Evaluating Complexity in Fire Emissions Modeling: Is More Better?

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ABSTRACT

Hundreds of Tg of gaseous non-methane organic compounds (NMOCs) are emitted globally to the atmosphere from biomass burning (BB). Estimates of NMOC emissions from these sources are highly uncertain, posing challenges to quantifying the effects of BB on air quality and climate. In this work, NMOC data obtained during the Fourth Fire Lab at Missoula Experiment were used to create an updated emissions speciation profile for coniferous canopy. These emissions were used as inputs to a modified box-model version of the gas-phase chemical mechanism MOZART-4; concentrations of gas-phase air pollutants and their precursors were predicted using the updated speciation profile and a default speciation profile. The updated speciation profile had a markedly different surrogate compound distribution than the default speciation profile. The sensitivity of modeled precursor and pollutant concentrations to these differences in the emission speciation profiles was evaluated using the box model. The box model results suggest that the differences in emitted compound distribution are likely to affect predictions of particulate matter and important gas-phase species including formaldehyde, acetaldehyde and methacryloyl peroxy nitrate (MPAN) in chemical transport models.

INTRODUCTION

Biomass burning (BB) – including wildfires, agricultural burning and prescribed fires – emits high levels of particulate matter (PM) and reactive trace gases to the atmosphere, thereby affecting air quality and climate. These reactive trace gases include a large number of non-methane organic compounds (NMOCs), many of which react photochemically to form ozone

(O_3) and secondary PM during plume evolution (Crutzen and Andreae, 1990). Model simulations of BB-derived O_3 and PM are characterized by significant uncertainties (e.g., Alvarado and Prinn, 2009; Heald et al., 2011; Alvarado et al., 2014; Amnuaylojaroen et al., 2014; Fiore et al., 2014). Model uncertainties are due in part to limitations associated with model inputs, including emissions. Due to chemical diversity and complexity, identification and quantification of the gaseous NMOCs emitted from fires has been incomplete (Akagi et al., 2011). In laboratory and field studies of BB emissions over the past few decades, 30-80% of the total NMOC mass remained uncharacterized or unidentified. Thus, models used to simulate fire emissions and plume chemistry have allocated total NMOC based on very limited chemical characterization of the emitted compounds.

Advances in analytical techniques have recently enabled improved identification and quantification of NMOC species in fire emissions. For example, during the Fourth Fire Lab at Missoula Experiment (FLAME-IV) the application of two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC-TOFMS) led to the identification and quantification of 708 compounds in BB emissions (Hatch et al., 2015); the application of proton-transfer-reaction time-of-flight mass spectrometry (PTR-TOFMS) and open-path Fourier transform infrared spectroscopy (OP-FTIR) led to an unprecedented identification of 80-96% of detected NMOC mass (Stockwell et al., 2015). In this work, the data from FLAME-IV were used to develop an updated NMOC speciation profile for coniferous canopy. A modified box model version of the MOZART-4 gas-phase chemical mechanism was then used to simulate concentrations of gas-phase species (e.g., peroxyacylnitrates (PAN), ozone (O_3), and secondary organic aerosol (SOA) precursors); the effects of incorporating enhanced knowledge of NMOC speciation were evaluated.

Although appropriate representation of emitted NMOCs in models is critical for the accurate prediction of downwind air quality (e.g., O_3 and SOA formation), the explicit simulation of hundreds of NMOCs is not possible in chemical transport models. Individual NMOCs therefore are mapped to a condensed number of surrogate species particular to a given gas-phase chemical mechanism; information on the chemical identities and properties of individual NMOCs is necessarily lost. Thus, in this work, an assessment of the process of mapping individual NMOCs to the surrogate compounds was performed, in addition to evaluating the changes in modeled pollutant and precursor concentrations as a function of changes in the identities and quantities of NMOCs emitted from coniferous fuels. Future work will focus on evaluating model skill in predicting BB-derived pollutants and precursors due to improved characterization of NMOCs with development of alternative lumping/mapping schemes and speciation profiles.

METHODS

Development of Speciation Profiles

NMOCs were measured during the FLAME-IV field campaign for a wide range of relevant fuels (Stockwell et al., 2014). Emission factors (EFs) for the identified NMOC species were calculated using the carbon mass balance method (Yokelson et al., 1999; Stockwell et al., 2014). A complete list of identified compounds and their respective EFs was developed for coniferous fuels using combined PTR-TOFMS, OP-FTIR and GC×GC-TOFMS data. The coniferous canopy average EFs reported in Stockwell et al. (2015) served as the starting point. EFs for compounds whose chemical formula was identified by GC×GC-TOFMS (Hatch et al., 2015) and

not by PTR-TOFMS/OP-FTIR were added to the total list of identified and quantified NMOC species, taking the average of EFs from black spruce and ponderosa pine burns. The final list of NMOC species and their respective EFs is considerably more complex than past results (e.g., (Andreae and Merlet, 2001); (Akagi et al., 2011); there are 344 compounds in the new compilation, compared to 99 reported by (Akagi et al., 2011).

Each of the individual compounds in the updated EF list were lumped into one of 34 MOZART-4 surrogate species (including a surrogate for compounds to be ignored in the chemical modeling) based on the following: 1) estimated OH reactivity, and 2) oxidation product distribution (Manion et al. 2013, IUPAC Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr/). This mapping to surrogates and the resulting speciation profile allow the explicit chemical species identified during FLAME-IV to be modeled using a simplified chemical mechanism. The updated speciation profile was compared with a speciation profile developed using a more limited data set (Wiedinmyer et al., 2011).

Box Modeling
To test the sensitivity of modeled chemistry to the changes in NMOC emissions (as represented by surrogates), a chemical box model was applied. The model simulates a mixed planetary boundary layer (PBL) with chemical species and reactions defined by an updated MOZART-4 mechanism. The box model is described in detail by Knote et al. (2014); in this work, the model set up and inputs, including initial and boundary conditions, were as described in Knote et al. (see Tables 2 and 3). Entrainment of air is enabled as the PBL grows in the model. The sensitivity of the modeled output to varying concentrations of NO and NO_2 in the initial and boundary conditions was tested (ppb NO/ppb NO_2: low NOx, 0.01/0.1; intermediate NOx, 0.1/1; and high NOx, 1/10). The results shown here are for a summer, cloud-free day at a latitude of 40 degrees north.

Constant emissions were emitted to the box during the model simulations. Emissions of the lumped MOZART-4 surrogates were calculated assuming a total NMOC emission factor of 41 g/kg (the sum of NMOC EFs from the composite EF list described above) and a biomass consumption rate of 39 Mg/ha (based on (Campbell et al., 2007). EFs for other species (CO, HONO, NH_3, NO, NO_2 and SO_2) were based on measurements from FLAME-IV (Stockwell et al., 2014; 2015).

Several model simulations were performed: DEFAULT (using the prior speciation profile for NMOC emissions from Wiedinmyer et al., 2011) and UPDATED (using the speciation profile for NMOC emissions developed in this work). The emissions of all compounds, including total NMOC, were constant for all simulations; only the speciation of the NMOC species was varied. The simulations were run for seven model days; however, the model reaches steady-state after 48 hours of simulation time (<5% change in modeled concentrations). Therefore, only the results of the first three days of each simulation are shown.

RESULTS

The inclusion of the newly identified and quantified NMOCs markedly changes the speciation profiles, as shown in Figure 1. In panels a and b, each of the 29 MOZART-4 surrogate species is represented by a colored wedge; only the top 5 (by mole fraction) are labeled. The offset wedges indicate a surrogate species with >3 carbon atoms (>C3 aldehdydes, alkanes and alkenes; benzene; toluene; xylene; monoterpenes; isoprene; methyl ethyl ketone; methacrolein, phenol, xylol, and cresol). The updated profile (Fig. 1b) has a higher percentage of >C3 compounds, particularly >C3 alkenes ("BIGENE") and lumped monoterpenes; the updated speciation profile also has a higher percentage of acetylene and a significantly lower percentage of hydroxyacetone. It is expected that such changes in the NMOC distribution (as represented by the MOZART-4 surrogates), would result in changes in chemical production rates and concentrations of compounds of interest from an air quality and climate perspective. This may be better evidenced by the results in panels c and d. Panels c and d illustrate the relative mass fractions of those surrogates that are likely SOA precursors in the default (Fig. 1c) versus updated (Fig. 1d) profiles. In the

Figure 1. Speciation profile for coniferous fuels: a) default, b) updated, c) default-likely SOA precursors, and d) updated-likely SOA precursors. In panels a and b, surrogate compounds are represented as percentages of total speciation profile; in panels c and d, surrogate compounds are represented as moles of species per area fire burned and pie charts are scaled to illustrate relative mass amounts.

MOZART-4 chemical transport model benzene, toluene, xylene, monoterpenes, and isoprene serve as SOA precursors. While the >C3 alkanes and alkenes do not serve as SOA precursors in MOZART-4, 5% (by EF) of the >C3 alkane and 15% (by EF) of the >C3 alkene surrogates have carbon numbers > 10 and are thus likely to form SOA (e.g., Ziemann 2011). The updated profile has a factor of ~3 greater total mass allocated to likely SOA precursors.

Modeled concentrations of O_3, formaldehyde, and a lumped terpene oxidation product (TERPROD) are shown in Figure 2 for the default versus updated speciation profiles. The concentration of O_3 (Fig. 2a) changes relatively little; the updated speciation profile produces an up to 9 ppb or 10% increase in O_3 at the highest NOx conditions. Concentrations of O_3 and

hydroxyl radical (not shown) are much more sensitive to the concentrations of NO/NO$_2$ used as initial/boundary conditions, as expected. Other modeling studies (e.g, (Carlton and Baker, 2011) have shown the relative insensitivity of modeled O$_3$ to changes in NMOCs. Other reaction products that have important atmospheric chemistry implications were more sensitive to the NMOC emissions input. For example, concentrations of acetaldehyde (not shown) and formaldehyde (Fig. 2b) increase by up to 180% and up to 50%, respectively, with the updated speciation profile in the intermediate NOx case. Products of terpenes, such as methacryloyl peroxy nitrate (MPAN), a primary product of isoprene oxidation (not shown) and TERPROD, a lumped product of monoterpene oxidation (Fig. 1c),

Figure 2. BOXMOX results for: a) ozone, b) formaldehyde, and c) a lumped terpene oxidation product.

exhibited factor of 15 (MPAN) and factor of 10 (TERPROD) increases. These increases are due to the increased allocations of total NMOC emissions to isoprene and lumped monoterpenes: six times more of each in the updated versus default simulations.

CONCLUSIONS AND IMPLICATIONS

This study represents an effort to: 1) highlight the advances in the identification and quantification of gaseous NMOC species in BB emissions, and 2) test the sensitivity of a widely-used gas-phase chemical mechanism to changes in the resultant NMOC speciation profile. The updated emissions measurements result in an allocation of more mass to oxygenated surrogates and terpenes than past summaries of coniferous fuel. There is a modest increase in simulated O$_3$ production using the updated NMOC speciation profile (high NOx conditions); a process analysis model is recommended to further evaluate whether competing influences are "buffering" changes in O$_3$ in the box model. The updated NMOC speciation profile leads to significant increases in important gas-phase compounds including acetaldehyde and formaldehyde. Further, with the updated speciation profile, the box model produced higher SOA precursor concentrations and representative oxidation products, which likely would lead to an increase in modeled SOA production in BB plumes. The results of this study highlight the

potential for further BB emissions characterization studies, with concerted model development efforts, to improve the accuracy of BB predictions using simplified mechanisms. Future efforts will include sensitivity analysis and validation using regional and global chemical transport models; such efforts will help determine the level of detail required in BB emissions inventories to achieve the desired level of accuracy in predictive models.

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