Multi-component atmospheric aerosols prediction by a multi-functional MC-HDMR approach

Kai Fu, Dong Liang, Wenqia Wang, Yu Cheng, Sunling Gong

Abstract
In this paper, a multi-functional moving-cut high-dimensional model representation (MC-HDMR) approach is developed for simulation of multi-component input and output aerosols. This method leads to an aerosol prediction database system based on full thermodynamic models such as ISORROPIA. The developed prediction system can efficiently compute the prediction of aerosol thermodynamic equilibrium in high-dimensional domains with a large range of aerosol concentrations from $10^{-9}$ mol m$^{-3}$ to $10^{-5}$ mol m$^{-3}$ and for different types of aerosols including aerosols containing sea salt component. Numerical computations show the great computational efficiency of the method that its CPU-time cost is much less compared to ISORROPIA. Three types of aerosols of urban, non-urban continental and marine are considered and the multi-component outputs predicted by the approach are in great agreement with those by ISORROPIA and AIM2. Actual aerosol examples in European and Asian cities are simulated by the approach and ISORROPIA and AIM2. Numerical results match very well and show heavier traffic pollution at the areas of HU02, IT01 and NL09 among six European stations, more anthropogenic pollution in Shanghai than other three Asian cities, and Hong Kong’s aerosols affected by the marine environment.

1. Introduction
Global climate change and warming in the atmosphere have been widely recognized. As one of the most important constituents of the atmosphere, aerosols have a direct radiative forcing by scattering and absorbing solar and infrared radiation in the atmosphere, while they have an indirect radiative forcing associated with the changes in cloud properties by decreasing the precipitation efficiency of warm clouds. In these processes, the physical state and composition of aerosols including the aerosol phases (i.e. gas, liquid and solid), the aerosol-associated water mass, and the multi-components of aerosols are of great significance. Numerical prediction has been playing an important role in the study of aerosols processes and distributions in the atmospheric environment (see, for example, Astitha et al., 2008; Benson et al., 2008; Chen et al., 2011; Cheng et al., 2010; Cheng et al., 2000; Fitzgerald, 1991; Hsieh et al., 2008; Liang et al., 2008; Piazzola et al., 2010; Pilinis & Seinfeld, 1987; Planche et al., 2010; Pöschl, 2011; Shipway & Abel, 2010, etc.).

Aerosol thermodynamic equilibrium prediction is a complex multi-phase, multi-component system that involves multiple composition outputs of gas, liquid and solid phases. The large scale predictions of aerosols contain simulations of different types of aerosols in multiple regions such as urban, non-urban continental and marine and at multiple levels in atmosphere. Several aerosol thermodynamic equilibrium modules have been built. In the early period, EQUIL (Bassett and Seinfeld, 1983), MARS (Saxena et al., 1986) and SEQUILB (Pilinis and Seinfeld, 1987) were widely used models for $\text{NH}_4^+\text{SO}_4^{2-}\text{NO}_3^-$ system. Then, numerous models were developed and applied to aerosol predictions, such as AIM (Wexler and Seinfeld, 1991), SCAPE2 (Kim et al., 1993), AIM2 (Clegg et al., 1998; Friese and Ebel, 1998).
improve the accuracy and efficiency of approximations to high dimensional systems. In this paper, we develop a multi-functional MC-HDMR approach for large scale aerosol predictions in multiple regions. This approach will build an aerosol prediction database system based on full thermodynamic model data. It thus is an extension to full thermodynamic models. For a general Na$^+\cdot$SO$_4^{2-}\cdot$NH$_4^+$\cdot$NO$_3^-$\cdot$Cl$^-\cdot$water system, we focus on the study of accuracy, efficiency, and the functions of the approach. The multi-functional MC-HDMR prediction system can compute aerosols concentrations in multiple regions and for different types of aerosols with different component inputs. The results show that this prediction system has great computational efficiency and save a lot of CPU-time comparing with the ISORROPIA system. For the actual examples, we make simulations of multi-phase and multi-component aerosol concentrations for three types of aerosols: urban, non-urban continental and marine, and calculate their particulate matter (PM) concentrations. The numerical results predicted by the multi-functional MC-HDMR approach are in great agreement with those by ISORROPIA and AIM2. The high PM concentrations show more serious pollution in urban area than in non-urban continental and marine areas. We also do some simulations of the multi-component aerosols measured at six stations in the European cities: K-Puszta (Hungary), Montelibretti (Italy), Kollumerwaard (Netherlands), Skreadalen (Norway), Birkenes (Norway) and Janiskoski (Russia), and in four Asian cities: Shanghai, Southern Taiwan, Seoul and Hong Kong. Numerical comparisons show clearly that the predicted concentrations of aerosols in European cities and in Asian cities by the multi-functional MC-HDMR method, the ISORROPIA and the AIM2 match very well. High simulated concentrations of HNO$_3$ show that there might be heavier traffics at the areas of HU02 (K-Puszta, Hungary), IT01 (Montelibretti, Italy) and NL09 (Kollumerwaard, Netherlands) among the six areas of European stations. The high simulated concentrations of aqueous SO$_4^{2-}$ in Shanghai might be influenced by anthropogenic emissions since Shanghai is the largest city in China. The large simulated values of solid NaCl and aqueous Cl$^-$ in Hong Kong show that the aerosols in this city is affected by the marine environment.

The paper is organized as follows. Section 2 gives the description of the multi-functional MC-HDMR approach. Numerical simulations of multiple component input and output aerosols are given in Section 3. Section 4 shows the computations of urban, non-urban continental and marine aerosols, and aerosols actual computations in European and Asian cities. Finally, conclusions are presented in Section 5.

2. The multi-functional MC-HDMR approach

The prediction of aerosol thermodynamic equilibrium is an input–output computational system. The inputs include the concentrations of sodium, sulfate, ammonium, nitrate and chloride components and environmental parameters of temperature and relative humidity, etc. The outputs are concentrations of multiple compositions in gas, solid and liquid phases. At different regions and levels in atmosphere, aerosols have significant spatial variations in particle concentrations, sizes and compositions (Pandis et al., 1995). The prediction of aerosols can be characterized into different types, such as urban, non-urban continental and marine aerosols. For such a complex aerosol prediction, the general aerosol thermodynamic
equilibrium models that use iterative methods in computation normally cost large CPU time. The large scale multi-region and multi-level prediction of aerosols in environment requires to develop efficient and multi-functional high-dimensional computation systems. The high-dimensional model representation is an efficient technique of obtaining high-dimensional outputs, which is constructed by low-dimensional component functions based on the measured data or simulated data by full thermodynamic models. Taking the advantage of moving cut HDMR method on high-dimensional input–output systems, we develop a multiple functional MC-HDMR approach for large scale multi-region and multi-level aerosol predictions by setting up a database computation system.

For a high dimensional vector function $\overline{F}(\mathbf{x})$, $\mathbf{x}\in\Omega\subseteq\mathbb{R}^n$, the general HDMR expansion can be written as

$$
\overline{F}(\mathbf{x}) = \overline{F}_0 + \sum_{i=1}^{n} \overline{F}_i(x_i) + \sum_{1\leq i\lesssim j \leq m} \overline{F}_{ij}(x_i, x_j) + \cdots,
$$

where $\overline{F}(\mathbf{x}) = (f^{(1)}(\mathbf{x}), f^{(2)}(\mathbf{x}), \ldots, f^{(m)}(\mathbf{x}))$ is the $m$-output vector function, in which $f^{(k)}(\mathbf{x})$, $k = 1, 2, \ldots, m$, are outputs. $\overline{F}_0$ is a constant vector over the entire domain $\Omega$, which denotes the zeroth order effect; $\overline{F}_i(x_i)$, $1 \leq i \leq n$, are the first order component vector functions, which describe the effects of the variable $x_i$, $1 \leq i \leq n$, acting independently; the second order vector functions $\overline{F}_{ij}(x_i, x_j)$, $1 \leq i \leq n$, give the cooperated effects of the variables $x_i$ and $x_j$, $1 \leq i < j \leq n$; and the higher order terms reflect the cooperative effects of multiple variables acting together.

Let $\mathbf{x} = (x_1, x_2, \ldots, x_n)\in\Omega$ be the cut point, the component vector functions $\overline{F}_0, \overline{F}_i(x_i)$ and $\overline{F}_{ij}(x_i, x_j)$ can be evaluated as follows:

$$
\overline{F}_0 = \overline{F}(\mathbf{x})
$$

$$
\overline{F}_i(x_i) = \overline{F}(x_i, \hat{x}^{(i)}) - \overline{F}(\mathbf{x})
$$

$$
\overline{F}_{ij}(x_i, x_j) = \overline{F}(x_i, x_j, \hat{x}^{(ij)}) - \overline{F}(x_i, \hat{x}^{(i)}) - \overline{F}(\hat{x}^{(i)}, x_j) + \overline{F}(\mathbf{x})
$$

where $(x_i, \hat{x}^{(i)}) = (\hat{x}_1, \ldots, \hat{x}_{i-1}, x_i, \hat{x}_{i+1}, \ldots, \hat{x}_n)$ and $(x_i, x_j, \hat{x}^{(ij)}) = (\hat{x}_1, \ldots, \hat{x}_{i-1}, x_i, \hat{x}_{i+1}, \ldots, \hat{x}_{j-1}, x_j, \hat{x}_{j+1}, \ldots, \hat{x}_n)$. Generally, the second order component HDMR approximation can provide a satisfactory approximation by

$$
\overline{F}(\mathbf{x}) \approx \overline{F}_0 + \sum_{i=1}^{n} \overline{F}_i(x_i) + \sum_{1\leq i\lesssim j \leq m} \overline{F}_{ij}(x_i, x_j).
$$

The HDMR technique has a broad area of applications on fully equivalent operational models, global uncertainty assessments, financial and econometric problems, etc. (Benson et al., 2008, Wang et al., 2005, Chowdhury & Rao, 2009). However, due to the complicated input–output relations, the HDMR methods defined on a whole domain can not obtain enough accuracy for high dimensional systems in large domains. By using multiple cut points, the multi-cut-HDMR method was studied in (Li et al., 2004) but numerical accuracies of simulations depend on the locations of multi-cut points. More recently, paper (Cheng et al., 2010) proposed the moving-cut HDMR method by combining with moving multiple local cut points, which can obtain accurate and efficient approximations to high dimensional systems.

The moving cut HDMR method (MC-HDMR) can be described as below.

1. Firstly, set up multiple moving cut points. For getting an accurate approximation, local cut points are moved into relatively smooth parts of the function distribution on the domain by doing that
   a. Give an initial point $\mathbf{x}_0$ in a local part of the domain.
   b. For some step length $H_i > 0$, consider the neighborhood $O(\mathbf{x}_0, H_i)$ along the $x_i$-direction and find a new cut point $\mathbf{x}_1$ by looping some steps in accordance to smoothness conditions. Then take $\mathbf{x}_1$ as the new initial point and further find other cut points starting from $\mathbf{x}_1$ along the $x_i$-direction.
   c. Starting from the found cut points, loop to find the local cut points along another direction until all directions.
2. Secondly, set up sub-domains (sub-regions) according to local moving cut points.
3. Thirdly, over sub-domains, the HDMR is applied to generate local approximations to $F(\mathbf{x})$. The first order component terms $\overline{F}_i(x_i)$ with the local moving cut points can be constructed as follows. Take $s$ values along the $x_i$-direction denoted by $x_i^1, x_i^2, \ldots, x_i^s$, and get the discrete database. Let $(x_i^1, \hat{x}^{(i)}) = (\hat{x}_1, \ldots, \hat{x}_{i-1}, x_i^1, \hat{x}_{i+1}, \ldots, \hat{x}_n)$, the first order component functions are defined as

$$
\overline{F}_i(x_i) \approx \sum_{j=1}^{s} \prod_{k \neq j} \frac{x_i^k - x_i^j}{x_i^k - x_i^j} \overline{F}(x_i^j, \hat{x}^{(j)}),
$$

where $1 \leq i \leq n$, and the approximations have $s$-1 order accuracy $O(h^{s-1})$, where $h = \max_{1 \leq j \leq s-1} |x_i^{j+1} - x_i^j|$. The second order component functions $\overline{F}_{ij}(x_i, x_j)$ can be constructed similarly.

Remark 1. In the approach of MC-HDMR, the high-dimensional functions are locally approximated by low-dimensional component functions over sub-domains. At the step 3 above, the database system of the low-dimensional component functions over sub-domains are set up by low-dimensional interpolations from the data, at nodes $(x_i^j, \hat{x}^{(j)})$, $1 \leq j \leq s$, computed by ISORROPIA. The prediction of multiple outputs are further obtained by (2.1).

Multi-region and multi-level prediction of aerosols has greatly been affected by the spatial variations in particle concentrations, sizes and compositions. In the non-urban area, the input components contain rich sulfate but poor sodium, while in the marine or the coastal area, it is sulfate rich but sodium rich. In some urban areas, both sodium and chloride are sometimes not included. For large scale predictions of aerosols, the multi-functional MC-HDMR approach is developed by building a predicting database system in the following steps.
1. Set up the appropriate input components and their size ranges for different sub-region predictions according to the features of the global prediction. Each built sub-region prediction contains a certain of input components and range sizes based on the aerosol types.

2. On each simulated sub-region, set up multiple local moving cut points, and set up their sub-domains for building local predicting systems.

3. On each predicted sub-region, build the moving cut HDMR predicting system by applying the local HDMR approach on sub-domains of local moving cut points.

4. Generate the multi-functional MC-HDMR simulation database system for multi-phase and multi-component aerosol prediction over multiple regions and levels.

5. Simulate the aerosol outputs by using the generated database of multi-functional MC-HDMR system.

**Remark 2.** At the steps 3 and 4, the database prediction system is built based on full thermodynamic equilibrium models such as ISORROPIA, as described in Remark 1. Thus, we can see that the prediction system is an extension of full thermodynamic models.

**Remark 3.** As an illustration of inputs and outputs in the multi-functional MC-HDMR approach, we explain them by an ammonium-sulfate only system. For this simple ammonium-sulfate only system, the input vector is $x = (T, RH, C_{SO_4}, C_{NH_4})$, which includes the input components of temperature, relative humidity, and the concentrations of sulfate and ammonium, respectively. There are seven outputs, i.e., $y = (f^{(1)}, f^{(2)}, \ldots, f^{(7)})$, where $f^{(k)}$, $k = 1, 2, \ldots, 7$, represent the predicted concentrations of the output components: gaseous species, NH$_3$, liquid aerosol species, NH$_4^+$, SO$_4^{2-}$, and NH$_3$(aq); solid aerosol species, (NH$_4$)$_2$SO$_4$, NH$_4$HSO$_4$ and (NH$_4$)$_3$H(SO$_4$)$_2$.

### 3. Multiple component input and output aerosol simulation

Aerosols in many regions, especially in marine or coast area, can be normally considered as a multiple input system including seven component inputs of sodium, sulfate, ammonium, nitrate and chloride components, and environmental parameters of temperature and relative humidity. The system contains multi-phase and multi-component outputs such as liquid phase components: aerosol water, aqueous NH$_4^+$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$ and HNO$_3$; solid phase components: NaNO$_3$, NH$_4$NO$_3$, NaCl, NH$_4$Cl, Na$_2$SO$_4$, (NH$_4$)$_2$SO$_4$, NH$_4$HSO$_4$ and (NH$_4$)$_3$H(SO$_4$)$_2$ and gas phase components: NH$_3$(gas), HNO$_3$(gas) and HCl(gas). The concentration sizes of these input components have a large rate from $10^{-10}$ to $10^{-5}$. The multiple input domain is denoted by $D$ with Sodium: $1.0 \times 10^{-9} - 1.0 \times 10^{-5}$ (mol m$^{-3}$); Sulfate: $1.0 \times 10^{-10} - 1.0 \times 10^{-6}$ (mol m$^{-3}$); Ammonium: $1.0 \times 10^{-10} - 1.0 \times 10^{-6}$ (mol m$^{-3}$); Nitrate: $10^{-10} - 1.0 \times 10^{-6}$ (mol m$^{-3}$); Chloride: $1.0 \times 10^{-8} - 1.0 \times 10^{-5}$ (mol m$^{-3}$); Temperature: 210–320 K; and Relative humidity: 0 – 9. The prediction database of the multi-functional MC-HDMR is built from the modeled outputs by ISORROPIA on the multiple input domain.

Firstly, we take 20,480 sample inputs over the domain $D$ for the accuracy test. The relative error is defined by

$$\text{Relative Error} = \frac{|\text{ISORROPIA} - \text{MC-HDMR}|}{|\text{ISORROPIA}|}.$$

where MC-HDMR represents the simulated results by the multi-functional MC-HDMR, while ISORROPIA represents the exact outputs from ISORROPIA. Table 1 shows the percentage rates of aerosol water, HCl (gas), NH$_3$(gas) and solid sodium chloride (NaCl) in the relative error. For example, it is clearly shown that for the output of NaCl (solid), there are 75.5%, 80.8% and 85.6% output data over total 20,480 outputs within 5%, 10% and 20% accuracies, respectively.

Then, Fig. 1 shows the prediction profiles of solid ammonia nitrate (NH$_4$NO$_3$) (left) and solid sodium nitrate (NaNO$_3$) (right) concentrations by ISORROPIA and the multi-functional MC-HDMR method along the relative humidity variable. The other input component values are temperature 298.15 K, sodium 2.57×$10^{-9}$ (mol m$^{-3}$), sulfate 1.02×$10^{-7}$ (mol m$^{-3}$), ammonium 5.88×$10^{-7}$ (mol m$^{-3}$), nitrate 4.76×$10^{-7}$ (mol m$^{-3}$) and chloride 2.56×$10^{-7}$ (mol m$^{-3}$) for solid ammonia nitrate output (left), while the input values are temperature 298.15 K, sodium 1.35×$10^{-7}$ (mol m$^{-3}$), sulfate 3.19×$10^{-8}$ (mol m$^{-3}$), ammonium 1.01×$10^{-9}$ (mol m$^{-3}$), nitrate 3.175×$10^{-8}$ (mol m$^{-3}$) and chloride 5.5×$10^{-9}$ (mol m$^{-3}$) for solid sodium nitrate output (right). We can see from Fig. 1 that both results of solid ammonia nitrate (left) and solid sodium nitrate (right) calculated by the multi-functional MC-HDMR match very well with those by ISORROPIA. As a multi-component mixture can reduce the mutual deliquescence relative humidity (MDRH) (see, Nenes et al., 1998), it is shown in Fig. 1 (left) that the predicted concentration of solid ammonium nitrate begins to decrease at about RH = 0.45 when the input concentration of sodium is 2.57×$10^{-9}$ (mol m$^{-3}$).

Figs. 2 and 3 give the concentration distributions of gas HCl and aqueous chloride ion simulated by the ISORROPIA and the multi-functional MC-HDMR method with two input component groups including the same components of temperature 298.15 K, sulfate 1.20×$10^{-7}$ (mol m$^{-3}$), ammonium 3.20×$10^{-7}$ (mol m$^{-3}$), nitrate 3.91×$10^{-7}$ (mol m$^{-3}$) and chloride 6.63×$10^{-6}$ (mol m$^{-3}$), but the different sodium component values of 1.78×$10^{-9}$ (sodium poor) and 6.32×$10^{-7}$ (mol m$^{-3}$) (sodium rich). The simulation results for the case of sodium poor by the ISORROPIA and the multi-functional MC-HDMR method are in great agreement while some differences happen for the case of sodium rich. From the figures in Figs. 2 and 3, we can see clearly that the concentration of input sodium has a significant influence on the outputs of gas HCl and aqueous chloride ion. The concentration of gas HCl is 6.6×$10^{-6}$

<table>
<thead>
<tr>
<th>Table 1 Percentage rates of outputs simulated by the multi-functional MC-HDMR approach.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Output</strong></td>
</tr>
<tr>
<td><strong>Accuracy 5%</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Aerosol water</td>
</tr>
<tr>
<td>HCl (gas)</td>
</tr>
<tr>
<td>NH$_3$(gas)</td>
</tr>
<tr>
<td>NaCl (solid)</td>
</tr>
</tbody>
</table>
Fig. 1. Solid ammonia nitrate (left) and solid sodium nitrate (right) as functions of relative humidity.

Fig. 2. Predicted concentrations of gas HCl when sodium is poor (left) and rich (right).

Fig. 3. Predicted concentrations of aqueous Cl$^-$ when sodium is poor (left) and rich (right).
when $\text{RH} \leq 0.6$ for the case of sodium poor, but it is $6.3 \times 10^{-6}$ (mol m$^{-3}$) when $\text{RH} \leq 0.6$ for the case of sodium rich, in Fig. 2. That is because less gas HCl will be generated when sodium is rich and more NaCl will be generated in the liquid mixture. On the other hand, we can see from Fig. 3 that the concentration of chloride ion is up to $1.5 \times 10^{-7}$ at $\text{RH} = 0.9$ when sodium is rich. That presents that more NaCl will dissolve in the liquid when the relative humidity values are high, and thus the concentrations of aqueous chloride ions at high relative humidities increase.

Numerical profiles of solid sodium sulfate ($\text{Na}_2\text{SO}_4$) and aqueous $\text{SO}_4^{2-}$ ion outputs as functions of relative humidity are shown in Fig. 4. The inputs are temperature 298.15 K, sodium $1.96 \times 10^{-8}$ (mol m$^{-3}$), sulfate $1.36 \times 10^{-8}$ (mol m$^{-3}$), ammonium $2.89 \times 10^{-8}$ (mol m$^{-3}$), nitrate $1.71 \times 10^{-8}$ (mol m$^{-3}$) and chloride $1.48 \times 10^{-8}$ (mol m$^{-3}$). When the relative humidity is below 0.75, the concentration of solid sodium sulfate is close to a constant value and the concentration of aqueous $\text{SO}_4^{2-}$ ion is almost zero. When the relative humidity is greater than 0.75, solid sodium sulfate concentration (left) decreases rapidly while the aerosol $\text{SO}_4^{2-}$ ion concentration (right) has a fast growth.

Further, we take comparisons of simulations by the ISORROPIA, the AIM2, and the multiple functional MC-HDMR method. ISORROPIA is a thermodynamic equilibrium aerosol model which is widely used, while AIM2 is regarded as a accurate thermodynamic model for gas/liquid/solid equilibrium calculations. Fig. 5 gives the concentrations of aerosol water, solid sodium sulfate ($\text{Na}_2\text{SO}_4$), solid ammonium chloride ($\text{NH}_4\text{Cl}$) and aerosol $\text{Cl}^-$ ion outputs as functions of relative humidity with the input data of temperature 298.15 K, sodium $2.57 \times 10^{-7}$ (mol m$^{-3}$), sulfate $1.02 \times 10^{-7}$ (mol m$^{-3}$), ammonium $5.88 \times 10^{-7}$ (mol m$^{-3}$), nitrate $4.76 \times 10^{-7}$ (mol m$^{-3}$) and chloride $2.56 \times 10^{-6}$ (mol m$^{-3}$). It is clear that the results calculated by the three methods are very close at most relative humidity values. The curves of $\text{Na}_2\text{SO}_4$, $\text{Cl}^-$ and $\text{NH}_4\text{Cl}$ output concentrations have the same jump point around $\text{RH} = 0.6$. But at $\text{RH} = 0.6$ and 0.65, the values of $\text{Na}_2\text{SO}_4$, $\text{Cl}^-$ and $\text{NH}_4\text{Cl}$...
predicted by the AIM2 have some differences from those by the other two methods.

Moreover, the CPU-time comparison between the ISORROPIA and the multi-functional MC-HDMR is presented in Table 2. The samples of the first group and the second group are in input domain $D$, and the last group is in sub-domain $D$ of sodium: $1.0 \times 10^{-2} - 1.0 \times 10^{-6}$ (mol m$^{-3}$); Sulfate: $1.0 \times 10^{-6} - 1.0 \times 10^{-2}$ (mol m$^{-3}$); Ammonium: $1.0 \times 10^{-7} - 1.0 \times 10^{-6}$ (mol m$^{-3}$); Nitrate: $1.0 \times 10^{-6} - 1.0 \times 10^{-7}$ (mol m$^{-3}$); chloride: $1.0 \times 10^{-6} - 1.0 \times 10^{-5}$ (mol m$^{-3}$); Temperature: 280–310 K; and Relative humidity: 0.3–0.9. For the first group data of 124,416 samples, it takes 27.14 seconds to simulate by the ISORROPIA, but only 0.687 seconds by the multi-functional MC-HDMR method. In the second group, there are 186,624 samples of data, the simulation requires 40.25 seconds by the ISORROPIA, and 0.945 seconds by the multi-functional MC-HDMR. For the last group which contains 262,144 input samples data, the total simulated CPU time by the multi-functional MC-HDMR has decreased to about 80 times, comparing with the CPU time by the ISORROPIA in the last group. We can see that the multi-functional MC-HDMR method can save a lot of CPU time in simulation.

Finally, we evaluate stable/metastable solutions and forward/reverse problems. For the prediction of concentrations of aerosols at chemical equilibrium, ISORROPIA can solve the problem in two states: “stable”, where salts precipitate when the aqueous solution is saturated, and “metastable”, where aerosol is an aqueous solution even if it is under supersaturated conditions. ISORROPIA can also solve two classes of problems: “Forward” and “Reverse”. In the prediction, the known quantities are temperature, relative humidity and the concentrations of ammonium, sulfate, sodium, chloride and nitrate, the concentrations of the species refer to the total (gas and aerosol) amount in the “Forward” problem, while they refer to the amount only in aerosol phase in the “Reverse” problem.

The results on stable and metastable solutions are presented in Fig. 6, which shows the concentrations of aerosol water and aqueous phase sodium as a function of relative humidity predicted by ISORROPIA and MC-HDMR. The input components are temperature 298.15 K, sodium $8.67 \times 10^{-9}$ (mol m$^{-3}$), sulfate $2.04 \times 10^{-8}$ (mol m$^{-3}$), ammonium $4.71 \times 10^{-7}$ (mol m$^{-3}$), nitrate $1.91 \times 10^{-7}$ (mol m$^{-3}$) and chloride $5.47 \times 10^{-9}$ (mol m$^{-3}$). Both predict similar concentrations of aerosol water and aqueous sodium in two states for all RHs, and the difference between the stable and metastable states can be found. The thermodynamic stable solution predicts the presence of aerosol water and aqueous sodium at RH > 0.5, while a mount of aerosol water can be found under RH = 0.5 in the metastable state, and sodium keeps in aqueous phase at all RH levels.

Using the output from the above forward problem (in stable state) as input to the reverse problem, the predicted concentrations of aqueous water and aqueous nitrate by the ISORROPIA and MC-HDMR are shown in Fig. 7 and the numerical results are in a good agreement. Comparing the predicted concentrations of aerosol water in Fig. 6 (left) and Fig. 7 (left), it can be clearly seen that the forward and reverse modes predict the same outputs when the same inputs are used.

Remark 4. As we focus on the aerosol problems without crustal species in the paper, the aerosol database prediction system of multiple functional MC-HDMR is generated by the updated source code of ISORROPIA 1.7, which produces identical results as the version ISORROPIA-II (as stated on the
A seven input components aerosol database prediction system is built by ISORROPIA in this study. In the future work, we will use ISORROPIA-II to generate the database prediction system for aerosol problems with crustal species, which will require to build a more complex eleven input components aerosol database prediction system by multiple functional MC-HDMR approach. The results predicted by AIM2 in this paper are calculated by the web site http://www.aim.env.uea.ac.uk/aim/aim.php.

4. Actual aerosol computations by multi-functional MC-HDMR

In this section, the multi-functional MC-HDMR approach is used on the simulation of real aerosol prediction problems. Three general types of aerosols are calculated, and we also compute the species concentrations in a few European and Asian cities.

4.1. Computation of three types of aerosols in different regions

First, we consider three types of aerosols in different regions of urban, non-urban continental and marine. Input components concentrations of ammonium, nitrate, sulfate, sodium and chloride for three types of aerosols are listed in Table 3 (Heintzenberg, 1989; Fitzgerald, 1991; Nenes et al., 1999). The urban data was selected from 21 experiments in American, Chinese, European and Japanese sites (Heintzenberg, 1989), while the non-urban data was averaged over 35 data sets from 16 experiments, which were taken on the continents away from large urban or industrial sources in USA, Sweden, Brazil, and UK (Heintzenberg, 1989). The concentrations for marine aerosols data were selected so that the amount of species are comparable to levels of experiments on different sites of Pacific, Atlantic and Indian Ocean (Fitzgerald, 1991, Nenes et al., 1999).

The simulated results of aerosol water, aqueous NH$_4^+$ and solid sodium chloride related to RH (10–90%) at temperature 298.15 K are shown in Fig. 8 for three types of aerosols. The concentrations of aerosol water in urban and marine cases are around 1.6×10$^{-6}$ (mol m$^{-3}$) at RH=0.9, while the output is much smaller, about 1×10$^{-6}$ (mol m$^{-3}$) at RH=0.9 for the case of non-urban, which is shown in Fig. 8 (a). The predicted concentrations of aqueous NH$_4^+$ in Fig. 8 (b) by the multiple functional MC-HDMR method is very close to the results by the ISORROPIA and AIM2 methods for most RH values, but there are some differences at the points RH=0.6 for the urban case and RH=0.7 for the non-urban case. For the marine case, there are zero outputs of aqueous NH$_4^+$ by three methods. Fig. 8 (c) presents the results of NaCl simulation. As there is no sodium and chloride in the urban area and only a little in the non-urban area, the concentrations of solid NaCl in urban and non-urban aerosols are zero. The predicted NaCl results in the marine case are in good agreement by the three methods.

Finally, we list the comparison of particulate matter (PM) in Table 4, which shows the total PM concentrations predicted at temperature 298.15 K and RH = 30%. The total PM concentrations are calculated by formulas (see, Metzger et al., 2002):

$$ PM_{s} = 62 \cdot NO_{3}^{−}(s) + 18 \cdot NH_{4}^{+}(s) + 96 \cdot SO_{4}^{2−}(s) $$
$$ PM_{aq} = 62 \cdot NO_{3}^{−}(aq) + 18 \cdot NH_{4}^{+}(aq) + 96 \cdot SO_{4}^{2−}(aq) $$
$$ tPM = PM_{s} + PM_{aq} $$

where t denotes sum of solid and aqueous PM, and the subscripts s andaq denote solid and aqueous, respectively.
The values of PM concentrations predicted by the three methods are almost same. The PM concentration is 0.6 $\mu$g/m$^3$ for the marine aerosol, while it is larger, 11.5 $\mu$g/m$^3$, for the urban aerosols. It shows more serious pollution in the urban area than in the marine area.

4.2. Actual aerosol computations in European cities

We consider aerosol computations in European cities based on the measured data at six stations: K-Puszta (Hungary), Montelibretti (Italy), Kollumerwaard (Netherlands), Skreadalen (Norway), and two sites in Austria.

---

**Fig. 8.** Predicted concentrations of aerosol water, aqueous NH$_4^+$ and solid NaCl as functions of relative humidity in three types of aerosols.
The results of simulation of HNO₃ (gas) are presented in the multi-functional MC-HDMR, which is shown in Fig. 9(c). AIM2 are a little bit higher than those by the ISORROPIA and are high concentrations of aqueous NH₄⁺. The multi-functional MC-HDMR are shown in Fig. 9. It includes the other stations except the components of sodium and chloride. The concentrations of HNO₃ (gas) at stations HU02, IT01 and NL09 are around 1×10⁻⁸ (mol m⁻³) at RH=0.9 in Shanghai, 3×10⁻⁶ (mol m⁻³) in Southern Taiwan and 4×10⁻⁹ (mol m⁻³) in Seoul, respectively. The predicted plots of aqueous NO₃⁻ in these three cities, respectively. However, the predicted curves of solid Na₂SO₄ in Shanghai, Southern Taiwan, and Seoul have a sharp decrease point at RH=0.7, which is just the point where the SO₄²⁻ concentrations are 1.8×10⁻⁷ (mol m⁻³), 1.2×10⁻⁷ (mol m⁻³) and 1×10⁻⁷ (mol m⁻³) in Shanghai, and about 6×10⁻⁸ (mol m⁻³) in Southern Taiwan and Seoul, and the SO₄²⁻ concentrations are 1.8×10⁻⁷ (mol m⁻³), 1.2×10⁻⁷ (mol m⁻³) and 1×10⁻⁷ (mol m⁻³) in these three cities, respectively. The predicted curves of aerosol water concentration start to increase at RH=0.5, and reach to 4×10⁻⁶ (mol m⁻³) at RH=0.9 in Shanghai, 3×10⁻⁶ (mol m⁻³) in Southern Taiwan and Seoul, respectively. The predicted plots of aqueous NO₃⁻ and SO₄²⁻ concentrations are in accordance with the same varied trend as aerosol water distribution. Both the ISORROPIA and the multi-functional MC-HDMR predict the existence of aqueous NO₃⁻ and SO₄²⁻ when RH is greater than 0.5. At RH=0.9, the aqueous NO₃⁻ concentration is 4×10⁻⁹ (mol m⁻³) in Shanghai, and about 6×10⁻⁸ (mol m⁻³) in Southern Taiwan and Seoul, and the SO₄²⁻ concentrations are 1.8×10⁻⁷ (mol m⁻³), 1.2×10⁻⁷ (mol m⁻³) and 1×10⁻⁷ (mol m⁻³) in these three cities, respectively. As Fig. 13 displays, in the Hong Kong area, the existence of aerosol water is predicted when RH is less than 0.7, which is just the point where the SO₄²⁻ distribution concentrations start to increase. When RH is less than 0.7, the concentrations of solid Na₂SO₄ keep constant values of 4×10⁻⁸ (mol m⁻³) in Shanghai, 3×10⁻⁶ (mol m⁻³) in Southern Taiwan and 4×10⁻⁹ (mol m⁻³) in Seoul, respectively. Fig. 13 presents the predictions of aerosol water, aqueous SO₄²⁻ and Cl⁻ and solid NaCl in Hong Kong, which mainly reflects the effect of sea salts.

### Table 4
Comparisons of total PM concentration (μg/m³) predicted at temperature 298.15K and RH = 30%.

<table>
<thead>
<tr>
<th>Aerosol type</th>
<th>PM concentrations (μg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ISORROPIA</td>
</tr>
<tr>
<td>Non-urban continental</td>
<td>7.19</td>
</tr>
<tr>
<td>Urban</td>
<td>11.52</td>
</tr>
<tr>
<td>Marine</td>
<td>0.66</td>
</tr>
</tbody>
</table>

### Table 5
Measured data (μg/m³) of ammonium, nitrate, sulfate and sea salt at six stations in European cities in 2000.

<table>
<thead>
<tr>
<th>Code</th>
<th>Station name</th>
<th>Country</th>
<th>Ammonium</th>
<th>Nitrate</th>
<th>Sulfate</th>
<th>Sodium</th>
<th>Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>HU02</td>
<td>K-Puszta</td>
<td>Hungary</td>
<td>1.90</td>
<td>2.76</td>
<td>4.95</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>IT01</td>
<td>Montelibreti</td>
<td>Italy</td>
<td>2.06</td>
<td>3.62</td>
<td>3.24</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NL09</td>
<td>Kollumerwaard</td>
<td>Netherlands</td>
<td>1.29</td>
<td>2.78</td>
<td>1.85</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO08</td>
<td>Sreadalen</td>
<td>Norway</td>
<td>0.28</td>
<td>0.51</td>
<td>1.04</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>RU01</td>
<td>Janiskoski</td>
<td>Russia</td>
<td>0.29</td>
<td>0.21</td>
<td>1.05</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO01</td>
<td>Birkenes</td>
<td>Norway</td>
<td>0.39</td>
<td>0.74</td>
<td>1.33</td>
<td>0.45</td>
<td>0.54</td>
</tr>
</tbody>
</table>
RH is bigger than 0.6, and the increase of aqueous SO$_4^{2-}$ starts from RH=0.8. The change points are later than in other cities of Shanghai, Southern Taiwan and Seoul. This may be caused by the high concentrations of sodium and chloride in Hong Kong. From the figures, we can also see that the concentration of solid NaCl decreases, and the concentration of Cl$^-$ increases greatly both from RH=0.6. At RH=0.9, the concentration of Cl$^-$ reaches to 2.5×10$^{-7}$ (mol m$^{-3}$). The main reason is that NaCl will not keep in solid for the high humidity values.

In Figs. 10–12, the concentration of aqueous SO$_4^{2-}$ in Shanghai is higher than those in southern Taiwan and Seoul, which indicates that there are more human activities in Shanghai, as SO$_4^{2-}$ is mainly influenced by the anthropogenic emissions. This is coincide with the fact that Shanghai is the largest city in China with over 16.74 million people. From Fig. 13, we can see Cl$^-$ is mainly deviated from NaCl dissolution, and the large amount of solid NaCl and aqueous Cl$^-$ indicates that the aerosols in Hong Kong is greatly affected by marine environment.

**Remark 5.** The traditional approaches used to perform the calculation of high-dimensional input–output problems, such as high order polynomials and standard high-dimensional look-up tables, etc., will lead to an exponential scaling of computational cost and also high memory requirement for solving high-dimensional equations. The HDMR approach transforms the high-dimensional problems into a set of lower-dimensional functions that can be easily computed and greatly reduces the computational complexity and CPU-time. The method has a low memory cost for high-dimensional approximations. In the multi-functional MC-HDMR system, the size of prediction database system depends on the aerosol input components and their size.

**Table 6**

<table>
<thead>
<tr>
<th>Site</th>
<th>Time</th>
<th>Ammonium</th>
<th>Nitrate</th>
<th>Sulfate</th>
<th>Sodium</th>
<th>Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shanghai, China</td>
<td>2003-2005</td>
<td>5.68</td>
<td>14.19</td>
<td>17.83</td>
<td>1.90</td>
<td>8.06</td>
</tr>
<tr>
<td>Southern Taiwan</td>
<td>2004</td>
<td>6.08</td>
<td>6.14</td>
<td>11.28</td>
<td>1.42</td>
<td>1.84</td>
</tr>
<tr>
<td>Hong Kong</td>
<td>1995-1996</td>
<td>1.08</td>
<td>4.21</td>
<td>10.77</td>
<td>11.13</td>
<td>16.80</td>
</tr>
<tr>
<td>Seoul, South Korea</td>
<td>2001</td>
<td>5.17</td>
<td>12.6</td>
<td>9.42</td>
<td>0.20</td>
<td>2.14</td>
</tr>
</tbody>
</table>
ranges and the behaviors of outputs. By considering these factors in the first step, the multi-functional MC-HDMR can arrange efficiently multiple sub-domains and moving local cut-points, which further reduces the database size and memory requirement. All the simulation tests in this paper are performed on an Intel CPU Core2 T2450 2GHZ machine with 1536 M RAM.

5. Conclusion

In this paper, we developed a multi-functional MC-HDMR approach for the multi-component input and output aerosol predictions. This method can be applied to simulate the predictions of aerosols in high dimensional domains with a large range of aerosol concentrations. The developed aerosol prediction system includes a prediction database built by the MC-HDMR approach based on data computed from full thermodynamic models such as ISORROPIA. It can efficiently compute aerosol concentrations in multiple regions and for different types of aerosols. Numerical results showed the great computational efficiency of the approach. The CPU-time cost by the approach is shown much less than that by the ISORROPIA. Actual aerosol examples in European and Asian cities are computed. The results obtained by the approach are in great agreement with the predictions of the ISORROPIA and AIM2. We observed from the results that there might be more traffic pollution at the areas of HU02, IT01 and NL09, and the concentration of aqueous SO$_4^{2-}$ in Shanghai is higher than that in both Southern Taiwan and Seoul which might be influenced by more anthropogenic activities, and aerosols in Hong Kong is affected by the marine environment. Meanwhile, the PM concentrations of aerosols in the urban, non-urban continental and marine areas are calculated, which showed more serious pollution in urban area. The developed approach can be applied for the

![Fig. 10. Predicted concentrations of aerosol water, aqueous NO$_3^-$ and SO$_4^{2-}$ and solid Na$_2$SO$_4$ as functions of relative humidity in Shanghai.](image)

![Fig. 11. Predicted concentrations of aerosol water, aqueous NO$_3^-$ and SO$_4^{2-}$ and solid Na$_2$SO$_4$ as functions of relative humidity in Southern Taiwan.](image)
large scale predictions of aerosols in multiple regions and levels in atmosphere.

Since the multi-functional MC-HDMR approach can set up an efficient prediction database system. ISORROPIA is a widely used aerosol thermodynamic equilibrium model in many 3D chemical transport models (CTMs), such as Community Multi-scale Air Quality Modelling System (CMAQ) (Binkowski and Roselle, 2003), Particulate Matter Comprehensive Air Quality Model with Extensions (PMCAQM) (Gaydos et al., 2007), and Weather Research and Forecasting/Chemistry model (WRF-CHEM) (Grell et al., 2005), etc. We will further apply the multi-functional MC-HDMR system into a 3D aerosol simulation model system and will carry out computation of 3D aerosol simulations as our future work. We may also consider aerosol problems with crustal species into the model system.

Acknowledgements

This work was partly supported by the National Basic Research Program (973) of China under the grant 2006CB403703. K. Fu was also supported by the China Scholarship Council for his visit to York University. D. Liang was also supported partially by Natural Sciences and Engineering Research Council of Canada. W. Wang was also supported partially by Natural Science Foundation of China (10671113). K. Fu and Y. Cheng also thank the Department of Mathematics and

Fig. 12. Predicted concentrations of aerosol water, aqueous \( \text{NO}_3^- \) and \( \text{SO}_4^{2-} \) and solid \( \text{Na}_2\text{SO}_4 \) as functions of relative humidity in Seoul.

Fig. 13. Predicted concentrations of aerosol water, aqueous \( \text{Cl}^- \), solid \( \text{Na}_2\text{SO}_4 \) and \( \text{NaCl} \) as functions of relative humidity in Hong Kong.
Statistics, York University for their visits to the department. We would also thank the Editor in Chief, the Associate editor and the referees for their valuable suggestions which have helped to improve the paper greatly.

References


