

IN-SITU MEASUREMENT AND CMAQ SIMULATION OF SO₂ OVER CENTRAL CHINA

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1. INTRODUCTION

In spring 2008, *in-situ* measurements of tropospheric SO₂ are conducted in central China. Vertical distribution of SO₂ is obtained from the surface to 4000 m. And the flight routes are selected according to the NASA OMI SO₂ products.

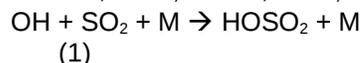
The numerical simulation of this campaign is conducted using the CMAQ v4.6 model. We use the WRF v3.1 model to provide the meteorological field and the NASA INTEX-B (2006) emission inventory for emission inputs. Two nested domains with 30/10 km resolution are defined, and the simulation period is 45 days with the first 15 days as spin-up. Improvements of SO₂ dry deposition and advection schemes have been done to modify the CMAQ systems, and 3 sensitivity runs are achieved.

The comparison of *in-situ* and remotely-sensed measurements with CMAQ simulation shows a reasonably consistent picture of tropospheric SO₂. And the CMAQ model tends to underestimate the SO₂ concentration within the PBL and overestimate it in the free troposphere (FT), probably caused by the parameterization of advectons. With the update of SO₂ dry deposition rate, CMAQ gives better evaluation of surface SO₂. The change of advection scheme supports the calculation of horizontal advection, which leads to less than 3% error in the sulfur balance and SO₂ lifetime as ~ 1.5 days.

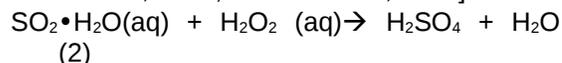
2. BACKGROUND

During the rapid economy growth in the last decades, the consumption and energy and raw materials has been drastically increased in China. Coal burning accounts for 70% of the total energy consumption in China [CESY, 2005], and the anthropogenic SO₂ emission is ~ 30.7 Tg in 2005 [Zhao *et al.*, 2009] and ~ 31.0 Tg in 2006 [Zhang *et al.*, 2009]. The enormous amount of sulfur emission causes environment problems, such as acid rain and smog [He *et al.*, 2002; Sun *et al.*, 2009].

The main chemistry of tropospheric SO₂ is the oxidization from the lower oxidation state S(IV) to higher oxidation state S(VI) [Finlayson-Pitts and Pitts, 1999; Hewitt, 2001; Seinfeld and Pandis, 1998]. In the gas phase, hydroxyl radicals (OH) play an important role [Atkinson *et al.*, 1976; Calvert *et al.*, 1978; Harris and Wayne, 1975; Harris *et al.*, 1980; Hewitt, 2001; Leu, 1982] as:



While in the aqueous phase, hydrogen peroxide (H₂O₂) oxidization is the major pathway [Martin and Damschen, 1981; Penkett *et al.*, 1979]:



The acidic sulfur-compounds produced by reaction (1) and (2) are neutralized by basic compounds such as NH₃, forming sulfate (SO₄²⁻) aerosols. These sulfur-compounds have profound impacts on both environments and human health [EPA, 2004; Hand and Malm, 2007; Schlesinger and Cassee, 2003; Watson, 2002]. Long range transports of sulfur-compounds [Igarashi *et al.*, 2006; Jaffe *et al.*, 1999; Kim *et al.*, 2001], it is important to study the chemistry, evolution and transportation of SO₂ in China.

3. AIRCRAFT CAMPAIGN IN CHINA

In spring 2008, a China-US joint aircraft campaign was carried out in Henan province of central China. Henan province is the most



Figure 1 Location of Henan province and Y-7 airplane

populous region of China with more than 100 million residents in 160,000 km². Coal mines and power plants are located in the west and south of

province, and coal is widely used for domestic cooking and heating.

A Y-7 turboprop transport aircraft (Figure 1) was employed as the airborne measurement platform. This airplane had the cruise speed of around 400 km/h, and was located at Zhengzhou Xinzheng International Airport (IATA code: CGO, 34°31'11"N, 113°50'27"E) during the one-month campaign. The aft facing inlet was installed on a rack to the left of fuselage as well as the T/RH probe provided by the local Henan Meteorological Bureau (HMB). Onboard was a modified TECO 42C SO₂ analyzer with detection limit of ~0.3 ppbv for 10 seconds average [Hains, 2007; Luke, 1997]

A typical flight included a spiral from 900 m to 4500 m and a descending to the CGO airport, providing the information within the PBL and in the FT respectively. Figure 2 demonstrates a sample of flight in 04/05/2008.

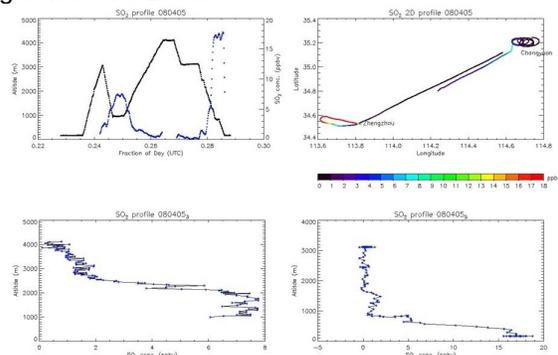


Figure 2 In-situ measurement of SO₂, 04/05/2008

Large spatial and temporal variations were observed. The average SO₂ profile is calculated (Figure 3), and the column content is 0.78 Dobson Unit (DU). We also present the mean

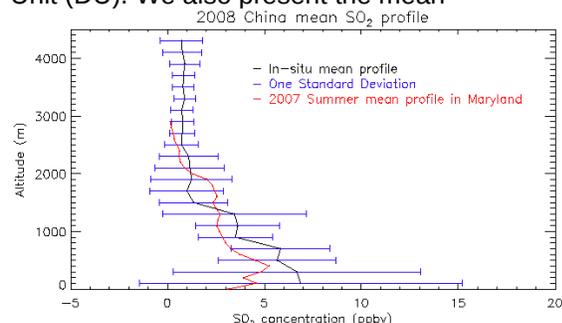


Figure 3 Average 2008 China SO₂ profile

SO₂ profile of 2007 summer in Maryland. The Maryland profile has higher SO₂ aloft (1500 to 2000 m) and less total column content.

4. WRF-CMAQ SIMULATION

4.1 WRF-MCIP System

Numerical simulation of the 2008 China campaign is conducted using the WRF-CMAQ system with WRF v3.1, MCIP v3.5 and CMAQ v4.6 models. The WRF model is driven by the NCEP FNL ds083.2 products (26 vertical levels from 1000 hPa to 10 hPa) and has two nested domain with 30/10 km resolution. The WRF outputs have 35 Eta levels from the surface to 50 hPa, and hourly resolution.

WRF outputs are processed by MCIP v3.5 to create meteorological fields for CMAQ. It is observed that the SO₂ mesophyll resistance (MR) is set as 0 in the dry deposition module of MCIP,

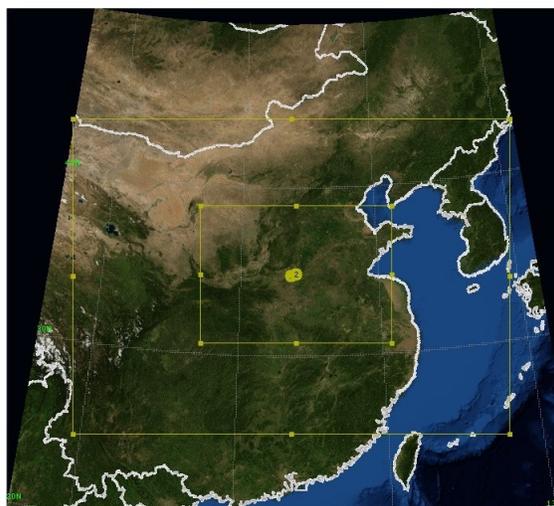


Figure 4 Demonstration of the WRF domains

which is much lower than the observation [Pfanzer et al., 1987]. So we correct the SO₂ mesophyll resistance to 8000 s/cm, and generated two sets of meteorological data (NoMR and MR).

4.2 NASA INTEX-B Emission Inventory

We use the NASA 2006 INTEX-B emission inventory to create 4-D emission input data for CMAQ. The INTEX-B emission inventory includes major pollutants (SO₂, NO_x, CO, PM₁₀, PM_{2.5}, BC, and OC) and 30 lumped VOC species for SAPRC-99 chemical mechanism with the spatial resolution of 0.5° × 0.5°. The emission inventory is interpolated to 30/10 km grids and allocated to 2 sectors, power plants and the others. The emission of power plants are located ~ 200 m above the surface due to statistics of regular stack heights, and 'the others' are on the surface. Four dimensional emission input files in netCDF format are created using IO/API library (Figure 5). The

seasonal and diel variations are ignored, leading to static emission fields.

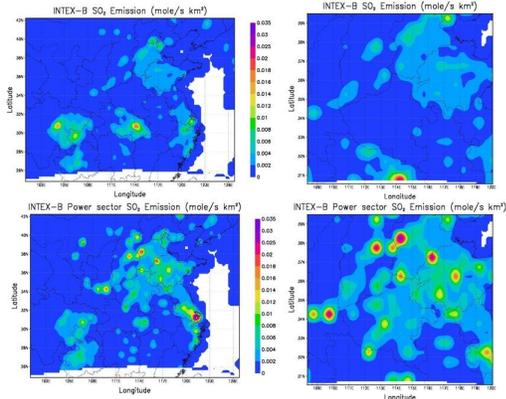


Figure 5 SO₂ emission map (left: coarse domain, right: nested domain)

4.3 CMAQ Simulation and Modification

The SAPRC-99 scheme services as the chemistry mechanism, and 45 days' simulation (March 14, 2008 to April 26, 2008) is conducted by CMAQ v4.6 with the first 15 days as spin-up. The CMAQ outputs have the hourly temporal resolution.

We have developed a module to calculate the horizontal advection of pollutants, which uses the Piecewise Parabolic Method (HPPM) instead of default Yamartino scheme (HYAMO) as the advection scheme. The information of horizontal advectons contains the absolute amount of transports at the domain boundaries, and is written to an individual output file (FTBNDY).

With the different sets of SO₂ mesophyll resistance (MR) and advection schemes (HYAMO to HPPM), we have 3 sensitivity runs as following: CMAQ_NoMR_HYAMO, CMAQ_NoMR_HPPM, and CMAQ_MR_HPPM.

5. CMAQ RESULTS

5.1 In-Situ Measurements Vs. CMAQ Simulation

The comparison of *in-situ* measurements and CMAQ simulation is illustrated in the Figure 6. The destination of research flight in 04/05/2008 is Changyuan, which is a hot SO₂ spot in the NASA OMI SO₂ map. The CMAQ captures the SO₂ vertical profile well, but it only indicates 0.47 DU column content, around half of the *in-situ* measurement 0.93 DU. During the descending

over the CGO, CMAQ fails to predict the very high SO₂ concentration near the surface. The similar

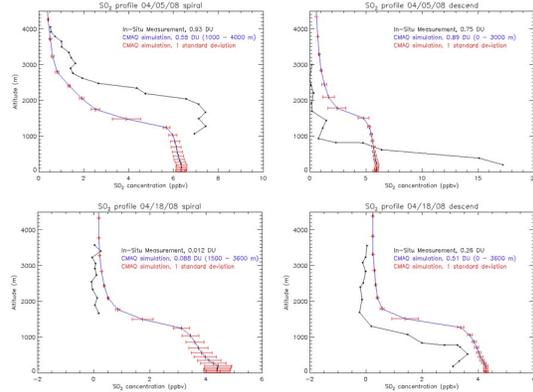


Figure 6 Comparison of *in-situ* measurement and CMAQ simulation in 04/18/2008

comparison for 04/18/2008 is demonstrated in Figure 6 bottom part. The spiral over Yexian (a weak OMI SO₂ spot) shows very little SO₂, 0.012 DU from the *in-situ* measurement and 0.088 DU from the CMAQ simulation. During the descending to CGO, CMAQ overestimates the SO₂ from 3000 m to surface. It is noticeable that the distribution of SO₂ has great spatial and temporal variability, and CMAQ tends to capture the picture but fails to reproduce the SO₂ profile accurately.

5.2 OMI SO₂ product Vs. CMAQ Simulation

The NASA OMI instrument is a UV/Vis solar backscatter spectrometer with high resolution (13 km × 24 km) and daily global coverage. The Band Residual Difference (BRD) algorithm is developed at NASA-GSFC/UMBC SO₂ group [Krotkov *et al.*, 2006] to measure volcanic sulfur emissions [Carn *et al.*, 2008; Yang *et al.*, 2007], industrial processes [Carn *et al.*, 2007] and anthropogenic emissions over northeastern China [Krotkov *et al.*, 2008]. We also compare the OMI SO₂ products with the CMAQ simulation (Figure 7). For the

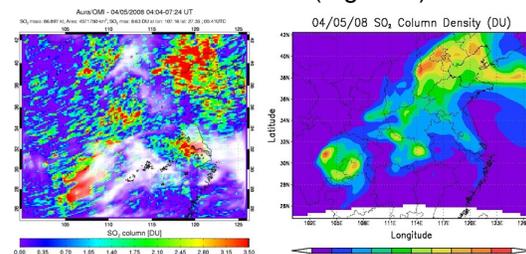


Figure 7 OMI and CMAQ SO₂ column map

For the remotely-sensed products, the cloud plays an important role in retrieval of the SO₂ column content. We use the criteria, cloud fraction less than 0.2, to select the valid SO₂ data, and the SO₂ active area is also calculated. For 04/05 of the coarse (10 km resolution) domain, OMI gives SO₂ burden of 86.9 kt in 4.60 mkm² and CMAQ simulates 70.1 kt SO₂ in 4.48 mkm². The valid SO₂ areas are very close, and the estimates of total SO₂ amount only have ~ 20% difference.

5.3 Improvement of SO₂ dry deposition

The mesophyll resistance of SO₂ is added to the MCIP code to calculate the dry deposition velocity. Figure 8, demonstrate the difference of

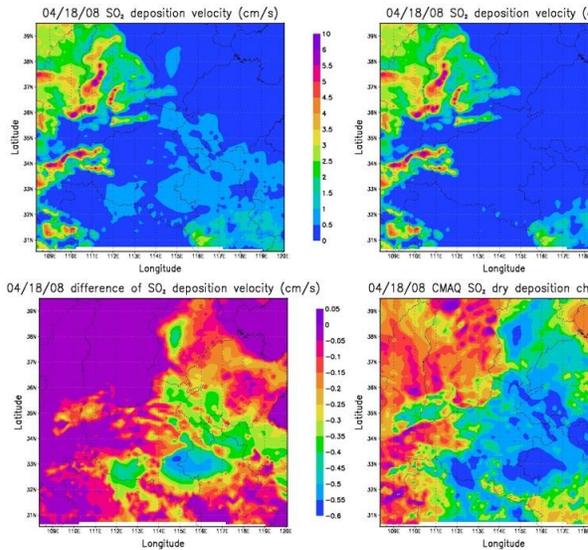


Figure 8, SO₂ dry deposition velocity 04/18/2008

CMAQ run without MR and with MR. It is noticeable that the adding of MR decreases the deposition velocity 20 to 50% in the center and east of the domain, leading to less than 0.5 cm/s ubiquitously, except in the mountainous northwestern area. It might be caused by the difference of vegetation coverage in the plains and in the mountains. The SO₂ dry deposition velocity is 0.2 ~ 0.4 cm/s in northern China [Sorimachi *et al.*, 2003], which is better simulated by the CMAQ run with MR.

The actual SO₂ dry deposition rates are calculated by the CMAQ model. The comparison of deposition rates in 04/18 is demonstrated in Figure 9. The SO₂ dry deposition rates are 600 ± 490 g/km² h⁻¹ and 430 ± 450 g/km² h⁻¹ for two sensitivity runs. A decrease of 300 to 600 g/km² h⁻¹

is ubiquitous in the center and south of domain with up to 70% decrease.

The mean SO₂ profiles are demonstrated in Figure 10. The CMAQ_MR_HPPM run with the

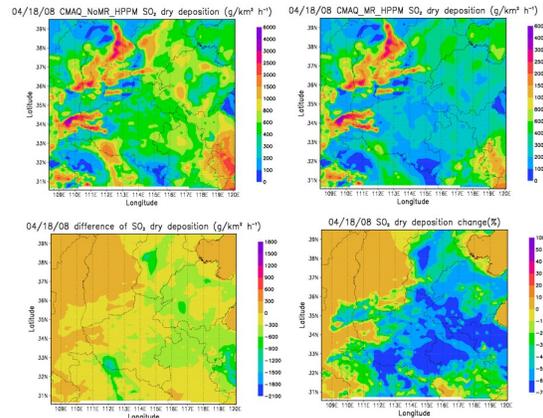


Figure 9, SO₂ dry deposition rate 04/18/2008

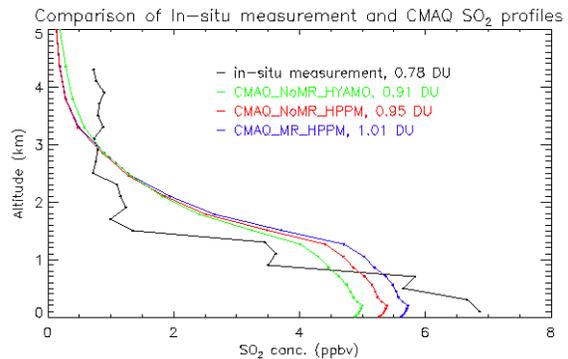


Figure 10 Results of CMAQ sensitivity runs

corrected SO₂ MR has the best evaluation of surface SO₂ concentration. All the runs underestimate the SO₂ concentration within the PBL and overestimate it in the FT, which indicates CMAQ tends to mix the lower atmosphere too fast in the PBL. It might be caused by the parameterization of PBL advectons in the WRF model. These runs also demonstrate higher SO₂ column contents than the *in-situ* measurements. The reason of this overestimate is probably due to the emission information of 2006.

5.4 Budget of Sulfur-compounds

With the module computing horizontal advection, we calculate the budget of sulfur-compounds in the nested domain (1.26 mkm²) in Figure 11. Assuming all the gaseous SO₂ left in the atmosphere is 100% converted to sulfate, the

difference of the sulfur budget has -0.4 kt difference, leading to 2.7% error with respect to the emission. The advectations have great day-to-day variability, and two cases are studied with

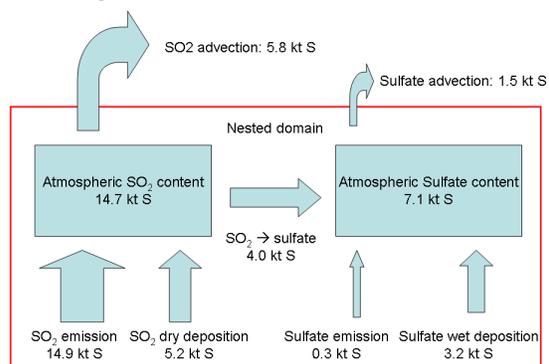


Figure 11 Budget of sulfur-compounds

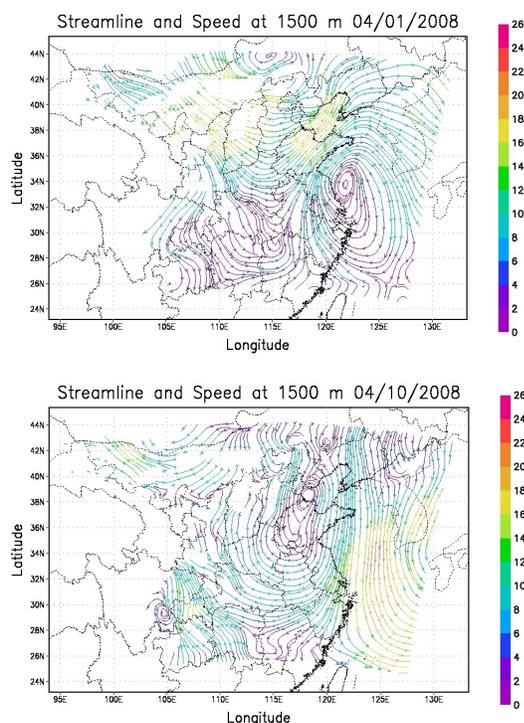


Figure 12 WRF streamlines

computing streamlines and wind speed at 1500 m. In 04/01, maximal advection of 17.8 kt S are exported out of the domain, and in 04/10, almost no S are transported. It is noticeable that the SO₂ advectations are determined by the atmosphere circulation.

During the period of simulation, on average ~11.6 kt of SO₂ (5.8 kt S) and ~4.5 kt of sulfate aerosols (1.5 kt S) are exported out of the domain daily, which equals to ~ 50% of the total SO₂ emission. The lifetime of SO₂ is calculated as 36.5 hours with oxidization and transport as sinks.

In the Figure 10, it is observed that the *in-situ* measurements show higher value of SO₂ concentration aloft (> 3000 m) and lower SO₂ column content. These indicate that the possibility that the real advection might be higher than the simulation of the CMAQ model.

6. CONCLUSION AND FUTURE WORK

We simulated SO₂ over central China using CMAQ v4.6 with improvements of the SO₂ dry deposition rate and advection scheme. The comparison of *in-situ* and remotely-sensed measurements with CMAQ simulation shows a reasonably consistent picture of the tropospheric SO₂. WRF-CMAQ has trouble with mixing leading to overestimate of SO₂ in the PBL and underestimate in the FT. On average, *in-situ* observations show more SO₂ aloft (above 3000 m altitude) than CMAQ simulation, indicating substantial export of S from central China. The model also indicates that ~ 50% of the S is exported and the SO₂ lifetime is ~ 1.5 days.

The uncertainties of our research mainly come from the uncertainties of emission inventory. The INTEX-B emission inventory focuses on the emission of 2006, and in 2006 to 2008 the control measures and clean acts for 2008 Beijing Olympic Games have been conducted decreasing the SO₂ emission drastically. The lack of temporal and diel variation of emission also increase the uncertainty of CMAQ results.

The potential future works include:

- 1) The improvement of SO₂ chemistry in CMAQ especially the aqueous chemistry in the cloud.
- 2) Long range transport of sulfur-compounds. The CMAQ model provides the information about the SO₂ plumes, which can also be monitored by the OMI instrument. The comparison of these two values can improve our knowledge of emission, evolution and transport of anthropogenic sulfur emission.
- 3) The CMAQ results indicate the accuracy of INTEX-B emission inventory, and are crucial for the development of next version of Asian emission inventory.

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