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SENSITIVITY ANALYSIS OF INDIVIDUAL VOC SPECIES TO REDUCTION OF ATMOSPHERIC OZONE

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Abstract: In this study the sensitivities of anthropogenic VOCs to the reduction of atmospheric ozone were investigated. CMAQv5.0.1 with WRFv3.4.1 were set up for the simulation in Japan on 2 domains, and emission inventories of precursors were introduced from JATOP (Japan AuTo-Oil Program) compiled in 2005. The resolutions of domains were 30km squares for parent domain covering most part of Japan and 10km squares for child domain covering Kinki area. SAPRC-99 model was adopted in CMAQ as gas phase chemistry. Biogenic emission was considered by using MEGANv2.04. Summertime simulation for one month including high concentration episodes of ozone in Japan was conducted and good performance was shown by the comparison with monitoring data. The sensitivity analysis of VOCs to ozone reduction in the child domain was conducted by estimating the reduction rates of ozone concentrations in case of 20 % reduced emission of each VOC species. From the summed emission amount in the child domain, seven species of VOCs such as with ALK3, ALK4, ARO1, ARO2, OLE2, ETHENE, HCHO were found to be dominant, therefore, the analysis were conducted the reduced emission of these seven species, respectively. The reduction rate of each grid was sorted by a photochemical index of the function of each VOC concentration divided by NOx concentration. The results showed remarkable decreases in case of the reduction of former five species. As the sum of reduction rates in case with individually reduced emission showed no differences from the rate in case with reduced emissions of five species, it was confirmed that the emission amount of VOCs has a linearity in the ozone reduction. From the sensitivity analysis, the sum of above five VOCs divided by NOx was proposed as a photochemical index for ozone reduction. The reduction rates on weekdays, weekends, and during high concentration episodes were estimated as a function of the index, respectively. In the case that the index was below 0.2, the reduction rates were more prominent. It was concluded that this index proposed in this study can help the policy makers to build the measures for ozone reduction.

Key words: WRF/CMAQ, VOCs, ozone, photochemical index, sensitivity analysis

INTRODUCTION

In Japan atmospheric ozone concentration has been increasing in spite of the reduction of the precursors such as NOx and VOCs by the national regulation. It is thought that the reasons is the non-linearity of ozone generation process and the uncertainty of biogenic VOCs emission. The non-linearity of ozone generation brought by ozone chemistry complexity, that is, under VOC-rich condition the ozone concentration is dominated by NOx, and in case of NOx-rich condition VOCs is dominant (Sillman et al., 1995). For environmental managements it seems to be useful the index showing which of them are influential in ozone reduction is developed. In this study the sensitivities of VOCs to ozone generation was investigated by WRF/CMAQ model. Through the results investigations of VOC species for effective reduction at a given point was conducted and an index stated the mixture condition of precursors were developed. Furthermore the distribution of index in Kinki area, located at the central part of mainland of Japan was calculated for a discussion of the availability for ozone control procedures. Biogenic VOC (BVOC) were also considered for simulation, however, sensitivity analysis of BVOC was not conducted because the emission amount of BVOC has the great uncertainty (Bao et al. (2008)). Some studies on the development of photochemical index were already conducted. Sillman et al. (2002) examined several kinds of indexes and applied to the high ozone episodes, however, the indexes indicated different values in case of less than 80ppb, 100-200 ppb, and more than 200 ppb. In addition, Xie et al. (2011) proposed the ratio of O_3/NOy as an index, and reported that the index is related to VOC-NOx sensitive conditions.

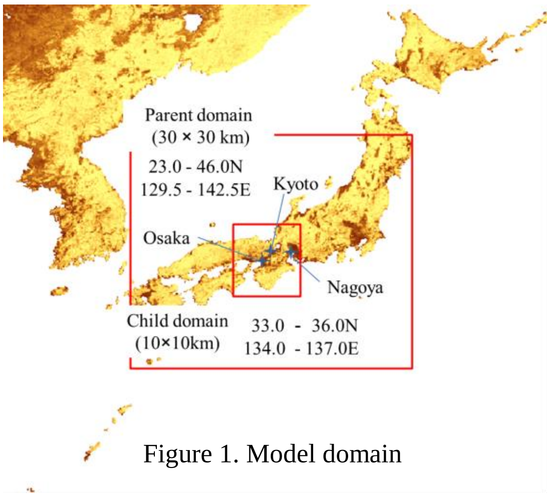

Figure 1. Model domain

In this study an index which consists of VOCs and NOx is developed from the result of sensitivity analysis by a chemical transport model. As VOCs has many components involved the species with less reactivity to NOx, the index should be developed as the function of effective species VOCs.

MODEL DESCRIPTION

In this study WRF3.4.1 and CMAQ5.0.1 were introduced for calculating the distribution of ozone. Model domain was set as Figure 1, which consists of coarse domain of 23.0-46.0 N, 129.5-142.5 E with 30km square grid and fine domain of 33.0-36.0 N, 134.0-137.0 E with 10km square grid in Lambert conformal conic projection. The number of the grid was 38 * 42 for coarse domain, 22 * 34 for fine domain, respectively. For vertical direction 27 layers were set from the ground to 50 hPa above. Emission inventories of precursors were introduced from JATOP (Japan AuTo-Oil Program) compiled in 2005. In conducting CMAQ model SAPRC-99 model was adopted in CMAQ as gas phase chemistry. Biogenic emission was considered by using MEGANv2.04. Running period was set to July 1 to 31, 2005, with 3 days pre-calculation at the end of June.

EMISSION INVENTORY

Emission inventory of anthropogenic precursors was an important factor of this analysis. In this study JATOP database was introduced as an anthropogenic emission summed at resolutions of 30km * 30km and 10km * 10km, and MEGANv2.04 was introduced as a biogenic emission. In this CMAQ calculation SAPRC-99 model were used as a gaseous chemical process, emission amount were re-compiled by the VOC species followed by the division of categories in SAPRC-99 model. Figure 2 shows the result of the re-compilation. ALK1-5, ARO1-2, OLE2, ETHENE, and HCHO were found to be dominant species in the domain.

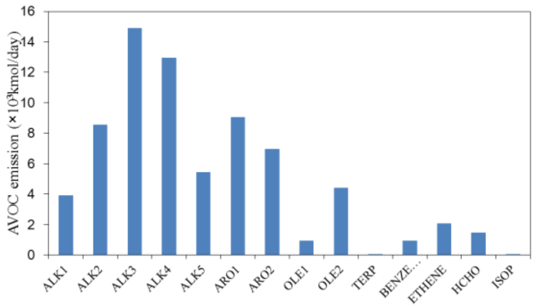

Figure 2. Emission amount of VOCs in the domain

Selection of VOC species for sensitive analysis

As potential contributions to the generation of ozone differ from VOC species, MIR (Maximum Incremental Reactivity) is used as one of the index for indicating the photochemical reactivity. VOCs with high MIR have a great potentiality of generating ozone. In this study ozone productivity P of each species i was evaluated by the following formula,

$$P = (MIRi * VOCi) / \Sigma (MIRi * VOCi) \quad (1)$$

MIR values taken from the table (Carter, 2000) were multiplied by the emission amount re-compiled above. Each VOC category has several species, for instance, ALK1 has 10 species, MIR value for each VOC category was assumed to the average of the values of those species.
The results of P are shown in

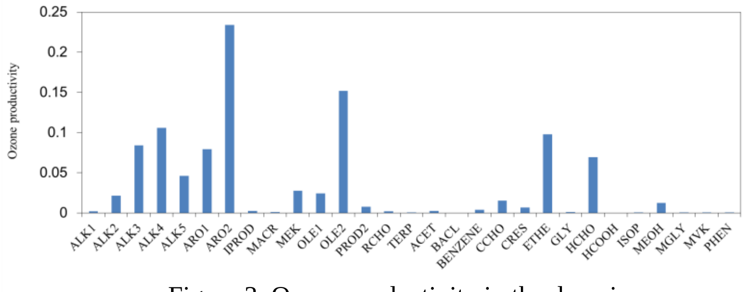

Figure 3. Ozone productivity in the domain

Figure 3. In Kinki area ALK3, ALK4, ARO1, ARO2, OLE2, ETHENE, and HCHO were found to be dominant species for ozone generation. Following the result, these 7 species were selected for sensitivity analysis and the simulation with reduced emission of these 7 species were conducted to be examined the influence of individual VOC to the ozone concentration changes.

CMAQ CALCULATION

CMAQ performance

CMAQ simulations were conducted through 1 to 31 of July, 2005 with 3 days of pre-running. In this simulations modules of gaseous chemistry were adopted SAPRC-99, that of aerosol were AERO5, and that of cloud mixture were ACM2, respectively. Firstly the comparisons of CMAQ model results with the observed values were conducted. The results are shown in Figure 4. Observed values were taken from national monitoring database in Osaka and Nagoya shown in Figure 1. Despite of the calculation in 10km * 10km of finer grid, the trend of variation of ozone concentration were comparably agreed with observed values. However, during long-range transport events the calculated values tend to be under-estimated. For a solution of this issues expanded domain should be introduced and considered the emission from the Asian continents. In this study the object of the study was to find the dominant species of VOCs from local sources and only the difference of concentrations with reduced emission were needed. The following analysis was continued with this calculating conditions hereafter.

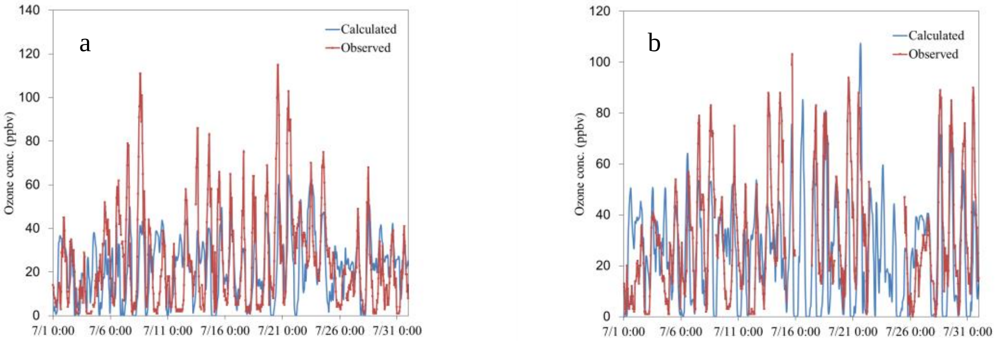

Figure 4. Comparison of the concentration at (a) Osaka and (b) Nagoya

Sensitivity analysis

The value of atmospheric concentration of VOC divided by the value of atmospheric concentration of NOx at a given place would be useful for the decision of control strategies, if the values were defined as the index of atmospheric photochemical state (Kleinman et al., 2000). VOCs comprise of several hundred components, some species should be selected on behalf of total VOC. As in the results of inventory analysis, 7 species of VOC was influential on ozone concentrations in this domain. Here WRF/CMAQ simulation with original emission inventories and with individually 20% reduced VOC emission were conducted to find the species in place of total VOCs in the index. Effectiveness were evaluated by the change rate (CR) of ozone concentration shown below,

$$[CR\ (\%)] = 100 * (C_{red} - C_{ori}) / C_{ori} \quad (2)$$

where C_{red} means ozone concentrations with reduced emission, and C_{ori} is ozone concentrations with original emission. In this analysis calculation results in the time of 12:00 ~ 16:00 of 1 ~ 7 in July, 2005 were picked up for the analysis of CR with high photochemical reactivity.

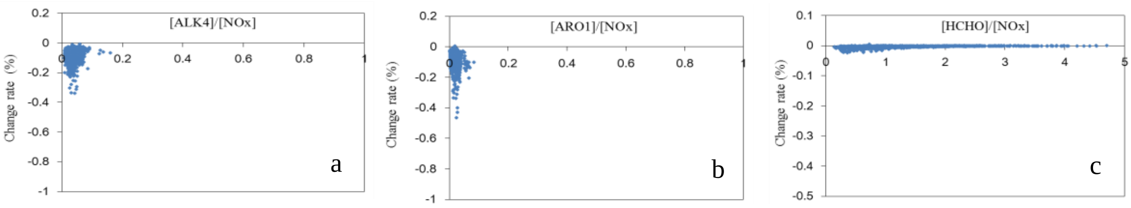

Figure 5. CRs with individually reduced emission of (a)ALK4, (b)ARO1, and (c)HCHO

Some results of CRs are shown in Figure 5. The concentration of target VOCs, such as ALK3, ALK4, ARO1, ARO2, OLE2, ETHENE, and HCHO divided by NOx concentration were candidates for an index. In the analysis of former 5 species, CRs indicated low values in case of low VOC/NOx values. However, latter two, ETHENE and HCHO did not contribute the ozone reduction.

Comparison of ozone CRs in case of 5 species reduction with the rate in case of total VOC reduction is shown in Figure 6. According to the CRs in each grid plotted in the diagram, CRs in case of 5 species were around 80 % of the CR in case of total VOC. Consequently these 5 species were confirmed to be dominant to the ozone concentration in Kinki area.

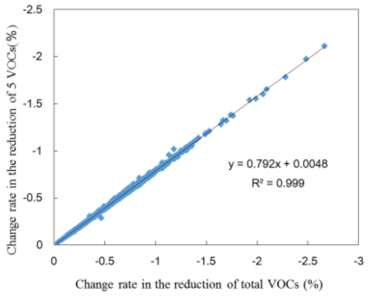

Figure 6. Comparison of the CR in reduction of 5 species and total VOCs

In constructing an index, a linearity of selected 5 VOC species should be checked. For this purpose the comparison of the sum of each CR in reducing individually with the CR in the simultaneous reduction of 5 species were conducted. According to Figure 7, each dot was well followed the diagonal line, that is, it was confirmed that these 5 VOCs have a linearity.

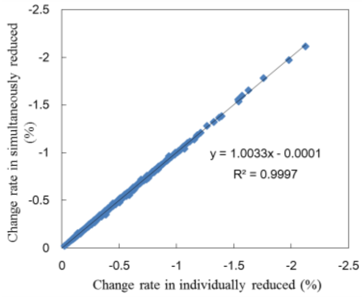

Figure 7. Comparison of the CR in individual simultaneous reduction

From the various sensitivity analysis, the index indicating the photochemical state in generating ozone was defined as below,

$$\text{Developed Index} = \{[ALK3] + [ALK4] + [ARO1] + [ARO2] + [OLE2]\} / [NOx] \quad (3)$$

where [VOCi] means the atmospheric concentration of i species. CRs with the index defined above is shown in Figure 8, CRs were gradually descending with the decrease of the index, especially in case of below 0.2 remarkable decline of CRs was found.

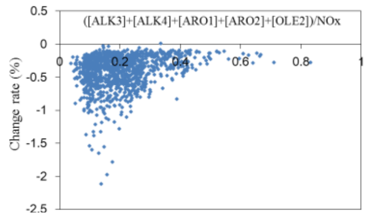

Figure 8. CRs with the index

Availability of the index under various ozone concentration ranges

To confirm the availability of proposed index, CRs were calculated on several days classified by its peak concentration. Here the days was picked up by the concentration ranges of 0 ~ 20, 20 ~ 40, 40 ~ 60, 60 ~ 80, 80 ~ 100, and more than 100 ppb from 1 to 31 on July in 2005. In those classification CRs with the proposed index are shown in Figure 9.

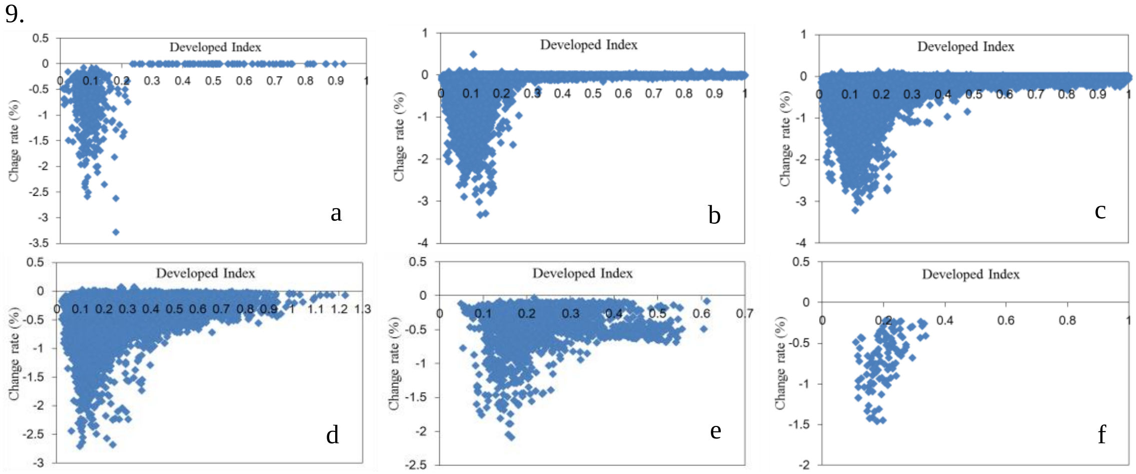

Figure 9. CRs of ozone in its peak of (a) 0-20ppb, (b) 20-40ppb, (c) 40-60ppb, (d) 60-80ppb,(e) 80-100ppb, and (f) more than 100ppb

In all ranges of concentration CRs were descending in case of the index of less than 0.2. Consequently the index was found to be available independently of concentration ranges.

Distribution map of the index and relationship with ozone reduction

Figure 10 shows the distribution of the index at Kinki area and the CR at the same time is shown in Figure 11. Similar distribution could be found. Where the index shows low has low CRs, that is, ozone was well removed. Low index areas are highly urbanized with high NOx emission area from mobile sources. In generally ozone concentration were dominated by the VOCs there, where VOC is more effective for ozone reduction than NOx. The distribution of this index was confirmed to be followed that. Consequently the index proposed would be an available for comprehension of photochemical state.

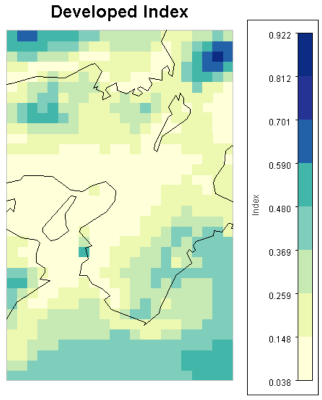

Figure 10. Distribution of the index averaged through July 2005

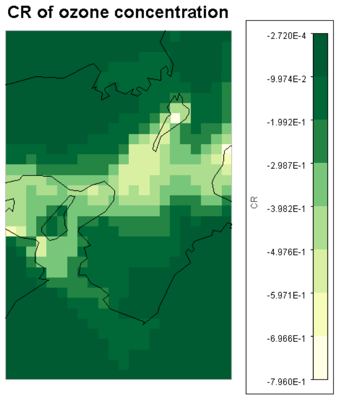

Figure 11. Distribution of the monthly averaged CR in July 2005

CONCLUSION

In order establish the index for indicating the photochemical status in generation of atmospheric ozone, sensitivity analysis of individual VOC species was conducted by using WRF/CMAQ model system. 5 species such as ALK3, ALK4, ARO1, ARO2, and OLE2 in SAPRC-99 showed remarkable contributions to ozone concentrations. In addition, it was found that emission amount of these species have a linearity to the ozone concentration. In this study the atmospheric concentration of sum of 5 species divided NOx concentration was proposed as an index, and examine the applicability of it to various concentration ranges. In every situations the decline of ozone concentration was found in case of the index of less than 0.2. These results concluded that this developed index would be one of the tools for representing the photochemical state in controlling the VOC sources.

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REFERENCES

Bao, H., Kondo, A. Kaga, A, Tada, M., Sakaguti, K., Inoue, Y., Shimoda, Y., Narumi, D., Machimura, T., 2008: Biogenic volatile organic compound emission potential of forests and paddy fields in the Kinki region of Japan, Environ. Res., 106; 156-169.

Carter, W. P. L., 2000: Documentation of the SAPRC-99 chemical mechanism for VOC reactivity assessment VOLUME 1 OF 2 DOCUMENTATION TEXT, Final Report to California Air Resources Board, Contract 92-329 and Contract 95-308 (http://www.cert.ucr.edu/~carter/pubs/s99txt.pdf).

Kleinman, L. I., 2000: Ozone process insights from field experiments – part II: Observation-based analysis for ozone production, Atmos, Environ., 34; 2023-2033.

Sillman, S., 1995: the use of NOy, H_2O_2, and HNO_3 as indicators for Ozone-NOx-hydrocarbon sensitivity in urban locations, J. Geophys. Res., 100; 14175-14188.

Sillman, S., He, D., 2002: Some theoretical results concerning O_3-NOx-VOC chemistry and NOx-VOC indicators, J. Geophys. Res., 107(D22), 4659, doi:10.1029/2001JD001123.

Xie, Y., Elleman, R., Jobson, T., Lamb, B., 2011: Evaluation of O_3-NOx-VOC sensitivities predicted with the CMAQ photochemical model using Pacific Northwest 2001 field observations, J. Geophys. Res., 116, D20303, doi:10.1029/2011JD015801.