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A process-analysis based study of the ozone weekend effect

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ABSTRACT

We have used the 3D photochemical model CMAQ to simulate the ozone weekend effect, a phenomenon in which urban areas can have higher ozone concentrations on weekends than on weekdays even though NO_x emissions are usually lower on weekends. A simulation containing a weekend is compared to hypothetical simulations in which the anthropogenic emissions for the weekend have been replaced by weekday emissions. The simulations are identical in all other respects. Process analysis is used to explain the results. We find that the weekend effect can be decomposed into an ozone titration component and an odd oxygen component, each contributing about half of the excess weekend ozone. The titration component simply requires that there be lower weekend NO_x emissions. The odd oxygen component additionally requires that on weekends there be a higher rate of OH + (VOC or CO) reactions, brought about by one or more of lower nitric acid formation, higher OH formation from O_3 photolysis, and higher VOC emissions. This causes higher weekend peroxy radical formation. The odd oxygen component also requires sufficiently high NO concentration even on the lower-NO_x weekends to propagate this higher rate of peroxy formation back to higher weekend OH formation.

1. Introduction

Urbanized regions have been observed to have higher ozone concentrations on weekends than on weekdays, a phenomenon known as the ozone weekend effect. Since the NO_x emissions that lead to ozone formation are usually lower on weekends this appears counter-intuitive. However, the chemistry of ozone production is complicated, ultimately depending on a combination of the concentration and time profiles of ozone precursors (NO_x and VOCs), their relative ratios, solar UV intensity, water vapor concentration, and meteorological conditions. The weekend effect was first observed in the 1970s (Cleveland et al., 1974; Lebron, 1975) and since then in many parts of the US and world. The statistical significance of the effect using a variety of statistical methods and surface ozone observations has been evaluated for all California (Marr and Harley, 2002a), for the California South Coast Air Basin (Blanchard and Tanenbaum, 2003), and for several (non-California) cities around the US (Pun et al., 2003). A recent study near Sacramento (Murphy et al., 2007) studies an urban plume as it advects downstream. The weekend effect has also been investigated with photochemical modeling (Marr and Harley, 2002b; Yarwood et al., 2008), and a combination of the modeling and observations (Fujita et al., 2003). A review by Heuss et al., 2003 discusses the magnitudes, geographical locations where it is observed, and possible causes of the weekend ozone effect. Several hypotheses have been proposed to explain the weekend effect: reductions in the mass of emitted NO_x, changes in the timing of NO_x emissions; carryover of O_3 from the previous day; increases in VOC emissions on weekends; and increases in photolysis rates due to weekend decreases in soot emissions. Most studies of this issue conclude that

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Notation

CMAQ	Community Multiscale Air Quality (model)
CCOS	Central California Ozone Study
Δ or Δ_{ED}	indicates weekend minus weekday difference of a quantity
HO_x	sum of OH and HO_2
IRR	integrated reaction rate
MM5	Mesoscale Meteorological model version 5
NO_x	nitrogen oxides, defined as the sum of NO and NO_2
O_x	odd oxygen, defined as the sum of O_3 and NO_2
ppm	parts per million by volume
ppb	parts per billion (10^9) by volume
PA	process analysis
SAPRC99	Statewide Air Pollution Research Center chemical mechanism (1999 version)
VOC	volatile organic compound
[X]	concentration of species X

reduction in the mass of emitted NO_x on weekends is the dominant cause of the ozone weekend effect (Marr and Harley, 2002a; Heuss et al., 2003; Jimenez et al., 2005). In this study, we use process analysis to explore this hypothesis further and focus on analyzing chemical pathways to improve our understanding of the underlying reasons for the weekend effect.

In this study the weekend effect is examined using a 3-D photochemical air quality model, CMAQ v4.5 (Byun and Schere, 2006). We compare results from a multi-day simulation that includes a complete weekend to two hypothetical cases in which the emissions of the two weekend days are replaced by weekday emissions. Process analysis is used to understand differences between species concentrations and chemical integrated reaction rates (IRRs) in the simulations, partitioning the weekend effect into its most influential components to provide an indication of their relative importance.

Section 2 contains a description of the details of model setup and emissions for the two simulations, and an overview of process analysis. Section 3 contains simulation results showing a weekend effect, followed by a review of odd oxygen production chemistry, and a quantitative analysis of weekday–weekend differences in the chemistry. Discussion and conclusions are presented in Section 4.

2. Methods

2.1. Modeling system

Model simulations use CMAQ version 4.5 with the SAPRC99 gas-phase chemical mechanism (Carter, 2000). The mechanism includes a total of 72 species and >200 reactions. VOC species are either represented explicitly or lumped into one of several alkane, olefin, aromatic and other organic classes. The modeling domain over Central California is shown in Fig. 1. The authors have applied CMAQ to this domain previously, as described with more simulation details and measures of the model performance in Harley et al. (2006), and Steiner et al. (2006); we present only a brief summary. The horizontal extent of the study domain is 384 km east to west, and 468 km north to south, with a horizontal grid resolution of 4 km. The vertical extent is from the surface to approximately 16 km above sea level (100 mbar pressure). Meteorological fields were developed by Bao et al. (2006) using the MM5 meteorological model. Boundary conditions are taken from the literature, as reported by Jin et al. (2008).

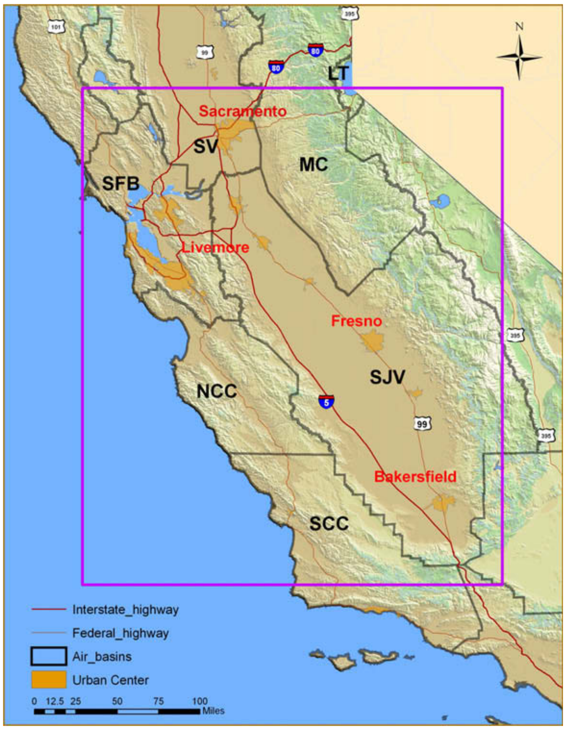

Fig. 1. Central California modeling domain used in this study.

Emissions are classified as area, point, biogenic and motor vehicle. With the exception of biogenics, typical weekday vs. weekend emissions are different. For example the motor vehicle emission inventory represents four distinct traffic activity patterns: weekday (Monday–Thursday), Friday, Saturday, and Sunday. Friday emissions differ from the other weekdays due to increased traffic and a broader afternoon peak traffic period. Motor vehicle emission timings are shifted on weekends due to the absence of morning commuter traffic, but still indicate a substantial amount of activity (Harley et al., 2005). Diesel truck traffic and associated NO_x emissions decrease significantly on weekends. The area and point source inventories also exhibit differences between weekday and weekend emissions but do not draw distinctions between Fridays and other weekdays, or between Saturdays and Sundays. Biogenic emissions, which are temperature and light sensitive, are determined by applying the meteorology of the actual day to a seasonally adjusted estimate of leaf cover. Hence there are day-to-day differences in our biogenic inventory but no specific weekday–weekend differences.