PM SIZE DISTRIBUTION IN SOUTHERN CHINA

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1. INTRODUCTION

As there have been closer economic ties between Hong Kong and the Pearl River Delta region, air pollution problems are inevitably affecting both sides as an entire regime. Respiratory malfunctioning and visibility impairment are related to particulate matters (PMs). However, studies show that the fine size of PMs, rather than their mass, determines how deep the PMs could penetrate the nostril into the respiratory system. The size, especially when near or within the range of wavelength of visible light (0.4-0.7 μm), happens to be most effective in scattering incoming sunlight, so that any object is poorly illuminated. To combat the PM problem, Hong Kong University of Science & Technology (HKUST) and Peking University (PKU) jointly conducted a measurement campaign in hope of understanding the size of ambient PM (Huang et al., 2006). With the help of positive matrix factorization (PMF), they resolve the bulk mass into condensation, droplet and coarse modes. They concluded the following. Ca^{2+} is in predominant coarse mode, occurring as soil particles. Na^{+} is also predominant coarse mode in sea salt, but a small fraction also occurs in droplet mode, which correlates moderately with droplet mode K^{+}. The moderate correlation suggests biomass burning source for the droplet Na^{+} and K^{+}. The biomass burning is also the major source for water soluble organic carbon (WSOC). Sulfate is mainly droplet mode, and the majority of it is formed through aqueous chemical reactions in cloud water. The similar aqueous pathway also applies to oxalate predominantly in droplet mode, however, it could be adsorbed onto alkaline coarse particles.

When air quality modeling system was set up adequately, we attempted to compare our model results with the measurement data in hope of understanding aerosol chemistry as well as assessing inadequacies in emissions, speciation profiles and/or any aerosol processes.

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2. MEASUREMENTS & CMAQ

Measurement

A ten-stage microorifice uniform deposit impactor (MOUDI, MSP Corp., Shoreview, MN) was used to collect aerosol samples whose size ranges between 0.056-18.0 μm. Details of equipment and setup can be referred to Huang et al (2006). Samples were collected 21-26 July, 12-26 August and last 18 days of December 2004, at the rooftop of a four-story high building in Shenzhen, immediately north to Hong Kong (Fig. 1). The collected PM_{10} samples were further analyzed chemically, and thus concentrations of Na^{+}, $NH4^{+}$, K^{+}, Mg^{2+}, Ca^{2+}, Cl^{-}, $NO3^{-}$, $SO4^{2-}$, oxalate, water soluble organic carbon (WSOC), OC and EC were determined. Since current versions of CMAQ do not explicitly model the concentrations of K^{+}, Mg^{2+}, Ca^{2+}, and oxalate, we omitted the first three ions for subsequent measurement-model comparisons. For organic species, we simply added up oxalate, WSOC and OC together.

CMAQ models

We used CMAQ v4.6 and CMAQ v4.7 to simulate the December case. Since the aerosol modules are different between the two versions, we will hereafter refer AE4 to Version 4.6, and AE5 to Version 4.7. In both models, simulations were made on three nested domains with resolutions 40.5-, 13.5- and 4.5 km, the last one shown in Figure 1. Boundary conditions were constructed from GEOS-Chem outputs, meteorology were extracted from MM5 outputs via MCIP v3.0. 20 vertical layers were used, up to top-level pressure of 100 mb. Emission data consists of two parts. One is based on a gridded emission dataset for the TRACE-P campaign in Asia (2003). It covers most parts of China. But since our major concern focuses on HK/PRD area, we replace the TRACE-P emissions in it with emission inventory

compiled by Hong Kong Environmental Protection Department (HKEPD) to refine the local details in this area. It is noted here that in Streets et al's report (2003), the uncertainty in TRACE-P EC emissions could be as high as 500%. Since this uncertainty might apply to the OC emissions as well, adjustments were made to the primary organic aerosol (POA) emissions. Ocean mask files for the nesting domains were constructed from the water body indicator contained in GRIDCRO2D, except that surf zone area has not been set.

One of the major differences between AE5 and AE4 is that coarse mode nitrate production is introduced in AE5, via the following reaction between hydrogen nitrate and sea salt:

$$HNO_{3(g)} + NaCl_{(s)} \rightarrow NaNO_{3(s)} + HCl_{(g)} \quad (1)$$

During the above reaction, nitrates combine with sodium so as to displace the chlorides.

The MOUDI data were taken mean over December to represent the average of the month and henceforth the winter. In both AE4 and AE5 versions, hourly outputs were also taken over the same periods for comparison.

PM species to be compared include Na^+, $NH4^+$, Cl^-, $NO3^-$, $SO4^{2-}$, OC and EC. In AE4, OC is the sum of organic species ORGA, ORGPA and ORGB, whereas in AE5, OC includes ALK, xylene groups, toluene groups, benzene groups, terpenes plus sequiterpene, isoprene groups, cloud-produced organics, primary organics, and aged OLGAs. In CMAQ, most output PM species except ACORS and ASOIL are represented in I, J, and/or K modes, representing generic Aitken, accumulation and coarse modes in modal distributions. To convert the output PM concentrations from continuous modal distributions into discrete size bins as in MOUDI data, we followed the calculation procedures laid out by Jiang et al (2006). Species ACORS and ASOIL were also converted to the discrete size bins as from K-mode. Thus the newly generated hourly bin-sized PMs were taken monthly or bimonthly averages so that they can be compared with the corresponding averaged MOUDI data. Results are described in the following section.

3. COMPARISONS WITH MODEL OUTPUTS

Figure 2 shows the bin distributed PM species for December, but now CMAQ AE5 is also included. Predictions of Na^+, $NH4^+$, $SO4^{2-}$, OC and EC are qualitatively similar in both AE5 and AE4. AE5 predicts lower PM concentrations than AE4 does, except for sodium. But perhaps the most noticeable feature is that AE5 predicts non-zero coarse-mode nitrate, but much less coarse-mode chloride than AE4. Even though AE5 gets the coarse-mode nitrate, it is still well below the measured data.

The apparent simultaneous increase in $NO3^-$ and decrease in Cl^- are possibly due to the HNO3-NaCl reaction in Equation (1), in which the solid phase chloride is displaced by the incoming gaseous nitrate. Hence the inadequate chloride emission is further consumed by the HNO3.

The low predicted Na^+ and Cl^- level may be due to the lacking of sea salt from the coastal surf zone. The simulation would have been improved with the presence of surf-zone area, which depends on the length of the coastline in each grid cell. Although CMAQ 4.7 (i.e., AE5) has been implemented with this feature, certain input data about the length of the coastline is not available. It is hoped that the sea salt prediction will be improved when the surf-zone area is calculated.

The overprediction of OC takes place in both AE4 and AE5, reasons being the definition of predicted OC as well as the strength of VOC emission inventory. Firstly, the predicted OC is really the sum of the aerosol organic species mass rather than of the carbon. Had the latter being counted, the model prediction would have been less overpredicted. Secondly, based on Streets et al's report (2003), the uncertainty in EC estimation can be as high as 500%. Since this uncertainty may apply to the OC emissions as well, adjustments are made to the primary organic aerosol (POA) emissions. In consequence, the OC is overpredicted.

4. FURTHER DISCUSSIONS

The AE5 prediction of coarse-mode nitrate could be enhanced by an additional reaction of HNO3 with calcium carbonate:

$$2HNO_{3(g)} + CaCO_{3(s)} \rightarrow Ca(NO3)_{2(s)} + H_2O + CO_{2(g)} \quad (2)$$

However, since CMAQ 4.7 does not explicitly model any particulate calcium, so at this stage it is not possible to implement the above reactions and therefore predictions of coarse mode nitrate cannot be further improved.

Although MOUDI chloride is predominantly in coarse mode in summer, an extra peak occurs around size range 1.0-1.8 μm in winter (Fig 2). In size range 0.56-3.2 μm, MOUDI sodium concentration level is also high in winter. These observations suggest that sea salt alone does not account for the entire size distributions of sodium and chloride. As remarked by Huang et al (2006), combustions such as biomass burning contribute to the fine mode sodium.

MOUDI data also contains binned concentration levels of inorganic ions such as potassium and calcium. Any working versions of CMAQ and emission processor SMOKE do not speciate those ionic aerosol species. Fortunately, Reff et al (2009) have undergone the study of the subject, and it is hoped that more comprehensive speciation profiles will become available in the next release of SMOKE and CMAQ.

5. ACKNOWLEDGMENTS

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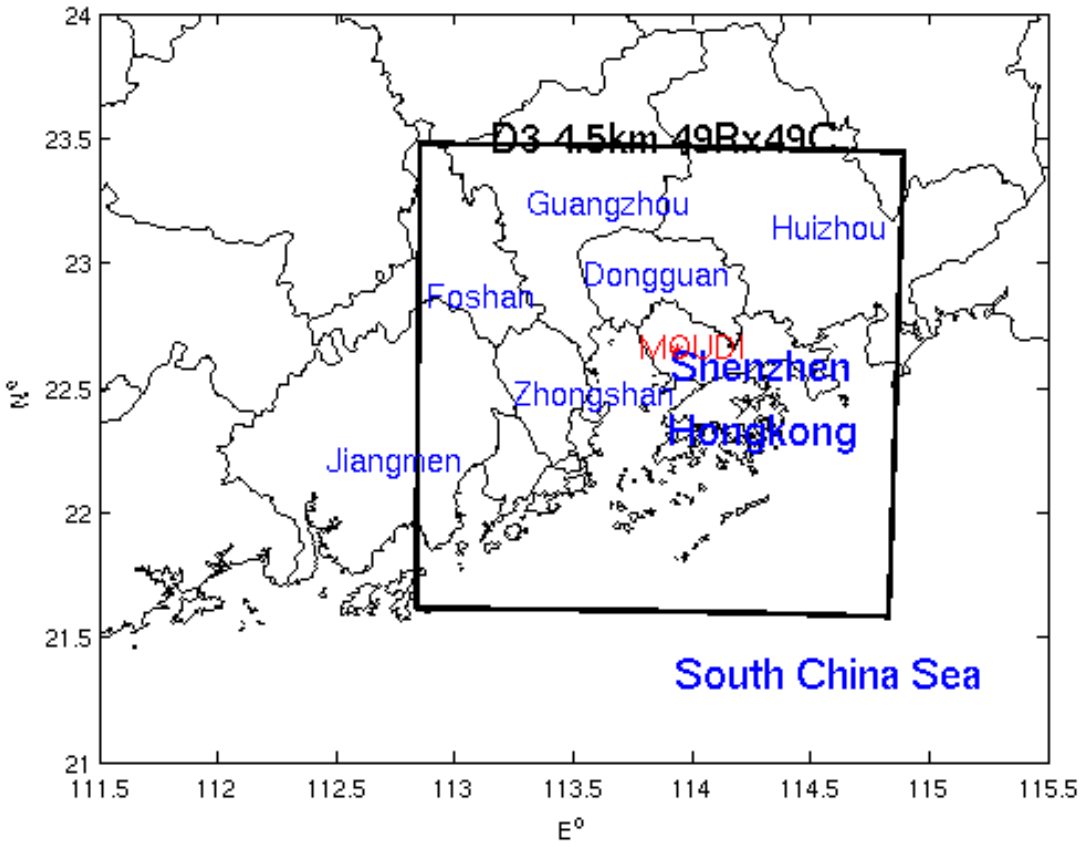

Fig.1. Computational domain and location of MOUDI measurement in Pearl River Delta

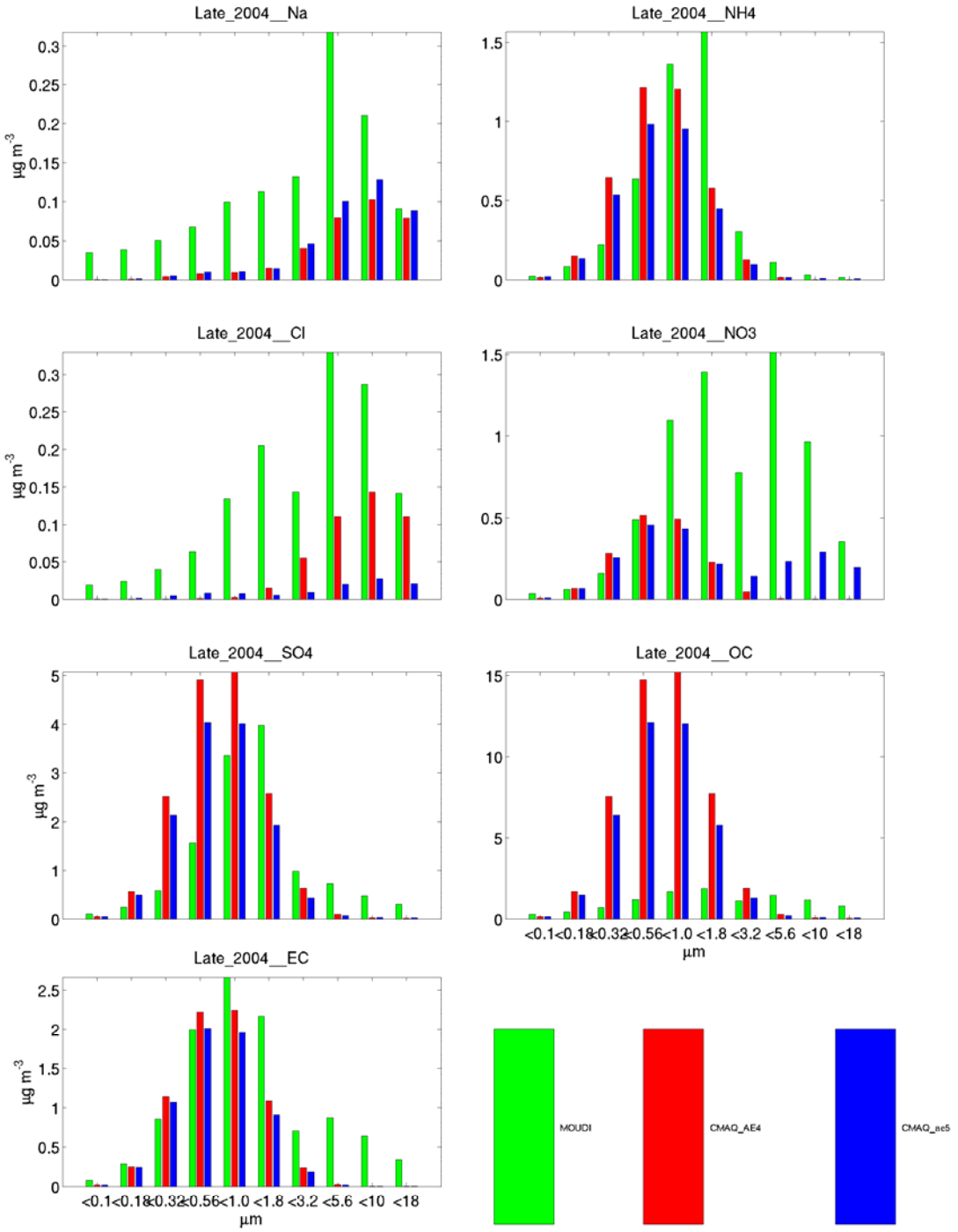

Fig.2. MOUDI (green) -CMAQ(AE4, red & AE5, blue) comparison for Dec 2004. Bin size is separated by 0.056, 0.1, 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6, 10.0 and 18 µm.