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An Acid Deposition Engineering Model

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Abstract

An acid deposition Engineering Model was developed by parameterizing the role of organics in the photochemistry and by simplifying liquid phase processes. This Engineering Model concept was implemented onto the Sulfur Transport Eulerian Model II (STEM II). The Engineering Model version of the STEM(STEM-ENG) saves the CPU time over 50 times and produces the upper and lower limit values predicted by the original STEM II. These limits obtained by the STEM-ENG can be used to estimate the importance of organics in acid and O3 production. The STEM-ENG with 30,000 grid points can be run on any recent PCs to give a quick assessment of air quality.

1. INTRODUCTION

For the past decades or so, several Eulerain atmospheric transport/chemistry/removal models have been developed to investigate acid production and photochemical smog formation. The STEM II[1], RADM[2] and ADOM[3] are the most comprehensive models formulated to date. However, these models require such large computational resources that only a limited number of computer simulation can be done with the current computational resources. Also being predominantely research/detailed-assessment oriented, the user should be very familiar with the model.

Furthermore, a detailed meteorological data and chemical species information should be prepared. Especially, 20 to 50 chemical species are usually used to represent organic species. However, the available emission inventory often fails to support this detail organic speciation. Only a few developed countries such as United States, European countries provide emission inventories with a limited organic speciation. For the East Asia region, the most of the reported organic emission is based either on the total hydrocarbon or on the non-methane hydrocarbon[4].

Until the emission inventory with detailed chemical speciation is established, the comprehensive Eulerian model is not able to ahieve its potential despite of consumption of large computational resources. Thus, for the case of limited emission inventory as the model with simplified organic speciation may still produce accurate results as the comprehensive Eulerian model[5]. These kinds of models can be named as an Engineering Model and can be used to evaluate the air quality in various conditions such as seasonal variations, different meteorological conditions and different regions due to their high computational efficiency. In the present paper, the Engineering Model was developed by parameterizing the role of organics such that the effect of organics can be estimated without having a detailed organic speciation. The parameterization was made such a way that it can be improved if

the field measurements or comprehensive modeling works are available.

2. DESCRIPTION OF THE ENGINEERING MODEL

A model simplification can be achieved by screening and lumping the processes and parameters with the guide of comprehensive model results and field measurements. The main idea for the Engineering Model is not to describe the processes containing large uncertainties, but to lump them into one or several representative processes. The parameters introduced in this process may be evaluated from comprehensive models and fed into the Engineering Model to enhance the predictability. In addition, the solution from the Engineering Model with changing value of lumped parameters within certain bounds suggests the range of solution the comprehensive model would provide. In this way, lumped parameters enable the Engineering Model to communicate with the comprehensive model and pipeline the findings from the comprehensive model to the Engineering Model. Furthermore, the Engineering Model keeps the same degree of detailedness as the field data so that it makes the best out of available field data at the present time.

2.1 GAS PHASE CHEMISTRY

The atmospheric chemistry represents one of the most complicated chemical network problem consisting of more than thousands of chemical species. The complexities of the atmospheric chemistry stem from organic species. Organics go through numerous oxidation and reduction reactions to increase or decrease oxidant level in the atmosphere. The explicit mechanism consisting of over 200 elementary reactions of atmospheric chemistry for the polluted region was developed[6] but is too complicated to be used for atmospheric models. Several simplified mechanisms[7,8,9] have been proposed for atmospheric models. Because these mechanisms were calibrated based on a limited atmospheric conditions, these mechanisms may fail to work for certain atmospheric conditions. In spite of these problems, the simplified mechanism is still complicated such that available source inventory can not support and it is responsible for more than 90 % of the computation time. Therefore, a parameterization of role of organic chemistry would save computational effort greatly without too much costing numerical accuracies. Because characteristics of the atmospheric chemsitry is significantly different bewteen daytime and nighttime it would be more efficient to differentiate daytime and nighttime atmospheric chemical mechanism. In daytime, organics affect photochemical reactivity by converting NO to NO_2 through multi-step chemical reactions. The produced NO_2 from organics photo dissociates to increase the O_3 concentration in the atmosphere. In the absense of organics, the destruction of O_3 by NO is equilibrated with production of NO_2 by photo dissociation resulting

$$\phi = k_1[NO_2]/k_2[NO][O_3]$$

where ϕ is called as the photo-stationary state number. And k_1 and k_2 is the photo dissociation rate constant of NO_2 and the reaction rate constant of $NO + O_3$ reaction, respectively. The photo-stationary state number should be equal to one if no organics are present. However, the photo-stationary state number usually deviates from one due to organics. According to measurements by several authors[10, 11, 12, 13] the photo-stationary state number varies diurnally between one and two for polluted area. The photo-stationary state number for remote area ranges from 1.5 to 2.5 except a few cases.

The Engineering Model accounts for the effect of organics by assuming the value of the photo-stationary state number. Because there is no need to explicitly represent individual organic species any more, the Engineering Model requires only 7 transport species, $NOx(NO+NO_2)$, $Ox(NO_2+O_3)$, SO_2, HNO_3, sulfate, NH_3, and H_2O_2. The daytime chemical reactions used for the Engineering Model includes the O_3 and H_2O_2 photolysis reaction, radical interactions and sulfate and nitrate formation reactions as shown in Table 1.

Table 1. Day time gas phase chemistry included in the Engineering Model

1. $NO_2+h\nu \rightarrow NO+O_3$
2. $NO+O_3 \rightarrow NO2+O_2$
3. $O_3+h\nu(+H_2O) \rightarrow 2OH(+O_2)$
4. $OH+NO \rightarrow 2HNO_3$
5. $HO+NO \rightarrow OH+NO_2$
6. $HO_2+HO \rightarrow H_2O_2+O_2$
7. $OH+CO(+O2) \rightarrow HO_2+CO_2$
8 $HO_2+O_3 \rightarrow OH+2O_2$
9. $SO_2+OH(+O2+H_2O) \rightarrow Sulfate+HO_2$

The use of photostationary state number not only removes all the explicit organic chemistry but also reduces the stiffness due to $NO-NO_2-O_3$ interactions so that the integration of chemical reaction equation is evaluated over 50 times faster than that of the Atkinson-Llyod-Winges mechanism[7]. The performance of the Engineering Model depends on smart selection of photo-stationary state number based on NOx and organics ratio and compositions of organics. On the other hand, the range of O_3 concentration level or acid production level can be esitmated by applying the lowest value and the highest value of the photo-stationary state number.

In nighttime, most of radical concentration becomes negligibly small due to absence of solar energy. The early atmospheric models such as STEM[14] and RTM[15] ignore nighttime chemistry. However, observations show that a significant amount of nitric acid is produced from the reaction between NO/NO_2 and O_3. On the other hand, the reaction of NO with O_3 to produce NO_2 is no longer balanced by NO_2 photo-dissociation. The reaction bewteen NO and O_3 is fast enough to titrate away either NO or O_3. Therefore, either NO or O_3 is assumed to be destroyed completely at nighttime in the Engineering Model. In addition the following reactions are considered to describe nitric acid formation.

$$NO_2+NO_3 \rightarrow N_2O_5$$
$$N_2O_5 \rightarrow NO_2+NO_3$$
$$N_2O_5+H_2O \rightarrow 2\,HNO_3$$

2.2 LIQUID PHASE CHEMISTRY

Active multi-step chemical reactions occur in cloud or rain droplets. In order to simulate interaction with the liquid phase properly, the absorption into and desorption from the liquid droplet as well as the liquid phase chemistry should be included. Because adding chemical species exchange between the gas phase and the liquid phase cause a numerical stiffness problem, the Engineering Model follows RADM model's treatment[2] which assumes the gas phase and the liquid phase are well-mixed. Only the following three liquid phase reactions directly related to the sulfate production are included in the Engineering Model.

$$OH+HSO_3^- \rightarrow 0.5\,SO_4^- + 0.5\,SO_4^= + OH$$
$$H_2O_2+HSO_4^- \rightarrow HSO_4^-$$
$$O_3+HSO_3^- \rightarrow HSO_4^- + O_2$$

3. COMPARISON OF THE ENGINEERING MODEL WITH THE STEM II

In order to evaluate the computational efficiency and accuracy, the Engineering Model was developed by modifying the Sulfur Transport Eulerian Model II(hereafter denoted as STEM II) and compared with STEM II. The reason for using the STEM II code is simply because the author is familiar with the model and the model is readily available to the author for modification. Any other comprehensive atmopheric model can be modified to become an Engineering Version of the model(hereafter denoted as STEM-ENG). The comparison of the CPU time for 46x64x11 grid system for a one day run is shown in Table 1. The STEM I is the model with only two transported chemical species with no organic chemical species. The STEM-C is the model with the same detailness as the STEM-ENG but the organic chemistry is lumped into one step as follows.

$$NMHC \rightarrow Products+O_3$$

The STEM-EM is slower than the STEM I but faster than the rest of the models. Becuase

the STEM I performs computations only for SO_2 and Sulfate and unable to estimate O_3 production due to organics, it is regarded as too simplified model. The STEM-C is similar to the STEM-ENG but more time consuming because it suffers from stiffness due to NO-NO_2-O_3 interaction as noted in the previous section. The other problem of the STEM-C is that it is very difficult to guess a reasonable ozone production rate from NHMC. This problem is circumvented in the STEM-ENG where the photostationary state number lies bewteen 1 and 2. The gas phase chemistry of the STEM-ENG was evaluated first by simulating the no cloud case and then the combined gas and liquid phase chemistry was discussed as below.

3.1 NO CLOUD CASE

The model simulation without cloud(hereafter denoted as no cloud case) provides a good test bed for the gas phase chemistry scheme of the Engineering Model. The one dimensional STEM I model was run for 10 days with an emission data base for a moderatelly polluted area. The concentration field at the end of 10 days was taken as the initial conditions for this study and the emission data for a typical remote area were chosen. This condition simulates the case that the polluted air mass is transported to a remote area. The initial concentration profiles and emission data can be found elsewhere[16].

Table 2. Comparison of CPU time of STEM-ENG with other versions of STEM*

	STEM -I	STEM -ENG	STEM -C	STEM -II
CPU TIME on HP720 workstation	2 mins	7 mins	45 mins	6.2 hrs

* Comparison was made based on 46x64x11 grid system for one day run. The time used for input and output was excluded for the CPU time estimation. The 720 HP workstation used here performs 54 MIPS and 10 MFLOPS.

The various photostationary state numbers were used by the STEM-ENG. The photostationary state number of one was chosen for the lowest possible number and that of two for the highest possible number. In addition, the photo-stationary state number calculated from the STEM II model simulation were also used. As shown in Figure 1, the STEM-ENG model successfully brackets the STEM II results for SO_2, sulfate, O_3, H_2O_2, OH and HO_2. Becuase it is very difficult to estimate the uncertainties of the STEM II model predictions caused by an inaccurate emission data base, the bounds which the STEM-ENG provids are very valuable in evaluating the importance of organics in given model conditions.The small overprediction of the STEM-ENG for HNO_3 is because the Engineering Model excludes organic nitrogen compounds which reduce the avialability of NOx to produce HNO_3. Nevertheless the overpredcition is less than 10% even for the highest value of HNO_3 of the STEM-ENG.

When the photo-stationary state number calculated from STEM II was employed, the STEM-ENG agrees quite well with STEM II for all the chemical species of concern. Even for the case of O_3 whose concetration is very sensitive to the photo-stationary state number, the relative concentration difference is less than 5 %. In order to increase the usability of the STEM-ENG, there must be a systematic way in estimating the photostationary state number other than using the STEM II model results. An investigation is being made to represent the photostationary state number as a function of organic reactivity. For the time being, the range of the photo-stationary number is estimated and then the STEM-ENG calculates the range of values instead of a sigle value for interested air pollutant concentration. If the calculated range of values is narrow, then the STEM-ENG model should be sufficient. Otherwise, the STEM II model should be used.

3.2 CLOUD CASE

The cloud case taken here is that precipitation occurs during 11 A.M. to 2 P.M.. The initial condition and emission strength was the

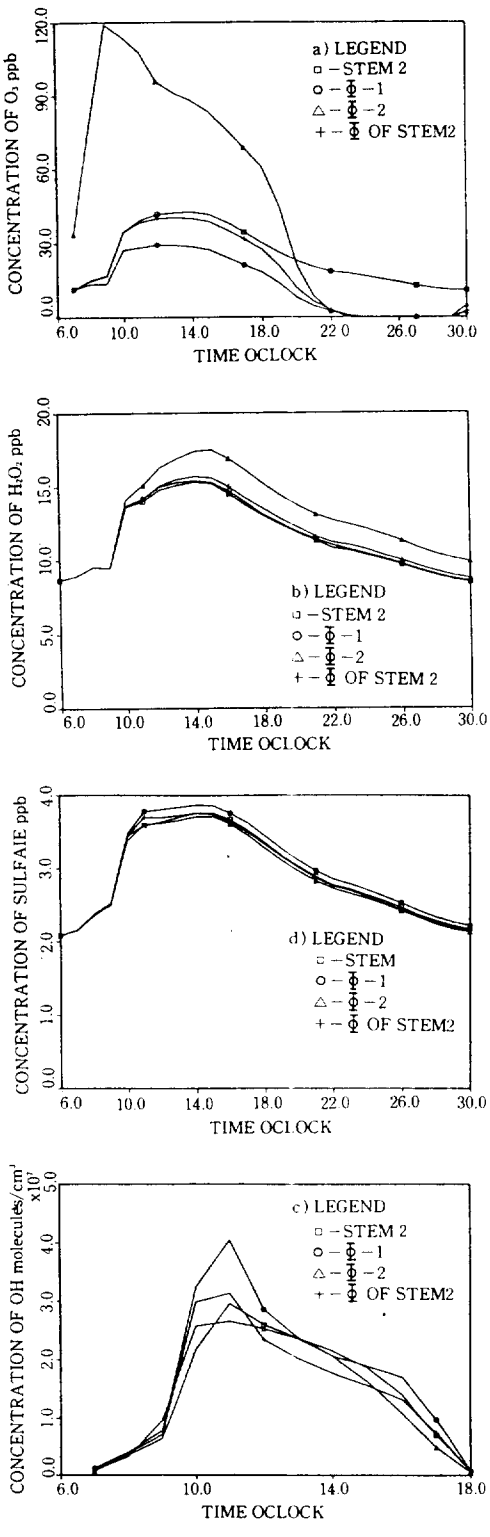

Fig. 1. The comparison of the major chemical species from the STEM-ENG with those from the STEM-II(no cloud case) (a) O_3, (b) H_2O_2 (c) OH (d) sulfate (e) HNO_3

same as the no cloud case. The model condition was described more detail elsewhere[16]. As discussed in Cho et al.[16], the sulfate is mainly from incloud production or from incorporation of the pre-existed sulfate aerosol. Incloud production of sulfate is larger than that of gas phase production of sulfate more than 30 times in this simulation. Therefore, the STEM-ENG model prediction of sulfate produced is not sensitive to the photo-stationary state number. The incloud sulfate production profile presented in Fig. 2 shows that the STEM-ENG model simulates the complicated incloud phase chemsitry properly without including radical interaction.

4. CONCLUDING REMARK

A new way of parameterizing complex photochemical reactions was implemented onto the STEM II to increase a computational efficiency. The resulting model named as STEM-ENG mak-es it quite possible to run a meso or regional scale simulation containing over 30,000 grid points on a personal computers. On the otherhand, a meso or regional scale model with much finer resolution can be run to investigate the importance of grid resolutions.

In developing a comprehensive atmospheric model, a detailed description of physical and chemical processes are included successfully

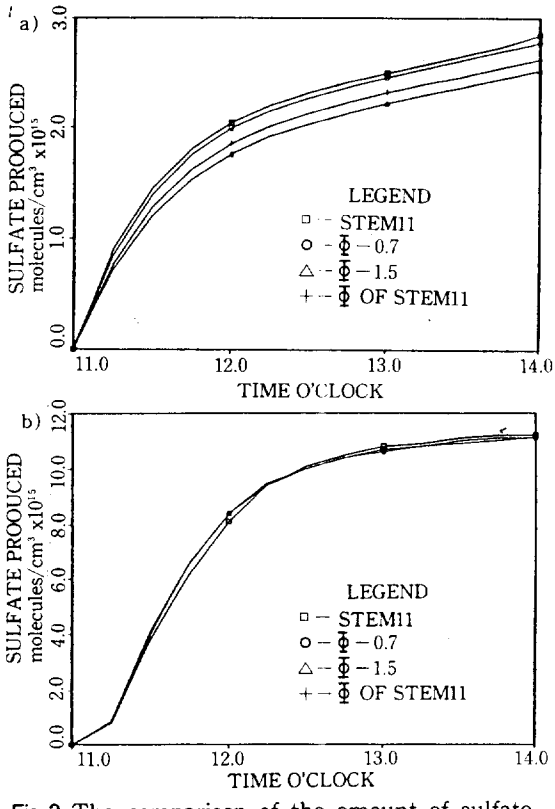

Fig. 2. The comparison of the amount of sulfate produced from the STEM-ENG with that from the STEM-Ⅱ(with cloud) (a) the amount of sulfate produced in cloud droplets (b) the amount of sulfate produced in rain droplets

into the model. However, considering the fact that the regional scale model employs 80-100km grid resolution and the meso scale model employs 10-20km grid resolution, these coarse grid resolutions can not resolve quite a few important atmospheric processes. It is a very difficult task to incorporate sub-grid scale phenomena into the coarse grid model. The usage of the STEM-ENG model allows one to examine small scale phenomena more closely by sacrificing some of photo chemical interactions.

An algorithm selecting the photostationary state number is currently being developed for better performance of the STEM-ENG. However, the present work shows that the STEM-ENG with using the maximum and minimum value of the photo-stationary state number should be enough to estimate most of acid precursors and acidifying materials. The STEM-ENG model is also currently being used to study the transport of air pollutants among China-Japan-Korea with two different grid resolutions; 10 km grid horizontal resolution and 80 km horizontal grid resolutions. The STEM II simulation in this area does not have a significant advantage over the STEN-ENG mainly because there are no credible speciated organic source inventory for organic species.

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공학적 산침적 모델에 관한 연구

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초 록

복잡한 광화학반응을 간략하게 처리하는 방법을 개발하고 다단계 액상반응 중에서 산의 생성에 직접 관련이 없는 반응을 생략하여 공학적 산침적모델을 개발하였다. 이러한 공학적모델의 개념을 적용하여 Sulfur Transport Eulerian Model II(STEM II)로부터 STEM-ENG를 제작하였다. STEM-ENG를 이용하면 STEM II보다 CPU를 약 30배나 절약할 수 있으면서도 STEM-II와 비견할 만한 정성적 결과를 얻을 수 있는 한편, 유기화합물이 산성물질과 오존형성에 미치는 영향의 크기를 예측할 수 있다. STEM-ENG는 workstation은 물론이고 PC를 사용하여도 운영이 가능하여 적은 비용으로 대기질을 평가할 수 있게한다.