6.01 SULPHUR CHEMISTRY AND ACID RAIN OVER CHINA. HOW TO COMPUTE THE CONTRIBUTION OF EACH PROVINCE?

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INTRODUCTION

Pollution due to SO2 remains an important issue in Asia. Several international research groups already did significant studies on this topic (see for example: Guttikunda S.K et al 2003). We propose in this paper to present a methodology to compute the contribution of several geographical zones regarding the total sulphur deposition (wet and dry). First approach used concerns a reduced chemical mechanism: the ozone and other pollutants (as OH) needed in the sulphur chemistry are not directly computed but taken from climatologic values. A second approach computes all the species concentrations using a complete photochemical mechanism (128 chemical reactions and 48 species). For this purpose, we adapted the CHIMERE-CHINA software to the specific Chinese data that was available. In our methodology, we first concentrated on the dry and wet deposition of sulphur dioxide (SO_2) and sulphates (SO_4^{2-}). This software was initially developed by the Pierre Simon Laplace Institute (CNRS, Paris, France). The regional version of the model, covering built up urban areas such as Paris, Lyons and Strasbourg, is widely used by the main French monitoring networks and the French government, together with the technical assistance of ARIA Technologies, for the ozone (O_3) and nitrogen dioxide (NO_2) forecast every few days. The purpose of this work was to deliver a complete tool to the Chinese operational administrations (SEPA-CNEMC) that can be used for air quality management and to test the various SO_2 emission reduction options. This document outlines the methodology adopted and gives first results from a simulation of the year 2000.

MODEL CONFIGURATION

In this paper, we compare SO_2 and SO_4 results given by:

(1) CHIMERE-CHINA 1.0 where OH, O_3 and H_2O_2 are not directly computed but climatological values are used. These values are imported, on monthly basis from the LMDz/INCA model (Hauglustaine et al., 2004).

(2) CHIMERE-CHINA 2.0 where OH, O_3 and H_2O_2 are computed using the "standard" photochemistry scheme as in the referenced version of CHIMERE-CONTINENTAL model.). LMDz outputs are used as boundary conditions in both versions

The great advantage of the CHIMERE-CHINA 1.0 is both to save CPU-time (very useful in test phase) and to avoid the difficult task of giving emission inventories for NO_x and VOC.
Both model versions are based the CHIMERE transport and chemistry model (CTM) previously developed for Europe and described in detail in Schmidt et al., 2001, Derognat .C, 2002 and on the web site http://euler.polytechnique.fr/chimere. In the following, we just want to stress some modifications with respect to the standard gas phase version of the CHIMERE model:

(1) *Reduced chemical mechanism in the gaseous phase*

For the purpose of this study, a reduced chemical mechanism specially shaped for sulphur chemistry was introduced into CHIMERE-CHINA 1.0. It only contains the following reactions.:

$SO_2 + OH + M \rightarrow SO_4^{2-} + HO_2$

$HO_2 + HO_2 \rightarrow H_2O_2$

$HO_2 + HO2 + H_2O \rightarrow H_2O_2$

$H_2O_2 + OH \rightarrow HO_2$

(2) *Introduction of aqueous chemistry*

Initially the chemical mechanism did not involve any chemistry in the aqueous phase ("cloud chemistry"). In the case of China, we introduced the aqueous transformation of SO_2 to SO_4^{2-} :

$SO_2 + O_3 \rightarrow SO_4^{2-}$

$SO_2 + H_2O_2 \rightarrow SO_4^{2-}$

(3) *Introduction of wet deposition*

The following processes are taken into account:

- Scavenging of SO_4 **aerosols** within clouds droplets based on parameterisations in *EMEP* (2000)
- Scavenging of **gaseous** species (SO_2 and H_2O_2) based on a similar approach but for a gas
- Scavenging of SO_4 aerosols within rain droplets using parameters fixed empirically by (*Berge et al*., 1993) Note that the main moisture loss process is scavenging in the clouds, rather than in rain droplets (EMEP, 2000).
- Scavenging of **highly soluble** gaseous species (HNO_3 and H_2O_2) in rain droplets (following *Seinfield and Pandis* , 1997)
- Scavenging of soluble to **low-solubility species** beneath the clouds : This process is not taken into account at the current stage of development because it is assumed to be slower than scavenging in the clouds. Moreover, it is assumed that a falling raindrop is quickly saturated and can no longer absorb compounds in the layers below the clouds.

(4) *Improving the calculation of the deposition velocity*

The Wesely (1989)'s calculation of the deposition rates, based on a resistance approach, was already introduced in the reference version of the CHIMERE code but with input data fitted for China. The calculation of the dry deposition of chemical compounds Land use description is a key issue to correctly deal with dry deposition. We opted to work with USGS data due to its higher resolution (URL:*http://gaia.umiacs.umd.edu.8811/landcover/index.html*). We simplified the classification to be closest to the 9 RIVM classes used over Europe. Then, we considered spatial variation, or seasonal variation as suggested by Wesely (1989) .

(5) *Model geometry*

- We selected a very light resolution to run one year with an acceptable CPU time:
- South-west point co-ordinates = 15°N – 90 ° E
- North-east point co-ordinates = 55°N – 150 °E
- Horizontal Resolution = 1 * 1 degree
- 7 vertical levels in sigma-P hybrid co-ordinates with top at 400 hPa

METEOROLOGICAL INPUT DATA

Meteorological data using (analyses, first guess of parameters as Horizontal wind, Temperature, Density, Specific humidity, Cloud liquid water content, Height of model layers, Low cloud fraction, Richardson number, Convective and large scale precipitation, and cloud cover) comes from ECMWF (http://www.ecmwf.int). Note that the local 3D precipitation is calculated from the precipitation rate on the ground (large-scale precipitation and convective precipitation from the ECMWF forecasts), proportionally to the cloud liquid water content.

EMISSION INPUT DATA

Anthropogenic emission

For CHIMERE-CHINE 1.0, hourly SO_2 emissions are needed, for CHIMERE-CHINE 2.0 in addition also NOx, VOC (volatile organic compound) and CO emissions. We used annual averages in a 1° deg. horizontal resolution specifically computed South East Asia (ACE-ASIA web side, see table 1) We deduced the seasonal variation from the GEIA (Global Emission Inventory Activity) data, which has the following characteristics Table 1.

Table 1 : Emission inventory sources

	ACE-Asia	GEIA
URL	http ://saga.pmel.noaa.gov/aceasia	http://weather.engin.umich.edu/geia/emits/so2.html
Year	2000	1995

The temporal variation of the emissions was taken into account using the emissions from the CHIMERE CONTINENTAL reference case (using information supplied by R. Friedrich, University of Stuttgart, Germany). Speciation of VOC are taken different from those used in Europe following KLIMONT Z. et al (2002) work (mainly for the Ethan and the O-xylen)

Biogenic emission

We directly used the monthly averages for the 1990 year available from the GEIA website and calculated using. This database shows clearly that the biogenic VOC contribution is very low season dependant and also generally low compared to anthropogenic VOC emission except in south of parallel 30°. We agree that improvement could be done, taking into account the solar radiation and the temperature. The emission of the “biomass burning” are also not considered in this version

COMPARISON WITH MEASUREMENTS

Daily SO_2 and NO_2 data from over 50 stations from the Chinese air quality network were available from June to December 2000, in addition to precipitation amount and SO_4 concentration for the whole year. The evaluation alongside the 50 stations database shows that the model is quite satisfactory on the North-East part but underestimates pollution in the south part (see figure 1). Similar results for sulphur species are obtained for both versions (CHIMERE-CHINA 1.0 and 2.0).

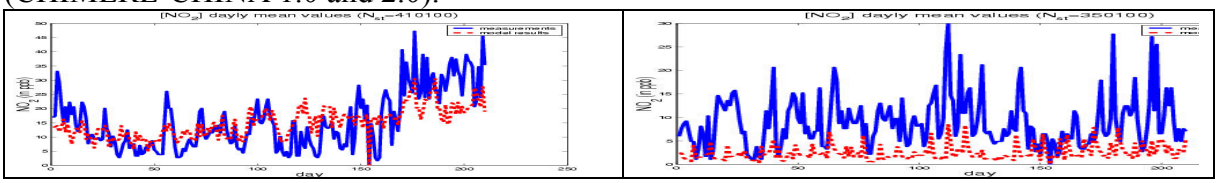

Figure 1. NO_2 Time series (Measurement = continue line, computation using CHIMERE-CHINA 2.0 = dot line) for a N-E station and (left) for a south station (right) Note: different vertical NO_2 scale (50 ppb left, 30 ppb right.

Results for H_2SO_4 in the rainwater show also that the model underestimates the observed values. Note that the large scale meteorological modelling (ECMWF) underestimates the precipitation rate as measured on the observation point. On the contrary, the seasonal tendencies are respected (figure 2). One reason for the strong underestimation in the wet H_2SO_4 deposition could be an underestimation of the SO_2 emissions, but an underestimation of a factor 5 does not seem probable. Another, more probable reason could be that many of the survey stations are located near strong emission sources, and are thus not representative

for the 1° model grid. A too slow conversion of SO_2 into H_2SO_4 is not a probable reason, because more than the half of emitted SO_2 is already wet deposited as H_2SO_4 in the model.

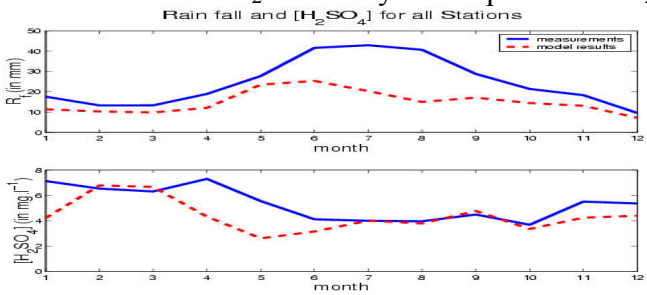

Figure 2. Rainfall (up) and H_2SO_4 (down) in the water rain time series (Measurement = continue line, computation using CHIMERE-CHINA 2.0 = dot line) average for all stations. Note: SO_4 concentrations are multiply per5

MAIN RESULTS OVER YEAR 2000

As results are very similar with both CHIMERE-CHINA 1.0 and CHIMERE-CHINA 2.0. we show here only results of CHIMERE-CHINA 1.0. Figure 4 summarizes the contribution distribution for each area to an other area over the whole year 2000. It has to be pointed out that several model uncertainties discussed already in the previous chapters can affect the results of this study. All factors influencing the transport time of sulphur species are important to that respect, for example the speed of SO_2 to SO_4 conversion. The precipitation distribution, the wet scavenging rates, etc.. A thorough sensitivity study to assess the impact of these processes has to await a future study. Thus present results have to be taken only as rough estimates.

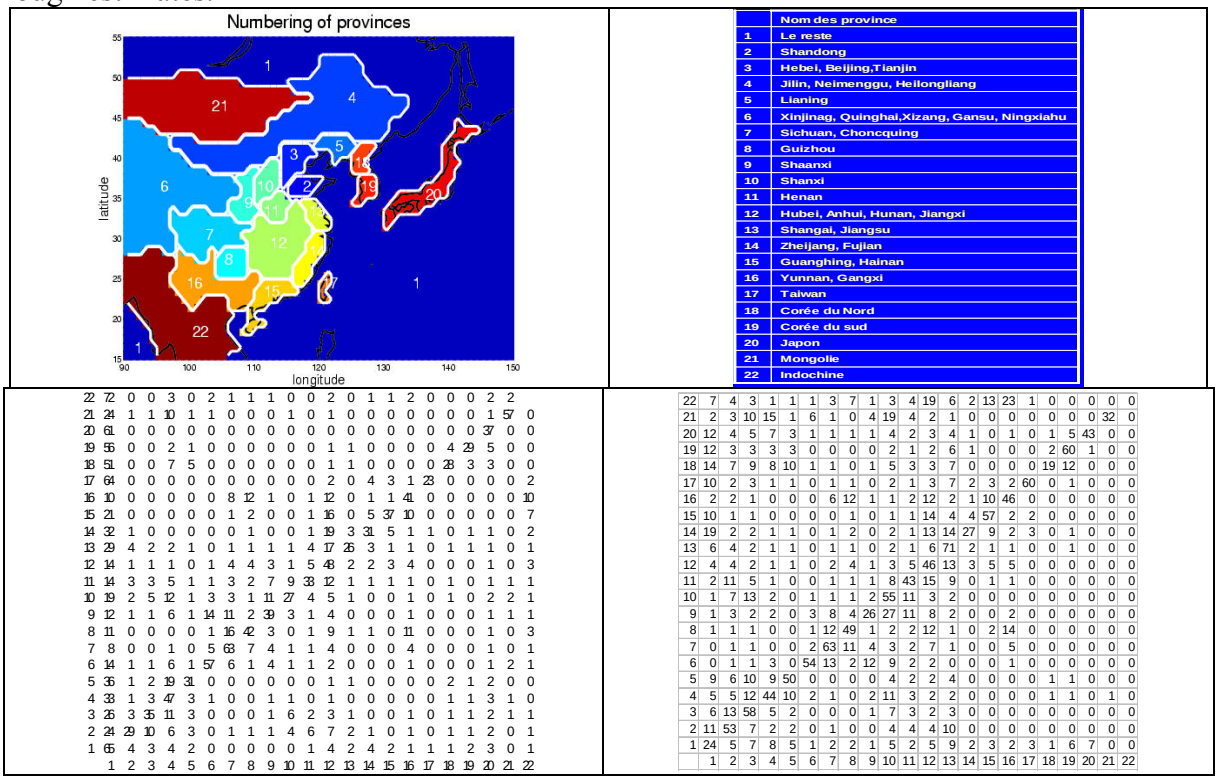

*Figure 4. The **left** table gives the "fate" of SO_2 emissions for different areas; for the **left** table rows represent the emitting areas and columns the receiving areas; the table has to be read line by line, the sum of each line is normalised to 100%.The **right** table gives the origin of deposited sulphur for different areas; rows represent now receiving areas and columns emitter areas; the table has to be read line by line, the sum of each line is normalised to 100%.*

CONCLUSION

This study has shown that data are available over China and can make progressing the understanding and elaboration of any air quality program. The CHIMERE-CHINA 1.0 using climatological values computed by LMDz is good enough to evaluate quick solution concerning sulphur chemistry Nevertheless, interest of version CHIMERE-CHINA 2.0 is required if Ozone is considered. Modelling over 2000 shows important ozone episode in the Northeast and especially in spring. In terms of environmental management, three important conclusions can already be drawn from this study:

- Emission reductions at a province level will in the most cases have positive results as about a half of the emissions originate in the considered areas themselves;
- Further reduction of sulphur deposition levels (the second half) need concerted efforts on a national level;
- Also long range transport of SO_2 emissions from country to country is an issue that needs consideration.

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ACKNOWLEDGEMENTS:

(1) European Centre of Medium Range Weather Forecast (ECMWF) is acknowledged for the use of meteorological data.

(2) This job was funded by the French Government (Ministry of Economy / DREE under a FASEP contract)