# Partitioning of nitrate and ammonium between the gas and particulate phases during the 1997 IMADA-AVER study in Mexico City

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## Abstract

The partitioning of nitrate and ammonium between the gas and particulate phases is studied combining available equilibrium models and measurements taken in Mexico City during the 1997 IMADA-AVER field campaign. Based on this analysis, there are no significant differences in model predictions, but some discrepancies exist between predictions and observations. The inclusion of crustal elements in the modeling framework improves agreement of model predictions for particulate nitrate against measurements by approximately 5%. Although some equilibrium aerosol models do not explicitly treat crustal elements, these species can be treated as equivalent concentrations of sodium. Atmospheric equilibrium models predict daily average $PM_{2.5}$ nitrate concentrations within 20% of the IMADA-AVER measurements at the MER site. Six-hour average $PM_{2.5}$ nitrate concentrations are predicted within 30–50% on average except for the afternoon sampling periods (12:00–18:00 h). Investigating the possible sources of these discrepancies, it appears that a dynamic instead of an equilibrium approach is more suitable in reproducing aerosol behavior during these afternoon periods. By applying the Multicomponent Aerosol Dynamic Model (MADM), model performance in predicting concentrations of particulate nitrate significantly improves during the afternoon periods. © 2001 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Several atmospheric models have been developed based on thermodynamic equilibrium principles to predict inorganic atmospheric aerosol behavior. 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, b), SCAPE2 (Kim and Seinfeld, 1995; Meng et al., 1995), EQUISOLV (Jacobson et al., 1996a), AIM2 (Clegg et al., 1998), ISORROPIA (Nenes et al., 1998a), GFEMN (Ansari and Pandis, 1999a) and EQUISOLV II (Jacobson, 1999). These models have been used in determining emissions control strategies (Watson et al., 1994; Ansari and Pandis, 1998; Kumar et al., 1998), in analyzing ambient measurements (Ansari and Pandis, 1999b, 2000) and directly in large-scale chemical transport models (Pilinis and Seinfeld, 1988; Lurmann et al., 1997; Jacobson et al., 1996b; Jacobson, 1997a, b, 1999; Meng et al., 1998; Nenes et al., 1998b).

Several studies have been performed comparing field measurements of inorganic gaseous species and their particulate forms versus theory (Tanner, 1982;

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Hildemann et al., 1984). Tanner (1982) compared theoretical equilibrium calculations versus observed partial pressure products of nitric acid and ammonia under conditions present on Long Island, New York and reported a general agreement although some differences were found. Hildemann et al. (1984) performed a similar comparison between equilibrium-based calculations and observed partial pressure products of nitric acid and ammonia and their particulate forms at different locations in Southern California. At inland sites like Anaheim and Rubidoux, an overall agreement was reported although some discrepancies were found at Long Beach. Although comparison of calculated and observed partial pressure products of $NH_3$ and $HNO_3$ can provide an alternative way of testing an atmospheric equilibrium model, interpretations of these comparisons are often difficult, especially in evaluating the ability of these models to reproduce particulate nitrate concentrations. Recently, an analysis of model performance against measurements has been performed by Kumar et al. (1998), Ansari and Pandis (1999b) and by Zhang et al. (2000). Kumar et al. (1998) compared the performance of several equilibrium models against measurements taken during the 1995 Integrated Monitoring Study (Chow and Egami, 1997). In these cases, the mean predictions of $PM_{10}$ nitrate and ammonium agreed within 20–30% of the corresponding measurements. Ansari and Pandis (1999b) compared the performance of SEQUILIB, SCAPE2, ISORROPIA and GFEMN and found a general agreement in predictions for particulate nitrate and total inorganic particulate matter (PM) over a broad range of temperature, relative humidity (RH) and composition. However, they found significant differences in predictions for particulate water and $H^+$ concentrations. Against measurements from the Southern California Air Quality Study (SCAQS, Lawson, 1990), all models qualitatively reproduced but generally underpredicted $PM_{2.5}$ nitrate concentrations (mean normalized biases less than $-30\%$). Zhang et al. (2000) compared the performance of SCAPE2, AIM2 and EQUISOLV II and found similar results in model predictions for total PM over a broad range of RH and composition although some differences over specific concentration and RH regimes were reported.

In the present study, four of the available equilibrium aerosol models (SEQUILIB, SCAPE2, GFEMN and ISORROPIA) are used as tools for studying $PM_{2.5}$ behavior in Mexico City. Specifically, the partitioning of nitrate and ammonium between the gas and particulate phases is investigated based on ambient measurements collected at several locations in Mexico City as part of the 1997 Investigación sobre Materia Particulada y Deterioro Atmosférico-Aerosol and Visibility Evaluation Research (IMADA-AVER) study. The equilibrium aerosol models are used for predicting aerosol behavior in Mexico City. Based on model performance, the resulting discrepancies are examined and modifications in modeling approaches and/or assumptions are proposed.

## 2. IMADA-AVER study

During the IMADA-AVER study, an intensive field campaign was carried out in Mexico City from 23 February to 22 March 1997 where extensive meteorological, air quality, and visibility measurements were taken for several sites throughout the metropolitan area of Mexico City. One of the purposes of IMADA-AVER is the use of the resulting database in testing, evaluating, and improving existing air quality models. A more detailed description of the IMADA-AVER field study is given by Edgerton et al. (1999).

Ambient $PM_{2.5}$ (particles with $d_p < 2.5\,\mu m$) and $PM_{10}$ (particles with $d_p < 10\,\mu m$) concentrations were measured over 6 h periods at the Merced (MER), Cerro de la Estrella (CES) and Xalostoc (XAL) sites and over 24 h intervals at the Tlalnepantla (TLA), Nezahuatcoyotl (NET) and Pedregal (PED) sites. Inorganic particulate species measured include nitrate, sulfate, chloride, ammonium, sodium, and potassium. Calcium and magnesium measurements are also available from elemental analysis. Gas-phase concentrations of nitric acid and ammonia were measured only at the MER site (located in downtown Mexico City). Hourly measurements of temperature and RH were obtained at the six sites from the Red Automática de Monitoreo Atmosférico (Atmospheric Monitoring Automated Network).

Since total (gas + particulate phase) nitrate and ammonium concentrations were collected only at the MER site, the gas- and particulate-phase concentrations measured specifically at this site will be analyzed. Fig. 1 shows the diurnal behavior and Table 1 shows the average and maximum values of 6 h average $PM_{2.5}$ measurements (Edgerton et al., 1999) and gas- and particulate-phase mass fractions (where applicable) for total nitrate (gas + particulate phase), total ammonia (gas + particulate phase), sulfate, and crustal species. There is enough available ammonia to fully neutralize the available sulfate and part of the nitrate to form $(NH_4)_2SO_4$ and $NH_4NO_3$. Nitrate occurred primarily in the gas phase during the afternoon sampling periods (12:00–18:00 h) where temperatures generally exceeded $20°C$, and in the particulate phase during the morning sampling periods (06:00–12:00 h). This is expected as high temperatures inhibit the thermodynamic formation of $NH_4NO_3$ whereas lower temperatures favor its formation. Nitrate remained primarily in the particulate phase (61% on average) while ammonia remained mainly in the gas phase (84% on average) over the measurement period of study (Table 1). Although not shown, 72% of $PM_{10}$ nitrate resided in $PM_{2.5}$; hence 28% of $PM_{10}$ nitrate was in the coarse mode.
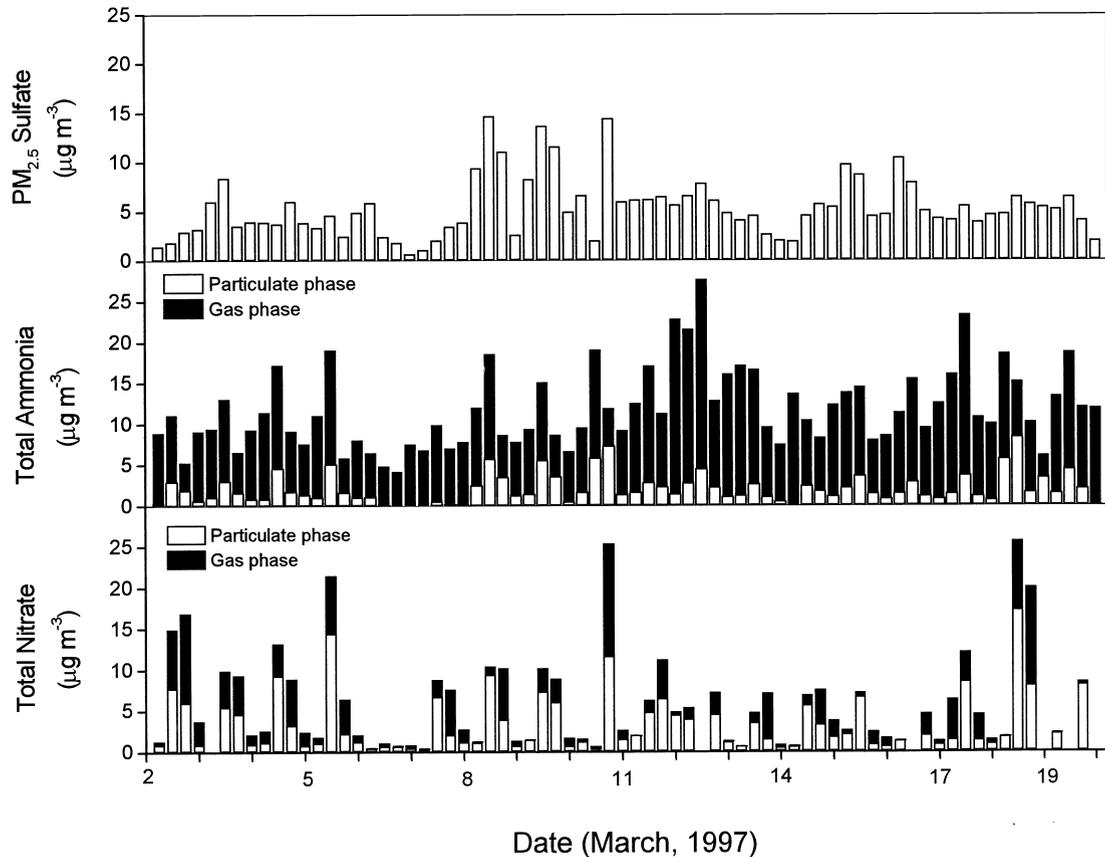
Fig. 1. Total sulfate, ammonia, and nitrate profile at the MER site over the period 2–19 March 1997.

Table 1
Measured $PM_{2.5}$ concentrations for inorganic species at the MER site, 2–19 March 1997 (Edgerton et al., 1999)

| Species | Mean observed ($\mu g\,m^{-3}$) | Maximum value ($\mu g\,m^{-3}$) | Gas phase (average value, %) | Particulate phase (average value, %) |
|---|---|---|---|---|
| Total nitrate | 5.9 | 25.6 | 39 | 61 |
| Total ammonium | 12.3 | 28.9 | 84 | 16 |
| Sulfate | 5.3 | 14.6 | 0 | 100 |
| Sodium[a] | 0.2 | 2.3 | 0 | 100 |
| Calcium[b] | 0.6 | 2.2 | 0 | 100 |
| Potassium[a] | 0.2 | 1.1 | 0 | 100 |
| Magnesium[b] | 0.1 | 0.3 | 0 | 100 |

[a] Water-soluble concentration (obtained by atomic absorption spectrometry).
[b] Total elemental concentration (obtained by X-ray fluorescence).

## 3. Equilibrium models

Given total (gas + particulate phase) concentrations of $HNO_3$, $NH_3$, $H_2SO_4$ and $HCl$, and temperature and RH as inputs, SEQUILIB, SCAPE2, ISORROPIA and GFEMN can be used to predict the partitioning of these inorganic species between the gas and particulate phases and within the particulate phase, between the aqueous and solid phases based on thermodynamic equilibrium. SCAPE2 also allows the inclusion of crustal species ($K^+$, $Ca^{2+}$, and $Mg^{2+}$) into its modeling framework. SEQUILIB, SCAPE2 and ISORROPIA treat the

equilibrium problem by solving a set of nonlinear algebraic equations (reaction equations) simultaneously with electroneutrality and mass conservation equations using Newton–Raphson and bisectional methods. As computational efficiency is a major priority in these models, each uses a simplified approach and/or simplifying assumptions in its modeling framework (i.e. simpler activity coefficients, divided RH and composition domains). Conversely, GFEMN uses an updated activity coefficient parameterization (Clegg et al., 1998) and a direct minimization of the Gibbs free energy of the system.

In calculating the deliquescence relative humidity (DRH) as a function of temperature for single salts, SCAPE2 and ISORROPIA use data from Wexler and Seinfeld (1991). ISORROPIA calculates DRH as a function of composition using phase diagrams generated by Potukuchi and Wexler (1995a, b). The direct minimization used in GFEMN allows it to implicitly calculate the temperature and composition dependence on the DRH. SEQUILIB does not predict DRH as a function of temperature nor composition. It is important to note that in the analysis presented here, an updated version of SEQUILIB (v2.3) is used where $K_{eq}$ ($T$) for $NH_4 NO_3$ (solid and aqueous) is in agreement with that in SCAPE2 and ISORROPIA.

## 4. Model performance

The ensuing analysis focuses on the behavior of $PM_{2.5}$ in Mexico City. Henceforth, particulate concentrations refer to $PM_{2.5}$ concentrations. The hypothesis of this work is that thermodynamic equilibrium is an adequate approach in modeling aerosol behavior for these size ranges. Small particles have greater surface area to mass ratios and thus faster equilibrium time scales as compared to large particles (Wexler and Seinfeld, 1990).

### 4.1. Role of crustal elements

To investigate the partitioning of nitrate and ammonia between the gas and particulate phases, the ambient 6 h averaged measurements are used to calculate the total concentrations of nitrate and ammonia. Total concentrations of nitrate included nitric acid determined by the denuder difference method (Shaw et al., 1982) using cellulose filters and an aluminum oxide-coated denuder, plus $PM_{2.5}$ non-volatilized and volatilized nitrate determined by a quartz/cellulose filter pack. These total concentrations of nitrate and ammonia along with measurements of sulfate, chloride, sodium, RH and temperature are used as inputs for the equilibrium models. During the IMADA-AVER campaign, gas-phase concentrations of $H_2SO_4$ and HCl were not measured, and we therefore assumed that the particulate measurements of sulfate and chloride are total (gas + particulate) concentrations of
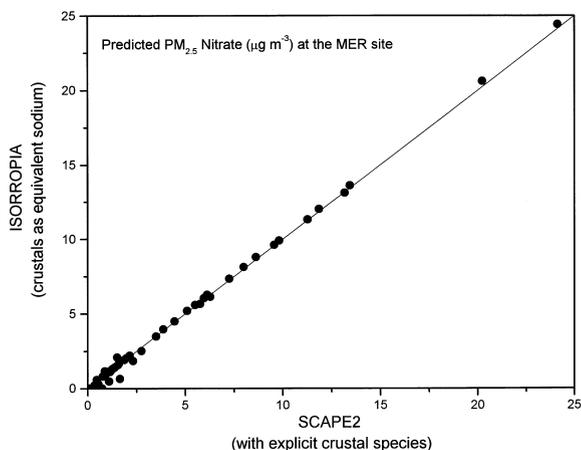


Fig. 2. Model comparison of predictions of particulate nitrate. Crustal elements are included as equivalent concentration of sodium in ISORROPIA.

sulfate and chloride. $H_2SO_4$ has a very low vapor pressure (Seinfeld and Pandis, 1998) and its gas-phase concentration is considered negligible. However, as crustal elements can influence the partitioning of total nitrate (Ansari and Pandis, 1999b; Jacobson, 1999), the importance of including crustal elements in the modeling framework is first examined. Crustal elements are usually represented by Al, Si, Fe, Ca, Mg, K, and Na (Kim and Seinfeld, 1995). Among them, Al, Si, and Fe compounds are not considered in the modeling framework, as they are present in the form of stable oxides (e.g. $SiO_2$) and do not participate in reactions. Conversely, Ca, Mg, K, and Na compounds generally exist as oxides and/or carbonates (e.g. $CaCO_3$) in ambient particles and can be transformed to water-soluble species. Therefore, in the following analysis we consider as crustal material the species Ca, Mg, K, and Na. Table 1 shows the average and maximum concentrations of crustal elements at the MER site over the measurement period. Although SCAPE2 allows the incorporation of crustal elements in its modeling framework, the others models used here (GFEMN, ISORROPIA and SEQUILIB) do not explicitly model crustal species. However, crustal elements could be modeled as equivalent concentration of sodium thus allowing their inclusion implicitly in GFEMN, ISORROPIA and SEQUILIB. Fig. 2 shows predicted particulate nitrate concentrations for SCAPE2 and ISORROPIA incorporating crustal elements in simulations. As seen, ISORROPIA with crustal element concentrations expressed as equivalent sodium performs almost as well as SCAPE2. Table 2 shows the performance of SCAPE2 and ISORROPIA in predicting particulate nitrate concentrations at the MER site. The models tend to underpredict $PM_{2.5}$ nitrate in both cases (with and without crustal elements). However, with the inclusion of

Table 2
Model performance with and without crustal species for $PM_{2.5}$ nitrate at the MER site, 2–19 March 1997

| Model | Aerosol behavior | Mean predicted ($\mu g\,m^{-3}$) | Mean observed ($\mu g\,m^{-3}$) | Mean normalized bias (%) | Mean normalized error (%) |
|---|---|---|---|---|---|
| SCAPE2 | With crustals | 3.44 | 3.21 | − 3 | 48 |
| | Without crustals | 3.16 | | − 22 | 55 |
| ISORROPIA | With crustals | 3.36 | 3.21 | − 14 | 61 |
| | Without crustals | 3.08 | | − 34 | 66 |
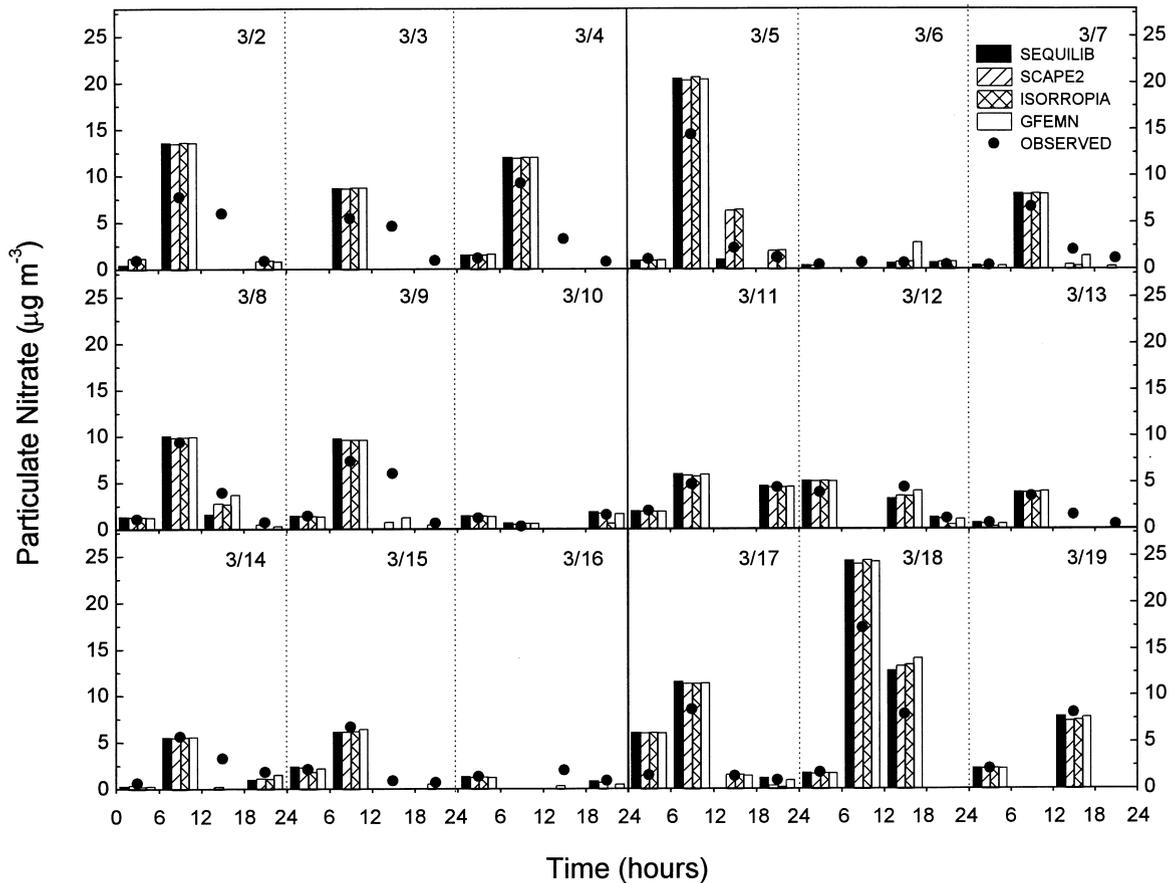


Fig. 3. Model performance for particulate nitrate against 6 h average IMADA-AVER measurements at the MER site over the period 2–19 March 1997.

crustal elements the mean normalized error and bias both decrease. Hence, in the following analysis, crustal elements are included in model simulations and as equivalent sodium concentrations in SEQUILIB, ISORROPIA and GFEMN.

### 4.2. Partitioning of nitrate and ammonium

As with the previous section, total ambient measurements are used as inputs for the equilibrium models. The partitioning of total inorganic species predicted by the models is then compared to gas- and particulate-phase measurements taken during the IMADA-AVER study.

Figs. 3 and 4 show predicted particulate nitrate and ammonium concentrations versus 6 h average measurements for the MER site. In general, predictions of the four models are similar, and no significant differences are observed. This finding is in agreement with that of Ansari and Pandis (1999b) concerning model performance. However, significant discrepancies exist between
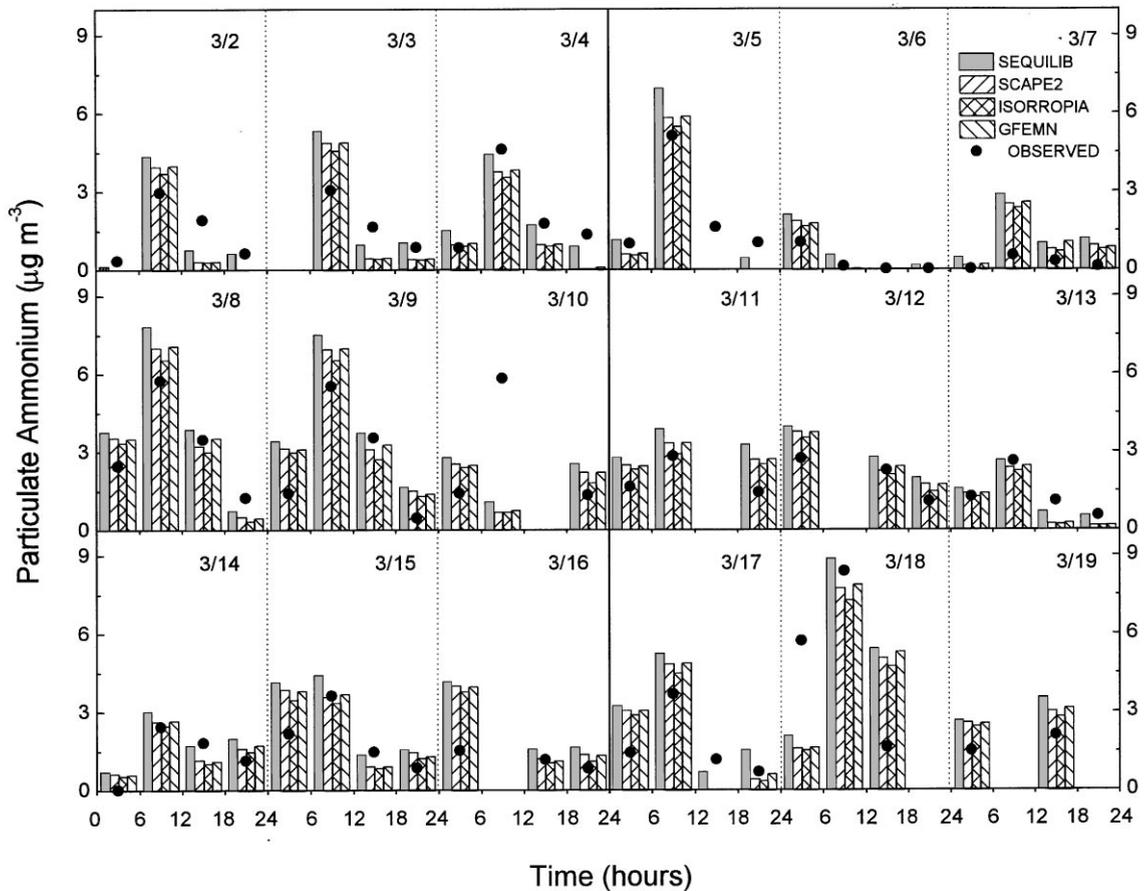
Fig. 4. Model performance for particulate ammonium against 6 h average IMADA-AVER measurements at the MER site over the period 2–19 March 1997.

predictions and observations, specifically for all of the afternoon sampling periods (12:00–18:00 h). All four models tend to overpredict particulate nitrate concentrations during the morning sampling periods (06:00–12:00 h) and underpredict during the afternoon sampling periods. For particulate ammonium (Fig. 4) there are no clear trends in the errors, which are larger in magnitude compared to those observed for particulate nitrate. Table 3 shows statistics of model performance for the results shown in Figs. 3 and 4. On average, all models underpredict particulate nitrate concentrations while ammonium concentrations are overpredicted for the MER site. Based on the mean normalized errors (50–60% for nitrate and 70–90% for ammonium) it appears that the models have difficulties in reproducing the 6 h observations at the MER site. Although not shown, the average predicted $NH_3$ fraction in the gas (85%) and particulate phases (15%) corresponds well with the average measured $NH_3$ fraction in these phases (84 and 16%, respectively).

Since air quality standards for particulate matter are often set for 24 h averaged values, our analysis is extended by comparing the average of four 6 h predictions versus the corresponding average of four 6 h average measurements for the 18-day study period. Figs. 5 and 6 show the results of this extended analysis for particulate nitrate and ammonium concentrations using SCAPE2. Predictions of the other models are not shown as they are similar to SCAPE2. For particulate nitrate and ammonium, there is a good agreement between the model predictions and measurements for 24 h averages. The statistics in Table 4 indicate an expected significant improvement in model performance for 24 h averages.

### 4.3. Duration of sampling periods

Given the discrepancies in model predictions, a discussion of possible sources of error is worthwhile. One possible source of error can be attributed to the duration of the sampling periods. The measurements obtained at

Table 3
Model performance against PM$_{2.5}$ measurements at the MER site, 2–19 March 1997

| Species | Model | Mean predicted ($\mu g\,m^{-3}$) | Mean observed ($\mu g\,m^{-3}$) | Mean normalized bias (%) | Mean normalized error (%) |
|---|---|---|---|---|---|
| Particulate nitrate | SEQUILIB | 3.22 | 3.21 | − 19 | 55 |
| | SCAPE2 | 3.44 | | − 3 | 48 |
| | ISORROPIA | 3.36 | | − 14 | 61 |
| | GFEMN | 3.37 | | − 12 | 57 |
| Particulate ammonium | SEQUILIB | 2.50 | 1.93 | 70 | 92 |
| | SCAPE2 | 2.08 | | 29 | 77 |
| | ISORROPIA | 1.80 | | 14 | 65 |
| | GFEMN | 2.11 | | 31 | 79 |
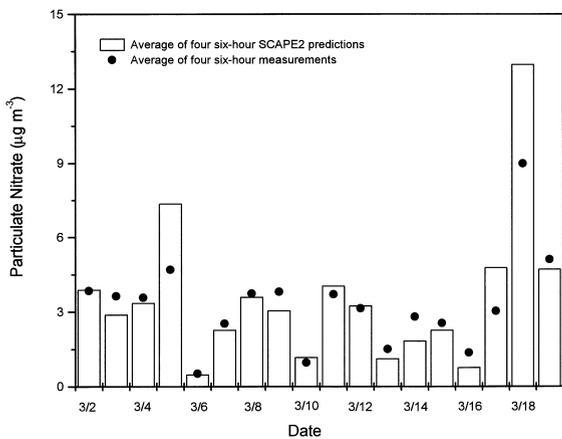


Fig. 5. Predicted particulate nitrate for the average of four 6 h SCAPE2 estimations against the corresponding IMADA-AVER measurements at the MER site over the period 2–19 March 1997.
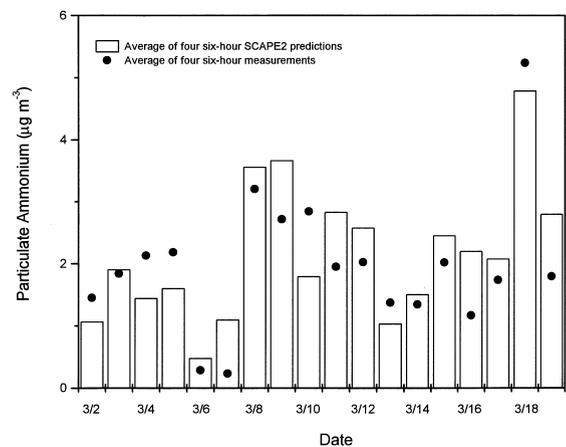


Fig. 6. Predicted particulate ammonium for the average of four 6 h SCAPE2 estimations against the corresponding IMADA-AVER measurements at the MER site over the period 2–19 March 1997.

the MER site were taken over 6 h periods, and for such a duration, where aerosol transport may occur and the ambient temperature and RH may vary significantly (Fig. 7), equilibrium models based on average conditions may not adequately reproduce aerosol behavior. To examine this hypothesis, SCAPE2 is used to predict measurements at the MER site using 1 h instead of 6 h averages of temperature and RH for each of the sampling periods. For each 6 h sampling period, six simulations were conducted using hourly measurements of temperature and RH, and constant total concentrations as inputs. Thus, 24 simulations were conducted for each day for the 18-day sampling period. The average predicted concentrations for these simulations are shown along with 6 h average simulations in Table 5. Overall, model performance in both cases is similar indicating using hourly resolution of temperature and RH does not significantly improve modeling performance. However, to ad-

equately test our initial hypothesis, hourly measurements of gas and particulate concentrations, in addition to RH and temperature are needed.

To further analyze the stated discrepancies, model predictions and measurements are stratified by sampling period. Fig. 8 shows predicted particulate nitrate versus 6 h averaged measurements for each sampling period for the MER site. As seen, slight overpredictions are observed for the morning sampling periods (00:00–06:00 and 06:00–12:00 h), and underpredictions are generally observed for the afternoon (12:00–18:00 h) and evening sampling periods (18:00–24:00 h). However, based on Fig. 8 and the corresponding statistics in Table 6, discrepancies in model predictions are highest for the afternoon sampling periods. Table 7 shows model performance for particulate nitrate over five RH regimes at the MER site, and as seen, the mean normalized error increases as RH decreases. The highest error occurs for the lowest RH

Table 4

SCAPE2 performance for 6 and 24 h average $PM_{2.5}$ measurements at the MER site, 2–19 March 1997

| Species | Duration (h) | Mean predicted ($\mu g\,m^{-3}$) | Mean observed ($\mu g\,m^{-3}$) | Mean normalized error (%) |
|---|---|---|---|---|
| Particulate nitrate | 6 | 3.44 | 3.21 | 48 |
| | 24[a] | 3.54 | 3.30 | 21 |
| Particulate ammonium | 6 | 2.08 | 1.93 | 77 |
| | 24[a] | 2.16 | 1.97 | 51 |

[a] The differences between 6 and 24 h observations (and predictions) are because 7 of the 18 daily average values were obtained with less than four 6 h measurements. No measurements were reported for several of the sampling periods.
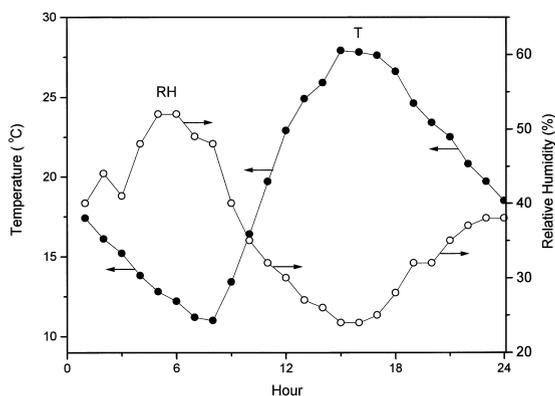


Fig. 7. Temperature and RH profile on 2 March 1997 at the MER site.

(RH < 50%) which are observed mostly during the afternoon sampling periods where temperatures generally exceeded 20°C at the MER site. Without considering the afternoon sampling periods (12:00–18:00 h), model performance for particulate nitrate improves significantly (mean normalized errors between 30 and 50%).

### 4.4. Bulk aerosol approach

The bulk aerosol approach (internal mixture assumption) implies that all modeled $PM_{2.5}$ particles have the same chemical composition. This assumption thus allows the mixing of acidic with alkaline particles which may introduce errors in predicting aerosol behavior. Such errors can be minimized by including multiple particle groups in the modeling framework (Pilinis and Seinfeld, 1987; Jacobson, 1999). However, this method has problems when the size resolved equilibrium approach is used to predict the behavior of dry particles (low RH). In the lower RH case, the partial pressure product for the formation of $NH_4NO_3$, $p_{NH_3}p_{HNO_3}$, is the same for all size sections, and thus, infinite solutions exist for distributing $NH_4NO_3$ mass over all size sections (Wexler and Seinfeld, 1990). In addition, since a single filter was used

to collect $PM_{2.5}$ in the measurement campaign, little information regarding the alkalinity and acidity of particles in different $PM_{2.5}$ size sections is available.

### 4.5. Deliquescence and efflorescence branch

The equilibrium aerosol models used in our analysis predict the partitioning of total nitrate between the gas and particulate phases using the deliquescence branch of aerosol behavior. Ansari and Pandis (2000), however, implicated the importance of considering metastable equilibrium states (efflorescence branch) at low to moderate particulate nitrate concentrations ( $< 8\,\mu g\,m^{-3}$ ). They found a difference of approximately 10% in particulate nitrate concentrations based on the deliquescence and efflorescence branches of aerosol behavior for simulations conducted over a broad range of temperature and RH. Using the efflorescence instead of the deliquescence branch of aerosol behavior (that is assuming that particles are liquid always), it appears that model performance could improve by 10% for Mexico City where average $PM_{2.5}$ nitrate concentrations are less than $8\,\mu g\,m^{-3}$. However, as aerosols are as probable to exist on the deliquescence versus efflorescence branch, the effect of metastable equilibrium states on the partitioning of nitrate between the gas and particulate phases most probably accounts for approximately 5% or so of the overall underprediction.

### 4.6. Equilibrium assumption

Based on its simplicity, computational efficiency and stability, the thermodynamic equilibrium modeling approach has been broadly used to predict partitioning of semi-volatile compounds between the gas and particulate phases (Stelson and Seinfeld, 1982; Pilinis and Seinfeld, 1987; Kim et al., 1993a, b; Kim and Seinfeld, 1995). However, in cases where the equilibrium time scale is long relative to the residence time of particles in a given environment, this approach may introduce errors in modeling aerosol behavior (Wexler and Seinfeld, 1990; Meng and Seinfeld, 1996). Large aerosol particles may

Table 5
SCAPE2 performance for 6 h of six 1 h average PM$_{2.5}$ measurements at the MER site, 2–19 March 1997

| Species | Duration | Mean predicted ($\mu g\,m^{-3}$) | Mean observed ($\mu g\,m^{-3}$) | Mean error ($\mu g\,m^{-3}$) | Mean normalized bias (%) | Mean normalized error (%) |
|---|---|---|---|---|---|---|
| Particulate nitrate | 6 h averages | 3.44 | 3.21 | 1.37 | − 3 | 48 |
| | Six 1 h averages | 3.01 | | 1.12 | − 10 | 42 |
| Particulate ammonium | 6 h averages | 2.08 | 1.93 | 0.96 | 29 | 77 |
| | Six 1 h averages | 1.96 | | 0.92 | 28 | 78 |
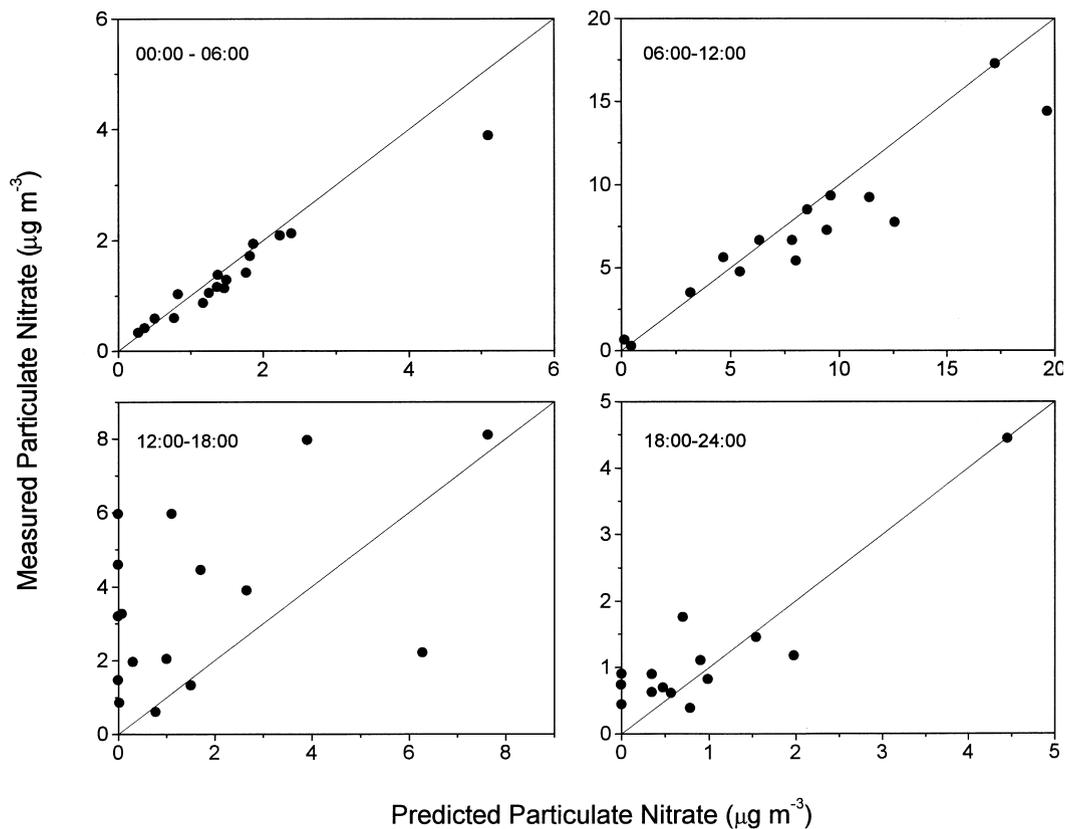


Fig. 8. Predicted particulate nitrate stratified by sampling period at the MER site over the period 2–19 March 1997.

require hours or even days to achieve equilibrium with the gas phase. In these cases, a dynamic instead of an equilibrium approach may be required to adequately predict the partitioning of semi-volatile compounds. Thus, in the following section, we briefly describe and apply a dynamic model to predict aerosol behavior for two sampling periods at the MER site.

### 4.7. Modeling aerosol dynamics

To analyze the validity of the equilibrium assumption used in our analysis, aerosol dynamics is simulated by using a fully dynamic mass transfer method for each aerosol size section. This approach should be in principle the most accurate (Meng et al., 1998; Capaldo et al., 2000) although it tends to be computationally more intensive than the equilibrium approach. In applying a dynamic approach in modeling aerosol behavior, the multicomponent aerosol dynamic model (MADM) recently developed by Pilinis et al. (2000) is used. A detailed description of MADM and its performance is given by Pilinis et al. (2000).

Since all of the afternoon sampling periods generally have the highest discrepancies between predictions and

Table 6
SCAPE2 performance for $PM_{2.5}$ nitrate by sampling period at the MER site, 2–19 March 1997

| Sampling period (h) | Mean predicted ($\mu g \, m^{-3}$) | Mean observed ($\mu g \, m^{-3}$) | Mean normalized bias (%) | Mean normalized error (%) |
|---|---|---|---|---|
| 0–6 | 1.5 | 1.4 | 11 | 18 |
| 6–12 | 8.3 | 7.1 | 15 | 29 |
| 12–18 | 1.7 | 3.6 | − 46 | 74 |
| 18–24 | 0.9 | 1.1 | − 21 | 47 |

Table 7
SCAPE2 performance for $PM_{2.5}$ nitrate by relative humidity at the MER site, 2–19 March 1997

| Relative humidity range | Percentage of measurements[a] | Mean predicted ($\mu g \, m^{-3}$) | Mean observed ($\mu g \, m^{-3}$) | Mean normalized bias (%) | Mean normalized error (%) |
|---|---|---|---|---|---|
| 20–40 | 17 | 3.7 | 3.9 | − 28 | 84 |
| 40–50 | 20 | 2.6 | 3.3 | − 24 | 56 |
| 50–60 | 20 | 1.6 | 2.2 | 0 | 35 |
| 60–70 | 27 | 4.6 | 4.4 | 6 | 20 |
| 70–80 | 16 | 1.9 | 1.6 | 23 | 23 |

[a] Percentage of measurements falling into specified RH range.

measurements, MADM is used in this period in place of the equilibrium models to predict aerosol behavior. Two days of the period of study (2 and 14 March 1997) have been chosen to simulate 6 h average aerosol behavior (12:00–18:00 h). As with the atmospheric aerosol equilibrium models, the ambient measurements are used to calculate the inputs for MADM. The gas and particulate composition measured at the MER site during the 2nd morning sampling periods (from 06:00 to 12:00 h) was used as the initial composition for 12:00. The particulate composition was initially distributed into 10 logarithmically spaced sections in the 0.05–10 μm range based on a typical urban size distribution (Wall et al., 1988). Although the particulate composition distribution in Mexico City may be different from that being used, it provides an initial approximation in performing the analysis. The sinks and sources of $NH_3$, $HNO_3$ and $H_2SO_4$ were estimated by taking the difference in total concentrations measured during the morning and afternoon sampling periods. Measured temperature and RH values are used as inputs to the model. Aerosol behavior was then simulated for 6 h (from 12:00 to 18:00 h) with a box (zero-dimensional) model. The major assumption of this approach is that the site is exposed to the same air mass during the 6 h simulation period. The average concentration of particulate nitrate predicted by MADM over the 6 h simulation period was then compared to the 6 h average measurement.

Fig. 9 shows the initial, final and average composition distribution of the inorganic species predicted by MADM for each aerosol size section for the afternoon

sampling period on 2 March, 1997. The first eight sections correspond to $PM_{2.5}$ whereas the latter two correspond to the coarse mode. It should be noted, however, that in the coarse mode (last two sections), nitrate was added (beyond what was measured) to neutralize the equivalent sodium concentrations since the measured aerosol was not neutral. Based on the initial, final, and average composition distributions, this added concentration of nitrate remained fairly constant, thus not affecting the nitrate concentration behavior in the $PM_{2.5}$ size sections. As seen in the initial distribution, the ammonium, nitrate and sulfate are distributed in the fine and coarse modes, while chloride (and mostly all sodium) is in the coarse mode. The final and average distributions show that nitrate is mostly in the coarse mode, while ammonium and sulfate are distributed in the fine and coarse modes. However, in section 8 (1–2.5 μm), the $PM_{2.5}$ section with the largest mass, some nitrate is present. Fig. 10 shows the $PM_{2.5}$ nitrate, ammonium and sulfate concentrations predicted by MADM for the 6 h simulation on 2 March 1997. For this period, MADM predicts an average $PM_{2.5}$ nitrate concentration of 2.8 μg m$^{-3}$ whereas the equilibrium models predict 0. In the equilibrium approach, $PM_{2.5}$ is treated as a single group of particles where the available sodium and ammonium have been fully neutralized with sulfate. In the dynamic approach, $PM_{2.5}$ is treated with eight separated particle group sections where some sodium and crustal material is present in the largest of the eight sections. Since there is not enough sulfate in this section (1–2.5 μm) to neutralize the existing sodium, nitrate is transferred from the gas to the particulate phase. Consequently, by
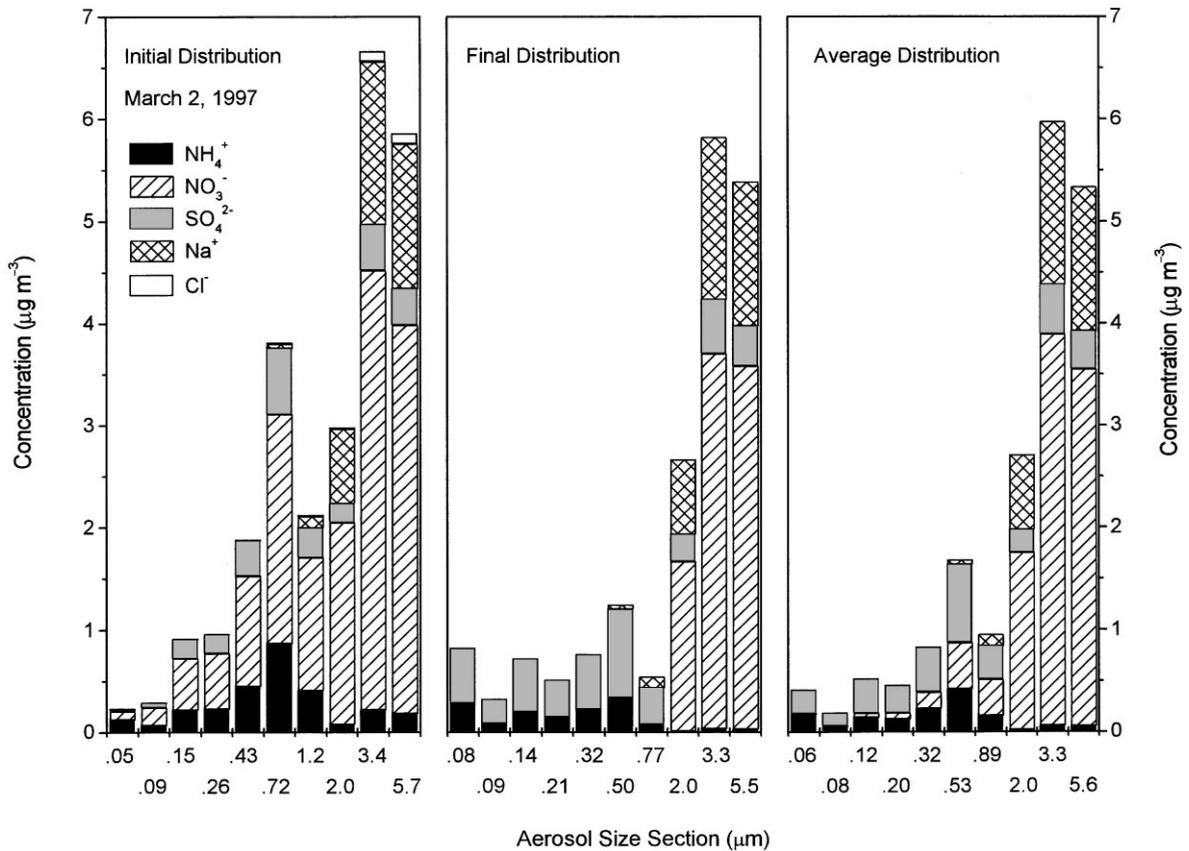
Fig. 9. Initial, final and average composition distribution of ammonium, nitrate, sulfate, sodium and chloride predicted by MADM for each aerosol size section for the 3rd sampling period on 2 March 1997 at the MER site.
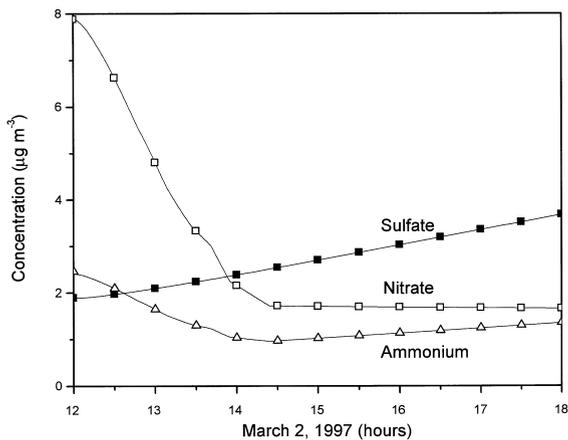


Fig. 10. MADM predictions of particulate nitrate, ammonium and sulfate for the 6 h simulation on 2 March 1997 at the MER site.

applying the dynamic approach, an average $PM_{2.5}$ nitrate concentration greater than that predicted by equilibrium is estimated.

MADM is used to simulate aerosol behavior for the afternoon sampling period on 14 March in a similar manner. Again, MADM predicts an average $PM_{2.5}$ concentration of $2.3\,\mu g\,m^{-3}$ for particulate nitrate while equilibrium models predict 0 (except SCAPE2 predicting $0.2\,\mu g\,m^{-3}$). MADM predictions for particulate nitrate and ammonium are shown along with SCAPE2 predictions in Table 8. The results indicate a significant improvement using the dynamic approach compared to the equilibrium approach for the two 6 h simulations. Hence, the results with MADM for the afternoon sampling periods are encouraging as they significantly reduce discrepancies with observations in this case.

## 4.8. Potential errors

In spite of the improvement in the results with MADM for the afternoon sampling periods, particulate nitrate concentrations are still underpredicted using the dynamic approach. Aerosol dynamics account for only a portion of the discrepancies shown in Figs. 3 and 4. The remaining error may be attributed to several different

Table 8
SCAPE2 and MADM performance for PM$_{2.5}$ species at the MER site on 2 and 14 March 1997 for the afternoon sampling periods (12:00–18:00 h)

| Species | Date | Mean predicted SCAPE2 ($\mu g\,m^{-3}$) | Mean predicted MADM ($\mu g\,m^{-3}$) | Mean observed ($\mu g\,m^{-3}$) |
|---|---|---|---|---|
| Predicted nitrate | 02/03/1997 | 0.00 | 2.80 | 5.95 |
| | 14/03/1997 | 0.23 | 2.29 | 3.25 |
| Predicted ammonium | 02/03/1997 | 0.31 | 1.32 | 1.89 |
| | 14/03/1997 | 1.15 | 1.94 | 1.80 |

sources. One of them may be the incomplete understanding of the different processes simulated (thermodynamics, dynamics). Furthermore, the modeling framework used models the same air mass. Considering the transport of air parcels into and out of the sampling area, especially over 6 h periods, this assumption may introduce errors in predicting aerosol behavior. Finally, the methods used in collecting samples during the field study are subject to experimental uncertainty for the difficult sampling of semivolatile inorganic compounds. Wolff et al. (1991), Solomon et al. (1992) and Chow et al. (1994) have reported significant losses of nitrate and ammonium on filter-based aerosol samples due to the decomposition of $NH_4NO_3$. Chow et al. (2000) describe the sampling methods for filter-based aerosol samples and evaluate the accuracy, precision and validity of the ambient aerosol measurements during IMADA-AVER. Edgerton et al. (1999) give additional details on analysis methods during IMADA-AVER. Finally, the sampling methods used allow the mixing of acidic and alkaline particles which may also lead to errors in predicting aerosol behavior.

## 5. Conclusions

The inclusion of crustal species is important in modeling aerosol behavior. These species can be treated as equivalent concentrations of sodium in models that do not explicitly include these species in their modeling framework. Against IMADA-AVER measurements, atmospheric equilibrium models predict daily average PM$_{2.5}$ nitrate concentrations within 20%. Six-hour average PM$_{2.5}$ nitrate concentrations are predicted within 30–50% on average except for the afternoon sampling periods where high temperatures (exceeding 20°C) and low RH are observed. However, in these cases, a dynamic instead of an equilibrium model improves significantly the agreement between predictions and measurements of particulate nitrate.

Based on the measurements taken during the IMADA-AVER study, a significant amount of sodium and crustal elements are present in PM$_{2.5}$. However, within PM$_{2.5}$, sodium and crustal elements are generally present in particles with diameters greater than 1 µm.

Thus, to lessen difficulties associated with the modeling of PM$_{2.5}$ levels that arise when sodium and crustal elements are present in the largest section, some measurements of the size-composition distribution could provide valuable input for models. In addition, to better understand the effect of the dynamic behavior of aerosols smaller sampling periods or continuous nitrate measurements would be helpful.

From a modeling perspective, it appears based on the results of Pilinis et al. (2000) that a dynamic approach is more accurate in terms of capturing overall aerosol behavior. However, based on its computational cost, it is expensive for aerosol behavior over a long period of time (days). A hybrid method such as that used by Capaldo et al. (2000) may be used instead. For these cases, concentrations of PM$_1$ are modeled with an equilibrium approach whereas coarse-mode species ($d_p > 1$ µm) are modeled with a dynamic approach.

Hence, based on our findings, it appears that the equilibrium approach reproduces the partitioning of nitrate between the gas and particulate phases under Mexico City conditions, except during periods where temperatures are high ($> 20°C$) and RH is low ($< 40\%$). In such cases, a dynamic approach is more suitable in modeling aerosol behavior.

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