicts less water as it predicts a low concentration of aerosol nitrate in this region. SEQUILIB does not predict any water. For RH > 0.63, SEQUILIB initially predicts higher aerosol water (due to high nitrate predictions), but converges to the results of GFEMN and SCAPE2 as RH increases. ISORROPIA predicts slightly less water, but also converges to the predictions of other models as RH increases beyond 0.80.

Remote Continental Aerosol

In many cases for remote continental aerosol, there is insufficient ammonia and sodium to fully neutralize the available sulfate (ammonia poor), and compounds containing the bisulfate and sulfate ion form such as NH_4HSO_4 and $(NH_4)_3H(SO_4)_2$ (letovicite). Model predictions of a remote continental aerosol showing the NH_4^+(aq) and aerosol water concentrations are shown in Figure 3. Although all models predict nearly identical total aerosol ammonium concentrations for this case, the predictions of the partitioning of the total aerosol ammonium between the solid and liquid phases is different. For the given concentrations, NH_4HSO_4 and letovicite are the major species forming along with small concentrations of Na_2SO_4. Thus a multistage deliquescence process results where NH_4HSO_4 deliquesces and is followed by the gradual dissolution of letovicite. GFEMN is able to predict multistage deliquescence and therefore predicts a gradual increase of NH_4^+(aq) until RH = 0.60, where it predicts a completely aqueous solution. For RH < 0.70, ISORROPIA and SEQUILIB predict similar and constant concentrations of NH_4^+, thus they are not able to predict the multistage behavior of the aerosol. SCAPE2 predicts a significantly lower concentration of NH_4^+(aq) because it partitions most of the available ammonia to letovicite instead of NH_4HSO_4. Hence, at low RH where all models predict the deliquescence of NH_4HSO_4, the NH_4^+(aq) predictions of

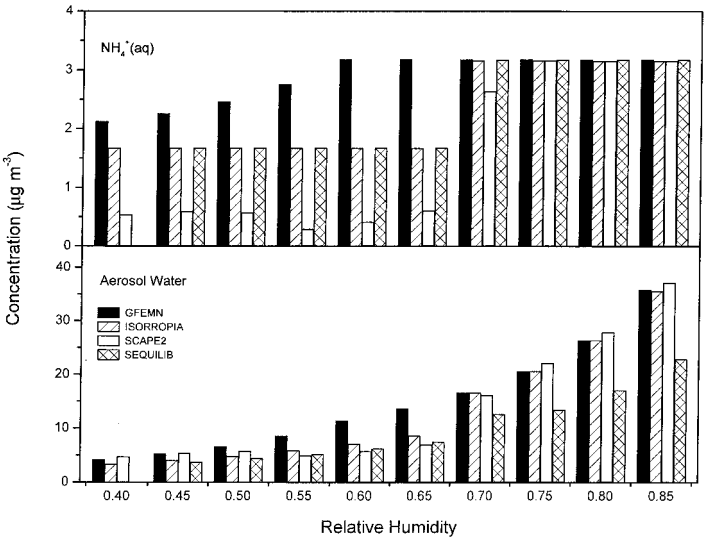


FIGURE 3. Predicted NH_4^+ and aerosol water concentrations as a function of RH for remote continental aerosol at 298.15 K. Model input: $NH_3^T = 3$ μg m^{-3}, $HNO_3^T = 10$ μg m^{-3}, $H_2SO_4 = 15$ μg m^{-3}, Na = 0.2 μg m^{-3}, HCl = 0.2 μg m^{-3}.

SCAPE2 are low. For RH > 0.70, all models predict similar concentrations of NH_4^+(aq) since each predicts the aerosol to be a completely aqueous solution.

Figure 3 also shows the aerosol water predictions of each model. These generally follow the trend in predictions of NH_4^+(aq) concentrations. For RH < 0.70, the aerosol water predictions of GFEMN are generally higher, as it predicts the gradual dissolution of letovicite in this range. SCAPE2, ISORROPIA, and SEQUILIB instead predict only the deliquescence of NH_4HSO_4 and little to no dissolution of letovicite resulting in a much lower concentration of aerosol water. SCAPE2, however, predicts similar water concentrations to ISORROPIA and SEQUILIB in this region despite predicting a lower NH_4^+(aq) concentration. For RH > 0.70, the system is completely aqueous and the results of GFEMN, ISORROPIA, and SCAPE2 are similar, whereas SEQUILIB predicts less aerosol water. SEQUILIB predicts less since it uses older binary water activity (Pilinis and Seinfeld 1987) in the ZSR relation; GFEMN, ISORROPIA, and SCAPE2 use updated data.

For the remote continental aerosol analyzed, species such as HSO_4^-(aq) and SO_4^{2-}(aq) form when deliquescence occurs. When HSO_4^-(aq) is present, a second dissociation may occur producing H^+(aq) and SO_4^{2-}(aq). Figure 4 shows model predicted H^+ concentrations for the remote continental aerosol. For RH > 0.70 where the system is completely aqueous, GFEMN predicts higher H^+ concentrations while ISORROPIA and SCAPE2 are in agreement. For RH < 0.70, SCAPE2 predicts similar H^+ concentrations to GFEMN, but significantly higher concentrations for RH < 0.50. Over this low RH region, ISORROPIA predicts a low concentration of H^+. The activity coefficient model of Clegg et al. (1998) used in GFEMN partitions total sulfate into H^+, HSO_4^-, and SO_4^{2-} and has been shown to accurately reproduce measurements for the dissociation of HSO_4^-

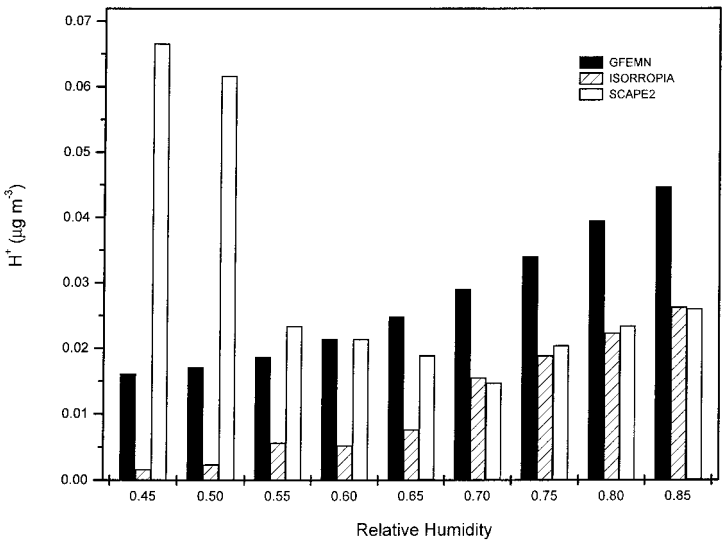


FIGURE 4. Predicted H^+ concentration for the remote continental aerosol examined in Figure 3.

into H^+ and SO_4^{2-} (Clegg and Brimblecombe 1995). Therefore, the prediction of GFEMN for the current system probably more accurately simulates the concentration of H^+. The simpler activity coefficient methods used in SCAPE2 and ISORROPIA cause difficulties in predictions of H^+. For example, in these models the binary activity coefficient for NH_4HSO_4 is approximated based on that of $(NH_4)_2SO_4$ and H_2SO_4 as parameters for its determination are not available. SEQUILIB was not formulated to predict H^+ concentrations.

Although not shown, all models predict nearly identical total dry inorganic PM concentrations. In ammonia poor environments, all compounds which may form (NH_4HSO_4, letovicite, $NaHSO_4$, etc.) have low vapor pressures and exist only in the aerosol phase; their aerosol concentrations are independent of temperature and RH. Components such as NH_4NO_3, whose aerosol concentration changes with RH and temperature because of its equilibrium with gaseous HNO_3 and NH_3, are not present in substantial concentrations in ammonia poor environments. The models examined partition sulfate, nitrate, and chloride to ammonia and sodium in nearly identical, stoichiometric amounts in ammonia poor environments and thus predict equivalent aerosol phase (total dry inorganic PM) concentrations.

Marine Aerosol

Significant quantities of sodium and chloride are present near coastal regions and along with nitrate have been measured in coarse particles where sulfate and ammonia salts are less abundant (Wolff 1984; Chow et al. 1994). Ammonia is normally not present in significant quantities in coarse marine aerosol, and therefore we neglect it for the following analysis. We focus on the differences in the partitioning of available HNO_3 and HCl to sodium. Figure 5 shows model predictions for a marine aerosol. The $NaNO_3$ predictions of GFEMN and ISORROPIA are similar and those of SCAPE2 and SEQUILIB are similar with the 2

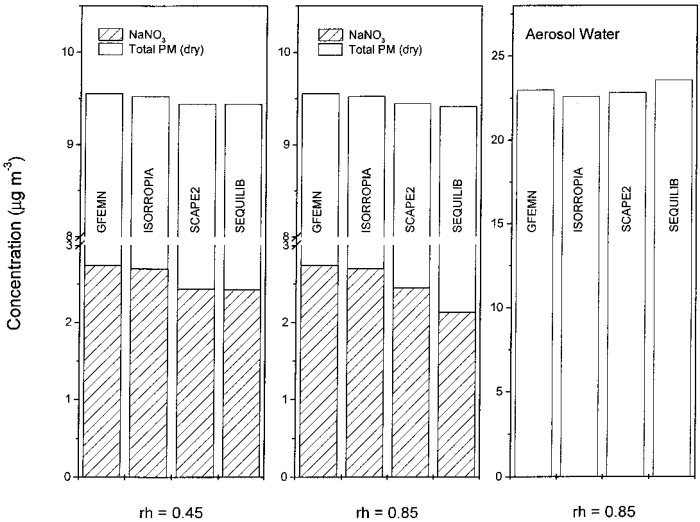


FIGURE 5. Predicted aerosol water and partitioning of HNO_3 and HCl to sodium for RH = 0.45 and RH = 0.85 at 298.15 K. Model input: $NH_3^T = 0$ μg m^{-3}, $HNO_3^T = 2$ μg m^{-3}, $H_2SO_4 = 3.13$ μg m^{-3}, Nal = 3.1 μg m^{-3}, HCl = 2 μg m^{-3}.

groups differing by approximately 10%. GFEMN and ISORROPIA predict higher concentrations of $NaNO_3$ and thus lower concentrations of NaCl. Two different approaches are used in partitioning HNO_3 and HCl to sodium to form $NaNO_3$ and NaCl. GFEMN and ISORROPIA predict that sodium will preferentially bind with any available HNO_3 to form $NaNO_3$. If there is not enough HNO_3 to fully neutralize sodium, the excess sodium binds with available HCl, thus forming NaCl and $NaNO_3$ (if HNO_3 is present). In this manner, GFEMN and ISORROPIA assume that sodium is not necessarily accompanied by an equivalent amount of chloride. SCAPE2 and SEQUILIB, however, assume that sodium is partitioned between $NaNO_3$ and NaCl through the following equilibrium reaction in the presence of HNO_3 and HCl:

$$NaCl(s) + HNO_3(g) \rightleftarrows NaNO_3(s) + HCl(g). \quad (4)$$

In this case, SCAPE2 and SEQULIB assume any sodium given as input corresponds to an equivalent amount of NaCl. For marine environments, where sodium is transported to the atmosphere as NaCl, the approach of SCAPE2 and SEQUILIB probably better reproduces aerosol behavior. However, in spite of differing approaches in partitioning HNO_3 and HCl to sodium, the resulting discrepancies in predictions of total PM and aerosol water are minor (Figure 5).

For high RH (RH = 0.85), the predictions of SCAPE2 and SEQUILIB are somewhat different (Figure 5). SCAPE2 does not predict a shift in the equilibrium state of Equation (1), whereas SEQUILIB shifts the equilibrium state in Equation (1) to favor formation of NaCl resulting in lower concentrations of $NaNO_3$.

OVERALL MODEL PERFORMANCE

Although the previous comparisons were instructive in illustrating some differences

in model predictions, overall model performance over an extended temperature, RH, and composition domain needs to be investigated. Considering the diurnal variation in the behavior of the ambient temperature, RH, and component concentrations, will SEQUILIB, SCAPE2, ISORROPIA, and GFEMN on average predict similar aerosol concentrations or will their predictions differ? Any resulting differences are important for applications such as large-scale aerosol transport models which rely on repeated equilibrium calculations covering the entire temperature, RH, and composition domain. Moreover, examining the CPU time consumed by equilibrium models in predicting aerosol behavior is necessary to determine any additional computational cost introduced by the incorporation of equilibrium models into large-scale chemical transport models.

To resolve the above issues, aerosol behavior was simulated for ammonia rich and ammonia poor environments using GFEMN, ISORROPIA, SCAPE2, and SEQUILIB with a large set of input data shown in Table 2. All scenarios in which sodium could not be fully neutralized by available sulfate, nitrate, and chloride or in which available sulfate existed as sulfuric acid, H_2SO_4 (aq), were eliminated from the input set. For the ammonia rich and ammonia poor environments, 768 and 1392 sets of conditions, respectively, resulted from the input.

Ammonia Rich Environments

Average predicted aerosol concentrations for ammonia rich environments are shown in Table 3 and in Figures 6–8. Table 3 also shows statistics of model predictions against those of GFEMN. Although such measures do not give insight to the cause of the discrepancies, they can provide valuable information about the magnitude of the discrepancy.

All models predict similar aerosol nitrate concentrations (Figure 6) with the highest on average predicted by SEQUILIB and the lowest by ISORROPIA. Although SCAPE2 and SEQUILIB predict low aerosol nitrate concentrations at low RH for the nonurban continental aerosol in

TABLE 2. Input for overall model behavior

Aerosol System	Variable	Value minimum	Value maximum	Increment
ammonia rich	temperature (K)	275	305	10
	relative humidity (%)	35	85	10
	H_2SO_4 ($\mu g\ m^{-3}$)	0.1	15	7.5
	HNO_3 ($\mu g\ m^{-3}$)	0.1	21	7
	NH_3 ($\mu g\ m^{-3}$)	0.1	9	3
	Na ($\mu g\ m^{-3}$)	1	1	N/A
	HCl ($\mu g\ m^{-3}$)	1	1	N/A
ammonia poor	temperature (K)	275	305	10
	relative humidity (%)	35	85	10
	H_2SO_4 ($\mu g\ m^{-3}$)	0.1	14	2
	HNO_3 ($\mu g\ m^{-3}$)	5	5	N/A
	NH_3 ($\mu g\ m^{-3}$)	0.1	4	1
	Na ($\mu g\ m^{-3}$)	0.1	2	0.5
	HCl ($\mu g\ m^{-3}$)	1	1	N/A

TABLE 3. Model performance against GFEMN for input given in Table 2

Species	Model	Mean Predicted ($\mu g\ m^{-3}$)	Mean Bias ($\mu g\ m^{-3}$)	Mean Normalized Bias, %	Mean Error ($\mu g\ m^{-3}$)	Mean Normalized Error, %
AMMONIA RICH ENVIRONMENTS						
	GFEMN	5.43				
Aerosol	ISORROPIA	5.33	−0.11	4.0	0.22	13.0
Nitrate	SCAPE2	5.42	−0.02	19.8	0.23	25.4
	SEQUILIB	5.46	0.02	21.0	0.26	26.1
Total PM	GFEMN	16.47				
	ISORROPIA	16.33	−0.58	4.2	0.77	5.4
	SCAPE2	16.45	−0.02	0.7	0.36	2.7
	SEQUILIB	16.56	0.09	0.1	0.46	3.1
	GFEMN	10.07				
Aerosol	ISORROPIA	7.97	−2.09	−13.4	3.13	38.7
Water	SCAPE2	10.62	0.56	214	2.30	241
	SEQUILIB	10.59	0.52	228	2.73	256
AMMONIA POOR ENVIRONMENTS						
NH_4^+(aq)	GFEMN	1.02				
	ISORROPIA	0.88	−0.14	−14.5	0.20	21.9
	SCAPE2	1.04	0.01	25.5	0.30	52.1
	SEQUILIB	0.92	−0.09	−7.6	0.25	30.3
H^+(aq)	GFEMN	0.006				
	ISORROPIA	0.013	0.007	369	0.010	403
	SCAPE2	0.019	0.013	1129	0.014	1134
	SEQUILIB	N/A	N/A	N/A	N/A	N/A
Total PM	GFEMN	12.70				
	ISORROPIA	12.71	0.00	0.0	0.07	0.6
	SCAPE2	12.72	0.02	0.1	0.09	0.7
	SEQUILIB	13.23	0.53	4.6	0.55	4.8
	GFEMN	7.95				
Aerosol	ISORROPIA	7.14	−0.82	−15.9	1.08	25.4
Water	SCAPE2	9.34	1.39	73.5	1.85	81.8
	SEQUILIB	6.27	−1.68	−19.1	2.46	41.0

Figure 1, over a broad temperature, RH, and composition domain their aerosol nitrate concentrations are similar to those predicted by GFEMN. The higher mean normalized bias and error of SCAPE2 and SEQUILIB compared to that of ISORROPIA indicate a higher overall discrepancy against predictions of GFEMN. ISORROPIA predicts slightly less aerosol nitrate (similar to its low prediction shown in Figure 1), but overall shows better agreement to GFEMN. Figure 7 indicates good agreement of all models for predictions of total dry inorganic PM. SEQUILIB predicts the highest average dry inorganic PM concentration because of its relatively high nitrate predictions over the RH range of 0.65–0.75 shown in Figure 1 where the

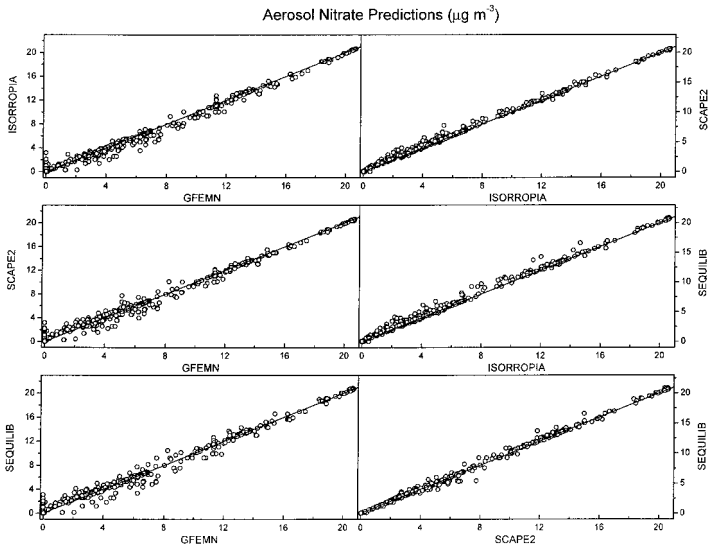


FIGURE 6. Model comparison of predictions of aerosol nitrate for ammonia rich environments from Table 2.

Pitzer method for calculating binary activity coefficient may be in error. Average total dry inorganic PM predictions of ISORROPIA are lowest, as expected, based on its lowest average prediction of aerosol nitrate. The low mean normalized bias and error of all models against GFEMN (< 6%) indicate overall agreement with GFEMN.

The most significant discrepancies in model predictions of ammonia rich envi-

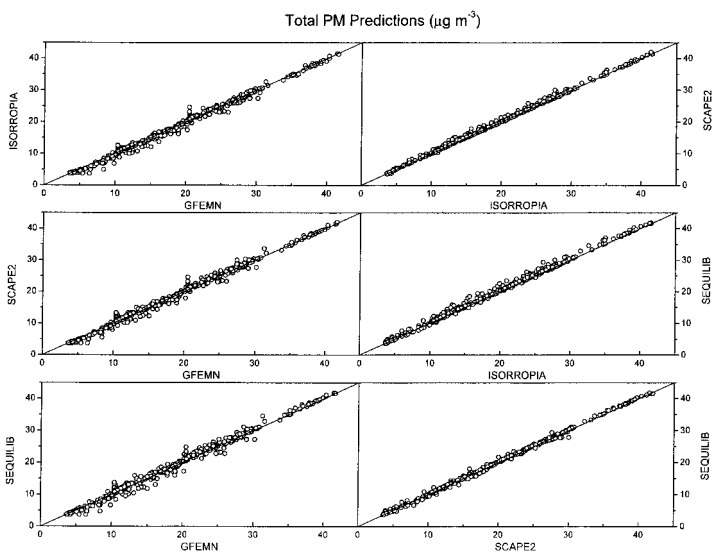


FIGURE 7. Model comparison of predictions of total PM for ammonia rich environments from Table 2.

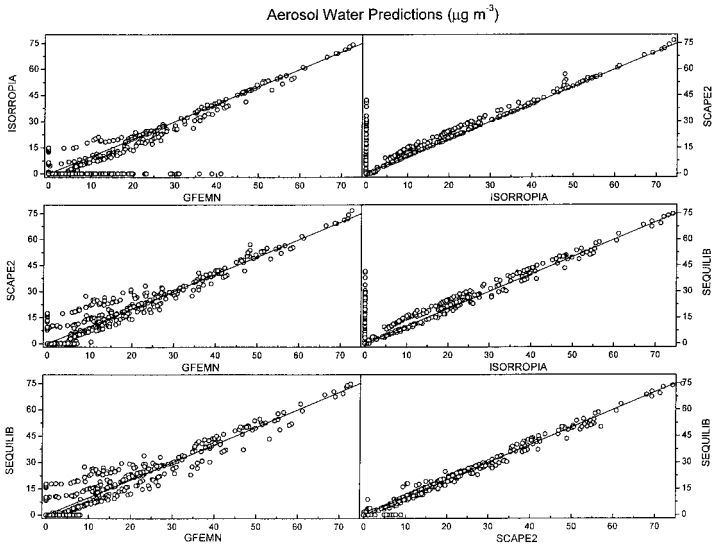


FIGURE 8. Model comparison of predictions of aerosol water for ammonia rich environments from Table 2.

ronments occur for aerosol water, as is evident by the scatter of predictions in Figure 8 and also by the high mean normalized bias and error in Table 3. SCAPE2 and SEQUILIB predict the highest average aerosol water concentrations. SCAPE2 often predicts water at even low RH (Nenes et al. 1998a), whereas SEQUILIB predicts higher water concentrations on average because of its high average aerosol nitrate and PM predictions. ISORROPIA, however, predicts significantly lower average water concentrations and thus in many cases, ISORROPIA predicts dry particles whereas GFEMN, SCAPE2, and SEQUILIB predict deliquescence behavior.

Ammonia Poor Environments

Average model predictions for ammonia poor environments are shown in Figures 9–12, and the resulting statistics of predictions against GFEMN are given in Table 3. All models predict nearly identical total aerosol ammonium concentrations but partition the total differently between the solid and liquid phases. For aerosol NH_4^+(aq), GFEMN and SCAPE2 predict similar results, whereas ISORROPIA and SEQUILIB predict similar yet lower mean concentrations (Table 3). However, as seen by the wide scatter in predictions in Figure 9, there are significant discrepancies in predicted NH_4^+ aerosol phase distribution for all models, with SCAPE2 having the highest mean normalized bias and error. For H^+ predictions, SCAPE2 and ISORROPIA predict significantly more H^+ than GFEMN does, as seen in Figure 10 and Table 3. Overall, there is poor agreement between models in predicting H^+; the mean normalized bias and error in these cases are significantly higher than for any other components. ISORROPIA and SCAPE2 tend to agree for predictions of H^+, more so when compared to each other than when compared to GFEMN. Based on the representative system shown in Figure 5, the high H^+ predictions of SCAPE2 occur at low RH. In addition, although Figure 5 shows that the predictions of ISORROPIA are

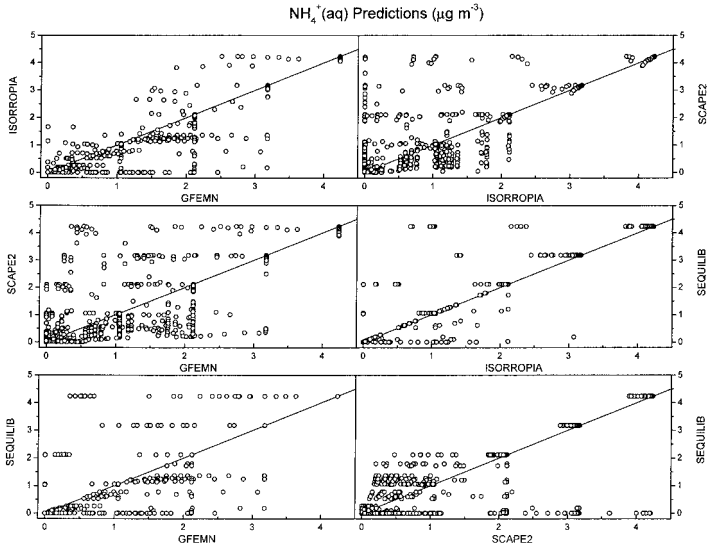


FIGURE 9. Model comparison of predictions of NH_4^+ for ammonia poor environments from Table 2.

less than that of GFEMN for this case, considering the broad ranges of temperature, RH, and composition examined from Table 2, ISORROPIA predicts on average higher H^+ concentrations overall. SEQUILIB makes no prediction of H^+. For mean predicted water concentrations, SCAPE2 again predicts the highest concentrations, whereas SEQUILIB predicts the lowest concentrations. Figure 11 shows the gen-

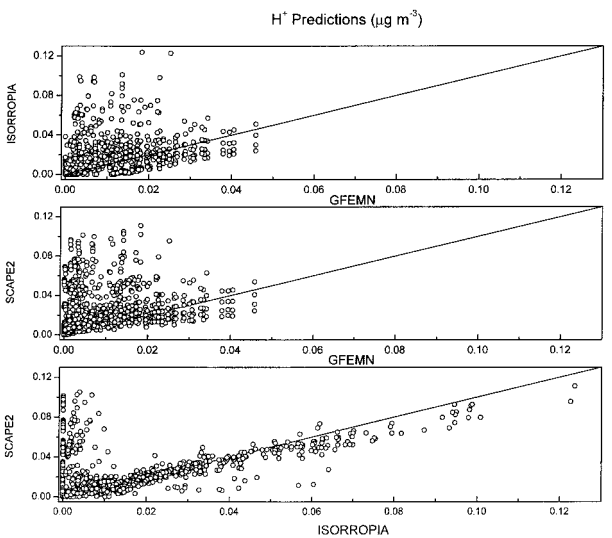


FIGURE 10. Model comparison of predictions of H^+ for ammonia poor environments from Table 2. Note: SEQUILIB makes no prediction of H^+.

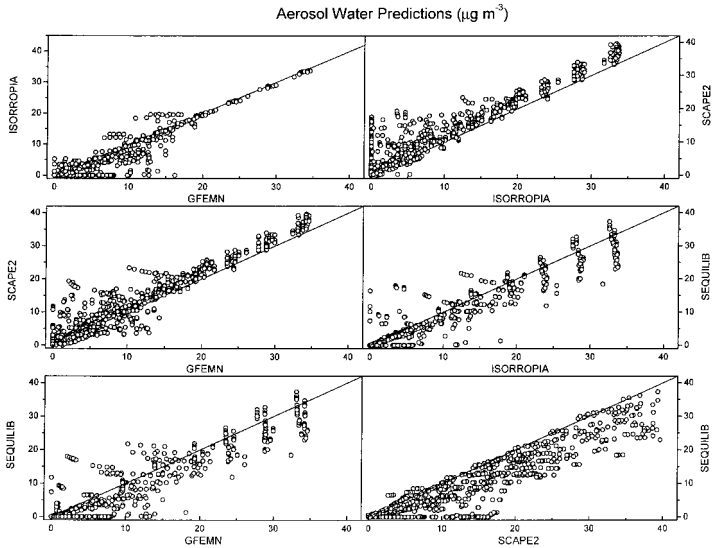


FIGURE 11. Model comparison of predictions of total PM for ammonia poor environments from Table 2.

eral wide scatter and discrepancies in model predictions for aerosol water as seen for NH_4^+ and H^+. Figure 12 and Table 3 also show that the predictions of total PM by all models are nearly identical except for those of SEQUILIB. SEQUILIB predicts higher concentrations since it assumes that there is always some sulfate present in the system. Overall for ammonia poor environments, ISORROPIA, SCAPE2, and SE-

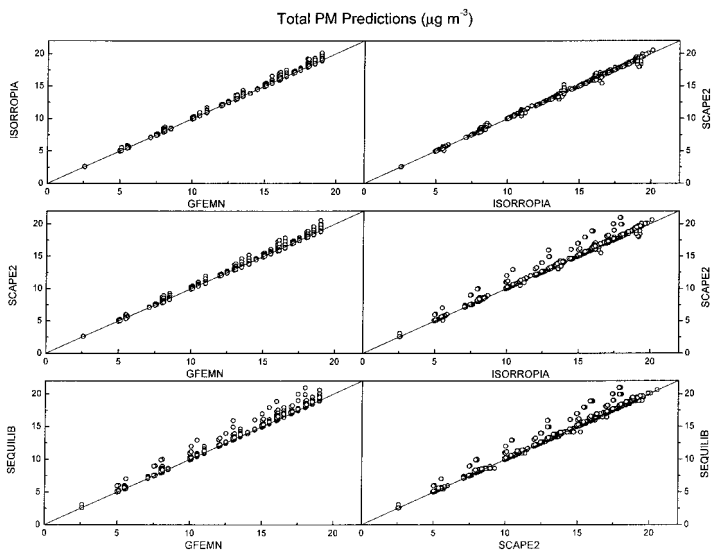


FIGURE 12. Model comparison of predictions of aerosol water for ammonia poor environments from Table 2.

QUILIB do not reproduce predictions of GFEMN, except for the predictions of total dry inorganic PM.

IMPLICATIONS FOR MODELING STUDIES

As mentioned in a previous section, the application of equilibrium models is widespread, for example, in large-scale transport models and in studies investigating emissions control strategies. Applying the calculations of one equilibrium model versus another in such studies may thus introduce discrepancies. Based on the results of the previous section, there are no major discrepancies in model predictions of aerosol nitrate and total dry inorganic PM. Thus for studies focusing primarily on total dry inorganic PM and aerosol nitrate behavior such as those by Watson et al. (1994a) and Kumar et al. (1998), the choice of equilibrium model is not consequential. Conversely, significant discrepancies between model predictions exist for aerosol water and H^+ predictions as evident by the wide scatter in data in Figures 8–11. It should be noted that SCAPE2 and SEQUILIB do predict similar aerosol water concentrations for ammonia rich environments. In general, in conducting studies to investigate atmospheric related issues such as acid rain, climate change, water content of aerosols, and the direct radiative affect on the energy balance of the planet, calculations of aerosol water and H^+ concentrations are important. Given that discrepancies exist in model predictions of these components, the use of one equilibrium model over another may produce differing results in some modeling studies.

CPU Consumption

Table 4 shows the CPU consumption of each model for the input in Table 2 as determined on an HP 9000 C100 workstation. The CPU consumption of ISORROPIA is lowest by more than an order of magnitude compared to SCAPE2 and SEQUILIB, making its use in large-scale atmospheric transport models attractive and advantageous. SEQUILIB is a factor of 4 faster in determining equilibrium composition compared to SCAPE2, whereas the minimization algorithm of GFEMN is orders of magnitude slower than SCAPE2 and SEQUILIB; its inclusion in large-scale transport models is not feasible, as it is more of a reference equilibrium model for determining accuracy and performance of models such as ISORROPIA, SCAPE2, and SEQUILIB.

TABLE 4. Total model CPU consumption for the 2160 simulations given in Table 2

Model	CPU Time (s)	CPU $CPU_{ISORROPIA}$
ISORROPIA	8.3	1
SEQUILIB	143.7	17
SCAPE2	577.2	69
GFEMN	93683.8	11287

MODEL PREDICTIONS AGAINST SCAQS MEASUREMENTS

Previously, model predictions were intercompared over a broad temperature, RH, and composition domain. Although such a comparison is instructive in determining modeling discrepancies, some of the models may encounter difficulties for more realistic concentrations and atmospheric conditions. During the 1987 SCAQS, an extensive database was compiled containing air quality measurements from several sites throughout Southern California. One of the purposes of SCAQS was to provide such a database for the testing, evaluation, and improvement of air quality simulation mod-

els (Lawson 1990). Thus, we examine model performance against measurements taken during SCAQS using models which rely on thermodynamic equilibrium principles alone to reproduce aerosol behavior. Instead of trying to predict the total species (nitrate, sulfate, ammonium, etc.) concentrations using a chemical transport model, we use the measurements to calculate these totals. The thermodynamic models are then used to simulate their partitioning between the gas and aerosol phases. Such a comparison will allow us to examine model predictions for realistic conditions and also enable us to quantitatively understand the thermodynamic uncertainty in comparison to other problems associated with equilibrium models and measurements.

Meteorological ambient $PM_{2.5}$ (particles with $d_p < 2.5$ μm) measurements were obtained during SCAQS and the inorganic portion of these measurements consisted of total nitrate, total ammonia, and sulfate measurements. Using the temperature, RH, and total ammonia, nitrate and sulfate concentrations of these measurements as inputs for the 4 equilibrium models, the models were used to reproduce observations. Figure 13 shows predicted aerosol nitrate concentrations against observations for 6 sites during August 27–29, 1987. Model predictions are in general agreement with measurements for the 3 day period. All 4 models generally underpredict observations, but accurately predict the diurnal variation of aerosol nitrate concentrations at Azusa (8/29), Claremont (8/29), Los Angeles (8/29), and Riverside (8/27, 8/29). GFEMN, ISORROPIA, SCAPE2, and SEQUILIB are in agreement with each other for all measurements shown in Figure 12. GFEMN occasionally predicts higher aerosol nitrate concentrations such as that for Azusa (9–13, 8/28/87) and Burbank (9–13, 8/28/87). This discrepancy is because of the different thermodynamic parameters GFEMN uses for the formation of NH_4NO_3 discussed in a previous sec-

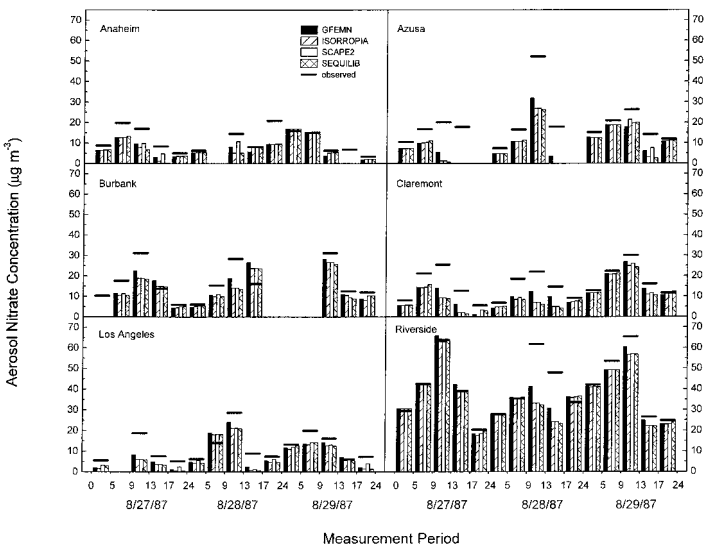


FIGURE 13. Model performance against SCAQS measurements for 6 observation stations over the period August 27–August 29, 1987.

tion. Table 5 shows the statistics of aerosol nitrate predictions against SCAQS observations for the equilibrium models. The statistics for all 4 models are similar, indicating minor discrepancies in predictions between the 4 models in this case. The mean bias and mean normalized bias for all models is negative, indicating an overall underprediction by the models.

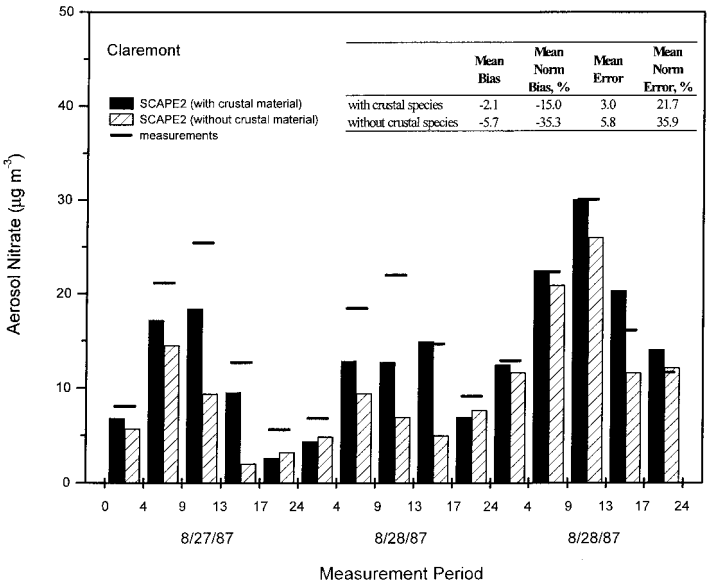
Given the general underprediction of measurements by the models in Figure 13, a discussion of the ambient measurements is worthwhile. Dust is a significant portion of total PM and, although it is abundant primarily in coarse particles, can constitute a significant fraction of $PM_{2.5}$. Crustal species (Al, Fe, Ca, K, etc.) found in dust can exist as nitrates (based on their alkalinity) such as $Ca(NO_3)_2$, $Mg(NO_3)_2$, and KNO_3, and their exclusion in our modeling study of SCAQS data may partially explain the underprediction of aerosol nitrate. To incorporate the influence of dust on the prediction of aerosol nitrate, we must first determine the composition and concentration of dust within $PM_{2.5}$. Watson et al. (1994b) used source profiles applicable to Southern California to apportion PM_{10} measurements taken during SCAQS and determined that during the summer at Claremont, paved roads acted as the major source contributing to the significant amounts of dust constituting total PM. The major species emitted from this source is crustal material (Ca, Al, Fe, K, Si); the weight percent of each species is given in Watson et al. (1994b).

Based on the $PM_{2.5}$ profile of the PRSCAB paved road dust used to apportion PM in Claremont (Watson et al. 1994b), the mass percent contribution of Ca, K, and Na is determined to be approximately 11.3, 3.2, and 2.9%, respectively. Applying these approximations to the $PM_{2.5}$ measurements, the concentrations of Ca, K, and Na can then be calculated for each of the 4, 5, and 6 h measurements made during SCAQS. Adding the calculated concentrations of Ca, K, and Na to the input used for the simulations in Figure 13, aerosol nitrate was predicted with SCAPE2 for Claremont in Figure 14. With crustal material, the mean normalized bias in the predictions of SCAPE2 is −15%, whereas excluding its contribution, the mean normalized bias is −35%. Thus for Claremont (a site with very high dust concentrations), the addition of crustal species increases the agreement of predictions to measurements by approximately 15%.

In spite of the inclusion of crustal material in evaluating model performance against SCAQS measurements, the predictions of SCAPE2 still generally underpredict measurements. Although part of this discrepancy may be a result of a low estimation of crustal species concentrations or the exclusion of some other species which

TABLE 5. Model performance for aerosol nitrate over six SCAQS observation stations on August 27–29, 1987

Model	Mean Predicted ($\mu g\ m^{-3}$)	Mean Observed ($\mu g\ m^{-3}$)	Mean Bias ($\mu g\ m^{-3}$)	Mean Normalized Bias, %	Mean Error ($\mu g\ m^{-3}$)	Mean Normalized Error, %
GFEMN	15.66		−4.16	−26.1	4.93	30.5
ISORROPIA	14.39	19.82	−5.43	−32.1	5.88	34.7
SCAPE2	14.91		−4.91	−26.7	5.40	29.7
SEQUILIB	14.51		−5.31	−30.3	5.81	33.3



	Mean Bias	Mean Norm Bias, %	Mean Error	Mean Norm Error, %
with crustal species	-2.1	-15.0	3.0	21.7
without crustal species	-5.7	-35.3	5.8	35.9

FIGURE 14. Performance of SCAPE2 including and excluding crustal species against measurements taken at Claremont during SCAQS.

binds to nitrate, the major cause of the underprediction is probably the bulk equilibrium assumption implicitly used in our analysis. Assuming that all $PM_{2.5}$ particles have the same chemical composition results in the mixing of acidic with alkaline particles introducing errors in the predictions of nitrate. These errors can be minimized with models employing multiple particle groups (Pilinis and Seinfeld 1987). Based on the limited example shown, however, the addition of crustal material in predicting aerosol nitrate behavior increases agreement with observations. Such an improvement stresses the role of crustal material in overall aerosol behavior and the importance of its inclusion in modeling studies of areas where dust is a significant component of total PM.

Thus, given the preceding analysis, we should not expect significantly differing model performance by improving the details of the NH_3-HNO_3-SO_4-H_2O system. The equilibrium approach gives reasonable results concerning nitrate partitioning, but some problems persist which are not attributed to the details of the NH_3-HNO_3-SO_4-H_2O system.

SUMMARY

Based on the analysis conducted between GFEMN, ISORROPIA, SCAPE2, and SEQUILIB, small discrepancies exist in their overall prediction of aerosol behavior. For ammonia rich environments, the mean predictions of aerosol nitrate and total dry inorganic PM agree within 3%. Compared to GFEMN, ISORROPIA has the lowest mean normalized bias and error (4–13%). For aerosol water, the mean prediction of ISORROPIA is lower than that of GFEMN, SCAPE2, and SEQUILIB by approximately 20%. Given the high mean normalized bias and error of ISORROPIA, SCAPE2, and SEQUILIB against predictions of GFEMN for aerosol water, the agreement in predic-

tions is not as good as for predictions of aerosol nitrate and total dry inorganic PM. In predicting overall aerosol behavior, however, the predictions of SCAPE2 and SEQUILIB are very similar.

For ammonia poor environments, there is close agreement in predictions of total PM; the mean prediction of SEQUILIB is approximately 4% higher than that of GFEMN, ISORROPIA, and SCAPE2. The models predict different deliquescence RHs, for many multicomponent systems, but for ammonia poor environments, these discrepancies do not introduce differences in total dry inorganic PM predictions. For NH_4^+(aq), H^+, and aerosol water predictions, the agreement, however, is not as good. Model predictions are within approximately 15, 30, and 70% for NH_4^+, aerosol water, and H^+ predictions, respectively. The differing and high mean normalized bias and error for model predictions against GFEMN for these 3 components show that the models may predict significantly different concentrations for ammonia poor environments.

Hence, in PM related studies where calculations of total dry inorganic PM and aerosol nitrate are important, significant discrepancies will not be introduced by using one equilibrium model versus another. However, for modeling studies relying on H^+ and aerosol water calculations (e.g., visibility and radiative forcing), using the calculations of ISORROPIA compared to SEQUILIB, for example, may introduce discrepancies.

For predicting the multistage behavior of aerosols, ISORROPIA incorporates a weighting system of "dry" and "wet" states to estimate the gradual dissolution of individual components in multicomponent systems. In many cases though, such a weighting system is inadequate in reproducing the multistage and gradual dissolution behavior of aerosol predicted by GFEMN. SCAPE2 and SEQUILIB predict nearly instantaneous deliquescence of multicomponent aerosols in most cases. It should be noted, however, that in general, since all of the aforementioned models use less than perfect parameterized fits to experimental data in their algorithms, errors may result in predicting aerosol behavior.

In reproducing ambient measurements during a summer period for observation stations during SCAQS, all equilibrium models qualitatively predict the diurnal variation and in some cases accurately predict aerosol nitrate concentration for several observation stations during SCAQS. In an attempt to explain the general underprediction of aerosol nitrate concentrations, the effect of crustal species on model predictions was explored. Model simulations, including the concentration of some crustal species, were performed with SCAPE2 and predictions better reproduced measurements. Based on the limited simulations performed with crustal species, it appears that in places where dust comprises a significant fraction of total PM, its role in aerosol nitrate chemistry is important and thus should not be neglected.

Finally, for inclusion with large-scale aerosol transport models, based on its computational rigor and general agreement with GFEMN in predicting aerosol behavior, ISORROPIA is the equilibrium model of choice. For cases where crustal elements are of significance, SCAPE2 is an alternative.

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