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Identification of chemical fingerprints in long-range transport of burning induced upper tropospheric ozone from Colorado to the North Atlantic Ocean

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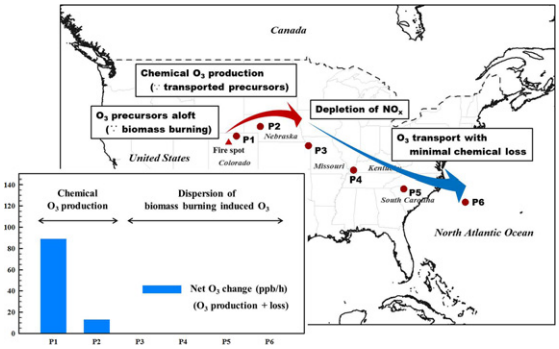
HIGHLIGHTS

- Identifying the behavior of biomass burning induced O_3 in the upper troposphere
- Evaluating the modeled upper tropospheric O_3 using aircraft measurement
- Investigating the primary sources for HO_x in the biomass burning plumes
- Clarifying the key drivers, sources, and sinks for biomass burning induced O_3
- Analyzing the O_3 sensitivity to NO_x and VOCs in the biomass burning plumes

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates a significant biomass burning (BB) event occurred in Colorado of the United States in 2012 using the Community Multi-scale Air Quality (CMAQ) model. The simulation reasonably reproduced the significantly high upper tropospheric O_3 concentrations (up to 145 ppb) caused by BB emissions. We find the BB-induced O_3 was primarily affected by chemical reactions and dispersion during its transport. In the early period of transport, high NO_x and VOCs emissions caused O_3 production due to reactions with the peroxide and hydroxyl radicals, HO_2 and OH. Here, NO_x played a key role in O_3 formation in the BB plume. The results indicated that HO_2 in the BB plume primarily came from formaldehyde ($HCHO + hv = 2HO_2 + CO$), a secondary alkoxy radical ($ROR = HO_2$). CO played an important role in the production of recycled HO_2 ($OH + CO = HO_2$) because of its abundance in the BB plume. The chemically produced HO_2 was largely converted to OH by the reactions with NO ($HO_2 + NO = OH + NO_2$) from BB emissions. This is in contrast to the surface, where HO_2 and OH are strongly affected by VOC and HONO, respectively. In the late stages of transport, the O_3 concentration was primarily controlled by dispersion. It stayed longer in the upper troposphere compared to the surface due to sustained depletion of NO_x. Sensitivity analysis results support that O_3 in the BB plume is significantly more sensitive to NO_x than VOCs.

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1. Introduction

The chemical ozone (O_3) production and loss at surface level are determined by the complex interplay between ambient nitrogen oxides (NO_x), volatile organic compounds (VOCs), and HO_x ($HO_2 + OH$) concentrations (Jeon et al., 2012, 2014; Lal et al., 2000; Lin et al., 1988; Seinfeld and Pandis, 2006). Unlike the surface, O_3 in the upper atmosphere can be affected by stratosphere-troposphere exchange (Lelieveld and Dentener, 2000), NO_x from lightning and aircraft emissions (Cooper et al., 2006; Grewe et al., 2001; Liu et al., 1980) and convectively lifted O_3 and its precursors from surface (Cooper et al., 2007). It sometimes shows significant enhancement resulting from Biomass Burning (BB) emissions transported aloft during a severe wildfire event (Cooper et al., 2006; Val Martin et al., 2006). Typical BB plumes sometimes reach the upper troposphere, and pyro-convective fire plumes can reach the stratosphere (Field et al., 2016). These plumes can result in the chemical production and/or loss of O_3 due to the presence of NO_x ($NO + NO_2$) and VOCs which are O_3 precursors. Several aircraft measurement-based studies have reported the composition of BB emissions and ratios of pollutant concentrations (e.g., $\Delta O_3/\Delta CO$, $\Delta NO_x/\Delta CO$) in the BB plumes (Akagi et al., 2013; Alvarado et al., 2010b; Liu et al., 2016). However, the characteristics of O_3 chemistry in the moving BB plume have rarely been reported in previous studies due to lack of measurements.

The Deep Convective Clouds and Chemistry (DC3) field campaign was conducted during 15 May–30 June 2012 using aircraft platforms and ground-based observations and happened to capture the High Park fire (Barth et al., 2015). The severe wildfire occurred in Fort Collins, Colorado of the United States (US) (Fig. 1), lasted between 8 June–1 July 2012 and burned 259 homes and 35,323 ha (Apel et al., 2015; Coen and Schroeder, 2015; Val Martin et al., 2013). During the campaign, clear BB signatures such as high CO and black carbon (BC) concentrations were coincidentally observed by two aircraft during 22–23 June 2012. The aircraft measurements also recorded significant enhancements in concentrations of O_3, NO_x, and VOCs due to the wildfire. The field campaign data is useful for analyzing O_3 chemistry in the BB plume but covers very limited areas and time periods. Modeling-based analysis can mitigate this drawback adding more information over larger length and time scales, but an accurate simulation of a BB event can be challenging due to uncertainties in fire emissions and plume rise height. To our knowledge, no previous studies have shown reasonable modeling results for the High Park fire event.

Here, we intend to reproduce this fire episode using the Community Multi-scale Air Quality (CMAQ) model (Byun and Schere, 2006) and investigate the O_3 chemistry in the upper troposphere associated with BB emissions during the event. We first evaluate the modeling results based on the aircraft measurements and conduct quantitative analysis on the characteristics of BB-induced O_3. Next, we report the chemical changes of O_3 in the transporting BB plume and their difference with respect to surface O_3 chemistry, illustrating the differences in O_3 chemistry drivers between the surface and aloft.

2. Material and methods

2.1. The modeling system

The CMAQ (v5.0.2) model was used to simulate the High Park fire event occurring in Colorado, US in June 2012. As shown in Fig. 1, the modeling domain was configured with a grid resolution of 12 km (459 × 299) covering the continental US with 33 vertical layers extending from the surface to 100 hPa. The CB05 and AERO6 modules were used for gas and aerosol phase chemistry mechanisms, respectively. Initial and boundary conditions were provided by a GEOS-Chem (v10-01) (Bey et al., 2001) simulation. Anthropogenic emissions were provided by the US Environmental Protection Agency (USEPA)'s National Emission Inventory of 2011 (NEI-2011) processed by the Sparse Matrix Operator Kernel Emissions (SMOKE, v3.6) model (Houyoux et al., 2000). Biogenic emissions were estimated by the Biogenic Emission Inventory System (BEIS, v3.14) (Pouliot and Pierce, 2009). Meteorological inputs were provided by the Weather Research and Forecast (WRF, v3.7) model (Skamarock et al., 2008). The North American Regional Reanalysis (NARR) data of the National Centers for Environmental Prediction (NCEP), which have spatial and temporal resolutions of 32 km and 3 h respectively, were used to determine the initial and boundary conditions for the WRF simulation. Grid analysis nudging technique (Jeon et al., 2015; Liu et al., 2012) was applied to enhance the model

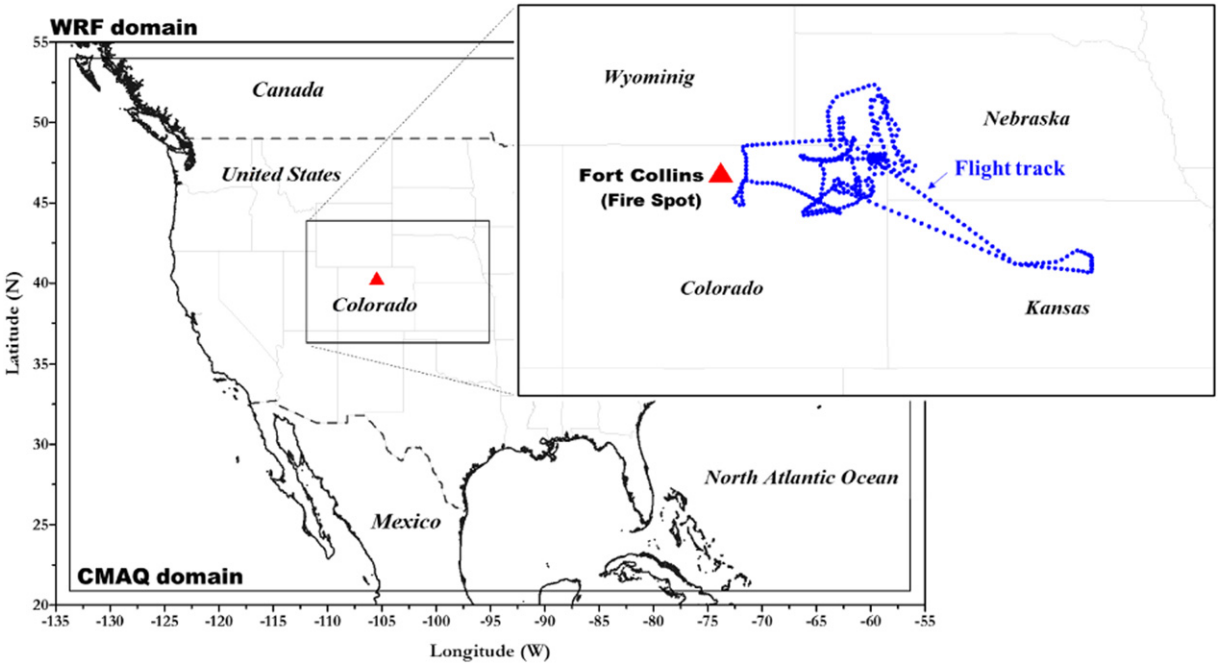

Fig. 1. Modeling domain for the WRF and CMAQ simulations. The red triangle denotes the location of the fire spot. The blue dots represent the flight track of DC-8 aircraft.