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Summertime weekly cycles of observed and modeled NO_x and O_3 concentrations as a function of land use type and ozone production sensitivity over the Continental United States

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Abstract

Simulation results from the Community Multiscale Air Quality (CMAQ) model version 4.7.1 over the Conterminous United States (CONUS) for August 2009 are analyzed to evaluate how satellite-derived O_3 sensitivity regimes capture weekly cycles of the U.S. EPA's Air Quality System (AQS) observed ground-level concentrations of ozone (O_3). AQS stations are classified according to a geographically-based land use designation or an O_3-NO_x-VOC chemical sensitivity regime. Land use designations are derived from the Advanced Very High Resolution Radiometer (AVHRR) global land cover characteristic data representing three features: urban regions, forest regions, and other regions. The O_3 chemical regimes (NO_x-saturated, mixed, and NO_x-sensitive) are inferred from low to high values of photochemical indicators based on the ratio of the HCHO to NO_2 column density from the Global Ozone Monitoring Experiment 2 (GOME-2) and CMAQ. Both AQS-observed weekly cycles of NO_x at measurement sites over AVHRR geographical regions and GOME-2 sensitivity regimes show high NO_x on weekdays and low NO_x on weekends. However, the AQS-observed O_3 weekly cycle at sites over the GOME-2 NO_x-saturated regime is noticeably different from that over the AVHRR urban region. Whereas the high weekend O_3 anomaly is clearly shown at sites over the GOME-2 NO_x-saturated regime in both AQS and CMAQ, the weekend effect is not captured at other sites over the AVHRR urban region. In addition, the weekend effect from AQS is more clearly discernible at sites above the GOME-2 NO_x-saturated regime than at other sites above the CMAQ NO_x-saturated regime. This study suggests that chemical classifications of GOME-2 chemical regime stations produces better results for weekly O_3 cycles than either the CMAQ chemical or AVHRR geographical classifications.

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1 Introduction

Photochemical ozone (O_3) production near the earth's surface depends on the chemical environment, which is heavily influenced by the ratio of volatile organic compounds (VOCs) to nitrogen oxide ($NO_x = NO + NO_2$) emissions. While biogenic sources (trees, grassland, water, and soil) are primarily responsible for VOC emissions in many parts of the country, man-made sources contribute the majority of NO_x emissions in the United States (US). According to the US Environmental Protection Agency (US EPA), anthropogenic NO_x emissions in the US are estimated to be 21.2 Tg per year (as in 2002), with 38 % from on-road vehicles, 22 % from electric generation power plants, 22 % from off-road equipment, 11 % from commercial fuel combustion, and the rest from industrial processes and miscellaneous sources. Because of the dominance of mobile sources, NO_x emissions demonstrate a clear daily and weekly pattern related to temporal variations in the human use of fossil fuels. Therefore, an investigation of the daily or weekly variations of surface O_3 concentrations could illuminate the controlling effects of the key precursors of O_3 concentrations. Previous studies have focused on daily or weekly O_3 variations over several metropolitan areas, including New Jersey, Southern California, Los Angeles, Atlanta, Chicago, Denver, New York City, Dallas, Houston, Phoenix, Washington, DC, Baltimore, and their neighboring regions (e.g., Lebron, 1967; Cleveland et al., 1974; Elkus and Wilson, 1977; Vukovich, 2000; Marr and Harley, 2002; Fujita et al., 2003; Qin et al., 2004; Blanchard and Tanenbaum, 2006; Shutters and Balling Jr., 2006; Blanchard et al., 2008; Yarwood et al., 2008). These studies have highlighted the weekend effect on urban regions, where higher ground-level O_3 concentrations occur during the weekends rather than weekdays. However, the peaks of their precursors show an opposite trend: The higher urban region O_3 concentrations during the weekends are attributed to lower surface NO_x emissions in a NO_x-saturated environment.

The relationship between the weekly cycles of NO_x concentrations and emissions has been investigated utilizing remote sensing NO_2 column density products. For

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example, Beirle et al. (2003) and Kaynak et al. (2009) examined the weekly cycle of the NO_2 column density using retrieval products from the Global Ozone Monitoring Experiment (GOME) and the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY), respectively, and found that temporal variations of the NO_x column density are proportional to those of the amount of NO_x emissions. In particular, Beirle et al. (2003) revealed lower GOME NO_2 column density on weekends and higher column density on weekdays over the US, European countries, Japan, and South Korea. Similarly, Kaynak et al. (2009) found relatively large SCIAMACHY NO_2 columns on weekdays and a significantly lower column density on weekends over polluted regions. However, no such large reduction has been found in rural areas. A strong correlation was also observed between the Ozone Monitoring Instrument (OMI)-derived surface NO_2 measurements and ground-based NO_2 measurements at the US Air Quality System (AQS) and Environment Canada's National Air Pollution Surveillance (NAPS) networks in polluted areas (Lamsal et al., 2008).

In addition to characterizing the weekly cycles of NO_x emissions, estimating a photochemical indicator, which is the ratio of VOCs to NO_x emissions, is crucial to a more thorough understanding of photochemical O_3 production because the photochemical environment strongly influences production. Sillman et al. (1990) and Sillman (1999) introduced a photochemical indicator that uses the ratios of certain chemical species to represent the O_3-NO_x-VOC sensitivity of a particular geographical area. Recently, Martin et al. (2004) and Duncan et al. (2010) utilized the ratio of satellite HCHO to the NO_2 column density from GOME (spatial resolution, 40 km × 320 km) and OMI (spatial resolution, 13 km × 24 km) as a photochemical indicator, which is consistent with the ratio of VOCs to NO_x emissions over the surface. Martin et al. (2004) used the GOME-derived indicator to characterize geographic regions (e.g., North America, Europe, and East Asia) as chemical regimes (NO_x-saturated and NO_x-sensitive regime). Using increased OMI-derived indicator, Duncan et al. (2010) found that most US cities had become more NO_x-sensitive regimes from 2005 to 2007.

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In this study, to investigate the difference between the weekly cycles of surface O_3 concentrations at EPA AQS stations over geographical regions and chemical regimes, we divide the 12 km CMAQ model grids covering the CONUS into two different types of satellite-derived classifications: the AVHRR-derived US Geological Survey Land Use Land Cover (USGS LULC) regions (referred to as "AVHRR regions", which consist of urban regions, forest regions, and other regions, Loveland et al., 2000) and GOME-2-derived chemical regimes (referred to as "GOME-2 chemical regimes", which are NO_x-saturated, NO_x-sensitive, and mixed regimes, Duncan et al., 2010). Furthermore, this study introduces CMAQ-derived chemical regimes (referred to as "CMAQ chemical regimes") to investigate the differences of weekly cycles of surface O_3 concentrations at AQS stations between the GOME-2 and CMAQ chemical regimes. In Sect. 2, we describe which measurement data are used for this study. Then, in Sect. 3, we provide a description of the CMAQ 4.7.1 model and in Sect. 4, a brief description of the methods used to define geographical regions and two different GOME-2- and CMAQ-derived chemical regimes. In addition, we investigate the variations in both the AQS-observed and CMAQ-simulated weekly cycles of daytime (01:00–05:00 p.m., local time) surface NO_x and O_3 concentrations at corresponding sites over AVHRR geographical regions and GOME-2 chemical regimes for August 2009 and the weekly cycles of NO_x and O_3 over GOME-2- and CMAQ-derived chemical regimes. Section 5 concludes and discusses the findings of this study.

2 Measurements

2.1 EPA Air Quality System (AQS) O_3 and NO_x

Hourly surface O_3 and NO_x concentrations are obtained from EPA AQS measurement networks (http://www.epa.gov/ttn/airs/airsaqs/detaileddata/downloadaqsdata.htm). The hourly-archived O_3 data from about 1100 measurement sites are utilized and mapped onto 12 km CMAQ model grid cells. The total number of CMAQ grids, including

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AQS O_3 measurement sites, is 874 (AVHRR urban region: 67 grid-cells, other region: 535 grid-cells, forest region: 272 grid-cells), 897 (GOME-2 HCHO/NO_2 < 1, GOME-2 NO_x-saturated regime: 58 grid-cells, 1 < GOME-2 HCHO/NO_2 < 2, mixed regime: 270 grid-cells, GOME-2 HCHO/NO_2 > 2, NO_x-sensitive regime: 569 grid-cells), and 875 (CMAQ HCHO/NO_2 < 1, CMAQ NO_x-saturated regime: 93 grid-cells, 1 < CMAQ HCHO/NO_2 < 2, mixed regime: 236 grid-cells, CMAQ HCHO/NO_2 > 2, NO_x-sensitive regime: 546 grid-cells). The hourly-archived NO_x data from 265 measurement sites are utilized and mapped onto 227 model grids (AVHRR urban: 41 grid-cells, other: 138 grid-cells, and forest: 48 grid-cells), 240 model grids (GOME-2 NO_x-saturated regime: 34 grid-cells, mixed regime: 90 grid-cells, NO_x-sensitive regime: 116 grid-cells), and 234 model grids (CMAQ NO_x-saturated regime: 55 grid-cells, mixed regime: 91 grid-cells, NO_x-sensitive regime: 88 grid-cells). The detection limit of surface O_3 and NO_x is 5 ppbv (J. Summers, personal communication from Choi et al., 2008). We filtered out some data for the study of the weekly cycles of surface NO_x and O_3 because the weather conditions during the period of the remnant low of Tropical Storm Ana affecting the US (17–19 August 2009) produced large uncertainties of its meteorological impact on O_3 chemistry.

2.2 AVHRR USGS LULC data and GOME-2 NO_2 and HCHO column data

USGS LULC data are taken from the Global Land Cover Characteristics Data Base Version 2.0. A detailed description of the data is provided at the site: http://edc2.usgs.gov/glcc/globdoc2_0.php. The 1 km resolution AVHRR-derived global land cover characteristic data from the National Center for Earth Resources Observation and Science at USGS, the University of Nebraska-Lincoln, and the Joint Research Center of the European Commission (Loverland et al., 2000) were used to provide 24 types of land use and land cover information (Anderson et al., 1976). For this study, over the CONUS, AVHRR USGS LULC data are grouped into three categories (urban region: 1, forest regions: 11–15, other regions: all the rest except urban regions, forest regions, and water bodies) and then mapped onto 12 km CMAQ model grid cells following Lambert

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conformal projection. A characteristic geographical region is determined based on the dominant land use class.

The remote sensing HCHO and NO_2 column densities are obtained from the retrieval products of the GOME-2 sensor, which is on board the EUMETSAT MetOp-A satellite. The instrument makes nadir measurements at 09:30 a.m. local time with the footprints of $40 \times 80\,km^2$. TM4NO_2A version 2.1 is used for GOME-2 NO_2 column density and TEMIS version 1.2 is for GOME-2 HCHO column density. The OMI products (01:40 p.m., local time) are thought to be more suitable for determining chemical regimes, but a midmorning time satellite instrument is used in this study as in the previous study by Martin et al. (2004), mainly because consistent dynamical random errors have appeared since January of 2009 in OMI product (http://www.knmi.nl/omi/research/science/) and OMI scientist teams keep working to consider these errors and preparing for a new product. The GOME-2 vertical NO_2 and the HCHO column density have a cell size of 0.25°, and some data are filtered out with cloud fraction >40 %. The details pertaining to the NO_2 retrieval algorithm using the DOAS approach and error analysis are provided by Boersma et al. (2004). The retrieval data used in this study are obtained from the European Space Agency (ESA) Tropospheric Emission Monitoring Internet Service (TEMIS) (http://www.temis.nl/airpollution/no2.html). A detailed description of the HCHO column product can be found in De Smedt et al. (2008), and the HCHO product is also from the TEMIS site (http://www.temis.nl/airpollution/ch2o.html).

2.3 Regional chemical transport model: CMAQ model version 4.7.1

CMAQ model version 4.7.1 (Foley et al., 2010) is based on the Carbon Bond 2005 (CB05) chemical mechanism, which includes aerosol components. The CMAQ model runs are setup with a horizontal resolution of 12 km with 22 vertical layers reaching from the surface to 100 hPa, derived by adapting a subset of the hybrid pure pressure and terrain-following σ-p coordinates of the Weather Research and Forecasting Non-hydrostatic Multi-scale Model dynamic core (WRF-NMM). The CMAQ vertical layer designation retains as much as one-to-one correspondence with that of the

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WRF-NMM in the lower troposphere, specifically in the planet boundary layer (Lee and Ngan, 2011). The CB05 (gas)-AQ (cloud)-AERO05 (aerosol) module in this model configuration considers O_3, PM, visibility, and acid deposition on the continental scale. The O_3 and $PM_{2.5}$ concentrations are driven by anthropogenic emissions based on the EPA National Emissions Inventory (NEI) for 2005. For Electric Generating Unit (EGU) point sources, Continuous Emission Monitoring 2007 is used to replace the 2005 NEI wherever applicable. Updated EGU emissions are further projected into 2009 using emission projection factors from the Department of Energy 2009 Annual Energy Outlook (AEO) report. All emissions that are independent from meteorological conditions are processed first using a modified version of the Sparse Matrix Operator Kernel Emission (SMOKE) model (Houyoux et al., 2000). The emission sectors that vary with meteorological conditions are simulated with various emission models in the PRE-processor to CMAQ (PREMAQ). In this study, monthly mean lateral boundary conditions derived from the GEOS-CHEM (Bey et al., 2001) global model simulation results are used for August 2009, in light of the findings of earlier CMAQ evaluations that emphasized the drawback of using the climatologically-averaged static boundary condition (e.g., Tong and Mauzerall, 2006; Tang et al., 2008).

3 Results

3.1 AVHRR geographical regions and GOME-2 and CMAQ chemical regimes

Previously, Kaynak et al. (2009) derived three geographical sites – urban, rural and rural-point (rural areas including large EGUs) – for their NO_x weekly cycle study. They chose seven urban sites using Census 2000, eleven rural sites far from both urban regions and large EGUs, and more than 100 rural-point sites. In this study, instead of selecting specific sites, we divide the entire CONUS domain into three AVHRR-based geographical regions – urban, forest, and other (Fig. 1) – to examine how surface O_3 concentrations vary at all the available EPA's AQS measurement sites over these geographical regions. Such a classification differs from that used in previous studies to

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characterize weekly cycles of O_3, including the weekend effect in several urban regions (e.g., Cleveland et al., 1974; Elkus and Wilson, 1977; Vukovich, 2000; Marr and Harley, 2002; Fujita et al., 2003; Lebron, 2004; Qin et al., 2004; Blanchard and Tanenbaum, 2006; Shutters and Balling Jr., 2006; Blanchard et al., 2008; Yarwood et al., 2008). In this study, all of the model grid cells and EPA AQS measurement stations are categorized using a dominant AVHRR land use type. The AVHRR urban regions, which represent cities and their surrounding areas, comprise the smallest portion of the three geographical regions. The AVHRR forest region is co-located with high canopy density, the data of which are obtained from http://edc2.usgs.gov/glcc/fao/forest_canopy_image.php (see Fig. 1).

Previous remote sensing studies (e.g., Martin et al., 2004; Duncan et al., 2010) characterized two or three different regimes, including the NO_x-saturated/NO_x-sensitive regime and the NO_x-saturated/mixed/NO_x-sensitive regime. In this study, as in studies by Martin et al. (2004) and Duncan et al. (2010), we first utilized the ratio of GOME-2 HCHO to the NO_2 column density to divide the CONUS into three chemical regimes by using O_3 sensitivity derived from the GOME-2 ratio. Figure 2 represents daytime (01:00–05:00 p.m., local time) surface O_3 differences between baseline CMAQ and CMAQ with a 30 % reduction of NO_x emissions (in red) and between CMAQ and CMAQ with a 30 % reduction in VOC emissions (in blue) in accordance with the ratio of GOME-2 or CMAQ HCHO to the NO_2 column density. No clear transitions take place among the NO_x-sensitive, mixed, and NO_x-saturated regimes, but the change in daytime surface O_3 is proportional to that in VOC emissions over a NO_x-saturated regime (for low HCHO/NO_2 ratio < 1), but surface O_3 is highly sensitive to the change in NO_x emissions over a NO_x-sensitive regime (for high HCHO/NO_2 ratio > 2). Over a mixed regime, some changes in surface O_3 are affected by those in VOC emissions, but more changes are affected by NO_x emissions changes (for ratios between 1 and 2). High O_3 sensitivity to changes in NO_x emissions was similarly shown as the ratio of HCHO to the NO_2 column density increased, as in previous studies by Martin et al. (2004) and Duncan et al. (2010). The CONUS domain is divided into three chemical

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regimes using two transitions (ratios are 1 and 2, see Fig. 2). The left panel of Fig. 3 identifies three regimes – NO_x-saturated, mixed, and NO_x-sensitive chemical regimes – using the transitions. This study further categorizes other chemical regimes using the ratios of CMAQ HCHO to the NO_2 column density (see the right panel of Fig. 3) to investigate how weekly cycles of NO_x and O_3 vary among the measurement stations of the GOME-2 and CMAQ chemical regimes of the CONUS.

Some data are filtered out when the NO_2 column density is less than 1×10^{15} molecules cm^{-2}, which is typical of regions in remote areas (Fig. 3). The distribution of two different chemical regimes derived by GOME-2 and CMAQ is generally consistent over the CONUS, but with clear differences over some areas (e.g., Houston, New Orleans, and Tampa, in Fig. 3). Thus, over such regions, another classification could introduce different surface O_3 sensitivity in model simulation. A zoomed-in regionalized study over the Southeastern US may highlight the differences among these chemical regime definitions. In addition, the NO_x-sensitive regimes (in red) from CMAQ are larger than those from GOME-2, implying higher surface O_3 sensitivity to changes in NO_x emissions in the model simulation.

3.2 Weekly variation of NO_x emissions

To understand the weekly cycle of the ground-level O_3 concentrations, we must evaluate the weekly variation of the emissions of O_3 precursor, NO_x. For the sake of consistency with the evaluation of the weekly O_3 cycle, only the daytime (01:00–05:00 p.m., local time) emissions inventory from CMAQ is used. The large weekday/weekend variations of NO_x emissions are shown at the EPA AQS stations over both the AVHRR regions and the GOME-2 regimes (Fig. 4). Over the urban regions and the NO_x-saturated regimes, the changes in weekday/weekend NO_x emissions are larger than those in other regions or regimes. From Friday to Saturday, NO_x emissions decrease by 29.4 %, 26.7 %, and 25.3 % over the urban, other, and forest regions, respectively. The reduction of NO_x emissions over the urban regions in this study is smaller than that of NO_x emissions (about 34 %) in the Los Angeles basin, estimated by Yarwood et

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al. (2008). Reductions are similarly estimated by 29.4 %, 26.6 %, and 26.4 % over NO_x-saturated, mixed, and NO_x-sensitive regimes, respectively. The greatest NO_x emissions are also shown on Friday over three AVHRR regions (7.76 $mols^{-1}$, 1.94 $mols^{-1}$, and 0.97 $mols^{-1}$) and GOME-2 regimes (5.25 $mols^{-1}$, 2.57 $mols^{-1}$, and 1.75 $mols^{-1}$). Thus, changes in the absolute amounts of NO_x emissions over the urban regions from weekdays to weekends are larger than those over NO_x-saturated regimes, but changes in NO_x emissions over other and forest regions are smaller than those over mixed and NO_x-sensitive regimes.

3.3 Weekly anomalies of AQS and CMAQ ground-level NO_x

We investigate weekly anomalies of ground-level AQS and CMAQ NO_x concentrations at EPA AQS stations over AVHRR geographical regions and GOME-2 chemical regimes. Only daytime (01:00–05:00 p.m., local time) observed and simulated NO_x concentrations are used. Weekly anomalies are estimated by subtracting averaged NO_x concentrations for each day from the average of all the available NO_x concentrations during the month over urban, forest, and mixed regions (see the two left columns of Fig. 5) or NO_x-saturated, mixed, and NO_x-sensitive regimes (see the two right columns of Fig. 5). The low weekend and high weekday NO_x are clearly shown at the stations located in all the AVHRR regions and GOME-2 regimes (Fig. 5).

Over urban regions and NO_x-saturated regimes, the AQS observation shows the smallest NO_x concentrations during weekends (on Sunday) and the largest NO_x concentrations during weekdays (on Thursday and Friday). The weekly pattern of NO_x concentrations over urban regions is similar to the weekly patterns of the NO_2 column density or the NO_2 mixing ratio in the previous studies (e.g., Beirle et al., 2003; Shutters and Balling Jr., 2006; Kaynak et al., 2009). In particular, Kaynak et al. (2009) showed the smallest NO_2 column density over urban regions on Sunday and the largest on Wednesday, Thursday, and Friday (e.g., Wednesday for Chicago; Thursday for Houston, Atlanta, New York, Phoenix; Friday for Los Angeles and Seattle). The CMAQ simulation shows a similar pattern for the smallest NO_x concentrations on Sunday and the

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largest on Thursday (over urban regions) or Wednesday (over NO_x-saturated regimes) instead of Friday, as in AQS. In general, the model simulated NO_x peaks occur one or two days earlier than the AQS-observed NO_x peaks. This shift in the highest NO_x day (Fig. 5) may contribute to the shift in the lowest O_3 day (Fig. 6), particularly at stations over urban regions or NO_x-saturated regimes because of relatively greater amount of NO_x emissions compared with other regions or regimes (Fig. 4). Details are described in the next section.

The weekly cycles of NO_x concentrations at AQS measurements sites over the AVHRR other region and GOME-2 mixed regimes in AQS are more or less similar to those in the AVHRR urban region and the GOME-2 NO_x-saturated regimes, respectively. CMAQ shows that the weekly cycle of NO_x concentrations at AQS sites over the AVHRR other region are similar to those over the AVHRR urban region. The simulated high-peak NO_x days (Tuesday–Thursday) over the NO_x-saturated regime shifted to late weekdays (Wednesday–Friday) over the mixed regime. In other words, whereas simulated weekly cycles of NO_x concentrations of urban and other regions are similar, simulated peak NO_x occurs two days later over mixed regimes than it does over NO_x-saturated regimes. Interestingly, the simulated NO_x cycle at AQS stations over mixed regimes is similar to the observed cycle at stations over NO_x-saturated regimes.

The AQS shows the largest NO_x concentration at stations over forest regions and NO_x-sensitive regimes on Friday, but CMAQ shows the largest NO_x concentrations in these areas on Thursday (Fig. 5). A study by Kaynak et al. (2009) also showed similar patterns of NO_2 column densities over their rural areas (large NO_2 column densities on Thursday and Friday and small column densities on Saturday and Sunday). The pattern of NO_x cycles at stations over the AVHRR forest regions in AQS and CMAQ is similar to that over the AVHRR other regions in AQS and CMAQ, respectively. Over forest regions and NO_x-sensitive regimes, the highest NO_x peak day occurs one day earlier in CMAQ (on Thursday) than in AQS (on Friday), which might be closely related to the one- or two-day shifts of low O_3 peak days during weekdays in CMAQ, compared to those in AQS.

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3.4 Weekly anomalies of AQS and CMAQ ground-level O_3

Weekly anomalies of ground-level O_3 concentrations from AQS and CMAQ are compared at the EPA AQS measurement stations over the AVHRR geographical regions and the GOME-2 chemical regimes. Weekly O_3 anomalies and weekly NO_x anomalies are estimated in the same way. Over urban regions, the largest observed ground-level O_3 concentrations occur on Tuesday, the same as those simulated by CMAQ (Fig. 6). The smallest O_3 concentrations occur on Friday in AQS, but on Thursday in CMAQ. The lowest O_3 days in AQS (on Friday) and CMAQ (on Thursday) correspond exactly to the highest NO_x days in the observation and the model, respectively. Blanchard et al. (2008) showed three different high O_3 peak days (on Sunday in Chicago, Dallas-Fort Worth, and Phoenix for all O_3 season days; on Tuesday in Chicago and Phoenix for high O_3 days; on Saturday in Dallas-Fort Worth for high O_3 days). From their study, over several urban sites for high O_3 days, the highest O_3 peak days, occur on Tuesday. From another study by Shutter and Balling Jr. (2006), high O_3 peak days in Phoenix occur on Sunday. Interestingly, in our study, the highest O_3 peak day over a NO_x-saturated regime is Sunday. The study by Blanchard et al. (2008) also showed various low peak days (on Monday in Chicago for high O_3 days; on Wednesday in Phoenix for all O_3 season days; on Thursday in Dallas-Fort Worth, Dallas-fort Worth , and Phoenix for high O_3 days; and on Friday in Chicago for all O_3 seasonal days). Our study shows that the lowest O_3 peak days occur on Friday (in AQS) and Thursday (in CMAQ) over both urban regions and NO_x-saturated regimes. A previous study by Blanchard et al. (2008) showed more diverse highest and lowest peak days than our study, likely resulting from the local characteristics of the measurement sites.

In general, previous studies clearly showed the weekend effect in several polluted areas (e.g., Cleveland et al., 1974; Elkus and Wilson, 1977; Vukovich, 2000; Marr and Harley, 2002; Fujita et al., 2003; Lebron, 2004; Qin et al., 2004; Shutter and Balling Jr., 2006; Yarwood et al., 2008), but this study did not show the weekend effect at AQS stations over the AVHRR urban regions in AQS nor in CMAQ. However, at other AQS

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sites over NO_x-saturated regimes, the weekend effect is clearly shown in both AQS and CMAQ, indicating a peak ground-level O_3 concentration on Sunday both in AQS and CMAQ. Both AQS and CMAQ also show the second highest peak on Monday. At AQS stations over NO_x-saturated regimes, AQS observations indicate the smallest O_3 on Friday, but the CMAQ simulation shows the smallest on Thursday (see Fig. 6). The difference between the observed and simulated lowest O_3 days is most likely the result of temporal variations of NO_x concentrations over the regime (see Fig. 5).

At AQS stations over the AVHRR other regions, the largest and smallest O_3 concentrations are shown on Wednesday and Sunday, respectively. The CMAQ model simulation results show the same highest and lowest O_3 days. Both AQS and CMAQ show negative anomalies on Saturday (Fig. 6), which are consistent with negative anomalies in NO_x concentrations (Fig. 5). At AQS sites over the mixed regime, both the AQS observation and the CMAQ simulation show the largest O_3 concentrations on Tuesday. The AQS observation shows the smallest O_3 concentrations on Sunday, but the CMAQ simulation shows the smallest on Thursday. The reason for negative anomalies on Thursday and Friday in CMAQ is not clear, but the AQS observation also shows similar negative anomalies on Friday and Saturday. The differences between the lowest O_3 days in AQS and those in CMAQ are likely associated with those over NO_x-saturated regimes. Similarly, low O_3 peak day occurs one day earlier in CMAQ (Thursday) than in AQS (Friday) during the weekdays. The transport of small O_3 concentrations over NO_x-saturated regimes might introduce small O_3 concentrations over its neighboring mixed regime. At AQS stations over forest regions, both AQS and CMAQ show the largest on Tuesday, but they show the smallest on Sunday or Thursday, respectively. At AQS stations over NO_x-sensitive regimes, both AQS and CMAQ show the largest O_3 concentrations on Tuesday, the second largest on Wednesday, and the smallest on Sunday.

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3.5 Weekly anomalies of NO_x and O_3 over the CMAQ chemical regimes

In this section, the effects of the difference between the GOME-2-derived chemical regimes and CMAQ-derived chemical regimes (see Fig. 3) on the weekly cycles of surface NO_x and O_3 concentrations are further investigated at the EPA AQS measurement stations. This study compares the weekly NO_x and O_3 cycles at the AQS stations over the two different NO_x-saturated regimes (from GOME-2 and CMAQ). The weekly cycles of NO_x at corresponding stations in AQS and CMAQ over two different chemical regimes (see the two right columns of Fig. 5 and the two left columns of Fig. 7) are generally similar. As we addressed in the previous section, the O_3 weekend effect in AQS and CMAQ (see the two right columns of Fig. 6) are clearly shown at AQS stations over the GOME-2 NO_x saturated regime, but high O_3 anomalies on Sunday and Monday are not obvious at the AQS stations over the CMAQ NO_x saturated regime in AQS (see the third column of Fig. 7). Interestingly, the pattern of weekly O_3 cycles over the CMAQ NO_x-saturated regime is similar to that over the AVHRR urban region (see the first column of Fig. 6). This finding indicates that CMAQ-derived NO_x-saturated regime stations might be characterized as urban region stations that, in reality, include some mixed regime stations or NO_x-sensitive regime stations. This finding further suggests that utilizing the GOME-2-derived photochemical indicator might define NO_x-saturated regime stations better than the CMAQ-derived photochemical indicator.

4 Conclusion and discussion

This study analyzes CMAQ-simulated weekly variations of O_3 and its precursors at EPA AQS stations over the AVHRR geographical regions and the GOME-2 chemical regimes of the CONUS for August 2009 and compares them to in-situ ground-level AQS observations. The CMAQ model generally captures the weekly cycles of ground-level NO_x and O_3 at AQS sites, except in some occasional shifts of high positive and negative anomalies during weekdays. Over AVHRR other and forest regions and GOME-2

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mixed and NO_x-sensitive regimes, both AQS and CMAQ show positive NO_x anomalies during weekdays and negative NO_x anomalies during weekends. Similarly, AQS and CMAQ show negative O_3 anomalies during weekends and positive O_3 anomalies during weekdays. However, AQS observations do not reveal any weekend effects (high O_3 weekly anomalies during weekends) at AQS stations over the AVHRR urban region, but they clearly show weekend high O_3 anomalies at other AQS stations over the GOME-2 NO_x-saturated regime, suggesting that characterizing the CONUS as GOME-2 chemical regimes is beneficial to analyzing weekly cycles (including the weekend effect). Over the AVHRR urban region and the GOME-2 NO_x-saturated regime, the greatest negative O_3 day differs slightly in AQS (on Friday) and CMAQ (on Thursday). The shift in the greatest negative O_3 anomaly day in CMAQ is likely to the result of the shift in the greatest positive NO_x day in the model, unlike those in AQS.

Furthermore, the weekly cycles of NO_x and O_3 over the two different chemical regimes from GOME-2 and CMAQ are analyzed and compared. A weekend effect is clear at AQS stations over the GOME-2-derived NO_x-saturated regime, but it is not at other AQS stations over the CMAQ-derived NO_x-saturated regime. After selecting a specific region of interest as a chemical regime using a satellite-derived photochemical indicator, we were able to compare observed O_3 weekly cycles with corresponding simulation results in order to evaluate model performance. Through the comparison, we could understand and even further forecast the highest and lowest O_3 anomaly days over the region.

The results of this research warrant future research that addresses several remaining issues. First, our definition of a "chemical regime" is loosely associated with satellite or land use-based characteristics. Besides inherent uncertainties from satellite retrievals and land use data, the categorization approach used to derive chemical regimes may not collocate with the actual chemical environment in the lower troposphere, where surface ozone is photochemically produced. The satellite HCHO and NO_2 columns represent the vertical accumulation of corresponding species from the ground to the top of the troposphere. The use of column data can be justified by the fact that the

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majority of emission sources of NO_x and VOCs originate at (mobile, area, and biogenic) or near (power plant sources, typically with chimney in the lower km) the earth's surface. Nevertheless, the potential impact of the vertical distribution of species, particularly those caused by the difference in chemical lifetime and emission source distribution, on the determination of a chemical regime must also be taken into account. Second, our study is also limited to one month (August 2009). It would be worthwhile to investigate how the chemical regime changes over space during other seasons/years. Both anthropogenic and biogenic emissions are expected to change from season to season/year to year in various directions, resulting in a so-called "seasonal transition" of the chemical regime (e.g., Jacob et al., 1996; Martin et al., 2004). While the static land use-based indicator may not capture such seasonal changes, a satellite- based dynamic indicator could more realistically reflect such a temporal evolution of the chemical environment on a similar order or the finer spatial resolution of CMAQ (12 km to 4 km), compared to the spatial resolution of remote sensing measurements.

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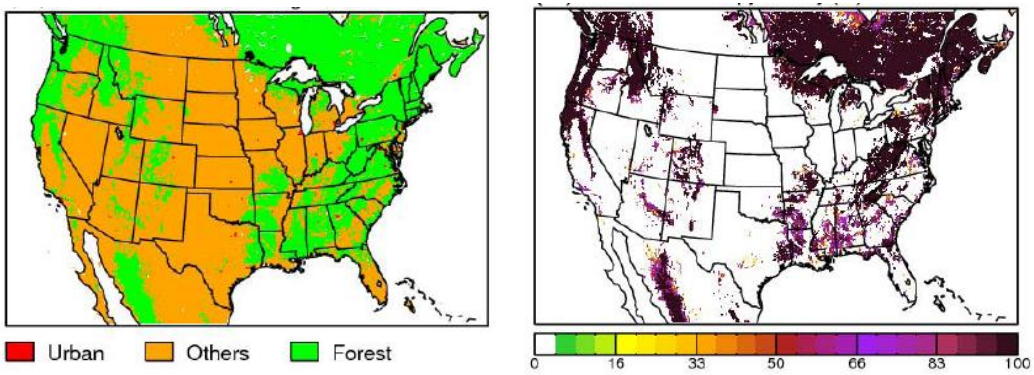

Fig. 1. Three AVHRR USGS LULC geographical regions (red: urban regions, including USGS LULC type 1; green: forest regions including USGS LULC types 11–15, and orange: other region including all the rest except urban region, forest region, and water bodies (Anderson et al., 1976; Loverland et al., 2000, left panel)) and canopy density mapped onto 12 km CMAQ model grids (the right panel, units in percentage, data are from http://edc2.usgs.gov/glcc/fao/forest_canopy_image.php).

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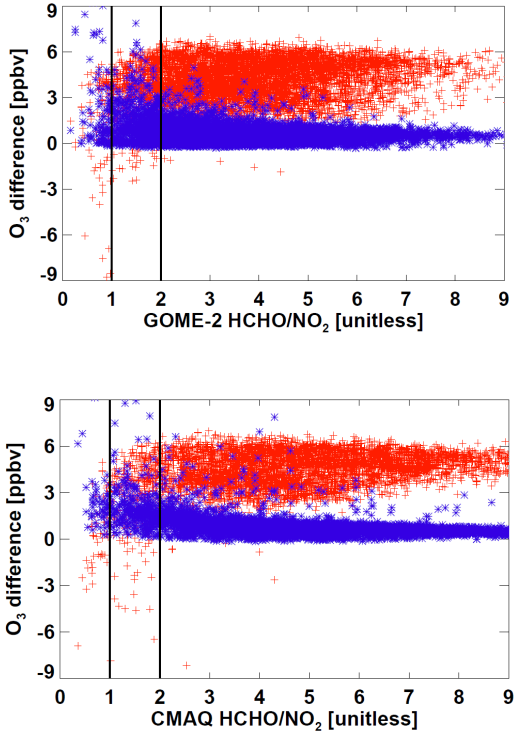

Fig. 2. Differences between the Surface O_3 in baseline CMAQ and CMAQ with 30 % NO_x (in red, baseline – NO_x sensitivity) or a reduction in VOC emissions (in blue, baseline – VOC sensitivity) in accordance with the ratios of the GOME-2 HCHO to NO_2 column density (upper panel) and the CMAQ HCHO to NO_2 column density (lower panel). The O_3 differences are estimated by averaging the data for daytime (01:00–05:00 p.m., local time) during August 2009 only when the GOME-2 NO_2 or CMAQ NO_2 column density is larger than 1.0×10^{15} molecules cm^{-2}. So that the trend can be more clearly observed, every five O_3 differences are averaged according to the GOME-2 or CMAQ ratios.

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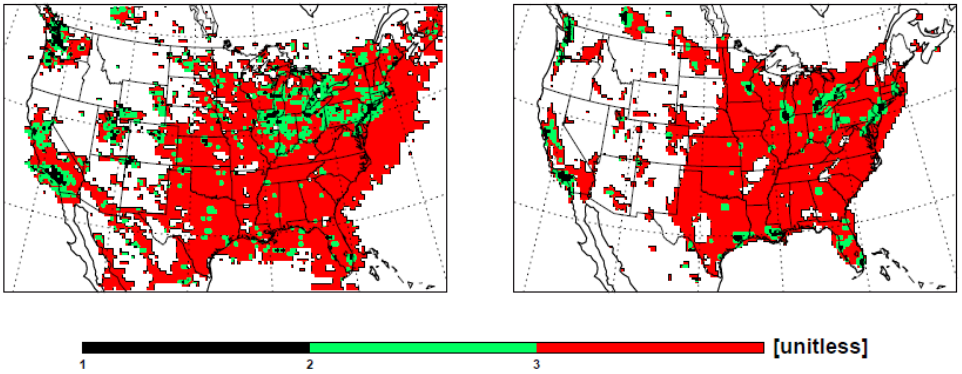

Fig. 3. Three GOME-2-derived and CMAQ-derived chemical regimes using two transitions (1 and 2, see Fig. 2) using the ratio of the GOME-2 HCHO to the NO_2 (left panel) and CMAQ HCHO to NO_2 column density (right panel). Black represents the category 1 region ($HCHO/NO_2 < 1$, a NO_x-saturated regime), green the category 2 region ($1 < HCHO/NO_2 < 2$, a mixed regime), and red the category 3 region ($HCHO/NO_2 > 2$, a NO_x-sensitive regime). The cell size (0.25°) of the GOME-2 HCHO and NO_2 column density data (from http://www.temis.nl/airpollution/) differs from that of CMAQ (12 km), and thus, both GOME-2 and CMAQ column density data are interpolated into 36 km for this comparison. Ratios are estimated only when the GOME-2 NO_2 column density is larger than 1.0×10^{15} molecules cm^{-2}.

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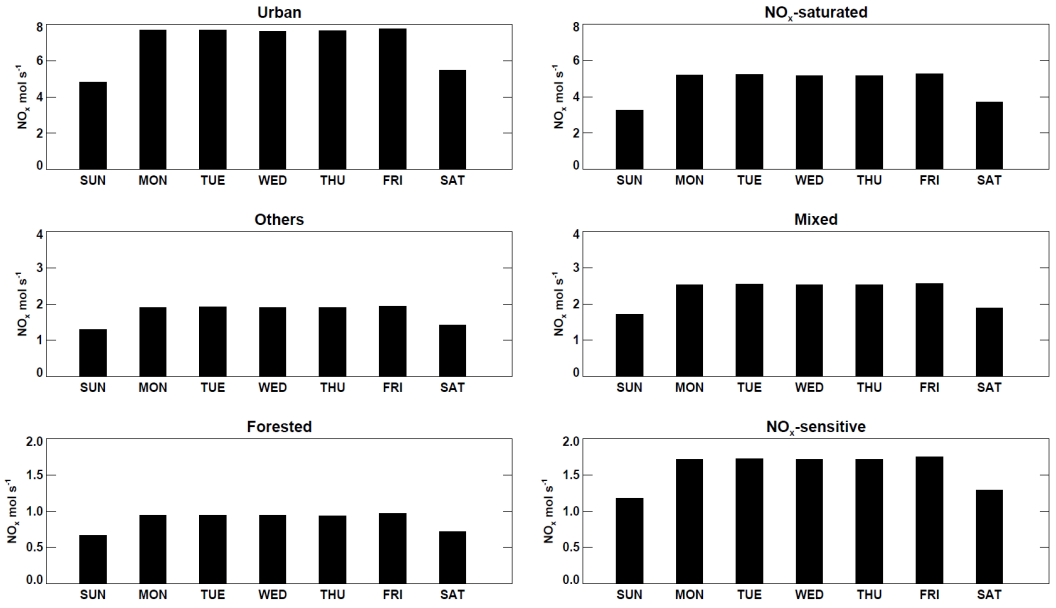

Fig. 4. Weekly variation in NO_x emissions at EPA AQS stations over three AVHRR-derived geographical regions (i.e., urban, other, and forest regions, left column) and GOME-2-derived chemical regimes (i.e., NO_x-saturated, mixed, and NO_x-sensitive regimes, right column) in CMAQ for August 2009. For the sake of consistency with the daytime O_3 comparison in Fig. 6, only daytime (01:00–05:00 p.m., local time) NO_x emissions are used; some data are filtered out during 17–19 August 2009, when Tropical Storm Ana strongly affected air quality over the eastern US.

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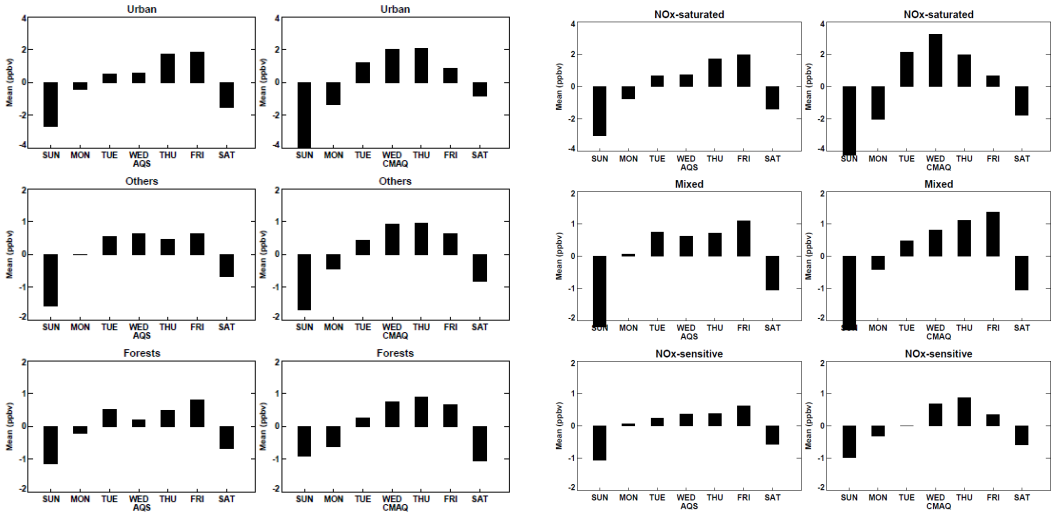

Fig. 5. Weekly anomalies of AQS-observed and CMAQ-simulated ground-level NO_x concentrations at EPA AQS stations over AVHRR-derived geographical regions (i.e., urban, other, and forest regions, left two columns) and GOME-2-derived chemical regimes (i.e., NO_x-saturated, mixed, NO_x-sensitive regimes, right two columns) for August 2009. For the sake of consistency with the daytime O_3 comparison in Fig. 6, only daytime (01:00–05:00 p.m., local time) NO_x concentrations are used; some data are filtered out during 17–19 August 2009, when Tropical Storm Ana strongly affected air quality over the eastern US.

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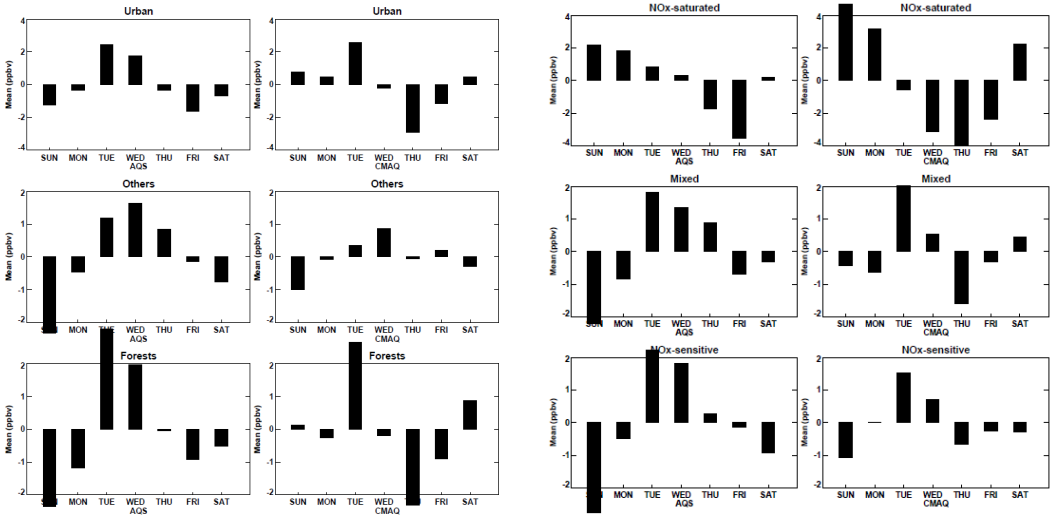

Fig. 6. The same as Fig. 5, but for ground-level O_3 concentrations.

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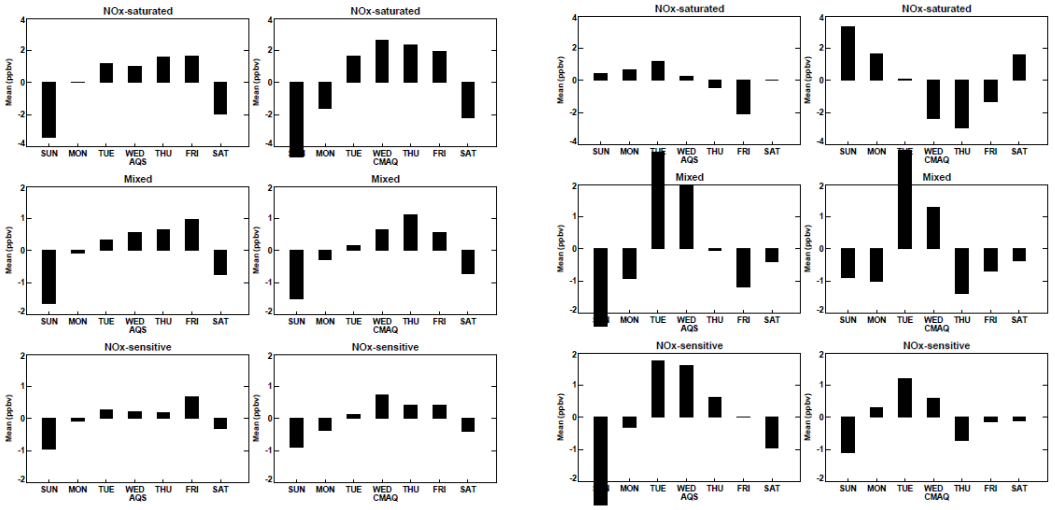

Fig. 7. Weekly anomalies of AQS-observed and CMAQ-simulated ground-level NO_x at EPA AQS NO_x stations (left two columns) and O_3 concentrations at EPA AQS O_3 stations (right two columns) over CMAQ-derived chemical regimes (i.e., NO_x-saturated, mixed, and NO_x-sensitive regimes, see the right panel of Fig. 3) for August 2009. Only daytime (01:00–05:00 p.m., local time) NO_x and O_3 concentrations are used; some data are filtered out during 17–19 August 2009, when Tropical Storm Ana strongly affected air quality over the eastern US.

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