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Is the size distribution of urban aerosols determined by thermodynamic equilibrium? An application to Southern California

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Abstract

A size-resolved equilibrium model, SELIQUID, is presented and used to simulate the size–composition distribution of semi-volatile inorganic aerosol in an urban environment. The model uses the efflorescence branch of aerosol behavior to predict the equilibrium partitioning of the aerosol components between the gas phase and a size-resolved aerosol population over the entire RH domain. Predictions of SELIQUID are compared against size-resolved composition measurements at different locations during the Southern California Air Quality Study. Based on the modeling results, the size distribution of sub-micrometer nitrate and ammonium can be determined by thermodynamic equilibrium when the RH > 60%. In cases where the RH < 60%, the assumption that all aerosol particles are metastable liquid solutions may introduce unacceptable errors. On the other hand, the equilibrium assumption, in some cases at least, introduces errors in the calculation of the coarse (particles with diameter > 1 μm or so) nitrate and ammonium that increase with particle size. Finally, the inclusion of crustal species is important in modeling the size distribution of coarse inorganic aerosols when the concentration of these species is high. The effect of these crustal species can be complex and counterintuitive. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

Atmospheric aerosols are suspended particles having diameters ranging from a few nanometers to tens of micrometers. Inorganic compounds typically comprise 25–50% of the mass of the aerosol (Gray et al., 1986) with sulfates, nitrates, ammonium, sodium and chloride being the dominant species. A portion of inorganic particulate matter (PM) is generally classified as crustal material or dust (~15% of total PM) with Ca, K, Mg, and Na being the major active constituents (Kim and

Seinfeld, 1995; Jacobson, 1999). Particles <2.5 μm in diameter are generally referred to as “fine” and those >2.5 μm diameters as “coarse” (Seinfeld and Pandis, 1998). Within a typical urban aerosol size distribution (Wall et al., 1988) sulfate, nitrate and ammonium can be found in both fine and coarse modes. Some of the nitrate is found in the coarse mode together with most of the sodium, chloride and the crustal components.

Atmospheric aerosols reduce the local visibility, air quality, and have adverse effects on human health. Simulating the aerosol size and composition distribution is an invaluable tool in increasing our understanding of aerosol behavior and in determining its role in atmospheric processes. Because of the complex chemical

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composition of the atmospheric aerosol (Seinfeld and Pandis, 1998), a number of approaches have been proposed to simplify the mathematical representation of an aerosol population. One of the most popular approaches is the division of the aerosol population into discrete size sections or bins, each with uniform composition.

Two main approaches have been used to predict the partitioning of semi-volatile species between the gas and aerosol phases. The first approach uses a fully dynamic mass transfer calculation for each aerosol size section (Meng and Seinfeld, 1996; Meng et al., 1998; Jacobson et al., 1996; Jacobson, 1997a,b; Sun and Wexler, 1998a,b; Pilinis et al., 2000). This approach is, at least theoretically, expected to be the most accurate although it is also the most computationally expensive (Pilinis et al., 2000; Capaldo et al., 2000). This computational cost often limits its use in large-scale atmospheric chemical transport models.

The second approach assumes that the two phases, gas and aerosol, are in thermodynamic equilibrium. This approach has been applied extensively in several atmospheric models (Bassett and Seinfeld, 1983; Saxena et al., 1986; Pilinis and Seinfeld, 1987; Kim et al., 1993a,b; Kim and Seinfeld, 1995; Meng et al., 1995; Jacobson et al., 1996; Clegg et al., 1998; Nenes et al., 1998; Ansari and Pandis, 1999a; Zhang et al., 2000). In most applications, the thermodynamic calculations neglected the differences in composition of different particles, and the aerosol population was treated as a “bulk” particulate phase. By assuming that all modeled particles (e.g. $\text{PM}_{2.5}$, PM_{10}) have the same chemical composition, this “bulk” approach often introduces errors in the partitioning calculations. To avoid these errors, the inclusion of multiple particle groups has been considered by some studies (Pilinis and Seinfeld, 1987; Jacobson et al., 1996; Jacobson, 1999). The size-resolved equilibrium approach was first used by Pilinis and Seinfeld (1987). These authors applied and evaluated their model, SEQUILIB, in a three-dimensional chemical transport model (Pilinis and Seinfeld, 1988). Wexler and Seinfeld (1990) recognized the two major weaknesses of the size-resolved equilibrium method, namely that the assumption is often not valid for coarse particles and that for solid particles it leads to infinite solutions. Because of these weaknesses, the approach was abandoned by atmospheric aerosol modelers. Recently, Jacobson (1999) revisited this modeling approach and showed excellent agreement between the predictions of his size-resolved model and ambient measurements in Southern California. At the same time, while some studies have shown the validity of the equilibrium approach (Jacobson, 1999), others (Allen et al., 1989; Harrison and MacKenzie, 1990; Wexler and Seinfeld, 1990, 1992; Ansari and Pandis, 1999b) have questioned this approach suggesting that under some conditions

this assumption is not valid. Furthermore, Meng and Seinfeld (1996), Dassios and Pandis (1999) and Cruz et al. (2000) have analyzed the corresponding equilibrium time scales for ammonium nitrate. Their findings suggest that aerosol nitrate associated with the sub-micrometer size range should be in equilibrium with the gas-phase species since the equilibration time is small compared to other relevant atmospheric time scales. On the other hand, for particles $> 1 \mu\text{m}$ or so the assumption of thermodynamic equilibrium is not applicable in general since the time scale for equilibration is of the order of an hour or more.

Given these rather contradicting results about the usefulness of the size-resolved equilibrium approach, we attempt here to take another critical look at this assumption using an extension of the equilibrium postulate to predict the partition of inorganic salts over a size- and composition-dispersed aerosol. The major advantage of the equilibrium approach is its speed and simplicity. Its major disadvantage is in predicting the behavior of dry particles (low RH). In these cases, the partial pressure product for the formation of NH_4NO_3 is the same for all size sections and consequently infinite solutions exit for the distribution of NH_4NO_3 over all size bins (Wexler and Seinfeld, 1990).

To resolve the weakness of applying the equilibrium approach on dry particles (low RH), an atmospheric model able to predict the partitioning of inorganic aerosol components between the gas-phase precursors and multiple aerosol size bins over the entire RH domain is presented here. The second goal of this work is to apply this model against ambient measurements and answer one of the most interesting questions regarding the inorganic aerosol size distribution: Is the size-resolved equilibrium approach adequate to predict the partition of inorganic salts among a size and composition dispersed aerosol?

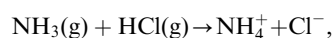
2. Model formulation

SELIQUID is based on the sectional equilibrium model SEQUILIB (Pilinis and Seinfeld, 1987). In predicting the equilibrium composition of all the size sections, the model finds the partial pressure of the volatile species in each bin, which are, at equilibrium, equal to the partial pressure of the volatile species over the total aerosol population. The partial pressure of the volatile compounds in each aerosol size section (bin) is determined by solving the system of equilibrium equations:

$$\frac{a_p^{v_{pj}}}{a_r^{v_{rj}}} = K_{eqj}(T), \quad (1)$$

where $K_{eqj}(T)$ is the equilibrium constant of the j th reaction, a_r and a_p are the activity of reactants and

products, respectively, and v_{rj} and v_{pj} are the stoichiometric coefficients of reactants and products in the j th reaction, respectively. To determine the equilibrium constant, $K_{eqj}(T)$, SELIQUID uses the thermodynamic data compiled by Wagman et al. (1982). It uses the ZSPOW nonlinear equation solver of the International Mathematical and Statistical Libraries (IMSL). Equilibrium expressions, such as Eq. (1) require mean mixed activity coefficients. For instance, for the equilibrium reaction



the corresponding species activities satisfy

$$\frac{a_{\text{NH}_4^+} a_{\text{Cl}^-}}{a_{\text{NH}_3\text{g}} a_{\text{HClg}}} = \frac{m_{\text{NH}_4^+} m_{\text{Cl}^-} \gamma_{\text{NH}_4^+ \text{Cl}^-}^2}{p_{\text{NH}_3\text{g}} p_{\text{HClg}}} K_{eqj}(T), \quad (2)$$

where m is the molality of the ion, p is the partial pressure of the gas, and $\gamma_{\text{NH}_4^+ \text{Cl}^-}^2$ is the mean mixed activity coefficient of NH_4Cl . In SELIQUID, mean mixed activity coefficients are calculated using Bromley's empirical method (Bromley, 1973), as described in Pilinis and Seinfeld (1987). With this method, one needs to know the mean binary activity coefficients. SELIQUID calculates the mean binary activity coefficients using the Kusik–Meissner method (Kusik and Meissner, 1978), which has shown a better performance over other mean binary activity coefficient methods (Kim et al., 1993b). The liquid water content in SELIQUID is calculated using the ZSR method (Robinson and Stokes, 1965).

In a number of applications of atmospheric aerosol thermodynamic models, it is assumed that particles are solid below their deliquescence relative humidity and liquid above it. In SELIQUID, when the RH decreases below the deliquescence relative humidity of the multi-component solution, solutions are considered to remain supersaturated (metastable equilibrium) and thus, no solid phase is permitted. This approach allows us to predict the equilibrium composition between the gas-phase precursors and the multiple aerosol size bins over the entire RH domain without encountering the infinite solution problem (Wexler and Seinfeld, 1990).

The treatment of crustal species in atmospheric particulate matter modeling was first considered by Kim and Seinfeld (1995) in their model SCAPE2. Previously, the models treated only sulfate, ammonium, nitrate, chloride and sodium. Since then, other studies (Jacobson, 1999; Ansari and Pandis, 1999b) have stressed the importance of including these elements in the modeling framework as they can influence the partitioning of total nitrate. For atmospheric particulate matter models that do not explicitly model crustal species, these elements can be modeled to a first approximation as equivalent concentration of sodium giving comparable results with SCAPE2 (Moya et al., 2001). SELIQUID allows the incorporation of crustal

species (calcium, potassium and magnesium) in its modeling framework, modeling them as equivalent concentrations of sodium. Moreover, with regards to calcium, SELIQUID considers the formation of calcium sulfate (gypsum) before the treatment of the dissolved form of calcium (Ca^{2+}) as equivalent concentration of sodium using the following chemical reaction:



A solid form of calcium is practically present in all cases considering the DRH of calcium sulfate ($\approx 97\%$), and the value of the solubility product constant at ambient temperature (around $4 \times 10^{-5} \text{M}^2$). If the formation of calcium sulfate is limited by the availability of sulfate, the remaining calcium along with the potassium and magnesium is treated as equivalent concentration of sodium. If the formation of the solid is limited by the availability of calcium, then practically all the available calcium precipitates as calcium sulfate.

The potential chemical components considered in SELIQUID are then the same gas and liquid components as SEQUILIB plus the solid form of calcium (calcium sulfate), plus the dissolved forms of calcium, magnesium and potassium considered as equivalent concentration of sodium.

3. Model performance

3.1. Model predictions against SCAQS measurements

To examine SELIQUID, predictions were compared against the eight-stage Berner impactor measurements of John et al. (1990) during the Southern California Air Quality Study (SCAQS). The 50% cutoff diameters for stages 1–8 were 0.075, 0.14, 0.27, 0.52, 1.04, 2.15, 4.25, and 8.2 μm , respectively. Fourteen cases at Long Beach (11 and 3 from the summer and fall sampling periods, respectively), four cases at Riverside (Rubidoux) and two cases at Claremont are discussed in this study. These cases were chosen from the SCAQS database as they include measurements of crustal species (calcium and magnesium). There is an additional case (1300–1630 PST on 28 August 1987 at Riverside) that will be discussed in this study. This is an interesting case as the ambient RH (45%) was below the DRH of NH_4NO_3 (62%) and will be useful to evaluate model performance at low RH conditions. The SCAQS database also contained gas-phase concentrations of NH_3 and HNO_3 , hourly temperature and RH values.

To predict the equilibrium partitioning between the gas-phase precursors and the multiple aerosol size bins, the measured impactor stage values and gas-phase concentrations are used to calculate the total concentrations of nitrate and ammonia. Total concentrations of nitrate and ammonia therefore include the gas-phase

concentrations plus the sum of the corresponding measured stage values. For instance, for PM_{10} simulations, total nitrate included nitric acid plus particulate-phase concentrations corresponding to the first five stages. During SCAQS gas-phase concentrations of HCl were not measured and we did not include HCl as model input. This assumption underestimates the availability of chloride in our system and will introduce some error. Sulfate, sodium, calcium and magnesium were constrained to their corresponding size bins during simulations. Particulate-phase concentrations of potassium were not available. Calcium and magnesium were measured only in stages 6 and 7 (2.15 and 4.35 μm 50% cutoff diameters, respectively). For stage 8 (8.2 μm 50% cutoff diameter) we have assumed the same values

for calcium and magnesium as those measured in stage 7 (Jacobson, 1999). Crustal species as well as nitrate concentrations were higher at Riverside than at Long Beach or Claremont. Crustal species (calcium and magnesium) were modeled in SELIQUID as equivalent concentrations of sodium. This treatment is expected to introduce additional error when the crustal species concentrations are high and will be discussed later.

Fig. 1 shows the predicted and measured size-distributed nitrate and ammonium concentrations for one of the 20 cases studied (Long Beach, 0500–0830 Pacific Standard Time (PST) on 13 November 1987). For this specific case, nitrate and ammonium predictions match the corresponding measurements suggesting that the equilibrium assumption is valid. Extending our analysis,

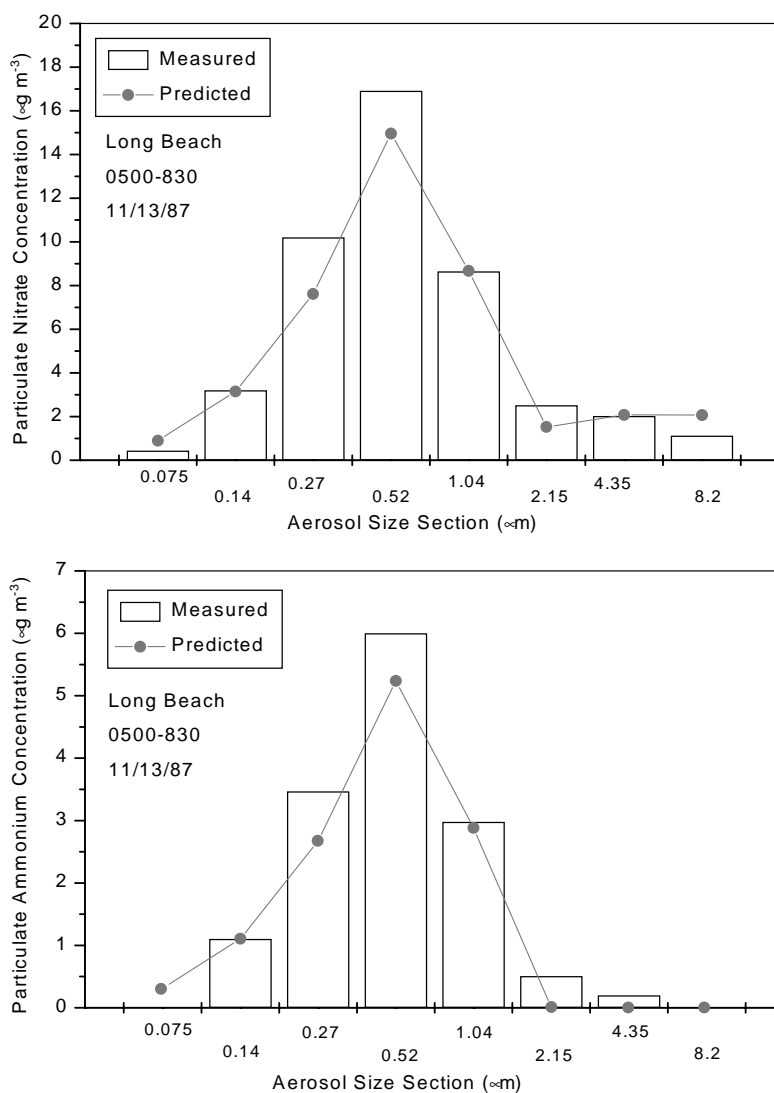


Fig. 1. Predicted versus observed size-resolved particulate nitrate and ammonium for measurements made at 0500–0830 PST on 13 November 1987 at Long Beach.

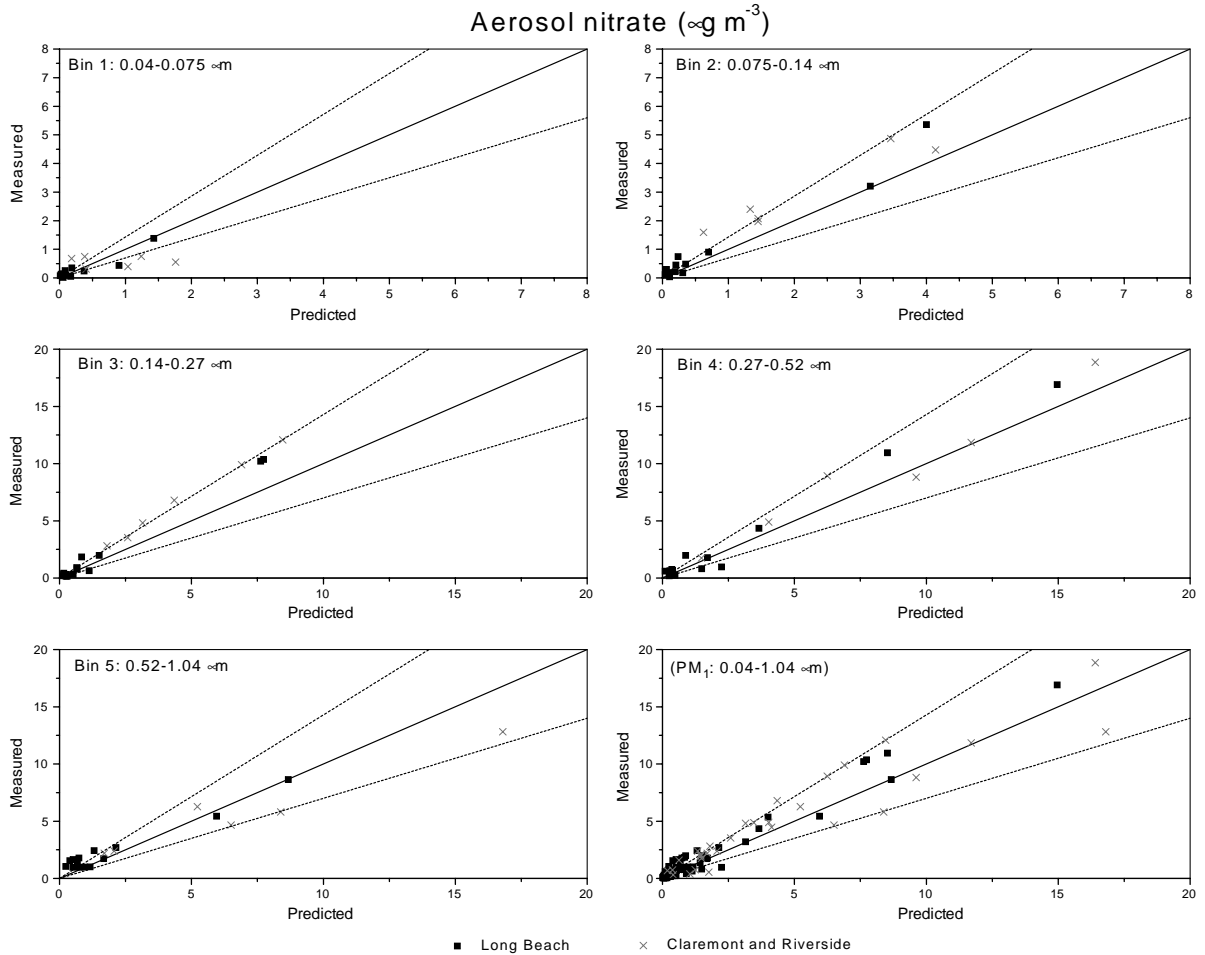


Fig. 2. Predicted versus observed particulate fine nitrate (size bins 1–5 and PM_{10}). Fourteen cases analyzed at Long Beach corresponding to measurements (John et al., 1990) made at 1300–1630 and 1700–0430 on 19 June 1987; 0500–0830, 0900–1230, 1300–1630 and 1700–0000 on 24 June 1987; 0500–0830 and 1300–1630 on 28 August 1987; 0500–0830 on 29 August 1987; 1700–0000 on 2 September 1987; 0500–0830 on 3 September 1987; 0500–0830 and 0900–1230 on 13 November 1987; and 0900–1230 on 11 December 1987. Four cases analyzed at Riverside corresponding to measurements made at 1700–0430 on 19 June 1987; 1700–0000 on 24 June 1987; and 0500–0830 on 28 and 29 August 1987. Two cases analyzed at Claremont corresponding to measurements made at 0500–0830 on 28 and 29 August 1987. The times are Pacific Standard Time (PST). The diameter ranges of each figure correspond to 50% cutoff diameters for the impactor. These are considered as sectional boundaries in SELIQUID simulations.

Figs. 2 and 3 show the predicted versus observed nitrate and ammonium concentration, respectively, for the sub-micrometer aerosol bins and for the total PM_{10} (first five aerosol size bins) for Long Beach, Claremont, and Riverside. Except for the low concentrations of stage 1 where some discrepancies can be seen, overall equilibrium calculations agree well (especially if one considers the experimental error) with the corresponding observed values suggesting that for sub-micrometer aerosols the equilibrium assumption is reasonable for all cases for all the three locations. The agreement between the predicted and measured PM_{10} nitrate indicates that such a model can reproduce the measured PM_{10} nitrate within 30%

under a variety of conditions with moderate or high relative humidity (see Section 3.4 for a discussion of a low RH case).

3.2. Size-resolved $\text{PM}_{\text{coarse}}$

Figs. 4 and 5 show the predicted versus observed nitrate and ammonium concentration, respectively, for bins 6, 7 and 8, corresponding to 2.15, 4.35 and $8.2 \mu\text{m}$ 50% cutoff diameters and for the total $\text{PM}_{\text{coarse}}$ (last three aerosol size sections). The nitrate predictions in bin 6 were reasonably accurate, but that accuracy decreased in bin 7 and further in bin 8. The disagreement between

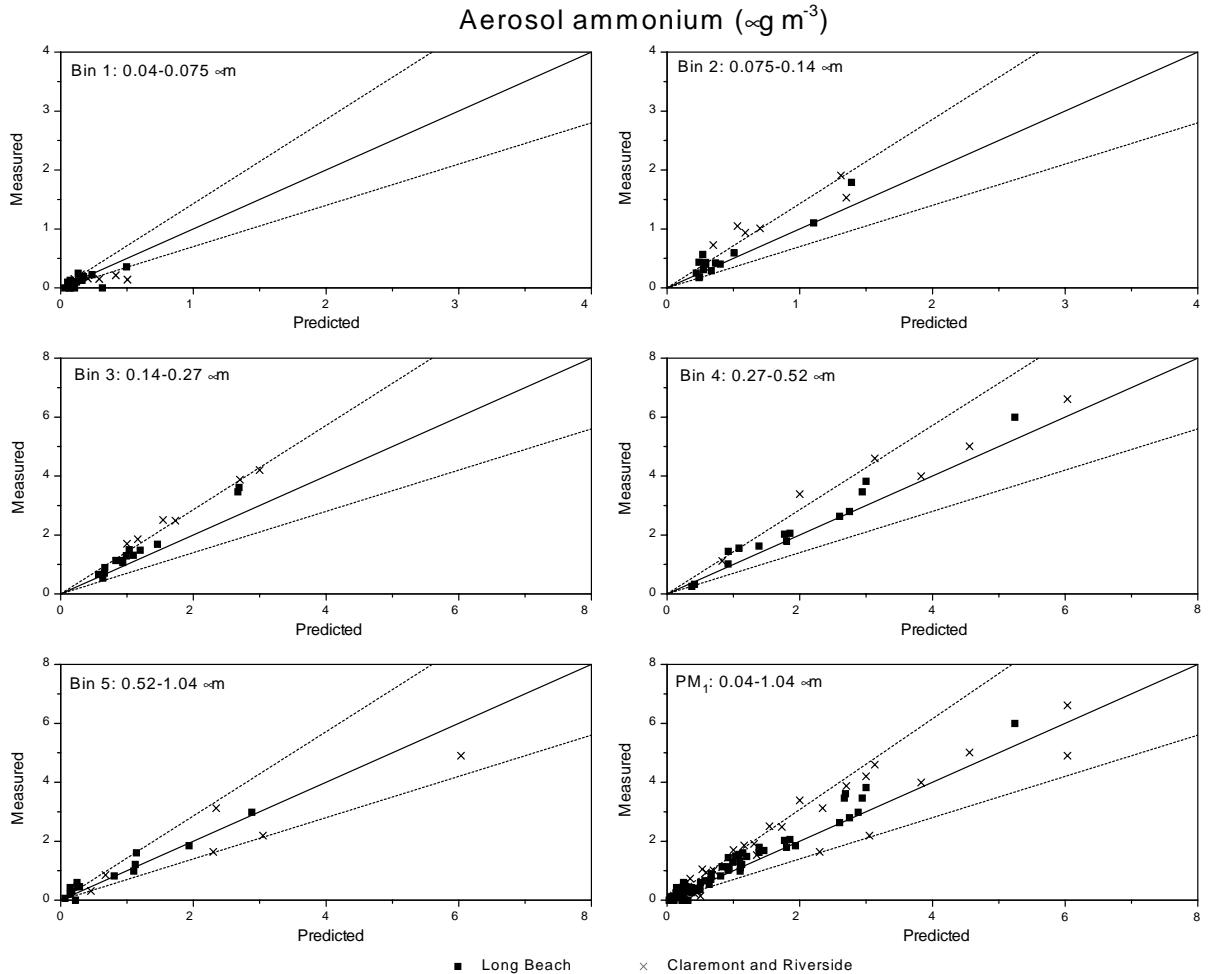


Fig. 3. Predicted versus observed particulate fine ammonium (size bins 1–5 and PM_{10}). Fourteen cases analyzed at Long Beach corresponding to measurements (John et al., 1990) made at 1300–1630 and 1700–0430 on 19 June 1987; 0500–0830, 0900–1230, 1300–1630 and 1700–0000 on 24 June 1987; 0500–0830 and 1300–1630 on 28 August 1987; 0500–0830 on 29 August 1987; 1700–0000 on 2 September 1987; 0500–0830 on 3 September 1987; 0500–0830 and 0900–1230 on 13 November 1987; and 0900–1230 on 11 December 1987. Four cases analyzed at Riverside corresponding to measurements made at 1700–0430 on 19 June 1987; 1700–0000 on 24 June 1987; and 0500–0830 on 28 and 29 August 1987. Two cases analyzed at Claremont corresponding to measurements made at 0500–0830 on 28 and 29 August 1987. The times are PST. The diameter ranges of each figure correspond to 50% cutoff diameters for the impactor. These are considered as sectional boundaries in SELIQUID simulations.

the predicted and observed nitrate values indicates that the equilibrium assumption introduces some errors that increase with particle size. Most of the error is contributed by the last size section where the model tends to over-predict the nitrate. The model fails to reproduce the coarse ammonium measurements (Fig. 5). The coarse particles are alkaline and the model predicts that little or no ammonium should be present in most cases. Based on the results showed in Figs. 2–5 and the experimental error of the measurements, thermodynamic equilibrium is a reasonable assumption for the calculation of the size-resolved partitioning of

semi-volatile compounds between the fine aerosol (PM_{10}) and the gas phase. Conversely, for larger particle size ranges ($> 1 \mu\text{m}$), the current equilibrium model was not adequate in reproducing observations in most of the cases tested. The disagreement can be the result of either the lack of equilibrium or weaknesses of SELIQUID and will be discussed in a subsequent section.

3.3. Size-resolved $\text{PM}_{2.5}$ and PM_{10}

Fig. 6 shows the predicted versus observed nitrate concentration for bins 1–6 ($\text{PM}_{2.5}$) and bins 1–8 (PM_{10}).

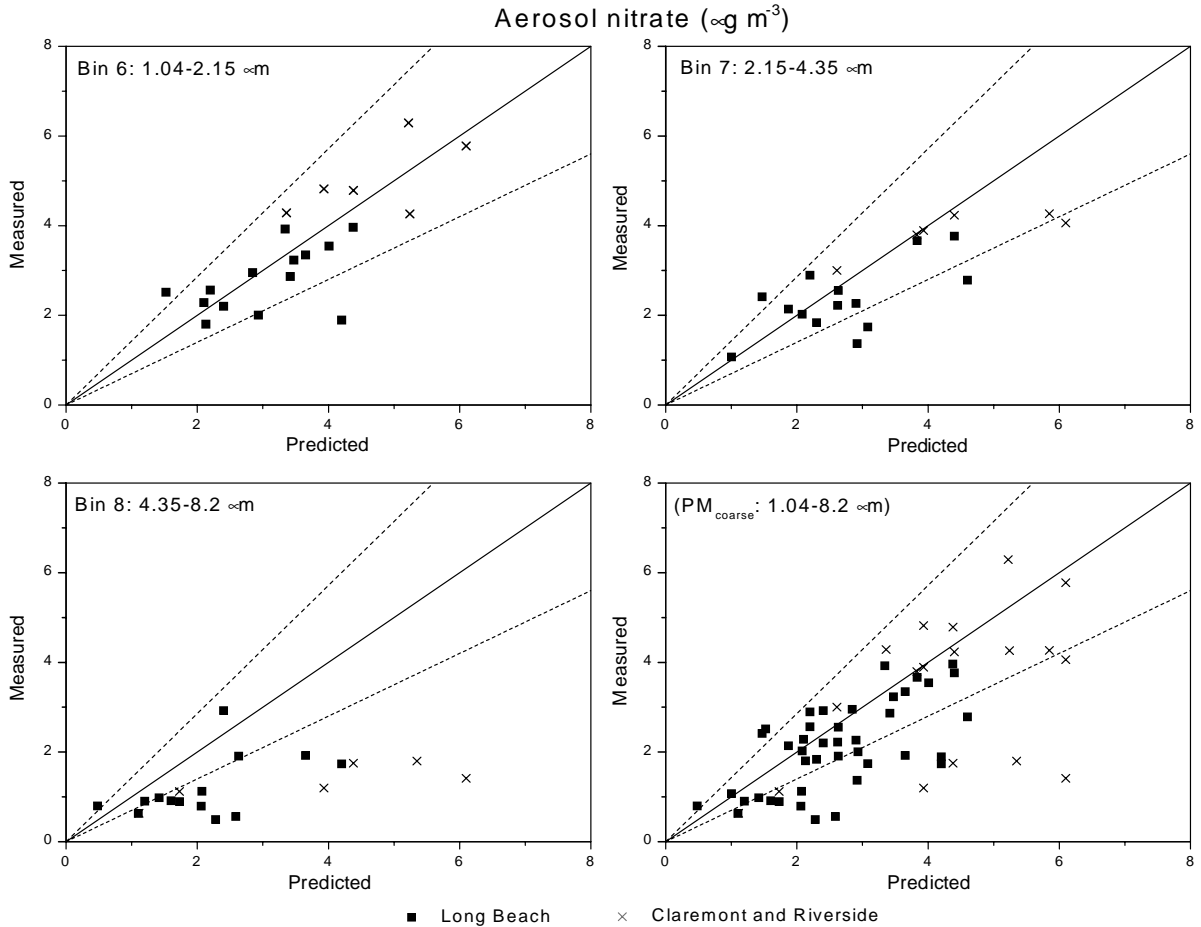


Fig. 4. Predicted versus observed particulate coarse nitrate (size bins 6–8 and $\text{PM}_{\text{coarse}}$). Fourteen cases analyzed at Long Beach corresponding to measurements (John et al., 1990) made at 1300–1630 and 1700–0430 on 19 June 1987; 0500–0830, 0900–1230, 1300–1630 and 1700–0000 on 24 June 1987; 0500–0830 and 1300–1630 on 28 August 1987; 0500–0830 on 29 August 1987; 1700–0000 on 2 September 1987; 0500–0830 on 3 September 1987; 0500–0830 and 0900–1230 on 13 November 1987; and 0900–1230 on 11 December 1987. Four cases analyzed at Riverside corresponding to measurements made at 1700–0430 on 19 June 1987; 1700–0000 on 24 June 1987; and 0500–0830 on 28 and 29 August 1987. Two cases analyzed at Claremont corresponding to measurements made at 0500–0830 on 28 and 29 August 1987. The times are PST. The diameter ranges of each figure correspond to 50% cutoff diameters for the impactor. These are considered as sectional boundaries in SELIQUID simulations.

Despite the weaknesses in reproducing the coarse aerosol concentrations, size-resolved $\text{PM}_{2.5}$ nitrate predictions are mostly within 30% of error. The low nitrate concentrations, which are subject to the largest experimental error, are the main exception. On the other hand, as seen in Figs. 4 and 5, the current size-resolved equilibrium approach introduces errors in modeling particles $>2.5\mu\text{m}$. Therefore for the cases under study, the present size-resolved equilibrium model, SELIQUID, will introduce errors above 30% in cases when the measured PM_{10} nitrate $<2.5\mu\text{g m}^{-3}$ and the PM_{10} ammonium $<1\mu\text{g m}^{-3}$.

3.4. Model performance at low relative humidity

To examine model performance at low RH, SELIQUID predictions were compared with measurements for the 1300–1630 PST period on 28 August 1987 at Riverside. In this case, the ambient RH was 45%. For low RH, SELIQUID assumes that the multi-component solution remains supersaturated (metastable equilibrium state), and therefore, no dry particles are considered in the modeling framework. Using the efflorescence branch of aerosol behavior (that is assuming that particles are liquid always) enables the model to predict the

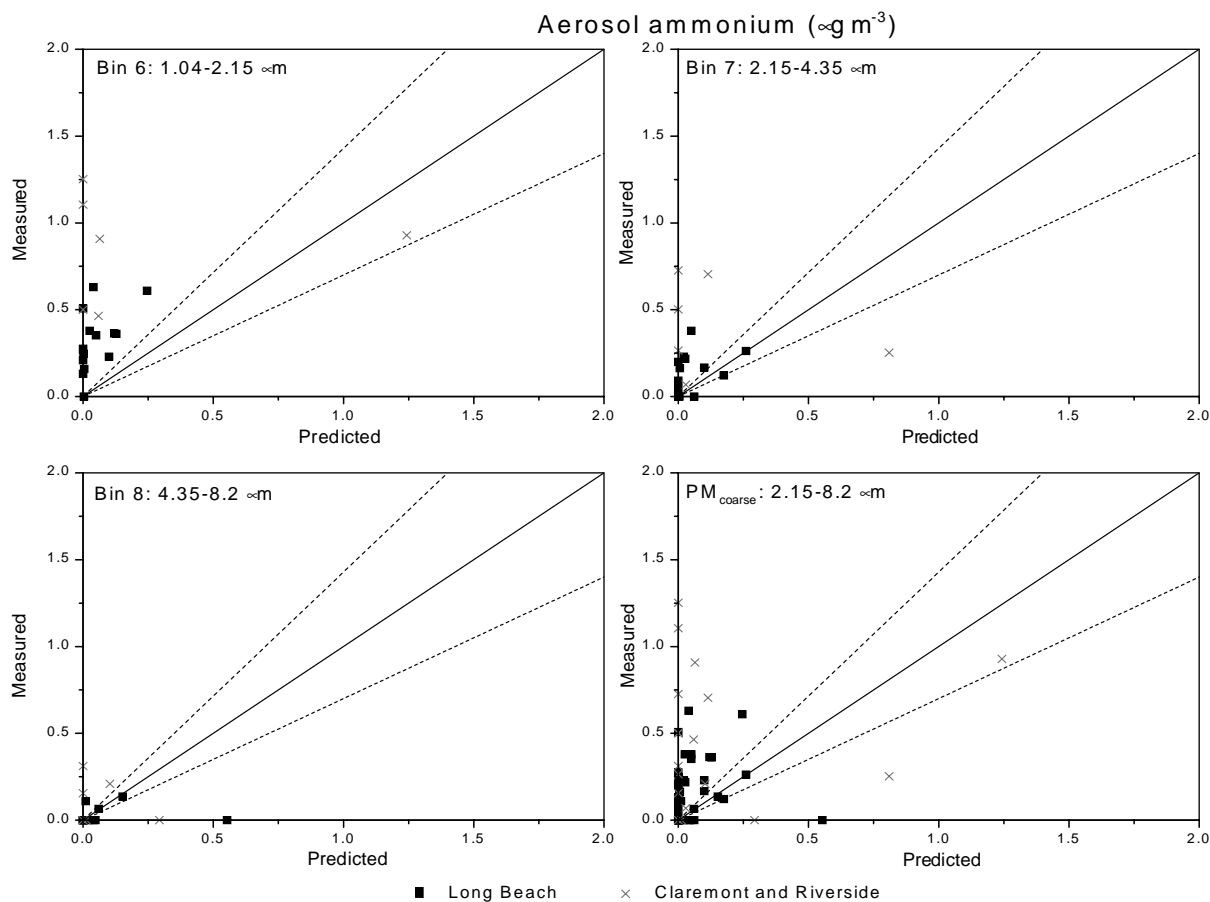


Fig. 5. Predicted versus observed particulate coarse ammonium (size bins 6–8 and PM_{coarse}). Fourteen cases analyzed at Long Beach corresponding to measurements (John et al., 1990) made at 1300–1630 and 1700–0430 on 19 June 1987; 0500–0830, 0900–1230, 1300–1630 and 1700–0000 on 24 June 1987; 0500–0830 and 1300–1630 on 28 August 1987; 0500–0830 on 29 August 1987; 1700–0000 on 2 September 1987; 0500–0830 on 3 September 1987; 0500–0830 and 0900–1230 on 13 November 1987; and 0900–1230 on 11 December 1987. Four cases analyzed at Riverside corresponding to measurements made at 1700–0430 on 19 June 1987; 1700–0000 on 24 June 1987; and 0500–0830 on 28 and 29 August 1987. Two cases analyzed at Claremont corresponding to measurements made at 0500–0830 on 28 and 29 August 1987. The times are PST. The diameter ranges of each figure correspond to 50% cutoff diameters for the impactor. These are considered as sectional boundaries in SELIQUID simulations.

equilibrium composition between the gas-phase precursors and the multiple aerosol size bins over the entire RH domain. As seen in Fig. 7, model predictions are in complete disagreement with observations suggesting that for low RH cases ($RH < 60\%$), the assumption that all aerosol particles remain in a supersaturated solution (metastable equilibrium) introduces errors. For this case, the observed PM_{10} nitrate was $42.8 \mu\text{g m}^{-3}$ while the predicted concentration by the size-resolved model is $19.2 \mu\text{g m}^{-3}$. So using a size-resolved equilibrium model like SELIQUID for low RHs not only introduces errors to the predicted size distribution, but also to the total aerosol concentration. The model over-predicts the equilibrium vapor pressure of nitric acid and ammonia

over the particles, artificially shifting the nitrate equilibrium towards the gas phase. This is indirect evidence that the particles were solid during this period and not metastable liquids. If a bulk (all particles are assumed to have the same composition) model (SEUILIB or ISORROPIA) is used for this period the predicted aerosol PM_{10} nitrate concentration is $40.1 \mu\text{g m}^{-3}$, in good agreement with the $42.8 \mu\text{g m}^{-3}$ measured. This agreement further supports the hypothesis that the particles were solid during this period and indicates that at low RH values, a bulk model may be more useful, at least for the total aerosol nitrate concentration, than a size-resolved equilibrium model like SELIQUID.

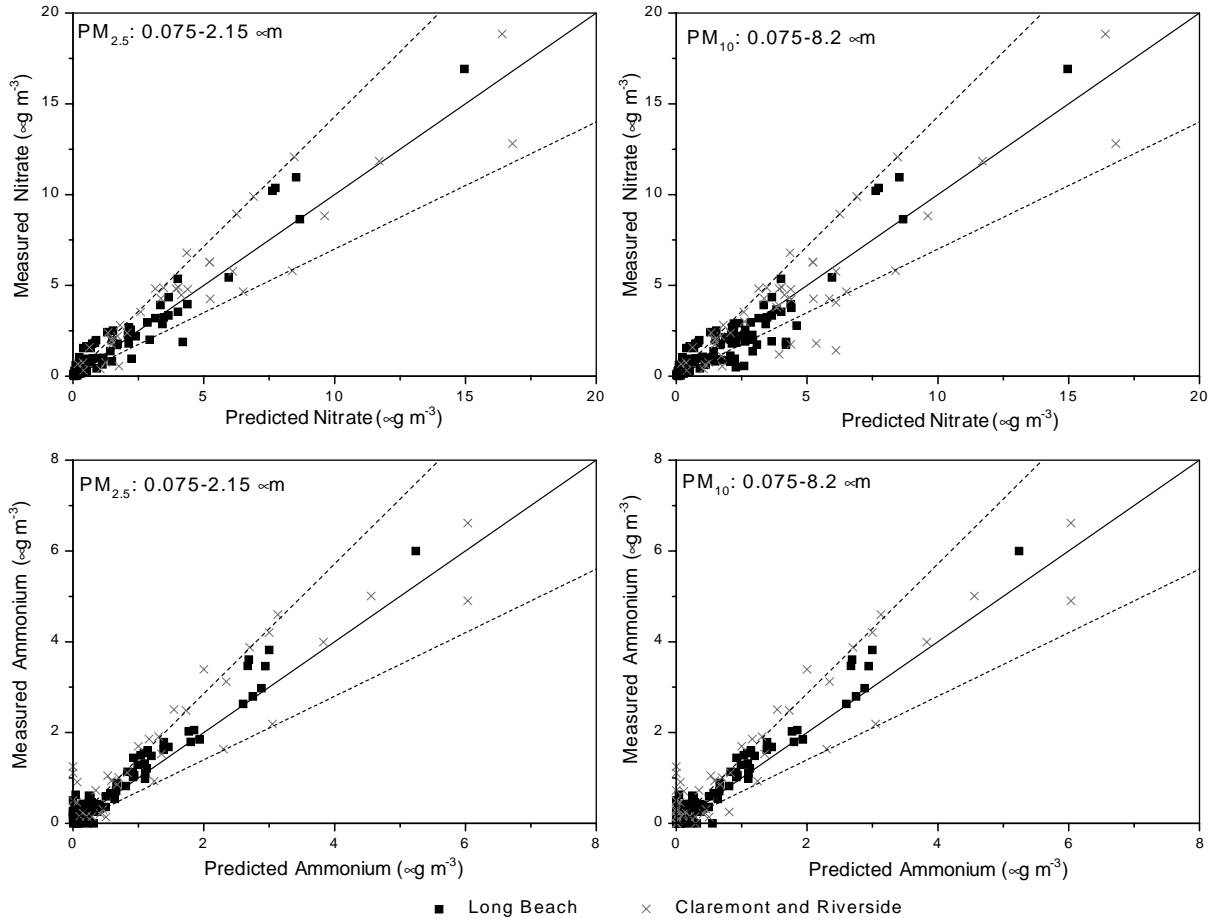


Fig. 6. Predicted versus observed $PM_{2.5}$ and PM_{10} nitrate and ammonium. Fourteen cases analyzed at Long Beach corresponding to measurements (John et al., 1990) made at 1300–1630 and 1700–0430 on 19 June 1987; 0500–0830 and 1300–1630 on 24 June 1987; 0500–0830 and 1300–1630 on 28 August 1987; 0500–0830 on 29 August 1987; 1700–0000 on 2 September 1987; 0500–0830 on 3 September 1987; 0500–0830 and 0900–1230 on 13 November 1987; and 0900–1230 on 11 December 1987. Four cases analyzed at Riverside corresponding to measurements made at 1700–0430 on 19 June 1987; 1700–0000 on 24 June 1987; and 0500–0830 on 28 and 29 August 1987. Two cases analyzed at Claremont corresponding to measurements made at 0500–0830 on 28 and 29 August 1987. The times are PST. The diameter ranges of each figure correspond to 50% cutoff diameters for the impactor. These are considered as sectional boundaries in SELIQUID simulations.

3.5. Sources of error

Given the discrepancies found between the predicted and measured PM_{coarse} nitrate and ammonium, a discussion of the possible sources of error is worthwhile. These discrepancies may be attributed to the equilibrium assumption implicitly used in our model, to our treatment of crustal species, to the lack of some necessary input information (total chloride concentrations, complete crustal species size distribution) or to the experimental error associated with field measurements of semi-volatile inorganic components.

The equilibrium assumption is expected to be inadequate for the modeling of coarse particles. Wexler

and Seinfeld (1990) estimated that the corresponding time scale for equilibration will be of the order of at least hours and will increase with particle size. This is consistent with the results shown in Figs. 4 and 5, where the error increases as particle size increases. Therefore, deviations from equilibrium are consistent both with the existing theory and also with the error dependence on size for these simulations.

The inclusion of crustal species in the modeling framework is important as these elements can influence the partitioning of total nitrate (Kim and Seinfeld, 1995; Ansari and Pandis, 1999a, b; Jacobson, 1999; Moya et al., 2001). These crustal species are found mainly on large particles (coarse mode) and as mentioned, they are

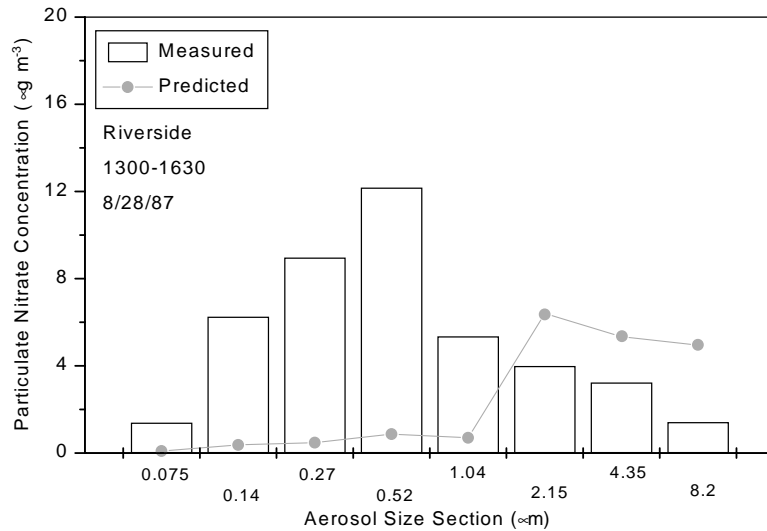


Fig. 7. Predicted versus observed size-resolved particulate nitrate for measurements made at 1300–1630 PST on 28 August 1987 at Riverside.

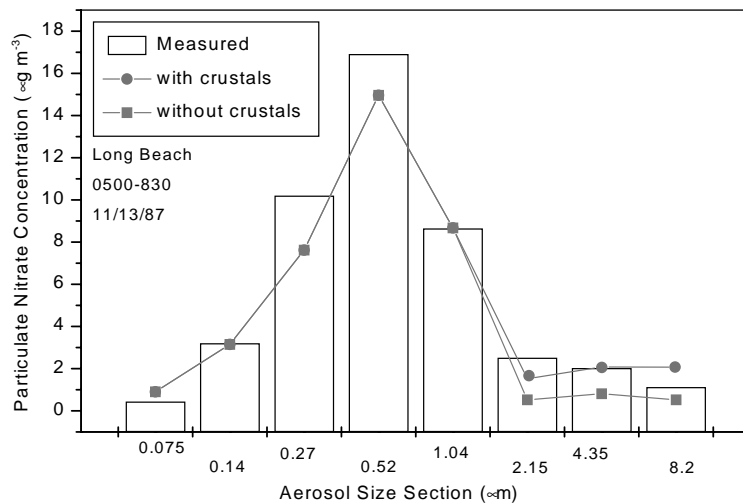


Fig. 8. Comparison of the predicted versus observed size-resolved particulate nitrate with (and without) considering crustal species as equivalent concentrations of sodium for measurements made at 0500–830 PST on 13 November 1987 at Long Beach.

treated as equivalent concentrations of sodium in SELIQUID. Fig. 8 compares the predicted equilibrium size-distributed nitrate concentrations versus measurements with and without including crustal species (calcium and magnesium) for one of the 20 cases studied (Long Beach, 0500–830 PST on 13 November 1987). For this specific case, model performance for the coarse particles improves with the inclusion of the $1.75 \mu\text{g m}^{-3}$ of calcium and $0.18 \mu\text{g m}^{-3}$ of magnesium. Extending our analysis for the 20 cases studied, Fig. 9 shows the predicted nitrate concentration versus the absolute

error, respectively, for bins 6, 7 and 8 and for the total $\text{PM}_{\text{coarse}}$. As seen the inclusion of crustal species increase predicted nitrate in bins 6, 7 and 8 (coarse-mode). The presence of calcium and magnesium decrease the available nitric acid gas shifting the nitrate equilibrium towards the particulate phase (Dentener et al., 1996; Tabazadeh et al., 1999). Fig. 9 also shows that the inclusion of crustal species tends to improve SELIQUID performance for aerosol bins 6 and 7 (overall predictions associated with smaller absolute errors), while for bin 8, model performance deteriorates after the incorporation

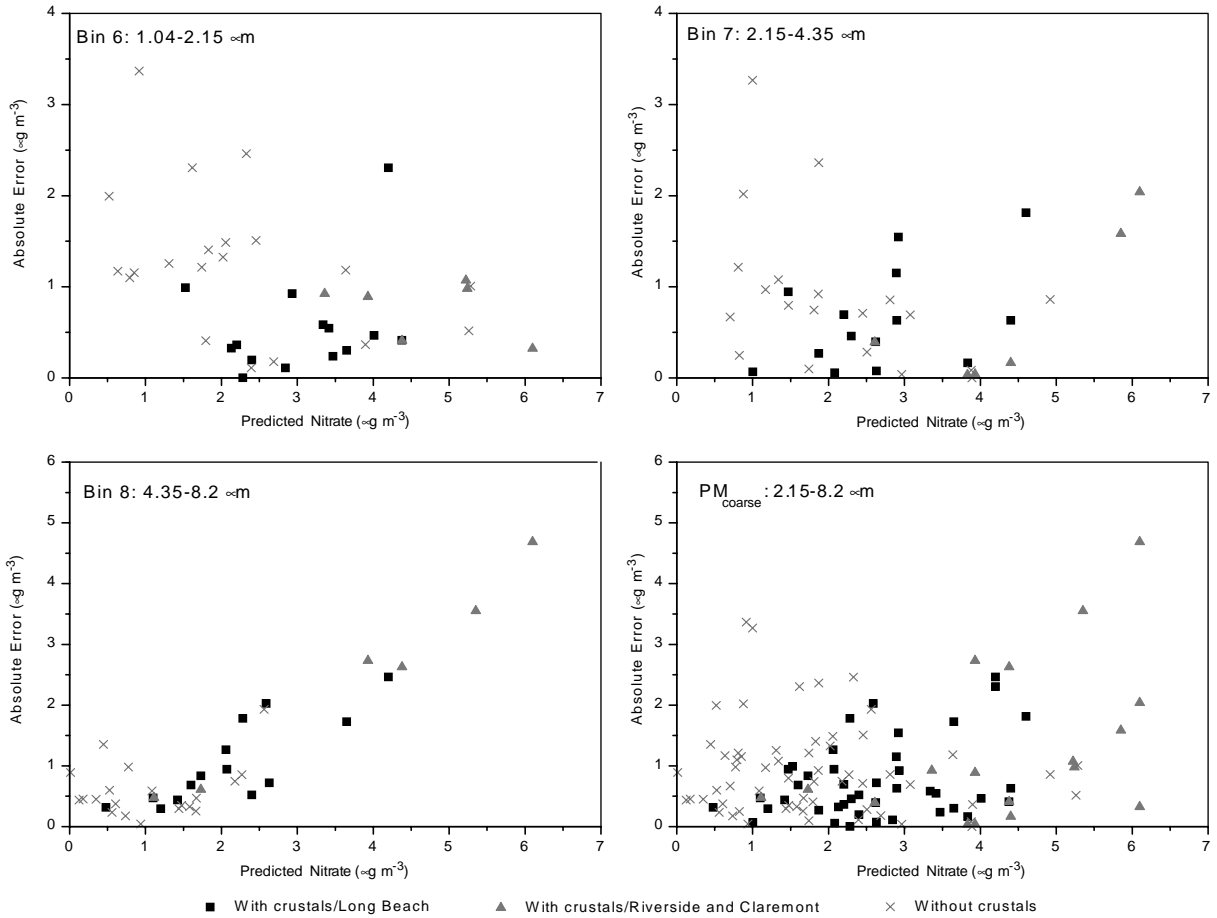


Fig. 9. Predicted particulate coarse nitrate (size bins 6–8 and $\text{PM}_{\text{coarse}}$) versus the absolute error. Fourteen cases analyzed at Long Beach corresponding to measurements (John et al., 1990) made at 1300–1630 and 1700–0430 on 19 June 1987; 0500–0830, 0900–1230, 1300–1630 and 1700–0000 on 24 June 1987; 0500–0830 and 1300–1630 on 28 August 1987; 0500–0830 on 29 August 1987; 1700–0000 on 2 September 1987; 0500–0830 on 3 September 1987; 0500–0830 and 0900–1230 on 13 November 1987; and 0900–1230 on 11 December 1987. Four cases analyzed at Riverside corresponding to measurements made at 1700–0430 on 19 June 1987; 1700–0000 on 24 June 1987; and 0500–0830 on 28 and 29 August 1987. Two cases analyzed at Claremont corresponding to measurements made at 0500–0830 on 28 and 29 August 1987. The times are PST. The diameter ranges of each figure correspond to 50% cutoff diameters for the impactor. These are considered as sectional boundaries in SELIQUID simulations.

of these elements (as equivalent concentration of sodium) in simulations. For this specific size bin, the errors in predicting particulate nitrate concentrations are larger at Riverside and Claremont than at Long Beach. Table 1 shows statistics of SELIQUID performance for the results shown in Fig. 9. Based on the mean errors, considering crustal species as equivalent concentrations of sodium in SELIQUID improves particulate nitrate predictions for aerosol bins 6 and 7. Conversely, for bin 8 the inclusion of these elements does not improve model performance. Overall model performance in predicting coarse-mode nitrate ($\text{PM}_{\text{coarse}}$) is practically the same incorporating (mean error $0.91 \mu\text{g m}^{-3}$) or not (mean error $0.92 \mu\text{g m}^{-3}$) crustal species as equivalent concentrations of sodium

Table 1
Particulate nitrate concentration averaged over 20 cases studied for bins 6, 7 and 8

Bin	Mean predicted ($\mu\text{g m}^{-3}$)		Mean observed ($\mu\text{g m}^{-3}$)
	With crustals	Without crustals	
6	3.55	2.20	3.47
7	3.22	2.10	2.80
8	2.60	1.06	1.23

in the modeling framework. A possible explanation for the discrepancies in bin 8 is that the treatment of crustal species as equivalent concentration of sodium in

SELIQUID may introduce some error when the concentration of crustal species is high. The potential dependence of the error on the concentration of crustal species is examined in Fig. 10. This figure shows the absolute error versus crustal species concentration (as equivalent sodium concentration) respectively, for bins 6, 7 and 8, and for the total PM_{coarse} , for the 20 cases studied. Equivalent concentrations of sodium in Fig. 10 included calcium concentrations after the formation of calcium sulfate. As seen, for bins 6 and 7 there is not a clear trend that the error increases as crustal species concentration increases. On the other hand, for several of the cases in bin 8, the error increases as crustal species concentration increases. Again, the largest errors in bin 8 are related to simulations performed at Riverside and Claremont, where the concentration of crustal species is

high. These findings suggest that apparently, in the largest aerosol size section ($8.2\mu\text{m}$ 50% cutoff diameter), when the concentration of crustal species is high, part of the error in the calculation of nitrate concentration may be due to our implicit treatment of crustal species (as equivalent concentration of sodium).

To further analyze this hypothesis, Table 2 compares the performance of SELIQUID and EQUISOLV II (Jacobson, 1999) in predicting coarse-mode nitrate concentrations for two Riverside cases (0500–0830 PST period on 28 and 29 August 1987) where the concentration of crustal species in the coarse mode is high. As seen, EQUISOLV II (that explicitly models crustal species) overall performs better than SELIQUID, particularly for nitrate predictions in the largest aerosol size section (bin 8). This finding further supports the

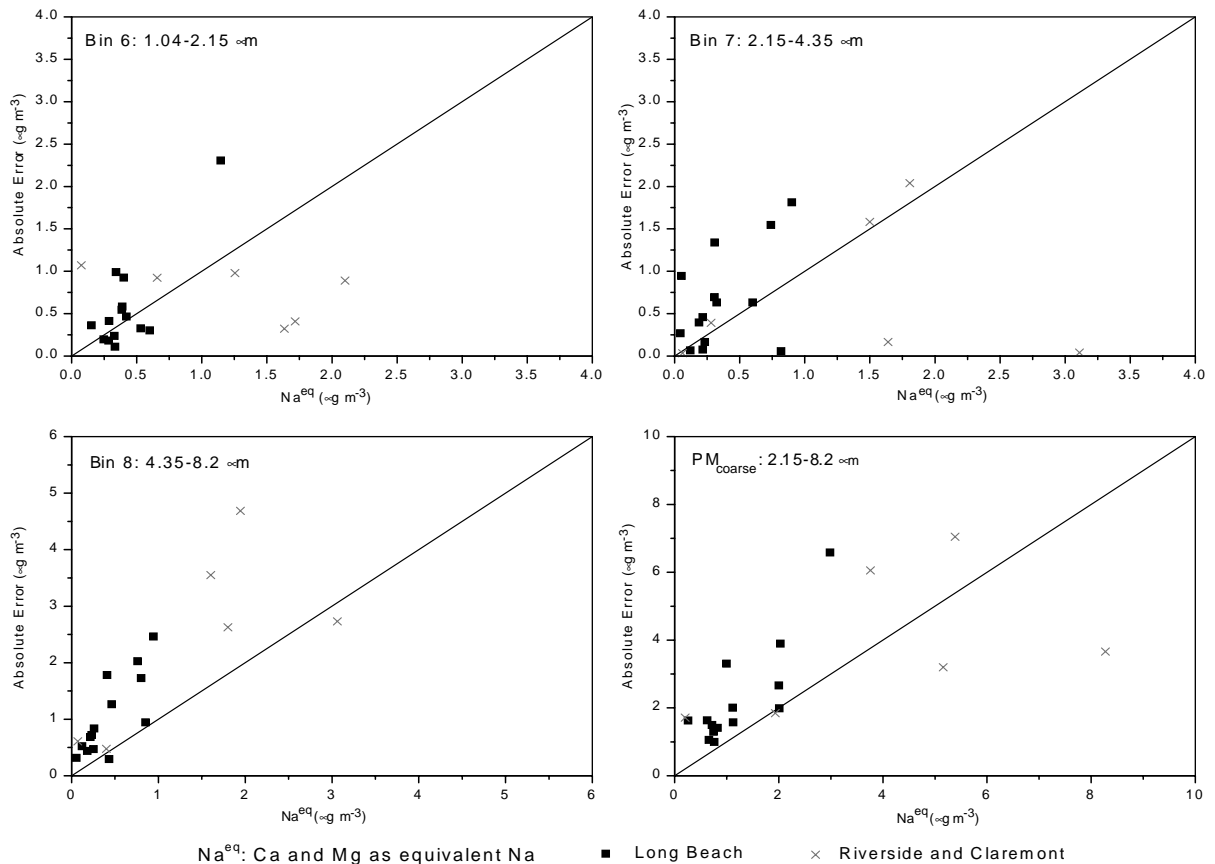


Fig. 10. Crustal species (calcium and magnesium) as equivalent concentration of sodium versus the absolute error. Fourteen cases analyzed at Long Beach corresponding to measurements (John et al., 1990) made at 1300–1630 and 1700–0430 on 19 June 1987; 0500–0830, 0900–1230, 1300–1630 and 1700–0000 on 24 June 1987; 0500–0830 and 1300–1630 on 28 August 1987; 0500–0830 on 29 August 1987; 1700–0000 on 2 September 1987; 0500–0830 on 3 September 1987; 0500–0830 and 0900–1230 on 13 November 1987; and 0900–1230 on 11 December 1987. Four cases analyzed at Riverside corresponding to measurements made at 1700–0430 on 19 June 1987; 1700–0000 on 24 June 1987; and 0500–0830 on 28 and 29 August 1987. Two cases analyzed at Claremont corresponding to measurements made at 0500–0830 on 28 and 29 August 1987. The times are PST. The diameter ranges of each figure correspond to 50% cutoff diameters for the impactor. These are considered as sectional boundaries in SELIQUID simulations.

Table 2
 SELIQUID and EQUISOLV II performance predicting coarse nitrate concentrations for the PST period 0500–0830 on 28 and 29 August 1987 at Riverside

Date	Bin	Predicted nitrate ($\mu\text{g m}^{-3}$)		Observed ($\mu\text{g m}^{-3}$)	Mean error ($\mu\text{g m}^{-3}$)	
		SELIQUID	EQUISOLV II		SELIQUID	EQUISOLV II
28 August 1987	6	3.90	3.83	4.82	0.89	0.99
	7	3.93	3.85	3.89	0.04	0.04
	8	3.95	1.52	1.20	2.73	0.32
29 August 1987	6	6.08	5.45	5.78	0.32	0.33
	7	6.10	3.85	4.06	2.04	0.21
	8	6.13	1.70	1.41	4.69	0.29

hypothesis that the implicit treatment of crustal species in SELIQUID may introduce additional errors when concentration of these species is high. Treating Ca^{2+} and Mg^{2+} as mole-equivalent Na^+ ions (e.g. $\text{Ca}^{2+} = 2\text{Na}^+$) may cause over-predictions of coarse-mode nitrate. For example, the binary activity coefficients of $\text{Mg}(\text{NO}_3)_2$ is larger than that of NaNO_3 in all cases where the molality of NaNO_3 is twice that of $\text{Mg}(\text{NO}_3)_2$. As a result, less nitrate can dissolve in water when Mg^{2+} is present in comparison with when Mg is “converted” to 2Na^+ . The binary activity coefficients of $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 are similar to each other when Ca^{2+} is converted to 2Na^+ .

Another possible source of error can be attributed to the lack of some necessary input information (complete crustal species size/composition distribution, total chloride concentrations). With regards to crustal species, there was a lack of data of particulate-phase concentrations of coarse-mode potassium, as well as particulate-phase concentrations of calcium and magnesium in the largest aerosol size section (bin 8). As mentioned, for this bin we have assumed the same values for calcium and magnesium as those measured in bin 7. To examine this assumption closely, we have performed few simulations analyzing the sensitivity of SELIQUID in predicting coarse-mode nitrate concentrations when crustal species concentration is changed. Table 3 shows the results of this sensitivity test applied to two Riverside cases (0500–0830 PST period on 28 and 29 August 1987). These two cases are characterized by high concentration of crustal species (particularly calcium) in the coarse mode. For instance, the calcium concentration at Riverside on 28 August was equal to 1.7, 2.7 and $2.7 \mu\text{g m}^{-3}$ (assumed) for bins 6, 7 and 8, respectively. The concentration of magnesium was significantly lower than the calcium concentration for the 20 cases studied. Particularly, for the two cases aforementioned, this concentration was in the range of $0.2\text{--}0.3 \mu\text{g m}^{-3}$ (total coarse-mode concentrations). As seen in Table 3, changes in the concentration of calcium

lead to significant changes in the resulting predicted coarse-nitrate concentration. Moreover, small changes in the concentration of magnesium (considering the low concentrations of this species) lead to larger changes in the resulting predicted coarse-nitrate concentration. These findings suggest that the inclusion of crustal species is very important in modeling the size distribution of coarse inorganic aerosols, particularly when the concentration of these species is high. Moreover, they suggest that small changes in the concentration of these species can lead to significant differences in the predicted coarse-nitrate concentration.

The assumption of neglecting total chloride concentrations in the model input may introduce some error in modeling the size distribution of inorganic aerosols. Measured particulate-phase concentrations of chloride are relatively low for the 20 cases studied (considering all size bins, the concentration range is $1\text{--}4 \mu\text{g m}^{-3}$, approximately). To examine the potential errors associated with this assumption, we have performed some simulations considering particulate-phase concentration of chloride (as equivalent concentration of sulfate) in the model input (gas-phase concentrations of HCl were not measured and we therefore did not include them in simulations). Fig. 11 shows the predicted equilibrium size-distributed nitrate concentrations with measurements for two of the cases studied (0500–0830 PST period on 28 August 1987 at Long Beach and Riverside). For these two cases, the measured particulate-phase concentration of chloride (considering all size bins) was around $2\text{--}3 \mu\text{g m}^{-3}$. As seen, model performance slightly improves ($\approx 3\%$) with the inclusion of particulate chloride in the model input for the Long Beach case while for the Riverside case model, performance (in the coarse mode) is practically the same including or not particulate chloride concentration in simulations. Although not shown, results of simulations for the 20 cases studied indicate that the inclusion of particulate chloride in simulations could change by $<5\%$ (in average) the overall predicted PM_{10} nitrate.

Table 3
 Predicted nitrate for Riverside cases, 28 and 29 August 1987 using as model input in bin eighth different crustal species (calcium and magnesium) concentration

Date: 28 August 1987				Date: 29 August 1987			
Treatment	Bin	Particulate nitrate ($\mu\text{g m}^{-3}$)	Mean error ($\mu\text{g m}^{-3}$)	Treatment	Bin	Particulate nitrate ($\mu\text{g m}^{-3}$)	Mean error ($\mu\text{g m}^{-3}$)
(a)	6th	4.82		(a)	6th	5.78	
	7th	3.89			7th	4.06	
	8th	1.20			8th	1.41	
(b)	6th	3.90	0.89	(b)	6th	6.10	0.32
	7th	3.93	0.04		7th	6.11	2.04
	8th	3.95	2.73		8th	6.03	4.69
(c)	6th	3.90	0.89	(c)	6th	6.64	0.86
	7th	3.93	0.04		7th	7.12	3.06
	8th	3.95	2.73		8th	4.01	2.60
(d)	6th	3.90	0.89	(d)	6th	7.00	1.22
	7th	3.93	0.04		7th	7.50	3.44
	8th	3.95	2.73		8th	2.93	1.52
(e)	6th	5.60	0.75	(e)	6th	7.00	1.22
	7th	5.50	1.59		7th	7.50	3.44
	8th	0.73	0.47		8th	2.94	1.53
(f)	6th	4.94	0.12	(f)	6th	7.40	1.62
	7th	4.94	1.05		7th	7.90	3.84
	8th	1.94	0.74		8th	1.74	0.33
(g)	6th	3.64	1.18	(g)	6th	5.26	0.52
	7th	3.89	0.00		7th	4.92	0.86
	8th	1.67	0.47		8th	2.27	0.86

(a) Observed.

(b) Bin 8th: Ca and Mg 100%.

(c) Bin 8th: 50% Ca and 100% Mg.

(d) Bin 8th: 50% Ca and 0% Mg.

(e) Bin 8th: 25% Ca and 100% Mg.

(f) Bin 8th: 25% Ca and 0% Mg.

(g) Without considering Ca and Mg.

Finally, the methods used in collecting samples during the field study are subject to experimental uncertainty for the difficult sampling of semi-volatile inorganic compounds. John et al. (1990) have reported volatilization losses of ammonium nitrate around 10% in the sampler (a nine-stage Berner cascade impactor) under hot, dry conditions.

4. Conclusions

Based on modeling results against SCAQS measurements, size-resolved PM_{10} nitrate and ammonium can be determined by thermodynamic equilibrium when $\text{RH} > 60\%$ (model predictions have an error of $< 30\%$ when the PM_{10} nitrate concentration exceeds $2 \mu\text{g m}^{-3}$). For cases where the $\text{RH} < 60\%$, the assumption that all aerosol particles remain in a supersaturated solution (metastable liquid solutions) may introduce

unacceptable errors at least in the case investigated here. In these cases, a bulk equilibrium model may prove more useful than a size-resolved model assuming metastable aerosol.

On the other hand, in modeling coarse particles (particles $> 2 \mu\text{m}$) the equilibrium assumption, in general, introduces errors that increase with particle size. For the cases studied, the present size-resolved equilibrium model, SELIQUID, will introduce errors above 30% in cases where the PM_{10} nitrate $< 2.5 \mu\text{g m}^{-3}$ and the PM_{10} ammonium $< 1 \mu\text{g m}^{-3}$. For higher concentrations of nitrate and ammonium, the model error remains $< 30\%$.

Finally, the inclusion of crustal species is important in predicting the partitioning of inorganic salts among a size- and composition-dispersed aerosol. The treatment of these species as equivalent concentrations of sodium in a size-resolved equilibrium model may introduce additional errors in predicting aerosol behavior when crustal species concentrations are high. Measurements

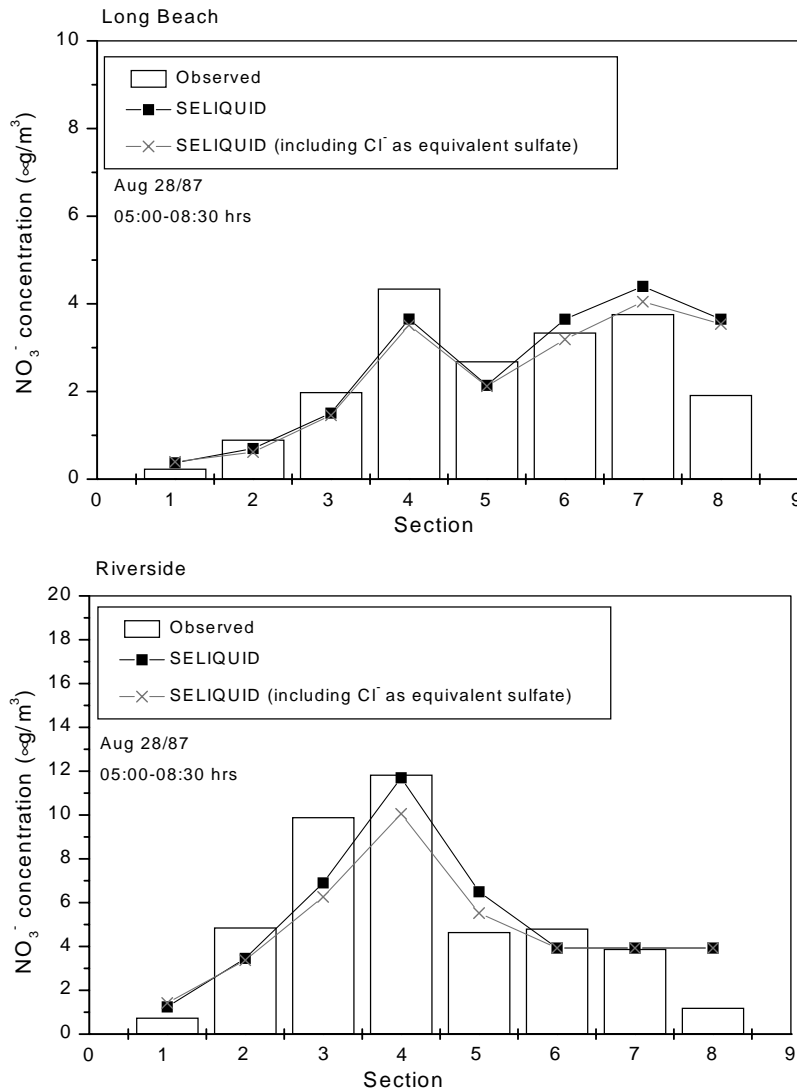


Fig. 11. Comparison of the predicted versus observed size-resolved particulate nitrate with (and without) considering particulate chloride concentrations as equivalent concentration of sulfate for measurements made at 0500–0830 PST on 28 August 1987 at Long Beach and Riverside.

of the complete size-composition distribution are important. The lack of measurements of the crustal species concentration in the 5–10 μm size range is an important weakness of the present dataset.

Hence, from a modeling perspective, size-distributed PM_{10} nitrate and ammonium can be determined by applying a size-resolved equilibrium model, like SELIQUID when the $\text{RH} > 60\%$. This equilibrium approach frequently results in greater errors in predicting coarse-particle composition than in fine-particle composition. These errors increase for low nitrate and high crustal species concentrations. For cases where $\text{RH} < 60\%$, a bulk equilibrium model may be more useful than a size-resolved one.

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