LONG-RANGE TRANSPORT AND TRANSFORMATION OF ACIDIFYING SUBSTANCES OVER EAST-ASIA

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The purpose of this study is to analyze long-range transport and transformation of acidifying substances over East-Asia. This is done through modeling of emission, meteorology, and atmospheric transport & chemistry. The Models-3 Community Multi-Scale Air Quality Modeling System (Models-3/CMAQ) coupled with the PSU/NCAR mesoscale model (MM5) is applied for this purpose and validated for March 2001. The simulated daily variation of surface SO_2 and NO_x concentrations shows some encouraging agreements with observation at two remote sites. However, underestimates of monthly mean concentration are found at some urban sites where the uncertainty in local emission has larger impact than that at remote and rural sites. Overestimates and larger vertical gradients are found at some sites with complex terrain. Wet depositions of sulfate, nitrate and ammonium are generally underestimated and have some dependence on both precipitation fields and site characteristics.

Key Words**:** *Long range transport, acid deposition, sulfur, nitrogen, East Asia, model evaluation*

1. INTRODUCTION

The long-range transport and fate of pollutants in Asia is an area of increasing scientific interest and political concern, as countries receive growing amounts of pollutants from neighboring and even distant countries.

This study aims at developing region-to-region source-receptor transfer matrices of acid deposition in East Asia. However, model results for long-range transport and deposition may contain large errors, due to the uncertainty in transport model, emissions and meteorological fields etc.

Comparing model results with measurements yields the most intuitive and most valuable means of model evaluation. This study applied the Models-3 Community Multi-Scale Air Quality Modeling System(Models-3/CMAQ) to East Asia and coupled with an emission processing module and the MOZART(Model for OZone And Related chemical Tracers) global chemical transport model for species boundary condition[1),2)]. The preliminary results of this modeling system are presented and validated for March 2001.

2. MODEL DISCRIPTION

The research framework and dataflow are presented in **Fig.1**. An Eulerian-type chemical transport model, CMAQ CTM, is used to calculate the distribution of trace gases in the troposphere and the quantities of acids deposited on the surface from specified emission distributions and meteorological scenarios.

The horizontal model domain is centered on East Asia with a grid resolution of 81km (**Fig.2**). In the vertical dimension, there are 23 layers for the meteorology and 12 layers for the chemical transport model in the sigma-p coordinates system unequally spaced from the ground to 13 km. Finer resolution is set in the lowest 2000 meters to better resolve the planetary boundary layer.

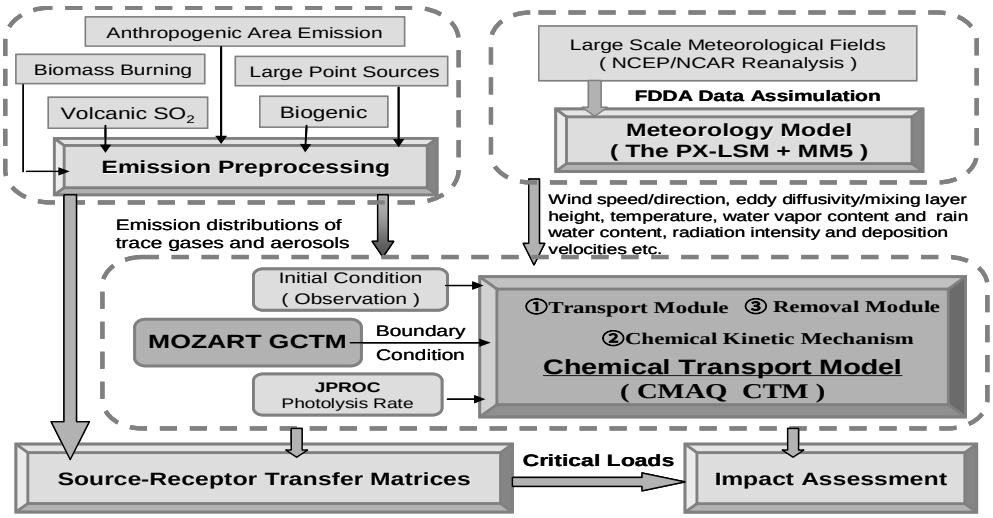

Fig.1 Research framework and data flow

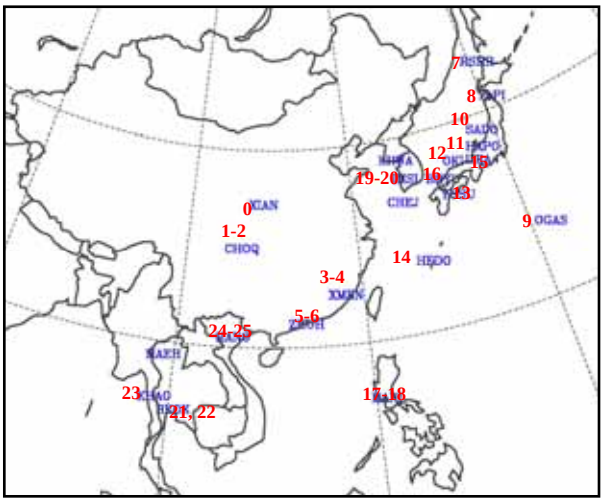

Fig.2 Model domain for chemical transport model. Also shown are the locations of observation sites used for model validation.

(1) Emission processing

For emissions, anthropogenic area emissions (0.5x0.5°) [3], large point sources, volcanic SO_2 and biogenic emissions (1.0x1.0°)[4] are taken into account in order to make a meaningful comparison between CTM results and observations. Raw emission data on lat-long coordinates with different grid resolutions are interpolated into a uniform Lambert projected map. Monthly allocation and chemical speciation are carried out to achieve the CTM input requirements. Speciation of VOC Emissions (Volatile Organic Carbons) is based on Carbon bond IV (CB4) chemical mechanism.

All large point sources are potentially elevated and injected into model layers according to stack parameters (physical stack height and diameter, exhaust temperature and velocity, and wind speed etc.)

The model-ready emission rates for primary acidifying substances are shown in **Fig.3**. The area of high population and intense industrial activity are clearly depicted.

(2) Meteorology

For Meteorology, NCEP/NCAR global meteorology reanalysis datasets (6hours interval and 2.5x2.5° resolution) are applied for MM5 initialization and boundary condition in a FDDA data assimilation mode **(Fig.1)** [5].

(3) Initial and boundary condition of chemicals

To evaluate the impacts of the anthropogenic emissions on the distributions of trace gases and aerosols, initial conditions of species in CMAQ were generally chosen at the lower end of their observed range[6].

The MOZART Global Chemical Transport Model was coupled to provide boundary condition for CMAQ. MOZART species are mapping into boundary CB4 species defined in CMAQ. Vertical linear interpolation based on height is performed to convert MOZART coordinates to model sigma-p vertical coordinates.

(4) Model evaluation

To evaluate the model performance, monthly and daily concentration in the lowest model layer (about 18m above ground) and accumulated wet deposition are compared with EANET surface observation. The locations of the observation sites are shown in **Fig.2**. Details on site characteristics and observation method can be found at EANET website (http://www.eanet.cc/).

Region-to-region source-receptor relationships and impact assessment of acid deposition in East Asia will be further discussed in a future paper.

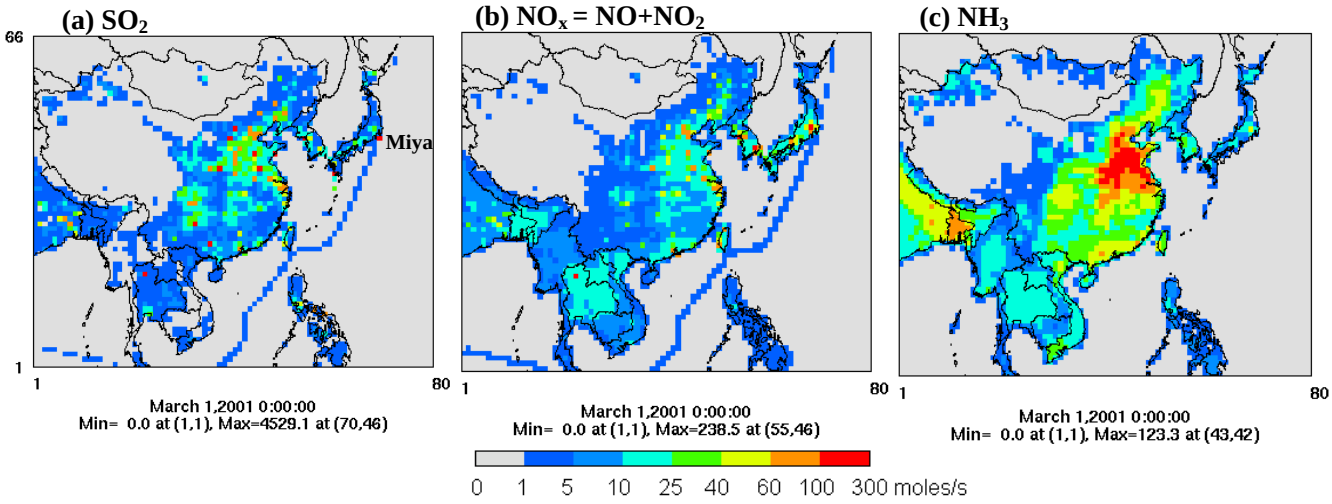

Fig.3 Model ready emission rates of acidifying substances in March 2001. (The location of maximum SO_2 emission also indicates the location of Miyakejima volcano.)

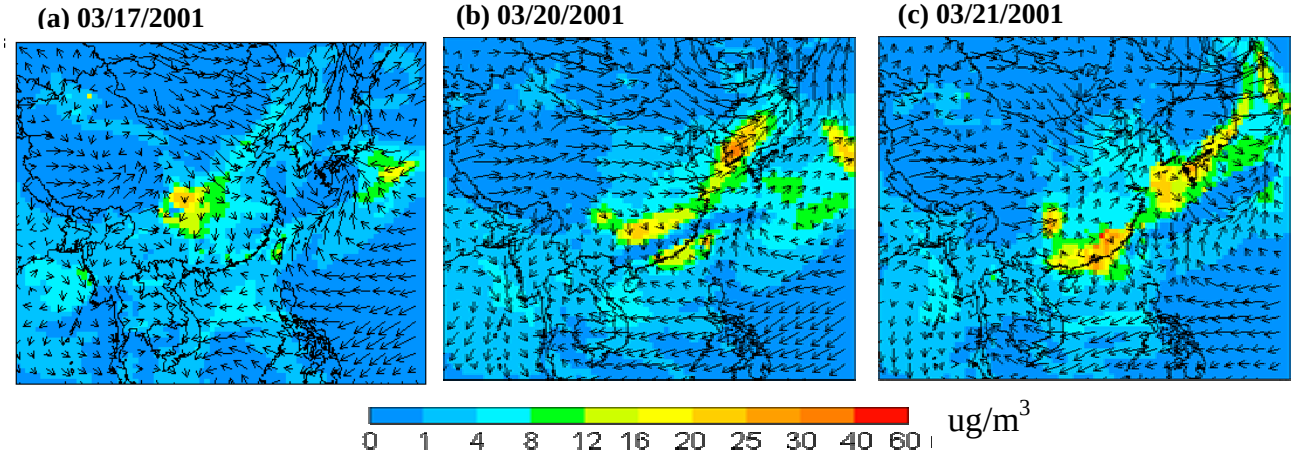

Fig.4 Horizontal distributions of sulfate concentration for the lowest model layer at 0900JST On 17 ~24 March 2001. Also shown are the surface wind vectors.

3. RESULTS AND DISCUSIONS

(1) Meteorological condition and transport pathways of Asian pollutants

Several studies indicate that middle latitude cyclones forming or intensifying near eastern Asia is a major transport mechanism of Asian pollutants[7]. During March 2001, two traveling low-pressure systems on 17-24 are the dominant meteorological features. Ambient SO_4^{2-} comes mostly from the oxidation of SO_2 released into the lower atmosphere as a result of fossil fuel combustion or volcanic eruptions. As shown in **Fig.4a**, on March 17 high concentrations of sulfate are mainly seen in Sichuan and east of Miyakejima volcano in association with strong emission flux. However in the next few days **(Fig.4b, c)** as the low pressure systems moved eastward, we find strong eastward and northeastward transport of SO_4^{2-} and its precursors from the Asian continent contributes to high SO_4^{2-} levels over the East China Sea and even over Northern Japan.

(2) Comparison with observations

(a) Monthly concentration

Comparison of monthly concentration of SO_2 (**Fig.5a**) shows a general agreement between heavily polluted area (central & southeast China) and relative clean area (Japan). Underestimates of SO_2 and NO_x concentration are found at two urban sites in Xiamen and Zhuhai (site 3, 5), also in Bangkok (site 21) for NO_x only. The uncertainty in local emission estimates and model spatial resolution tends to have stronger effect on these urban sites than remote sites.

Overestimates are mainly found in site 0(central China) and site 10, 11 & 15(Japan). An et al. (2003)[8] found the similar errors at Japanese sites and attributed this to the uncertainty of the other volcanic emission. However, this can not explain the overestimate of NO_x concentration. We found these sites are located at mountainous area with complex terrain. **Fig.5** also shows the comparison of surface concentration and mean concentration at

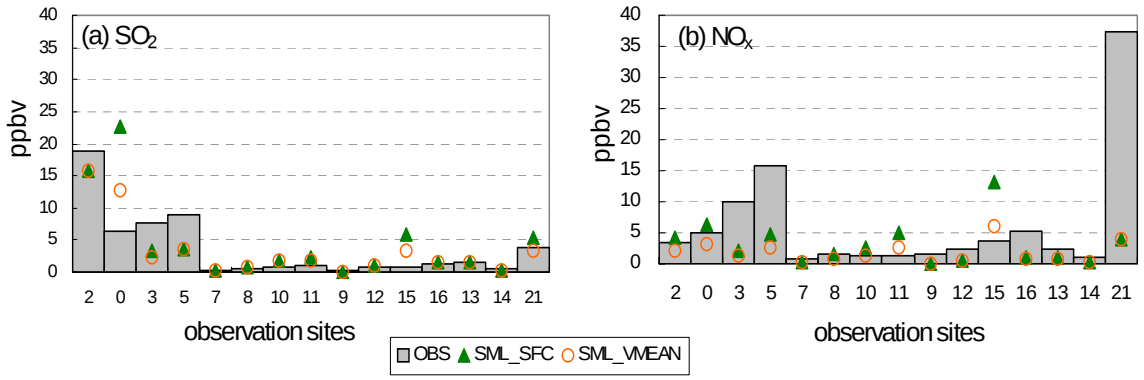

Fig. 5 Comparison of monthly surface concentration at 18 m (marked as green triangle) and mean concentration at 18~300m (marked as orange circle) above ground with EANET observations (For Chinese sites, NO_x includes NO_2 only.)

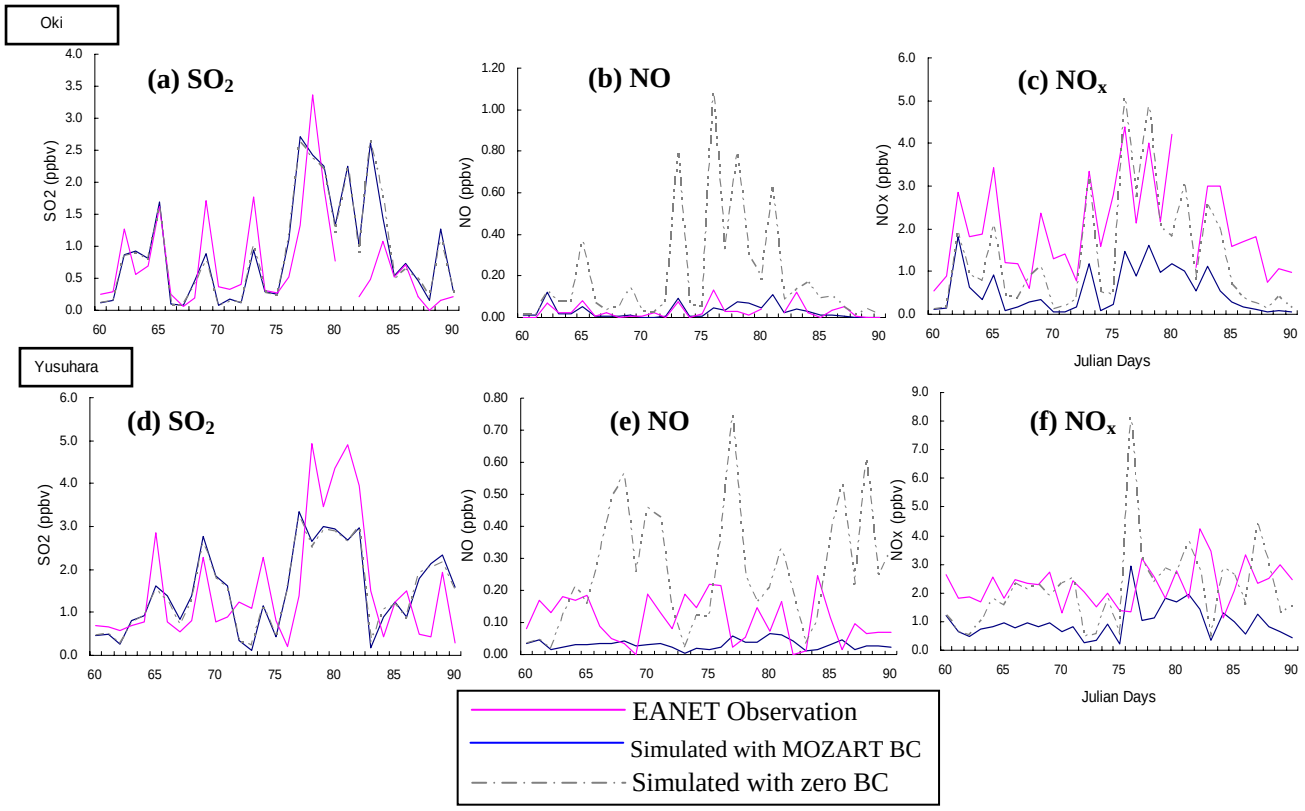

Fig.6 Time series of modeled and observed SO_2, NO, NO_x surface concentrations at two remote sites

18~300m above ground. Vertical gradients of concentration at site 0 and site 15 are larger than for other stations. The overestimates may be due to the complex terrain which is sensitive to model vertical resolution.

(b) Time-series of daily concentration

To evaluate the impact of boundary influx, two model scenarios are conducted; one with MOZART-coupled boundary condition, the other one with zero boundary influx. Concentrations at remote sites depend primarily on transport processes. In order to decrease the effects of volcanic emission uncertainty, two Japanese remote sites Oki (12) and Yusuhara (13) are selected to investigate time-series of daily concentration**.**

Fig.6 (a, d) shows that the timing of peaks and low concentration of SO_2 at these two sites are reasonably captured by the model. And boundary condition has less impact on SO_2 concentration. The good agreement between simulated and observed results implies that the SO_2 emissions, wind fields and transport processes & chemical mechanism were reasonably well reproduced by CMAQ CTM. This also owes to the assimilation of large scale reanalysis data to MM5. The peak concentration on March 17~24 is related to two moving low pressure systems as discussed in Section 3 (1).

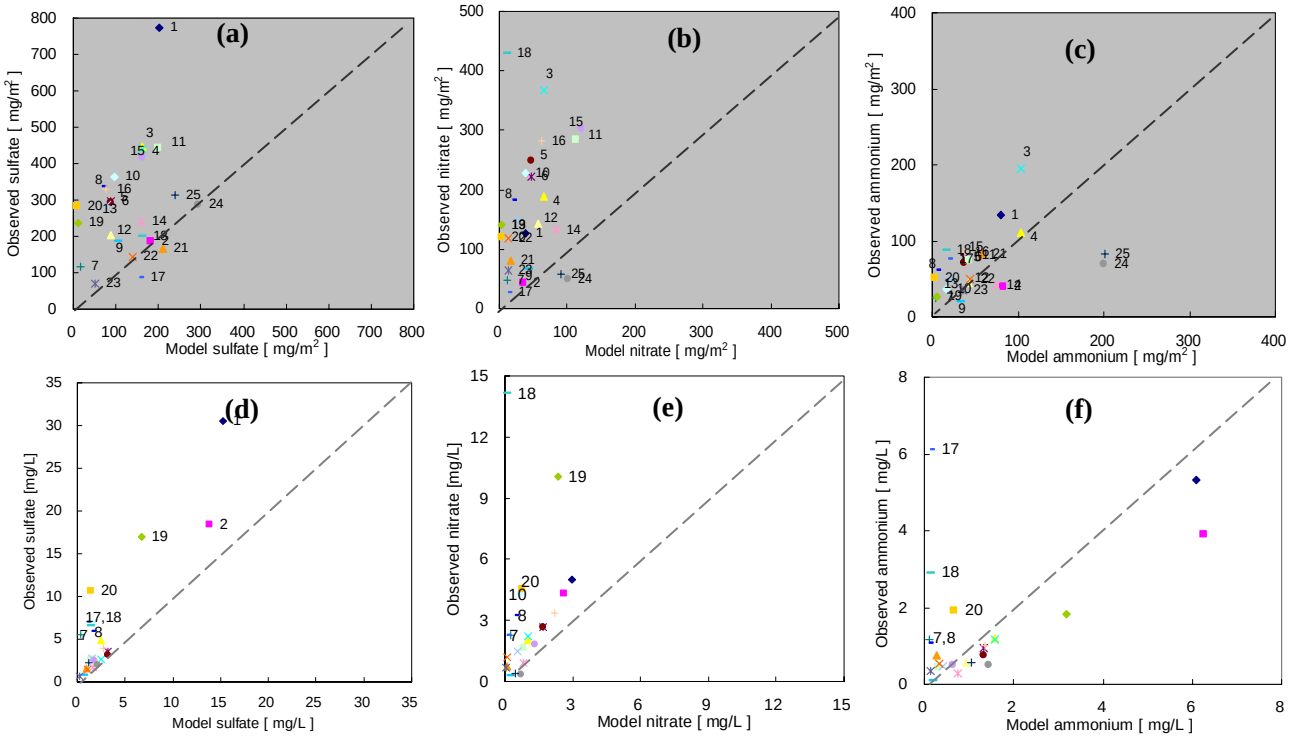

Fig.7 Comparison of wet deposition (a, b, c), and concentration precipitation (d, e, f) (numbers with point indicate the ID of observation sites)

Fig.6b,c,e,f indicates that the model performance for nitrogen species is lower than that for SO_2. Nitrogen species have higher uncertainty in emission estimates (±16% for SO_2 and ±37% for NO_x) [4], and much more complicated chemical reactions in the photochemical oxidant cycle. NO concentration fluctuates abnormally when boundary influx of all species are set to zero. With the MOZART boundary influx, time series of NO concentration **(Fig.6b, e)** has a higher agreement with the observation. NO_x are oxidized into nitric acid or aerosols with the existence of higher active oxygen concentration. This also indicates the selection of O_3 boundary condition will make a significant difference to nitrogen species.

(c) Monthly accumulated wet deposition

Wet deposition amount is very sensitive to precipitation, gas to aerosol conversion rates and removal rate.

Fig.8 shows that overestimates in precipitation are mainly found in Southeast Asia. A similar pattern is found when comparing the wet deposition amounts of sulfate, nitrate and ammonium **(Fig.7a, b, c)**. To eliminate the effect of bias in precipitation amount, we also compare concentration only **(Fig.7d, e, f)**. The bias in Thailand and Vietnam are removed, but underestimates still exist around Chongqing (1, 2), North Japan (7, 8), Manila (17, 18), and South Korea (19, 20).

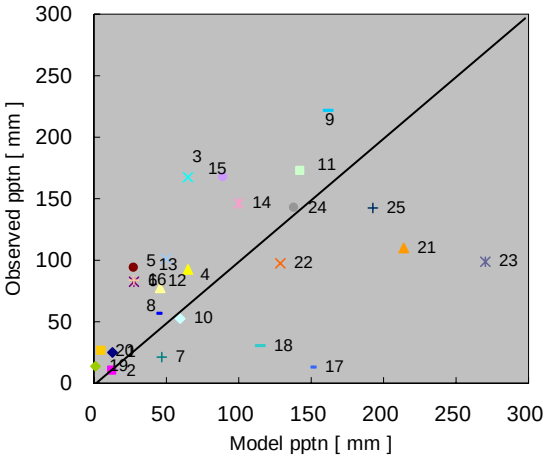

Fig.8 Comparison of precipitation

We identified some possible effects from precipitation aqueous chemistry, emission and transport process by analyzing the bias pattern in precipitation, deposition and concentration.

The underestimate of precipitation in South Korea may affect the aqueous chemistry from gas to aerosols. However, this is not the case for North Japan and Manila. The bias in North Japan may come from the emissions in Russian which are not included in the raw emission inventory[3]. In the case of Manila, The precipitation is even more overestimated, while deposition amount are still underestimated. This implies the anthropogenic emissions in Manila, especially NO_x and NH_3, may be underestimated.

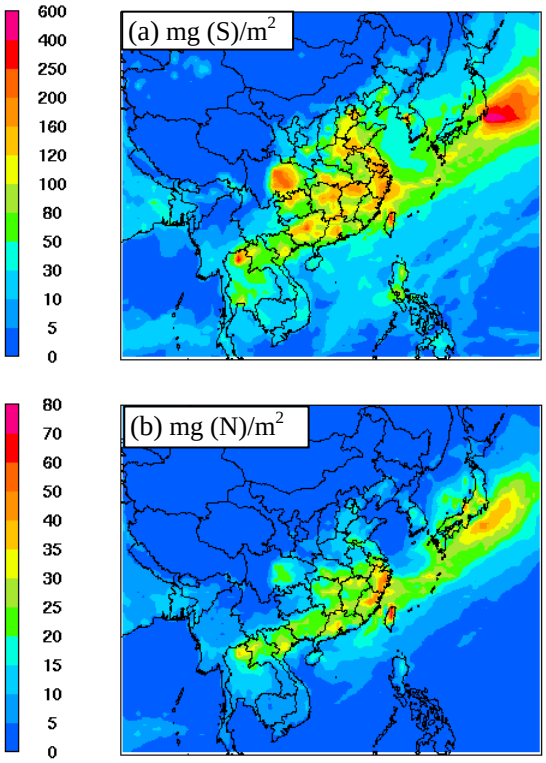

Fig.9 Distribution map of monthly sulfur and oxidized nitrogen deposition in March 2**001**

(3) Acid deposition in East Asia

Fig.9 shows the distribution maps of monthly sulfur and oxidized nitrogen (NO_x, HNO_3 and aerosol NO_3^-) depositions in March 2001. These maps provide an Asia-wide perspective on acidic deposition, which is due predominately to sulfur species at present, but with a growing contribution due to nitrate. Ammonia (deposition not shown) in rainwater acts as a base, neutralizes the strong acids and elevates the pH of precipitation. However, after it is deposited on soils biochemical processes cause ammonia to act as a strong acidifying agent.

The strong continental outflow of acidifying pollutants from East Asia is clearly depicted in **Fig.9**. An important question to address is what fraction of the acid deposition at a given location is due to local emissions? The environmental implications of acid deposition need to be evaluated by comparing deposition values with the sensitivity of received ecosystems. Research on region-to-region source receptor relationships will need to be further developed to address the environmental challenges.

4. SUMMARY

We apply a long-range transport modeling system to East Asia and evaluate model results for March 2001.

The simulated daily variation of surface SO_2 and NO_x concentrations showed some encouraging agreements with observation at two remote sites. However, underestimates of monthly mean concentration are found at some urban sites where the uncertainty in local emission has larger impact than that at remote and rural sites. Overestimates and larger vertical gradients are found at some sites with complex terrain. Wet depositions of sulfate, nitrate and ammonium are generally underestimated and have some dependence on both precipitation fields and site characteristics.

The regional aspects of acid deposition pose a significant challenge to East Asia. Research and political implications of long-range transport, source-receptor relationships and impact assessment of acid deposition in East Asia will need to be further developed.

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REFERENCES

1) Byun, D.W., Ching, J.K.S. (Eds.), 1999. Science algorithms of the EPA models-3 community multi-scale air quality (CMAQ) modeling system. NERL, Research Triangle Park, NC

2) Holloway, T. et al. (2006) "Impacts of Global Emissions on Asian Air Quality". *Atmospheric Environment*. (To be submitted)

3) Streets, D.G., et al., 2003. A inventory of gaseous and primary aerosol emissions in Asia in the year 2000. *Journal of Geophys. Res.* 108 (D21), 8809

4) Granier, C. et al., 2005. POET, a database of surface emissions of ozone precursors, available on internet at http://www.aero.jussieu.fr/projet/ACCENT/POET.php

5) Grell, G. A., J. Dudhia, and D. R. Stauffer, 1994: A description of the fifth-generation Penn State/NCAR mesoscale model (MM5). NCAR Tech. Note NCAR/TN-398+STR, 117 pp

6) Carmichael, G.R., et al., 1998. Tropospheric ozone production and transport in the springtime in East Asia. *Journal of Geophys. Res.* 103, 10,649-10,671

7) Fuelberg, H. E., et al., 2003. Meteorological conditions and transport pathways during the Transport and Chemical Evolution over the Pacific (TRACE-P) experiment, *J. Geophys. Res.*, 108(D20), 8782

8) An, J., ea al., 2003. Simulated impacts of SO2 emissions from the Miyake volcano on concentration and deposition of sulfur oxides in September and October of 2000. *Atmospheric Environment*, 37, 3039-3046

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