STUDYING THE METHOD FOR SENSITIVITY ANALYSIS OF OZONE FORMATION IN URBAN AND RURAL AREAS USING CMAQ

Nguyen Phuoc Quy An

The University of Danang, University of Science and Technology; ngphquyan@gmail.com

Abstract - The majority of ozone formation occurs when NOx, CO and VOC react in the atmosphere in the presence of sunlight. However, the ratio of VOC and NOx largely influences the formation of ozone. Therefore, the Community Multiscale Air Quality (CMAQ) modeling system is used in a sensitivity analysis of ozone with nine different emission scenarios by reducing VOC and NOx emissions. The capital metropolis of Seoul and the island of Gang-hwa, considered as typical urban and rural sites respectively, are chosen for the scope of this study. From the results of the sensitivity analysis of ozone formation in urban and rural areas, it is considered that ozone concentration in urban and rural appear in VOC limited area of EKMA (Empirical Kinetic Modeling Approach).

Key words - ozone; analysis; CMAQ; sensitivity; urban; rural

1. Introduction

The levels of air pollutants are increasing rapidly in many mega cities of the developing world. Urban air pollution has increased rapidly with urban populations, numbers of motor vehicles, and fuel with poor environmental performance, badly maintained roads and ineffective environmental regulations. Ozone is one of the air pollutant emissions which are the predominant factors affecting air quality. Ozone is the most severe air pollution problems in the world. It has serious impacts on human health and ecosystems, and is very difficult to control. In particular, the ground level ozone is responsible for a variety of adverse effects on both human being and plant life. To protect the humankind from such adverse health effects, early information and precautions of high ozone level need to be supplied in times.

Tropospheric ozone is a trace gas which plays a key role in the oxidizing capacity of the atmosphere. Ozone also exerts a significant influence on the radiation budget of the atmosphere owing to its properties as a greenhouse gas. Major ozone sources and sinks in the troposphere are the air mass exchange between the stratosphere and troposphere, in photochemical production or destruction and surface dry deposition. Taking into account that ozone precursors are also anthropogenically emitted, tropospheric background ozone levels have been modified during the last century [3]. Moreover, it can be swept away by prevailing winds, thus leading to higher ozone concentrations in places far from the sources of emission of the ozone precursors. Thus, the concentration of ozone in different areas is not similar, especially in the urban and in the rural.

Ozone is a secondary pollutant formed through the oxidation of volatile organic compounds (VOC) in the presence of nitrogen oxides (NOx) and sunlight followed by the combination of molecular oxygen (O_2) and triplet oxygen radical (O_3P) [2]. Thus, the sensitivity analysis of ozone will be performed by reducing VOC and NOx emissions. Sensitivity analysis is the study of how the variation in the output of a statistical model can be attributed to different variations in the inputs of the model. In this study, sensitivity of ozone formation in the urban and the rural of Korea will be analyzed. The capital metropolis of Seoul and the island of Gang-hwa, considered as the typical urban and rural, respectively, are chosen for the scope of this study. In the sensitivity study, the peak O_3 concentration for each scenario will be compared with the base-case. Special emphasis will be focused on the impact of VOC and NOx emission sources. Besides, sensitivity analysis of ozone formation indicates that reducing VOC or NOx emission affect the greatest reduction or increase in peak of ozone concentration in the urban and in the rural.

The Community Multiscale Air Quality (CMAQ) modeling system is used in a sensitivity analysis of ozone with 9 different emission scenarios by reducing VOC andNOx emissions using the same meteorological input and chemical transport schemes. The meteorological field is the Mesoscale Model, Version 5 (MM5) and the emission inventory model is Sparse Matrix Operater Kernel Emissions (SMOKE) Modeling System. In addition, this study will analyse the effect of VOC and NOx on the sensitivity of ozone formation in the urban and in the rural to have projects which can control strategies for VOC and NOx emissions to reduce ozone concentration in Seoul and Gang-hwa.

2. Research Overview

2.1. Ozone

2.1.1. Sources of ozone precursors

A problem of increasing concern is the presence of photochemical smog in some urban and industrial regions. The photochemical reaction of NOx (NO + NO_2) and VOC in the presence of sunlight originate in photochemical smog. It is chemically characterized by a high level of oxidant compounds, mainly O_3.

NOx and hydrocarbon emissions from traffic are high in urban areas so ozone tends to accumulate rapidly. A considerable effect on the oxidizing capacity of the troposphere which affects human health by causing symptoms such as irritated eyes, cough, headache, chest pains and, in extreme cases, lung inflammation coming from the concentration of ozone. The ozone is also associated with the corrosion of urban structures, the toxic plants and leading to a decrease in vegetation. Moreover, ozone can be swept away by winds so the higher ozone concentration appears in places far from the sources of the emission of the ozone precursors. Many regions worldwide have been plagued by the air pollution of high surface ozone arising from photochemical formation and accumulation. The ozone is photochemically produced and can accumulate to hazardous level in favorable weather conditions, in the presence of volatile organic compounds (VOC) and nitrogen dioxides (NOx).

2.1.2. Ozone control strategies

It is difficult to apply an optimized control strategy for ozone, since complex chemical mechanisms are involved in ozone generation. The ozone isopleth plot has been used as a basis for applying control strategies historically. The relationships between maximum ozone concentrations and mixtures of NOx and VOC are shown in the isopleths plot. The result of VOC and NOx mixtures being irradiated in photochemical chambers is the isopleths plot. The O_3 - NOx – VOC can be illustrated by isopleths plots generated from applying a basic ozone model called the Empirical Kinetic Modeling Approach (EKMA) to VOC and NOxconcentrations [4]. The peak ozone as a function of the ratio of VOC to NOx concentrations is shown in this graph. There are two regimes with different O_3 - NOx – VOC sensitivities, they are referred to as “limited” in the graph, they are VOC limited and NOx limited.

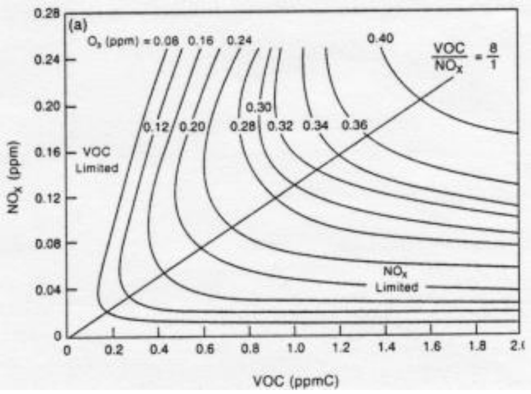

Figure 1. *A typical EKMA 2-dimensional depiction of ozone isopleths generated from initial mixtures of VOC and NOx in air [4]*

A constant VOC/NOx ratio = 8/1 is represented by the straight line in the center of Figure 1, the ozone isopleths is bisected by this line. Transition from the fairly vertical lines in the left side of EKMA graph where ozone changes are fairly sensitive to changes in VOC limited to the mostly horizontal on the graph’s right where ozone changes are quite responsive to NOx limited.

The VOC limited (VOC sensitive) represents an urban area with low VOC/NOx ratios. In urban areas, NOx emission has much greater influence and there is relatively little biogenic VOC to offset the NOx. In this area, when reducing VOC, ozone concentrations are most efficiently lowered. On the contrary, the NOx limited (NOx sensitive) is typical of less urbanized, more rural air massed where biogenic VOC are much bigger contribution to VOC levels. In NOx limited area, when reducing NOx the ozone concentrations are lower than moving downward to lower ozone isopleths.

On the basis of these isopleths, the EKMA plot shows that VOC only control strategies could reduce ozone concentrations more effectively in low VOC/NOx ratio areas. Any reduction of NOx initially have an adverse effect on the ozone air quality for low VOC/NOx ratio condition.

It is not realistic however, to use the ozone isopleths as a basis for control strategies without detailed investigations of VOC and NOx levels within a region. In the real atmosphere, deposition process, existence of particulate matter, turbulence and variations in radiation are believed to be the primary causes of deviations from chamber studies. Another difficulty in applying the ozone isopleths method, is that the VOC/NOx ratio at a monitoring site may not represent ratio in a region. The other approach in determining an optimal control strategy for ozone is to use air quality models. Air quality models have the capability to include the emission and meteorological characteristics of a region, therefore, they could be better tools to provide bases for optimal ozone control strategies.

2.2. Model descriptions

CMAQ modeling system is the air quality modeling system used in this study. The primary modeling components in the CMAQ modeling system include: Mesoscale Model Version 5 (MM5) is a meteorological modeling system for the description of atmospheric states and motions, Sparse Matrix Operating Kernel for Emissions (SMOKE) models for processing man-made and natural emissions that are injected into the atmosphere, and the chemical transport model used in this study is the Community Multiscale Air Quality Model (CMAQ).

2.2.1. Mesoscale Model Version 5 (MM5)

The Mesoscale Prediction Group in the Mesoscale and Microscale Meteorology Division, National Center for Atmospheric Research (NCAR) provide and support for MM5 (Mesoscale Model Version 5) modeling system software. MM5 was developed in cooperation with The Pennsylvania State University (Penn State) and the University Corporation for Atmospheric Research (UCAR).

2.2.2. Sparse Matrix Operating Kernel for Emissions (SMOKE)

The Sparse Matrix Operator Kernel Emissions (SMOKE) Modeling System was created by the MCNC Environmental Modeling Center (EMC) to allow emissions data processing methods to integrate high-performance-computing (HPC) sparse-matrix algorithms. An effective tool for emissions processing in a number of regional air quality modeling applications is the SMOKE prototype available since 1996. The support of the U.S Environmental Protection Agency (EPA) redesigned and improved SMOKE in 1998 and 1999 for use with EPA’s Models-3 Air Quality Modeling System.

A lot of criteria gaseous pollutants such as carbon monoxide (CO), nitrogen oxides (NOx), volatile organic compounds (VOC), ammonia (NH_3), sulfur dioxide (SO_2), particulate matter (PM) pollutants such as PM 2.5 microns or less (PM2.5) and PM less than 10 microns (PM10), as well as a large array of toxic pollutants, such as mercury, cadmium, benzene and formaldehyde can be processed by SMOKE. SMOKE can process no limitation regarding the number or types of pollutants.

The resolution of the emission inventory data is converted to the resolution needed by an air quality model is the purpose of SMOKE.

2.2.3. Community Multiscale Air Quality (CMAQ)

A third-generation air quality model is the EPA Community Multiscale Air Quality (CMAQ) modeling system. CMAQ requires two primary types of inputs: meteorological information and emission rates from sources of emissions that affect air quality. The meteorological model generates gridded meteorology for input to both CMAQ and the emissions model. The emission model is required to convert annual, county-level emissions estimates to gridded hourly emissions formatted for CMAQ.

The five main CMAQ programs are:

- The meteorology-chemistry interface processor (MCIP): MCIP is used to preprocess the data from a meteorological model for CMAQ and SMOKE.
- The initial conditions processor (ICON): a binary net CDF initial conditions file is created by ICON for input to CCTM.
- The boundary conditions processor (BCON): a binary net CDF lateral boundary conditions file is created by BCON for input to CCTM.
- The clear-sky photolysis rate calculator (JPROC): Physical information about photoreactive molecules into clear-sky photolysis rate look-up tables is converted by JPROC for input to CCTM.
- The CMAQ chemistry-transport model (CCTM): CCTM run last in the sequence of programs. All of the other CMAQ programs the emission and meteorological models are used to prepare the inputs to CCTM. CCTM can produce estimates of pollutant concentrations, wet and dry deposition rates and visibility metrics at a time granularity.

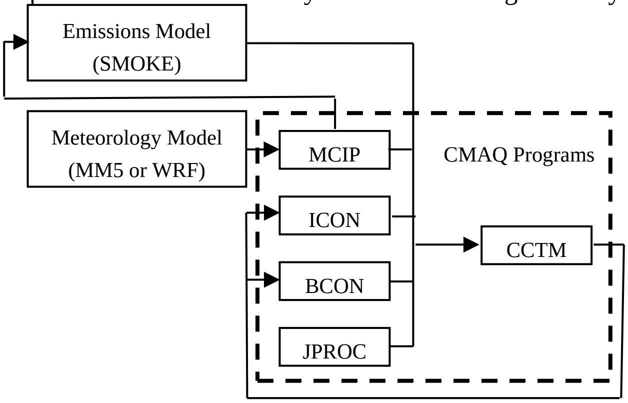

Figure 2. *The CMAQ modeling system [1]*

3. Research Methodology

3.1. Modeling conditions

3.1.1. Study period and domain

There was a rapid ozone formation event on August 23, 2007 and the ozone concentration in Gang-hwa is higher than Seoul in this day. Therefore, this study selects the simulation period from August 19 to 25, 2007.

There are 3 model domains in this study: domain 1 includes East Asia, domain 2 includes South Korea, domain 3 includes Seoul & Gang-hwa.

3.1.2. Meteorological fields

In this study, the MM5 (Mesoscale Model, Version 5) is used to produce and provide meteorological fields for CMAQ (wind, temperature, water mixing ratio, precipitation, surface variables and others). The domain 1 for nesting process is 102×102 grid numbers in plane with 27 km grid resolution for East Asia, the domain 2 of MM5 includes 61×61 grid numbers in plane with 9 km grid resolution for South Korea, and there are 52×49 grid numbers in plane with 3 km grid resolution in domain 3 for Seoul and Gang-hwa.

3.1.3. Emission inventory data

The emission inventory data use for domain 1 is from INTEX-B emission inventory derived from CGRER (Center for Global and Regional Environmental Research). SO_2, CO, NOx, PM10 and VOC emissions are based on INTEX-B emission inventory. Gridded data from 0.5˚×0.5˚ INTEX-B gridded emissions datais converted into 1˚×1˚ gridded emissions data. The emission data of domain 2 (9km x 9km) and 3 (3km x 3km) are from CAPSS, 2007 (Clean Air Quality Policy Support System in Korea). The spatial resolution of CAPSS data is 1 km x 1km. CAPSS data includes point, mobile and area emission sources from the plants and fugitive dust. VOC emission input includes anthropogenic emission. The emission inventory data are sorted according to source classification codes (SCC) for each pollutant and county. They are converted into the IDA (InventoryData Analyzer) format.

3.1.4. Air quality model

The chemical transport model used in this study is CMAQ (Community Multiscale Air Quality Model). The emission inventory data is converted by SMOKE modeling system into hourly emission data for CMAQ modeling. The gridded emission inventory is generated by SMOKE and meteorological fields are generated from MCIP, the CMAQ Chemical Transport Model (CCTM) calculates the chemical reactions, transport and atmospheric deposition of all participating species according to specified physical and chemical options.

3.2. Evaluation of model performance

The CMAQ performance is evaluated by comparing the observation data and the simulated results. Observed Ozone concentration used in this study is from the National Institute of Environmental Research in Korea 2007. The CMAQ output data in net CDF format was statistically analyzed. The statistical are calculates for 10 sites over the simulation period (August 19-25, 2007) and each hour over total sites.The statistical treatments of the data are shown in Table 1.

Mean bias (MB) can indicate whether the simulations under or over estimate the concentration at each hour of each site. As a mean normalized bias (MNB), this performance statistic averages the model/observation residual, paired in time, normalized by observation, over all monitor times/locations, a value of zero would indicate that the model over predictions and model under predictions exactly cancel each other out. As a mean normalized gross error (MNGE), this performance statistic averages the absolute value of the model/observation residual, paired in time, normalized by observation, over all monitor times/locations, a value of zero would indicate that the model exactly matches the observed values at all points in space/time. The mean fractional bias (MFB) normalizes the bias for each model-observed pair by the average of the model and observation before taking the average. Correlation coefficient (R) between modeling and observation concentrations can verify the ability of the model in predicting the variations of observed concentrations.

Table 1. *The statistical treatment methods for the comparison of data*

Mean bias (MB): $\overline{a_{mod}(x,t) - a_{obs}(x,t)}$
Mean normalized bias (MNB): $\overline{\left(\frac{a_{mod}(x,t) - a_{obs}(x,t)}{a_{obs}(x,t)}\right)}$
Mean fractional bias (MFB): $\frac{\overline{a_{mod}(x,t)} - \overline{a_{obs}(x,t)}}{0.5 \times \overline{(\overline{a_{mod}(x,t)} + \overline{a_{obs}(x,t)})}}$
Mean absolute gross error (MAGE): $\lvert a_{mod}(x,t) - a_{obs}(x,t)\rvert$
Mean normalized gross error (MNGE): $\overline{\left(\frac{\lvert a_{mod}(x,t) - a_{obs}(x,t)\rvert}{a_{obs}(x,t)}\right)}$
Correlation coefficient (R): $\frac{\overline{(a_{mod}(x,t) - \overline{a_{mod}}) \times (a_{obs}(x,t) - \overline{a_{obs}})}}{\left[\overline{(a_{mod}(x,t) - \overline{a_{mod}})^2}\right]^{0.5} \times \left[\overline{(a_{mod}(x,t) - \overline{a_{mod}})^2}\right]^{0.5}}$

$a_{mod}(x,t)$: *Modeling concentrations*

$a_{obs}(x,t)$: *Observation concentrations*

3.3. Sensitivity analysis

The sensitivity analysis of ozone formation evaluates the impact of changing emission inventory on ozone formation in the urban and the rural of Korea. This study evaluates the difference in peak ozone concentrations by reducing VOC and NOx emission using the same meteorological input and chemical transport schemes. In order to analyse the effects of VOC and NOx emissions on the sensitivity of ozone formation, the study performs 9 scenarios. Because the level of effect of VOC and NOx on ozone formation is not similar, this study reduces 10%, 25%, 50% of VOC; reduces 10%, 25%, 50% of NOx; reduces 10%, 25%, 50% of VOC and NOx to analyse the sensitivity of ozone formation.

4. Results and discussion

4.1. Evaluation of air quality modeling performance

The observation data is compared with the base case simulated results to evaluate CMAQ performance by using the algorithms in Table 1. Generally, the mean bias (MB) is negative, so the observation ozone concentration is higher than modeling ozone concentration at all sites. The correlation coefficient (R) between observation and modeling ozone concentrations for all sites are from 0.347 to 0.580. The correlation coefficient of average 8 hours are higher than 1 hour, they are from 0.439 to 0.679.

4.2. Sensitivity analysis of ozone formation

This study compares the ozone concentration of average all grids in Gang-hwa and Seoul (including West Seoul and East Seoul) including base case and 9 scenarios in 3 days (August 22, 23, 24).

In Gang-hwa, the sensitivity of ozone concentration in August 23 is highest and much higher than on August 22, 24 because the ozone concentration is highest on this day.When reducing 50% VOC, ozone concentration decreases than base case. On the contrary, reducing 50% NOx, ozone concentration increase than base case. As a result, ozone concentration in Gang-hwa appears in VOC limited area of EKMA figure. In addition, reducing 50% VOC and NOx, ozone concentration decreases than base case so ozone concentration in Gang-hwa appears on the left of EKMA figure.

When reducing 50% VOC, ozone concentration in East Seoul decreases than base case. On the contrary, reducing 50% NOx, ozone concentration increases than base case. As a result, ozone concentration in East Seoul appears in VOC limited area of EKMA figure. In addition, reducing 50% VOC and NOx, ozone concentration decreases than base case so ozone concentration in East Seoul appears on the left of EKMA figure. The ozone concentration in West Seoul is similar to that in East Seoul.

On August 22, the sensitivity of ozone formation in Gang-hwa is lowest because this day has the heavier rain than East Seoul and West Seoul.NOx emission in East Seoul is higher than in West Seoul but VOC emission in West Seoul is higher than in East Seoul, so the emission in East Seoul and West Seoul are similar. However, the sensitivity of ozone formation in West Seoul is 10.98% higher than the sensitivity of ozone formation in East Seoul. The wind direction in Seoul is West North from 1:00 – 10:00 and East North from 10:00 – 24:00 so West Seoul is affected by emission from East Seoul on August 22. As a result, the sensitivity of ozone formation in West Seoul is higher than in East Seoul because of the wind speed and wind direction.

On August 23, the sensitivity of ozone formation of average all grids in Gang-hwa is highest, it is 34.45% higher than the sensitivity of ozone formation in East Seoul and 23.41% higher than the sensitivity of ozone formation in West Seoul. The sensitivity of ozone formation of average all grids in West Seoul is 9.84% higher than the sensitivity of ozone formation in East Seoul. However, the emission in Gang-hwa is lowest and the emission in East Seoul and West Seoul are similar in this day. The wind direction in Seoul is East almost the day, the wind direction are East North and East South at some hours and the wind speed in East Seoul is lower than in West Seoul. The sensitivity of ozone in Gang-hwa is highest because Gang-hwa is affected by other areas. The sensitivity of ozone formation in West Seoul is higher than in East Seoul because West Seoul is affected by East Seoul.

On August 24, the sensitivity of ozone formation in

West Seoul is highest, but the emission in West Seoul is similar to that in East Seoul. The sensitivity of ozone formation of average all grids in West Seoul is 25.2%l higher than the sensitivity of ozone formation in East Seoul because the wind direction in Seoul are East and East South with high wind speed almost the day and the wind direction change many directions with low wind speed some hours.

5. Conclusions

The Community Multi-scale Air Quality (CMAQ) modeling system has been designed to approach air quality as a whole by including state-of-the-science capabilities for modeling multiple air quality issues, including tropospheric ozone. This study used MM5 - SMOKE - CMAQ modeling system to analyse the sensitivity of ozone formation in urban (Seoul includes East Seoul and West Seoul) and rural (Gang-hwa). The nine different sensitivity scenarios (reducing 10%, 25%, 50% of VOC; reducing 10%, 25%, 50% of NOx; reducing 10%, 25%, 50% of VOC and NOx) were analysed in August 22, 23, 24, 2007. The average all grids in each region are chosen to analyse the sensitivity of ozone formation in this study.

From the results of this study, some conclusions can be brought out: The ozone concentration in Seoul almost decreases earlier than in Gang-hwa within a day. Ozone concentration in Gang-hwa, East Seoul and West Seoul almost appears in VOC limited area of EKMA figure. Therefore, VOC control strategy could be the best approach in reducing peak ozone formation in Gang-hwa, East Seoul and West Seoul. NOx emission in East Seoul is highest, VOC emission in West Seoul is highest and VOC emission could be the best way to reduce ozone concentration in Gang-hwa, East Seoul and West Seoul. For this reason, reducing VOC emission may reduce the ozone concentration in East Seoul, West Seoul and Gang-hwa, especially, reducing VOC emission in West Seoul. The sensitivity of ozone formation in West Seoul is higher than in East Seoul because the wind creates the transport of ozone from East Seoul. On August 23, the emission of Gang-hwa is lowest but the sensitivity of ozone formation in Gang-hwa is highest because of the wind direction and wind speed. The transport of ozone precursors from Seoul can cause significant ozone production in Gang-hwa on August 23, 2007.

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