

Sensitivity of Ozone Concentrations to Initial Concentrations Applying the Carbon Bond Mechanism IV

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The Carbon Bond Mechanism IV has been developed for use in urban- and regional-scale oxidant models. The photochemical mechanism, CBM4, contains extensive improvements to earlier carbon bond mechanisms in the chemical representations of aromatics, biogenic hydrocarbons, peroxyacetyl nitrates, and formaldehyde. Ozone is produced mainly by nitrogen oxides and hydrocarbon. By altering the initial concentrations of the mechanism, an analysis of the sensitivity of ozone concentrations to VOC/NO_x ratios and VOC composition is conducted in this one-dimensional mechanism. Note that it is considered a chemical mechanism in order to understand the photochemical reactions within this mechanism. It analyzed the results of these simulations by applying a NO_x-sensitive and a VOC-sensitive regime. These sensitivity regimes are changed to match the relative contribution of VOC and NO_x concentrations to ozone production in simulations of two sets.

Key words : Carbon bond mechanism; sensitivity, Ozone production, Hydrocarbon, Nitrogen oxides

1. Introduction

Ambient concentrations of secondary pollutants are influenced by atmospheric emissions, meteorology, and heterogeneous and homogeneous chemistry. The chemistry is one of the most important components that determines pollutant concentrations since it is responsible for the non-linearity of secondary pollutant formation.¹⁻⁵⁾

A fully explicit mechanism for representing gas-phase atmospheric chemistry would contain upwards of 20,000 reactions and several thousand species. The chemical mechanisms used in air quality simulation models (AQSMs) have been highly generalized and simplified representations of the homogeneous chemistry. These chemical mechanisms adopt the lumped structure approach used in Carbon Bond Mechanism IV (CBM4) and the lumped molecule approach used at the Statewide Air Pollution Research Center (SAPRC), in the Regional Acid Deposition Model (RADM)

and in the Regional Atmospheric Chemistry Mechanism (RACM) in order to condense mechanisms into an appropriate size for use in grid models. Very recently, a third method, which will be referred to as the morphecule approach, has been developed.^{1,3)}

Photochemical reaction mechanisms describe how volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) interact to produce ozone and other oxidants. These mechanisms have been developed and detailed to select chemical reactions, which have an effect on photochemical oxidants, since the 1970s. *Adrian M. Hough*¹ compared 20 mechanisms and found that most of the mechanisms, published between 1985 and 1987, tended to produce similar results for ozone (O₃) and nitric acid (HNO₃) but predictions for peroxy acetylnitrate (PAN) and hydrogen peroxide (H₂O₂) differed by up to a factor of 2. *Gery et al.*⁴⁾ explained the detailed mechanism, CBM-EX and the condensed mechanism, CBM4 and showed agreement with the results of two mechanisms regarding the smog chamber data. *Marcia M. Dodge*²⁾ compared versions of the CBM4, CAL and RADM mechanisms and found that the

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mechanisms yielded nearly identical predictions for O₃, PAN, and HNO₃ under most conditions, although differences were noted in simulations carried out at low VOC/NO_x ratios, at low temperatures or with high levels of aromatic hydrocarbons.

In this study, the features of CBM4 that have proved its availability for urban- and regional-scale air pollution will be described through sensitivity studies conducted for VOC/NO_x ratios and an initial VOC mixture composition.²⁾

2. Description of Carbon Bond Mechanism IV

Since 1976, researchers at Systems Applications International have been developing carbon bond mechanisms for use in AQSMs. The current version of the CBM4, which is used in the Urban Airshed Model (UAM-V)⁶⁾, the Regional Oxidant Model (ROM) and several other AQSMs, is a lumped structure mechanism where organics are divided into smaller reaction elements based on the types of carbon bonds in each species.¹⁻⁵⁾

An overview of the general characteristics of the mechanism is provided in Table 1. The CBM4 treats the reactions of four different types of species: (1) inorganic species such as O₃, various NO_x species and HO_x radicals that are treated explicitly with no lumping; (2)

organic species such as formaldehyde, ethene and isoprene that, because of their unique chemistry or special importance in the environment, are treated explicitly; (3) organic species such as PAR, OLE and ALD2 that are represented by carbon bond surrogates; and (4) organic species such as TOL and XYL that are represented by molecular surrogates.⁴⁾

Carbon bond surrogates are used to describe the chemistry of three different types of carbon bonds commonly found as parts of larger organic molecules. The single-bonded one-carbon-atom surrogate, PAR, is used to represent the chemistry of alkanes and most of the alkyl groups found in other organics. The carbon bond surrogate, OLE (olefin), which contains two carbon atoms, is used to represent the carbon-carbon double bonds that are found in 1-alkenes. The third surrogate, ALD2, which also contains two carbon atoms, is used to represent the -CHO group and adjacent carbon atom in acetaldehyde and higher aldehydes. It is also used to represent 2-alkens since these species react very rapidly in the environment to produce aldehyde products. Two molecular surrogates represent the chemistry of aromatic hydrocarbons. The surrogate TOL is a seven-carbon species used to categorize monoalkylbenzene structures, and its chemistry is based on the reactions of toluene. XYL is

Table 1. Characteristics of the CBM4

Number of reactions	81
Inorganic reactions	30
Organic reactions	40
Photolytic reactions	11
Number of species	34
Inorganic species	15
Primary organics	9
Alkanes	1
Alkenes	2
Aromatics	2
Biogenic VOCs	1
Aldehydes	2
Nonreactive VOCs	1
Organic products	4
Organic radicals	3

*PAR, ETH, OLE, TOL, XYL, FORM, ALD2, ISOP, NR

Table 2. Representation of Selected Organics in the CBM4

Organic Species	Representation
n-Butane	4 PAR
2,2,5-Trimethylpentane	8 PAR
Ethene	1 ETH
Propene	1 OLE + 1 PAR
trans-2-Butene	2 ALD2
Toluene	1 TOL
m-Xylene	1 XYL
Ethylbenzene	1 TOL + 1 PAR
Trimethylbenzene	1 XYL + 1 PAR
Isoprene	1 ISOP
Formaldehyde	1 FORM
Acetaldehyde	1 ALD2
Propionaldehyde	1 ALD2 + 1 PAR
n-pentane	5 PAR

eight-carbon surrogate used to represent dialkylbenzenes and trialkylbenzenes, and its chemistry is based on *m*-xylene. Table 2 provides examples of how selected organics in the CBM4 are partitioned among the organic groupings explained above.^{3,4)}

The CBM4, like most mechanisms in use for a long period, is frequently updated to correct errors or incorporate new information obtained in kinetic and mechanistic studies. Since its inception in the mid-1980s, the CB4 has undergone several revisions. The kinetics for the reaction of acetyl peroxy radicals with NO and NO₂ and the thermal decomposition of PAN were updated based on recent experimental results. The formaldehyde absorption cross-sections recommended for use with the mechanism were also revised to be consistent with new laboratory data. To limit the number of organic intermediates included in the mechanism, CB4 developers created chemical operators such as XO₂ and XO₂N. To improve H₂O₂ predictions, the reaction XO₂ + HO₂ → (no products) was added to the mechanism. Very recently, the chemistry included in the CB4 mechanism for isoprene was revised. The reaction scheme used for this organic is now based on the one-product condensed mechanism developed by Carter (1996).^{3,4)}

3. Numerical simulation

In order to investigate the sensitivity studies of this box mechanism, only chemical mechanisms were included in this research, excluding the meteorological and emission mechanisms.

3.1. Base run

The base run was carried out for 2 days using a diurnally-varying photolysis rate, and a constant profile related zenith angle. The simulation was commenced assuming a clear day and initial concentrations of NO_x, O₃, CO and VOC from the Busan Clean Air Act 21. The base run concentration-time profiles obtained for the ozone, NO_x and oxidant products are shown in Figure 1.

3.2. Sensitivity of Ozone concentrations to various conditions

In this chapter, initial concentrations were created to set up good results of the sensitivity studies of ozone. The other conditions were identical to those of the base run.

3.2.1. Base case

For the initial concentrations of the base case, we referred to the research of Marcia C. Dodge²: [NO_x] = 0.06 ppm, [VOC] = 0.54 ppm C, [CO] = 1.2 ppm and [H₂O] = 20,000 ppm. It was considered to be an urban simulation which had a VOC/NO_x ratio of 9.

The tendencies of ozone and other oxidants obtained from the base case were similar to those of the base run (Fig. 1). The concentrations of the oxidants, however, were relatively lower than those in the base run because the initial ozone concentration was excluded from the simulation of the base case.

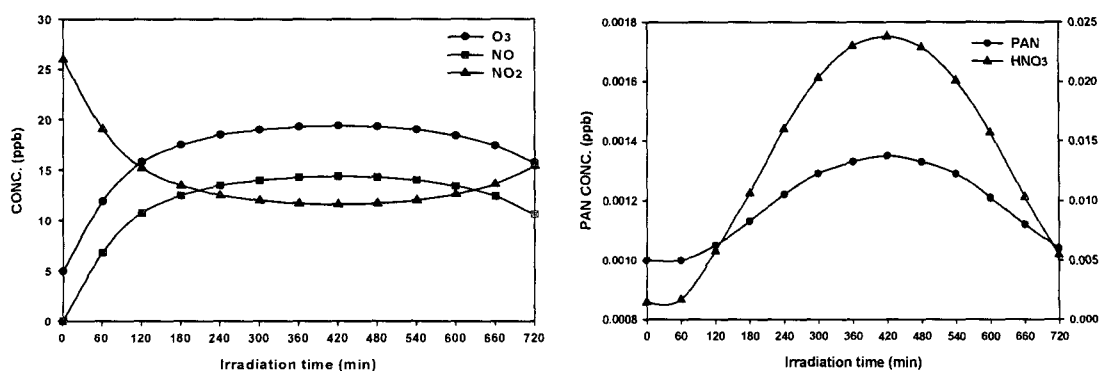


Fig. 1. Calculated concentrations of selected oxidant species as a function of time for base run.

3.2.2. Sensitivity of O_3 concentrations to VOC/ NO_x ratios

It is generally known that for some conditions the process of ozone formation is controlled almost entirely by NO_x and is largely independent of VOC, while for other conditions ozone production increases with increasing VOC and does not increase (or sometimes even decreases) with increasing NO_x .⁷⁻⁹⁾

To investigate the sensitivity of O_3 concentration to VOC/ NO_x ratios, simulations were conducted in two sets. In one set, $[NO_x]_i$ was held constant at 0.06 ppm and $[VOC]_i$ was varied from 0.1 to 1.0 ppm C. In the other set, $[VOC]_i$ was held constant at 0.54 ppm C and $[NO_x]_i$ was varied from 0.01 to 0.1 ppm.²⁾ It was found that the VOC/ NO_x ratio increases with increasing $[VOC]_i$ when $[NO_x]_i$ is constant and decreases with increasing $[NO_x]_i$ when $[VOC]_i$ is constant.²⁾

The maximum O_3 predictions obtained for these two series of simulations are shown in Figure 2. When $[NO_x]_i$ is constant, the ozone increase rate grows with increasing $[VOC]_i$ up to 0.6 ppm C and diminishes relatively with increasing $[VOC]_i$ (See Fig. 2(a)). When $[VOC]_i$ is constant, the ozone increase rate grows with increasing $[NO_x]_i$ up to 0.06 ppm and decreases and converges at a relatively low concentration, with increasing $[NO_x]_i$ (See Fig. 2(b)). These findings show that low VOC/ NO_x ratios correspond to VOC-sensitive chemistry and that high VOC/ NO_x ratios correspond to NO_x -sensitive chemistry.

To examine the sensitivity of O_3 concen-

trations to urban and rural areas, initial VOC/ NO_x ratios were set up. An urban and a rural area were represented by VOC/ NO_x ratios of 9 and 24, respectively, and these ratios were determined by NO_x concentrations when the VOC concentration of 0.54 ppm C was constant. Two additional sets of simulations were run to apply to NO_x -sensitive and VOC-sensitive regimes. In one set, $[NO_x]_i$ was held constant and $[VOC]_i$ was reduced from 10% to 100%. In the other set, $[VOC]_i$ was held constant and $[NO_x]_i$ was reduced from 10% to 100%.

The NO_x - and VOC-sensitive regimes are determined by their relative impacts of NO_x or VOC. The VOC-sensitive regime refers to situations in which a percent reduction in VOC would result in a significantly greater decrease in O_3 relative to the same percent reduction in NO_x . The NO_x -sensitive regime refers to situations in which a percent reduction in NO_x results in a significantly greater decrease in O_3 relative to the same percent reduction in VOC.⁷⁾

The results obtained in these simulations are shown in Figure 3. In the case of a VOC/ NO_x ratio of 9 (Fig. 3(a)), it was divided between VOC-sensitive and NO_x -sensitive at approximately an 85% reduction rate. In the case of a VOC/ NO_x ratio of 24 (Fig. 3(b)), it was divided identically at an 80% reduction rate. The ozone reduction rate was higher at the ratio of 9 than at the ratio of 24 in the case of the $[VOC]_i$ reduction and was lower at the ratio of 9 than at the ratio of 24 in the case of the $[NO_x]_i$ reduction. It may appear that urban areas are VOC-sensitive and rural areas are NO_x -sensitive.

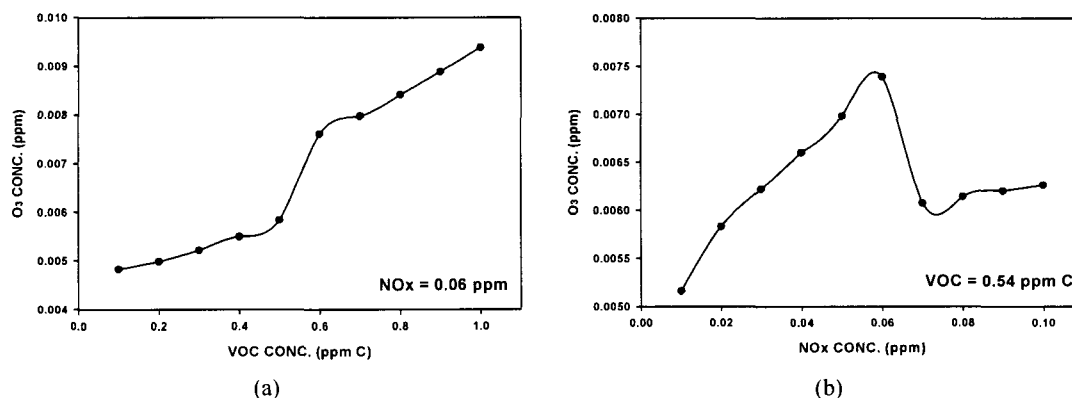


Fig. 2. Predicted maximum O_3 concentration as a function of $[VOC]_i$ and $[NO_x]_i$ for base case.

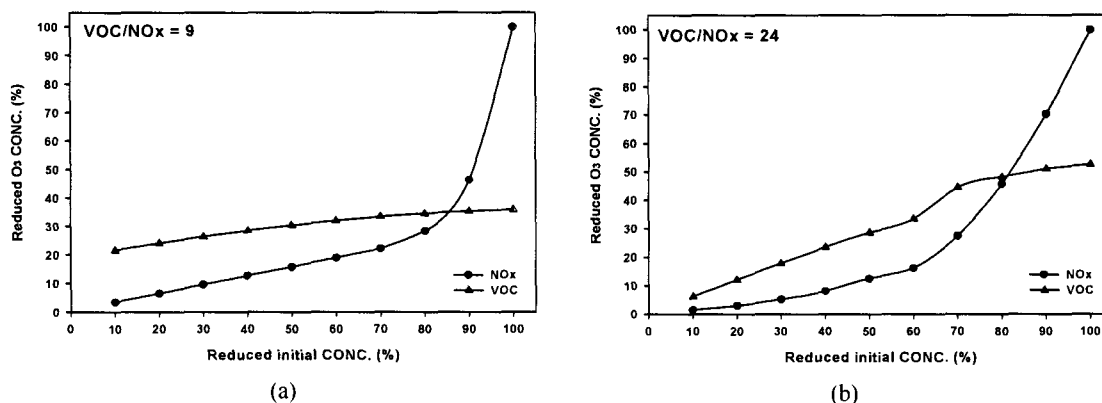


Fig. 3. Calculated maximum O₃ concentration reduction rate as a function of reduction rates for initial NO_x and VOC concentration.

3.2.3. Sensitivity of O₃ concentrations to VOC composition

Although the impact of VOC on ozone chemistry is frequently expressed in terms of VOC/NO_x ratios, the true impact of VOC is related more closely to the reactivity of the VOC species with respect to OH rather than to the total amount of VOC.^{2,7-12)}

To assess whether the effect of VOC composition is specific to a particular group of organics, simulations were conducted using VOC mixtures that contained only one class of VOCs (either aromatics, alkenes or alkanes). The VOC mixtures for the three sets of simulations are given in Table 3. Note that 10% initial aldehyde was added to the alkane simulations, since an alkane-only mix generated extremely low levels of O₃ at all VOC concentrations. Also, the VOC mixture simulations were conducted at

VOC/NO_x ratios of 9 and 24 to conform with urban and rural areas.

Maximum O₃ concentrations obtained in the VOC-mixture simulations are compared to the base case in Fig. 4. The first VOC composition, the aromatic mixture, did not affect ozone production in either VOC/NO_x ratio. The alkene mixture was a potent influence on ozone formation in both ratios, however, its potentiality for ozone formation was higher in urban areas than in rural areas. The final VOC composition, the alkane and aldehyde mixture, was also a potent influence on ozone formation in both ratios. However, its potentiality for ozone formation was higher in rural areas than in urban areas.

To investigate the sensitivity of O₃ concentration to urban and rural areas, the alkenes simulation, which had a large potential for ozone formation, was selected from among the three mixtures. It was applied to the method described in the previous section.

The results obtained from the simulation of the alkene mixture are shown in Fig. 5 and are more suitable to the sensitive regime than the total amount of VOC. In the case of a VOC/NO_x ratio of 9 (Fig. 5(a)), it was divided between VOC-sensitive and NO_x-sensitive in about 70% of the reduction rates. In the case of a VOC/NO_x ratio of 24 (Fig. 5(b)), it was shown to be NO_x-sensitive in most reduction rates. Similarly, considering the total amount of VOC, urban areas are VOC-sensitive and rural areas are NO_x-sensitive.

Table 3. Ingredients of simple organic mixtures

VOC-mixture	
Aromatics	toluene
	xylene
	trimethylbenzene
Alkenes	ethene
	propene
	trans-2-butene
Alkanes/aldehydes	PAR
	formaldehyde
	acetaldehyde

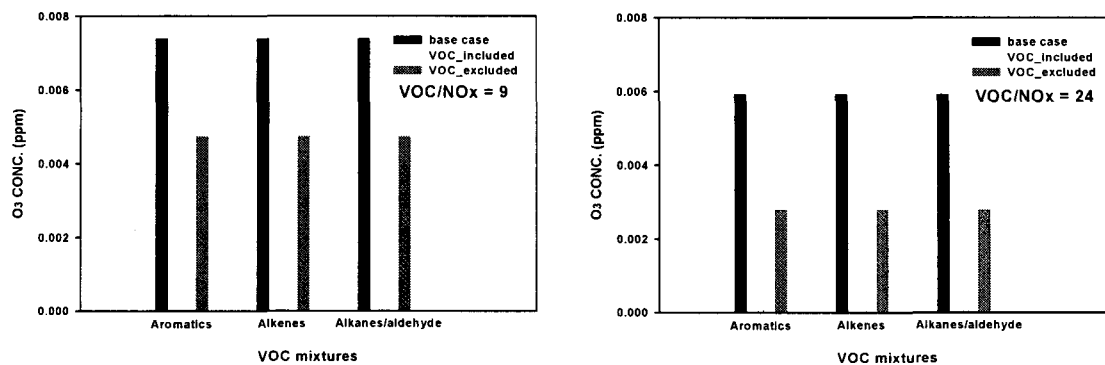


Fig. 4. Comparison of maximum O₃ concentrations for the simple organic mixture runs.

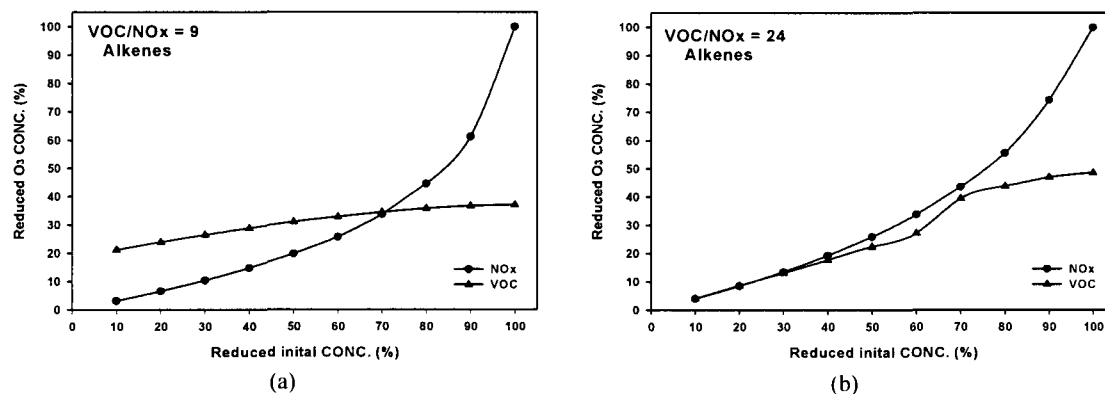


Fig. 5. Calculated maximum O₃ concentration reduction rate as a function of reduction rates for Alkene mixture.

4. Discussion

In this study, simulations of two groups were conducted to investigate the sensitivity of ozone to controlling initial concentrations: VOC/NO_x ratio and VOC composition.

The results obtained in these simulations can provide judicial standards for NO_x-sensitive and VOC-sensitive analysis: 1) high VOC/NO_x ratios correspond to NO_x-sensitive chemistry and low VOC/NO_x ratios correspond to VOC-sensitive chemistry; 2) urban areas are VOC-sensitive and rural areas are NO_x-sensitive; 3) Among the VOC compositions, the alkene mixture is the most potent influence on ozone production.

This sensitive regime can be applied to ozone-decrease scenarios if and when simulations of the same conditions are well conducted in a three-dimensional CBM4. Using the sensitive regime may decrease ozone concentrations when the VOC/NO_x ratio of emission and the VOC composition of the subject area are known.

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