

DEVELOPING CHEMICAL MECHANISMS THAT ARE MORE ROBUST TO CHANGES IN ATMOSPHERIC COMPOSITION

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1. INTRODUCTION

Gas-phase chemical mechanisms widely used for 3-dimensional (3-D) air quality modeling are primarily designed to model O₃ formation from typical urban ambient volatile organic compounds (VOCs) mixtures. In these chemical mechanisms such as the SAPRC (Carter, 1990, 2000, 2010a,b,c; Hutzell et al, 2012) and Carbon Bond (CB; Gery et al, 1989; Yarwood et al., 2005, 2010; Whitten et al, 2010) chemical mechanisms, highly condensed reactions of a limited number of model species are used to represent the atmospheric reactions of many different reactive VOCs by using assumptions on the average air compositions of major VOC classes (e.g., alkenes) or major carbon bond types (e.g., terminal C=C bonds). However, atmospheric composition is not constant and temporally and spatially changes. As a result, certain compounds may warrant more attention for some areas than for other areas, and certain compounds may need more attention due to changes in emissions over time. However, using more detailed and larger chemical mechanisms does not guarantee significantly better model predictions (e.g., predicted O₃ concentrations) than relatively compact chemical mechanisms while demanding more resources such as more computer memory, disk storage, and computational time. In this study, we will present a practical and scientifically reasonable approach to developing chemical mechanisms that are more robust to temporal and spatial changes in atmospheric composition.

2. IMPORTANCE OF CHEMICAL COMPOSITION

Chemical mechanisms for use in air quality models such as the Community Multiscale Air Quality (CMAQ; <http://www.cmaq-model.org/>) modeling system and the Comprehensive Air Quality Model with Extensions (CAMx; <http://www.camx.com>) are developed for use under various atmospheric conditions. Therefore, those chemical mechanisms need to represent the atmospheric reactions of numerous chemical compounds emitted from various emission sources so that their air quality impacts can be assessed. In general, different compounds react differently, which results in different impact on ozone formation. The maximum incremental reactivity scale (MIR; Carter, 1994, 2010a) is an example of quantifying ozone impacts to effectively control emissions to reduce ozone. Therefore, in regard to developing chemical mechanisms, atmospheric composition data are useful for judging which compounds need more attention than other compounds.

Preparation of model-ready emissions data involves two different speciation processes: one is mechanism-independent and the other is mechanism-dependent (Fig. 1). To speciate emissions, first, emission speciation profiles are used to map total VOC emissions or "total organic gases (TOG)" emissions into specific compounds (e.g., ethene and propene). SPECIATE (U.S. EPA, 2011) is one of best resources for these speciation profiles. Then, these compounds are represented in terms of model species of a chemical mechanism chosen for the air quality modeling. Note that this second step is mechanism-dependent. A chemical speciation database managed by Carter is a useful resource for mapping chemical compounds into model species (Carter, 2011). These two steps are combined into one step for chemical speciation in emission processing systems such as the Sparse Matrix Operator Kernel Emissions (SMOKE, <http://www.smoke-model.org/>) by using GSPRO files that are used to directly map emissions into model species. SMOKE's GSPRO files are

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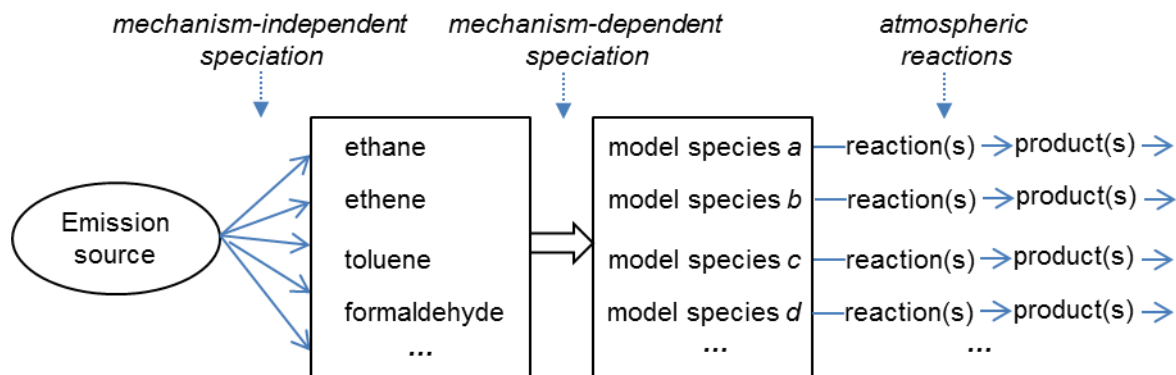


Fig. 1. Schematic representation of speciating emissions and representing atmospheric reactions of model species used for compounds emitted from the emission source.

mechanism-dependent and are prepared by a pre-processor to SMOKE called the Speciation Tool.

Inaccuracy in the chemical composition data used to generate speciation profiles (e.g., those available in SPECIATE) and errors in applying mapping rules used for preparing model-ready emissions (Fig. 1) will be translated into inaccurate or inconsistent model results. For example, in profiles 8750 and 8751 of SPECIATE version 4.3 (U.S. EPA, 2011) that are used to speciate exhaust emissions from gasoline fueled light-duty vehicles, the mass fractions for 3-methyl-1-butene are about 6%, and the mass fractions for isopentane are about 0.2%, which is inconsistent with results of many previous tunnel and ambient studies (e.g., Conner et al, 1995; Millet et al, 2005; Warneke et al, 2007; Harley, 2009) and needs further investigation. Active communication among researchers in the fields of emissions, chemical mechanisms and air quality modeling needs to be maintained to improve the accuracy and transparency of mapping emissions into model species which is necessary to prepare model-ready emissions data for air quality modeling.

3. IMPLICATIONS OF CHANGES IN ATMOSPHERIC COMPOSITION

Atmospheric composition can be influenced by changes in fuels, technologies and emission standards over time. Therefore, chemical mechanisms need to address changes in emissions that will be translated into changes in atmospheric composition. Atmospheric composition can be non-negligibly different at different locations due to differences in emission activities. For example, the air composition in the greater Houston area in southeast Texas is influenced by emissions from petrochemical

facilities and is often markedly different from that of the typical composition in most urban areas (e.g., see Table 3 of Heo et al (2010)). Industrial emissions can influence air quality in areas where industrial sources such as refineries, chemical plants and oil and gas production facilities are concentrated.

The fact that atmospheric composition can be non-negligibly changed over time and can be much different at different locations has multiple implications on developing chemical mechanisms for air quality applications. First, mechanisms that determine lumping by assuming a typical average atmospheric composition (e.g., SAPRC) could use a broader range of atmospheric chemical composition. Second, the number of separately represented compounds (e.g., ethene and isoprene in SAPRC and CB) can be selectively increased to limit the inaccuracy in model results due to lumping with other compounds. For example, when the reactivity is dominated by a few reactive compounds, the reactions of those compounds can be much better represented by using their own model species than by using lumped model species (Heo et al, 2010 and 2012). Third, information on optimum size of chemical mechanisms for use in 3-D modeling needs to be obtained because using a larger chemical mechanism does not guarantee more accurate model predictions but results in extra burdens such as requiring more computational resources for preparing emissions data and model simulations. Fourth, additional mechanism evaluation data are needed to develop chemical mechanisms that are more robust to changes in atmospheric composition caused by changes in emissions. More detailed chemical mechanisms use a larger number of reaction parameters that need to be based on well-established basic

laboratory data, reliable theoretical data or environmental chamber data produced under well-controlled and atmospherically-relevant experimental conditions.

4. PROPOSED APPROACH TO DEVELOPING CHEMICAL MECHANISMS

In this section, we will propose an approach to developing chemical mechanisms whose ozone predictions are relatively more robust to changes in atmospheric composition.

4.1 Examining the Relative Importance of Different Compounds

“Which compounds deserve relatively more detailed representation in a chemical mechanism?” is a complicated question because atmospheric composition temporally and spatially changes and the relative importance of different compounds is also variable. However, atmospheric abundance and reactivity can be used in ranking compounds. Speciated ambient VOC measurements are useful for this, and emission inventories evaluated against ambient measurements and speciation profiles such as those of SPECIATE (U.S. EPA, 2011) are also valuable to judging which compounds need more attention. Kinetic and mechanistic information (e.g., IUPAC, 2012; NASA/JPL, 2012) should be useful in ranking the relative importance of different compounds as well; relevant reactivity scales such as the MIR scale (Carter, 1994, 2010a) can be also useful.

In assessing the relative importance of compounds emitted from emission sources, the variability of emissions needs to be considered. For example, industrial alkene emissions in southeast Texas tend to be highly variable in emission strength and timing (Webster et al, 2007). For regions with emission sources that are highly variable enough to significantly increase atmospheric reactivity, major components of such emissions may need to be treated as relatively important compounds.

4.2 Representing Relatively Important Compounds

The reactions of relatively important compounds can be best described by representing those compounds explicitly by their own model species; e.g., using ETHENE in SAPRC-07 (Carter, 2010a) and ETH in CB05 (Yarwood et al,

2005) for ethene, one of major contributors to ozone formation in most urban areas. The reaction products can be represented by explicit model species (e.g., HCHO in SAPRC-07 for formaldehyde) or lumped model species (e.g., RCHO in SAPRC-07 for C3+ aldehydes). For example, adding just one additional species to explicitly represent propene and using the reactions of that explicit model species resulted in ozone predictions that were more robust to changes in the propene concentration (Heo et al., 2010, 2012). Note that the toxics version of SAPRC-07, SAPRC-07T (Hutzell et al, 2012), uses model species to explicitly represent propene, 1,3-butadiene, alpha-pinene, toluene, *o/p/m*-xylene, 1,2,4-trimethylbenzene and ethanol as well as ethene, isoprene, benzene and acetylene that are explicitly represented in the standard condensed version of SAPRC-07 (Carter, 2010c).

4.3 Representing Less Important Compounds

Lumped model species can be used to represent multiple compounds whose atmospheric reactions are kinetically and mechanistically similar to each other. Lumped model species can be used to represent numerous compounds (i.e., various alkanes) that are emitted in a relatively small amount and/or have low reactivity; this approach is better than just disregarding the reactions of those numerous minor compounds. The reactions of relatively less important compounds can be represented by using these lumped model species so that the size of the chemical mechanism can be constrained and suitable for use in 3-D models.

4.4 Evaluating Mechanisms with Experimental Data

Chemical mechanisms developed for use in 3-D air quality models need to perform well under targeted atmospheric conditions. However, evaluating chemical mechanisms under ambient conditions by carrying out 3-D air quality modeling is confounded by other factors such as emissions and meteorology. Uncertainties and errors in emissions and meteorology data can mislead modelers in evaluating the performance of a chemical mechanism. Therefore, evaluating chemical mechanisms with experimental data before incorporation into 3-D models is a useful approach to evaluating chemical mechanisms

while focusing on chemistry and minimizing the impact of uncertainties in emissions and meteorology.

Environmental chamber data produced under well-characterized and well-controlled conditions can be useful in evaluating mechanisms (Dodge, 2000; Carter et al, 2005). Chamber experiments for mechanism evaluation should be carried out by using atmospherically relevant experimental conditions whenever possible. Emission controls have lowered NO_x (NO and NO₂) concentrations in most areas in the U.S. Therefore, as noted by Carter et al (2005), chamber experimental data produced by using lower initial NO_x concentrations than previously used need to be expanded, particularly for evaluating mechanisms for aromatics such as toluene and ethylbenzene (Carter et al, 2005; Carter, 2010a, Whitten et al, 2010).

Detailed field measurement data can be useful to evaluate mechanisms with constrained box modeling, and can also be used to challenge assumptions that are used during mechanism development but are not fully tested by evaluation using environmental chamber data. Rigorous mechanism evaluation using experimental data will contribute to producing evidence of the credibility of chemical mechanisms used in air quality models.

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