

1 **Ozone trends over the United States at different times of day**

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9 **Abstract**

10 In the United States, the decline of summertime daytime peak ozone in the last 20 years has been
11 clearly connected to reductions in anthropogenic emissions. Yet questions remain on how and
12 through what mechanisms ozone at other times of day have changed over the recent decades.
13 Here we analyze the interannual variability and trends of ozone at different hours of day, using
14 observations from about 1000 US sites during 1990–2014. We find a clear diurnal cycle both in
15 the magnitude of ozone trends and in the relative importance of climate variability versus
16 anthropogenic emissions to ozone changes. Interannual climate variability has mainly been
17 associated with the de-trended fluctuation in the US annual daytime ozone over 1990–2014, with
18 a much smaller effect on the nighttime ozone. Reductions in anthropogenic emissions of nitrogen
19 oxides have led to substantial growth in the US annual average nighttime ozone due to reduced
20 ozone titration, while the summertime daytime ozone has declined. Environmental policymaking
21 might consider further improvements to reduce ozone levels at night and other non-peak hours.

22 **1. Introduction**

23 Tropospheric ozone is a potent pollutant damaging human and ecological health. The United
24 States Environmental Protection Agency (EPA) targets the maximum daily 8-hour average
25 (MDA8) ozone levels for regulation, with a current standard at 70 parts per billion (ppb). The
26 Global Burden of Disease assessment (Brauer et al., 2016;Lim et al., 2012;Forouzanfar et al.,
27 2015;Forouzanfar et al., 2016), however, estimates the threshold level (below which exposure to
28 ozone is not harmful) to be between 33.3 $\mu\text{g}/\text{m}^3$ and 41.9 $\mu\text{g}/\text{m}^3$ (between 15.5 ppb and 19.5 ppb).
29 Further, additional epidemiological evidence has shown that there is not a real threshold, and
30 ozone has adverse health effects at all concentrations (Bell et al., 2006;Peng et al., 2013;Yang et
31 al., 2012).

32 Chemically, surface ozone is produced in the sunshining daytime and destroyed mainly by
33 nitrogen oxides (NO_x) at night, with a transition between production and destruction in the dawn
34 and dusk hours. Understanding of ozone changes and drivers at different times of day might
35 provide additional information to assist further ozone mitigation policymaking beyond the MDA8

1 regulation. Previous observational and modeling studies have revealed important impacts of
2 varying climate conditions and anthropogenic precursor emissions on the near-surface daytime,
3 MDA8 or daily mean ozone over the United States (US) (Jacob and Winner, 2009; Fiore et al.,
4 2015). A particular finding for these studies is that the US emission reductions have decreased
5 the summertime daytime peak ozone over much of the United States (Cooper et al., 2012; Lefohn
6 et al., 2010; Simon et al., 2015; Strode et al., 2015).

7 In addition, most studies on the US ozone trends/variability tend to focus on ozone changes in a
8 particular season and/or over a particular region – for example, summertime ozone (Rieder et al.,
9 2015; Lu et al., 2016; Reddy and Pfister, 2016) over the eastern US (Zhang and Wang, 2016;
10 Rieder et al., 2015; Shen et al., 2015) or springtime ozone (Cooper et al., 2010) over the western
11 US (Lin et al., 2015). Lin et al. (2017) analyzed the various driving factors of the US MDA8
12 ozone trends by season and region, with no discussion on ozone at other hours.

13 Bloomer et al. (2010) analyzed the 1989–2007 changes in the diurnal cycle of ozone observed
14 from five stations over the eastern US. They showed ozone reductions at most times of day in the
15 warm seasons due to emission reductions, in contrast to the increases in winter. Jhun et al. (2015)
16 used a statistical model of ozone, nitrogen oxides and several meteorological parameters to
17 analyze the ozone trends over 1994–2010 measured at over 100 sites across the US. They linked
18 the observed reductions in nitrogen oxides to reductions in warm season peak ozone and to
19 enhancements in cold season peak ozone and warm season nighttime ozone. Overall, the
20 historical changes of ozone at night and other non-peak hours and their underlying climatic or
21 emission causes have been much less studied compared to those for peak ozone.

22 Here, with the usage of hourly data observed at about 1000 sites from the Air Quality System
23 (AQS) network, we contrasted the interannual variations of the daytime versus the nighttime US
24 ozone over 1990–2014, and also estimated the trends for ozone at the different hours of the day.
25 We further quantified the individual effects of interannual climate variability and anthropogenic
26 emissions on the ozone change, by using three climate indices and simulations of the chemical
27 transport model (CTM) GEOS-Chem. We focused on the large-scale features of annual mean US
28 averaged surface ozone and the impacts of broad changes in emissions and climate. We also
29 contrasted the ozone changes and drivers between the eastern and western US and between
30 different seasons, with complementary discussions for individual locations and land use types
31 (urban, suburban and rural).

32 The manuscript is structured as follows. Section 2 introduces the observation data, climate
33 indices, and GEOS-Chem simulations. Section 3 analyzes the linear trends for annual mean
34 hourly, daytime mean, nighttime mean and daily mean ozone. Section 4 compares the observed
35 ozone trends and interannual variability with three climate indices relevant to the US air quality.
36 Section 5 uses four GEOS-Chem simulations, with perturbed emissions and meteorological
37 inputs, to quantify the individual effects of climate variability and anthropogenic emissions.
38 Section 6 concludes the study.

1 **2. Data and Methods**

2 **2.1 Ozone measurements**

3 Hourly measurements of ground-level ozone over 1990–2014 are taken from about 1000 AQS
4 sites (http://aqsd1.epa.gov/aqsweb/aqstmp/airdata/download_files.html). For a given year, the
5 number of measurement sites vary from 825 to 1295 (see Fig. 1 for site distribution). The fraction
6 of hours in any year with missing data ranges from 21.3% to 28.5%. As indicated in Fig. 1, the
7 AQS network includes rural (42% of sites on average), suburban (40%) and urban (18%) sites,
8 based on the official site description document. We mapped the ozone measurements on a 2.5°
9 long. x 2° lat. grid to facilitate a comparison with GEOS-Chem simulations. For each hour, we
10 averaged all available data in a given grid cell. In order to contrast the daytime and nighttime
11 ozone changes and their underlying drivers, we calculated daily mean, daytime (07:00–19:00
12 local time) mean, and nighttime (19:00–07:00 local time) mean ozone mixing ratios from the
13 gridded hourly data. We averaged the daily data to produce monthly mean and then annual mean
14 values. We finally selected a total of 124 grid cells with annual average values available in all
15 years.

16 ***Robustness of data selection method***

17 To test the robustness of ozone trends results against the data/site selection method, we used four
18 alternate methods to choose sites, as follows.

19 The first alternate choice concerns the number of sites in a particular grid cell for geographical
20 representativeness, and it excludes 24 out of the default 124 grid cells that cover less than three
21 sites each.

22 The second choice concerns the temporal continuity of valid data at each site, and it only includes
23 sites with valid data in at least three years for every five years (1990–1994, 1995–1999, etc.) –
24 this leads to a total of 94 valid grid cells that cover 131 rural sites, 164 suburban sites, and 102
25 urban sites. The spatial distribution of ozone trends in these 94 grid cells is consistent with the
26 trends in the default 124 grid cells (not shown), although the (number and locations of) sites in
27 each common grid cell differ between the two site selection methods.

28 The third choice is much stricter, and it only selects 70 sites (24 rural sites, 27 suburban sites, and
29 19 urban sites) with valid hourly data in 75% or more of hours during 1990–2014.

30 The last choice is more complex, and is similar to the method adopted by Cooper et al (Cooper et
31 al., 2012). At a given site, if more than 50% of hourly data are missing in any daytime or
32 nighttime, then the particular day is discarded. If more than 50% of days in any season do not
33 contain valid data, then the particular season is discarded. For any season, there must be valid
34 seasonal mean data in at least 20 out of 25 years during 1990–2014, otherwise data in all years
35 for the particular season are discarded. These criteria lead to 82 sites with valid data, including 30

1 rural sites, 34 suburban sites, and 18 urban sites.

2 Table 1 shows that our default data selection method lead to ozone trends similar to the four
3 alternate methods, for the US mean ozone on an annual basis. Across the five methods, the
4 growth rates are about 0.14–0.17 ppb/yr for the US annual mean daily mean ozone, 0.06–0.09
5 ppb/yr for the daytime mean ozone, and 0.21–0.24 ppb/yr for the nighttime mean ozone.
6 Furthermore, the interannual variation of US annual ozone in our default case is highly correlated
7 to the other four cases, no matter whether the time series are de-trended ($R = 0.84$ – 0.95). We thus
8 conclude that our ozone trends and variability results are robust against our choice of sites/data.

9 **2.2 Climate indices**

10 We relate the interannual variability of ozone to two major climate indices relevant to the US air
11 quality (Sutton et al., 2007; Lin et al., 2015): the Atlantic Multi-decadal Oscillation (AMO;
12 <https://www.esrl.noaa.gov/psd/data/timeseries/AMO/>) index and the Oceanic Niño index (ONI;
13 http://origin.cpc.ncep.noaa.gov/products/analysis_monitoring/ensostuff/ONI_v5.php).

14 De-trended annual AMO index time series over 1990–2014 is calculated from the unsmoothed
15 Kaplan sea surface temperature (SST) dataset of the National Oceanic and Atmospheric
16 Administration (NOAA) Earth System Research Laboratory
17 (<http://www.esrl.noaa.gov/psd/data/correlation/amon.us.data>). Observational and model studies
18 have shown that the recent multi-decadal fluctuations in Atlantic SST were associated with
19 large-scale climate anomalies (Enfield et al., 2001; Johannessen et al., 2004; Hu et al., 2011;
20 Oglesby et al., 2012) important for the ozone chemistry. The warm conditions in the North
21 Atlantic Ocean (positive AMO) have been associated with increased air temperatures at northern
22 latitudes (by more than 3 °C locally especially in winter) (Johannessen et al., 2004) and reduced
23 summertime rainfall and increased droughts over much of the US (Enfield et al., 2001; McCabe
24 et al., 2004). Delworth and Mann (2000) showed evidence of AMO-related variations in sea level
25 pressure (SLP), and hence atmospheric circulation, in the North Atlantic region. Such
26 AMO-associated meteorological changes can alter the distribution of tropospheric constituents
27 (Olsen et al., 2016), including ozone (Shen et al., 2015; Lin et al., 2014). For example, warmer
28 temperature under a positive AMO phase tends to enhance the ozone production over the US (Lin
29 et al., 2014); less precipitation means less cloudy and higher radiation for photochemistry
30 (Kunkel et al., 2008); and the change in circulation affects the ozone transport (Fu et al., 2015).

31 De-trended annual ONI index time series over 1990–2014 is calculated from the NOAA Climate
32 Prediction Center dataset
33 (http://www.cpc.ncep.noaa.gov/products/analysis_monitoring/ensostuff/ensoyears.shtml). The ONI
34 index refers to ERSST.v4 SST anomalies in the Niño 3.4 region, as an indicator of the El
35 Niño-Southern Oscillation (ENSO). These SST anomalies are associated with global climate
36 variability, including changes in the temperature and precipitation patterns over the United States
37 (Ropelewski and Halpert, 1987; Yu et al., 2012; Yu and Zou, 2013; Liang et al., 2015), through

1 alterations in atmospheric circulations and teleconnection patterns (Bjerknes, 1969; Enfield,
2 1989). The Niño 3.4 index (referred as ONI here) has been widely used to examine the impact of
3 ENSO on surface ozone over the United States (e.g., Lin et al., 2015; Xu et al., 2017). Xu et al.
4 (2017) showed that over 1993–2013, the monthly ozone decreases (increases) during El Niño (La
5 Niña) years, with the amplitude varying from 0.4 ppb (for the US average) up to 1.8 ppb (for the
6 southeastern US) per standard deviation of the Niño 3.4 index. The La Niña years (strongly
7 negative ONI) tend to be associated with a more meandering jet over the central western US in
8 favor of stratosphere-troposphere exchange (STE) of ozone but not transport from Asia (Lin et al.,
9 2015).

10 In order to indicate the climate variability that influence the whole US, we combined the
11 de-trended and normalized AMO and ONI indices to obtain a third index, named AMONI:
12 $AMONI = AMO_{detrended_{normalized}} - ONI_{detrended_{normalized}}$. The normalization could adjust the AMO
13 and ONI values measured on different scales to a common scale and keep the individual
14 characteristics of the original AMO and ONI indices. The negative sign for ONI in the formula
15 accounts for the negative correlation between de-trended ozone and ONI anomalies (see Sect. 4).
16 Thus a positive AMO and a negative ONI, both of which are closely related to higher ozone
17 mixing ratios over the US, contribute to a positive AMONI index.

18 A recent work by Shen et al. (2017) developed two metrics, MAM- Δ SST and MAM- Δ SLP, to
19 study June-July-August (JJA) MDA8 ozone variability across much of the eastern US. They
20 found that MAM- Δ SST is highly correlated to the summer ozone ($R = \sim 0.7$), which level of
21 correlation is comparable to our results for daytime and daily mean ozone (see Sect. 4).

22 **2.3 Model simulations**

23 We used the global chemical transport model GEOS-Chem (version 9-02,
24 http://wiki.seas.harvard.edu/geos-chem/index.php/Main_Page) to simulate the US surface ozone
25 changes over 2004–2012. GEOS-Chem has been used extensively for ozone studies (e.g., Shen et
26 al., 2015;Fu et al., 2015;Yan et al., 2016;Zhang and Wang, 2016). Here, the model is run at a
27 horizontal resolution of 2.5 °long. x 2 °lat. with 47 vertical layers (including 10 layers of ~ 130 m
28 thickness each below 850 hPa), as driven by the GEOS-5 assimilated meteorological fields. The
29 model is run with the standard HO_x-NO_x-VOC-ozone-aerosol chemistry (Mao et al., 2013) with
30 some recent updates (Yan et al., 2014). The Linoz scheme is used for the stratospheric ozone
31 production (McLinden et al., 2000). Vertical mixing in the planetary boundary layer employs a
32 non-local scheme implemented by Lin and McElroy (2010). Model convection adopts the
33 Relaxed Arakawa-Schubert scheme (Rienecker et al., 2008).

34 A “Control” simulation includes variations in meteorology and anthropogenic emissions, and
35 three sensitivity simulations keep meteorology or anthropogenic emissions constant throughout
36 the years. As the GEOS-5 meteorological fields are only available from December 2003 to March
37 2013, all GEOS-Chem simulations are from December 2003 through December 2012, with

1 results analyzed for 2004–2012.

2 *Emissions in the “Control” simulation of GEOS-Chem*

3 Global and regional anthropogenic emission inventories used here are summarized in Yan et al.
4 (2016). Global anthropogenic emissions for CO and NO_x from 2004 to 2008 are taken from the
5 Emission Database for Global Atmospheric Research (EDGAR) v4.2 inventory. Global
6 anthropogenic emissions of NMVOC use the REanalysis of the TROpospheric chemical
7 composition (RETRO) monthly global inventory for 2000 (Hu et al., 2015). Emissions over China,
8 Asia, the US, Mexico, Canada and Europe are further replaced by the MEIC (base year is 2008;
9 www.meicmodel.org), INTEX-B (base year is 2006 (Zhang et al., 2009)), NEI05 (base year is
10 2005, <ftp://aftp.fsl.noaa.gov/divisions/taq/>), BRAVO (base year is 1999 (Kuhns et al., 2003)),
11 CAC (base year is 2005, http://www.ec.gc.ca/pdb/cac/cac_home_e.cfm), and EMEP (base year is
12 2005 (Auvray and Bey, 2005)) regional inventories, respectively. Emission data include monthly
13 or seasonal variability (Yan et al., 2016).

14 Most anthropogenic emission inventories provide data for a base year. In order to simulate the
15 interannual variability of ozone, we scaled NO_x and CO emissions from the base year to other
16 years between 2004 and 2012. Over the US, China and Canada, emissions of NO_x are scaled
17 based on the tropospheric NO₂ columns from OMI measurements (Lin et al., 2015;Vinken et al.,
18 2014). For the US (for CO), Canada (for CO), and Europe (for NO_x and CO), emissions are
19 scaled according to NEI (<http://www3.epa.gov/ttn/chief/trends/index.html>), Environment Canada
20 National Pollutant Release Inventory Trends (<http://www.ec.gc.ca/inrp-npri/>), and European
21 Monitoring and Evaluation Program (<http://www.emep.int/>). For regions not affected by the
22 above scaling processes, NO_x and CO emissions are scaled according to EDGAR (for 2004–
23 2008), or to changes in total and liquid fuel CO₂ emissions, respectively, following van
24 Donkelaar et al. (van Donkelaar et al., 2008) (for 2009–2012). CO₂ emissions are taken from the
25 Carbon Dioxide Information Analysis Center (<http://cdiac.ornl.gov/>).

26 Monthly biomass burning emissions are taken from the Global Fire Emissions Database version 3
27 (GFED3) (van der Werf et al., 2010). Other natural emissions (lightning NO_x, soil NO_x, and
28 biogenic NMVOC) are parameterized based on model meteorology. Lightning NO_x emissions are
29 parameterized based on cloud top heights (Price and Rind, 1992), and are further constrained by
30 the lightning flash counts detected from the satellite instruments (Murray et al., 2012;Murray et
31 al., 2013). Soil NO_x emissions follow Hudman et al. (2012). Biogenic emissions of NMVOC
32 follow the Model of Emissions of Gases and Aerosols from Nature (MEGAN v2.1) with the
33 Hybrid algorithm (Guenther, 2007;Guenther et al., 2012).

34 Figure 2 shows monthly anthropogenic and natural emissions of CO, NO_x, and NMVOC over the
35 United States from 2004 to 2012, as used in the “Control” simulation. Averaged over 2004–2012,
36 the US emissions (from all sources) are about 69.4 Tg/yr for CO, 6.6 TgN/yr for NO_x, and 34.0
37 TgC/yr for NMVOC. Anthropogenic emissions are the dominant source for CO, are comparable

1 to natural sources for NO_x, and are a minor source for NMVOC. Anthropogenic emissions of
2 NO_x and CO decline rapidly at rates of 0.25 TgN/yr (4.1%/yr relative to 2004) for NO_x and 2.7
3 Tg/yr (3.2%/yr) for CO. Natural emissions vary from one year to another with no obvious trends.

4 The “Control” simulation accounts the interannual variations in climate and anthropogenic
5 emissions of NO_x and CO. Between 2004 and 2012, anthropogenic emissions of NO_x and CO in
6 the US decline by 33% and 26%, respectively (Fig. 2a,b). As the US anthropogenic emissions of
7 NMVOC are smaller than natural emissions by a factor of about 7 (Fig. 2c), their reduction from
8 2004 to 2012 (by ~ 9%) is not included here. A sensitivity simulation suggests that including
9 changes in anthropogenic NMVOC emissions result in ozone changes from 2004 to 2012 very
10 close to the “Control” simulation (see Sect. 5.1).

11 **3. Observed ozone trends at different times of day**

12 The black line in Fig. 3 shows the 1990–2014 US average ozone trends at the individual hours of
13 the day (local standard time). At nighttime hours, the US annual mean ozone grows relatively
14 constantly at a statistically significant rate of about 0.2 ppb/yr. The growth rate declines in the
15 morning hours and increases during the late afternoon hours. The minimum growth rate is located
16 at around 14:00, when the ozone level peaks, and is slightly negative (but insignificant) with a
17 value of -0.01 ± 0.16 ppb/yr. The general characteristics of ozone trends are consistent with the
18 results of Jhun et al. (2015). The ozone trends for individual hours tend to weaken the diurnal
19 cycle of ozone – in particular, the diurnal range of ozone (i.e., maximum – minimum) is reduced
20 by 15% from 26.4 ppb in 1990–1994 to 22.4 ppb in 2010–2014. The contrasting ozone trends
21 between the daytime and the nighttime are indicative of distinctive causes. Hereafter we will
22 focus on trends and (de-trended) variability in the daytime mean, nighttime mean and daily mean
23 ozone, unless stated otherwise.

24 Table 2 shows the 1990–2014 trends for the US annual average daytime, nighttime and daily
25 mean ozone, and Fig. 4a shows their time series. The US annual average daily mean ozone grows
26 at a rate of 0.16 ppb/yr (P-value < 0.01 according to an F-test). The growth mainly reflects
27 enhanced nighttime mean ozone (at 0.21 ppb/yr, P-value < 0.01). The daytime mean ozone grows
28 at a much lower rate of 0.09 ppb/yr (P-value < 0.05). The implied total growth from 1990 to 2014
29 is about 4.1 ppb, 2.3 ppb and 5.3 ppb for daily mean, daytime and nighttime ozone, respectively.
30 Similar to the enhanced US annual average ozone, increasing trends of ~1 ppb/yr in the annual
31 mean ozone are observed at mountainous sites (e.g., Tanimoto et al., 2009) and regional
32 background stations (e.g., Wang et al., 2009) in Asia. In contrast, European annual mean ozone
33 levels have on average been decreasing during the last 20 years (e.g., Sicard et al, 2013).
34 Furthermore, annual mean surface ozone at a background station in eastern China has declined
35 (Xu et al., 2008).

36 Table 2 also differentiates the ozone trends for individual seasons over the eastern and western
37 United States (separated by 100 °W). Overall, the growth rates are higher over the west than over
38 the east, and the regional difference reaches about 0.15 ppb/yr in summer (June, July and August)

1 for daytime, nighttime and daily mean ozone. Seasonally, the most significant growth occurs in
2 spring, with growth rates at 0.17–0.26 ppb/yr for the US average daytime, nighttime and daily
3 mean ozone. For the nighttime ozone, the range of growth rates across the seasons is smaller over
4 the west (0.17–0.30 ppb/yr) than over the east (0.05–0.24 ppb/yr). For the daytime ozone over the
5 east, the increases in spring, fall and winter (0.07–0.15 ppb/yr) are contrasted by a reduction in
6 summer (-0.11 ppb/yr), resulting in a weakened trend for the annual mean ozone (0.06 ppb/yr).
7 The decreases in summertime ozone are associated with reductions in the US anthropogenic
8 emissions of precursor gases NO_x, carbon monoxide (CO), and non-methane volatile organic
9 compounds (NMVOC) revealed from the National Emissions Inventory (Fig. 4b), reflecting the
10 success in controlling peak-level ozone (Cooper et al., 2012; Lefohn et al., 2010; Simon et al.,
11 2015). Similarly, a substantial decrease in precursor concentrations over the last decades in
12 Europe, in line with the long-term emission declines (Colette et al., 2011; Wilson et al., 2012),
13 has resulted in a reduction in ozone episodes (Guerreiro et al., 2014). In contrast, the warm
14 season afternoon ozone over eastern China has been growing at rates of 1–3 ppb/yr over the past
15 20 years (Sun et al., 2016; and references therein) as a result of rapidly growing precursor
16 emissions.

17 Figure 5 further shows the spatial distribution of ozone trends across the 124 grid cells for daily
18 mean, nighttime mean and daytime mean ozone in individual seasons. The nighttime ozone has
19 grown or remained constant in most seasons and grid cells, although ozone reductions are also
20 visible in the summertime eastern US and at sparse places in other seasons. For the daytime
21 ozone, the summertime declines over the eastern United States and southern California are
22 contrasted by the summertime increases at other places and the springtime increases over most
23 regions. The springtime daytime increases over the western US are consistent with the MDA8
24 ozone growth rates (0.2–0.5 ppb/yr) reported by Lin et al. (2017). Averaged across all seasons,
25 the nighttime ozone has grown in most grid cells, while the daytime ozone has grown over the
26 west with mixed trends over the east (Fig. 5b, c). The spatial distribution of the trends in the
27 annual daily mean ozone (Fig. 5a) much resembles the trends in the nighttime ozone. The local
28 patterns in ozone trends reflect the effects of small-scale emission, chemical and/or
29 meteorological features (Cooper et al., 2012; Jhun et al., 2015; Simon et al., 2015; Strode et al.,
30 2015).

31 Table 3 presents the trends at the 5th, 50th and 95th percentiles for the daytime mean, nighttime
32 mean and daily mean ozone, separately for urban, suburban and rural sites. For each site, we
33 calculated daily mean, daytime mean, and nighttime mean ozone mixing ratios in each day, and
34 then computed the 5th, 50th, and 95th ozone percentiles in each year. We then averaged the
35 annual data over each site type (rural, suburban, or urban) for a subsequent trend analysis.
36 Overall, the 50th percentile trends are positive for daytime, nighttime and daily mean ozone at all
37 site types, consistent with the trends in the US annual mean ozone (Table 2).

38 Table 3 shows that for the nighttime mean ozone, trends at the 5th, 50th and 95th percentiles are
39 relatively consistent: the 5th percentile ozone grows by 0.19–0.21 ppb/yr across the three site

1 types, the 50th percentile ozone grows by 0.19–0.22 ppb/yr, and the 95th percentile ozone
2 increases at 0.22–0.27 ppb/yr.

3 Table 3 further shows that for the daytime mean ozone, trends at the 5th and 95th percentiles
4 differ greatly, and there are only small differences across the rural, suburban and urban sites. The
5 5th percentile daytime mean ozone grows rapidly by 0.28–0.29 ppb/yr across the three site types,
6 while the 95th percentile ozone declines by 0.13–0.21 ppb/yr. At the rural sites, the growth rate is
7 about 0.29 ppb/yr (P-value < 0.01) at the 5th percentile and -0.13 ppb/yr (P-value < 0.01) at the
8 95th percentile. For the 50th percentile daytime mean ozone, trends differ greatly between rural,
9 suburban and urban sites: the growth rate varies from 0.02 ppb/yr (statistically insignificant,
10 P-value = 0.95) for the rural sites to 0.19 ppb/yr (P-value < 0.01) for the urban sites.

11 Overall, the distinctive trends at the three percentiles reflect a decrease in the peak ozone
12 contrasted by an increase in the low ozone (Table 3), a decrease in summer compensated by an
13 increase in other seasons (Table 2), and stronger tendency of ozone growth over the west than
14 over the east (Table 2 and Fig. 5).

15 Our daytime results in Table 3 are consistent with Cooper et al. who examined the afternoon
16 ozone trends over 1990–2010 at 53 rural sites (Cooper et al., 2012). Our 5th and 95th percentile
17 daytime ozone trends at rural, suburban and urban sites are also broadly consistent with Simon et
18 al. who analyzed the trends over 1998–2013 in the MDA8 ozone (Simon et al., 2015). The
19 summertime decreases, largest at the 95th percentile, and wintertime increases in the 50th to 5th
20 percentiles over the eastern US are also showed in the MDA8 ozone results of Lin et al. (2017)
21 for 70 rural sites. Note that these previous studies (Cooper et al., 2012; Simon et al., 2015; Lin et
22 al., 2017) were focused on the high-ozone afternoon hours and excluded the low-ozone early
23 morning hours that have experienced notable ozone growth (black line in Fig. 3).

24 **4. Relationship between de-trended ozone and climate variability**

25 We relate the interannual variability of ozone to AMONI, AMO and ONI. We de-trended the
26 time series of ozone and climate indices with linear fit for a subsequent statistical analysis;
27 de-trending the ozone time series removed the effects of continuously rising Asian emissions and
28 declining US emissions (Zhang et al., 2008; Lin et al., 2008; Huang et al., 2008; Cooper et al.,
29 2010; Simon et al., 2015; Jhun et al., 2015; Verstraeten et al., 2016; Lin et al., 2017).

30 Figure 6a-c shows the time series of de-trended annual AMONI, AMO, and ONI indices between
31 1990 and 2014, in comparison with the de-trended ozone data. The three indices are interannually
32 consistent with the daytime and daily mean ozone anomalies. The AMONI anomaly correlates
33 strongly to the daytime ($R = 0.71$, P-value < 0.01 by a one-sided T-test) and daily mean ($R = 0.62$,
34 P-value < 0.01) ozone anomalies, stronger than AMO and ONI. The negative AMONI anomalies
35 in the early 1990s, 2009 and 2014, contributed by negative AMO and positive ONI (El Niño-like),
36 correspond to negative anomalies in the daytime and daily mean ozone. By comparison, the
37 positive AMONI anomalies around the late 1990s and early 2000s are associated with positive

1 ozone anomalies.

2 Figure 7a, b further shows the correlation between de-trended AMONI and de-trended daily and
3 daytime mean ozone in individual grid cells. The AMONI-ozone correlation is positive and
4 statistically significant over most of the eastern US, and it reaches 0.82 over parts of the southeast.
5 A positive AMONI anomaly is associated with increased temperature over the east (Fig. 8c),
6 which enhances biogenic emissions, changes chemical reaction rates, and changes atmospheric
7 circulation that overall lead to increased ozone formation/buildup (Jacob and Winner, 2009; Shen
8 et al., 2015; Fu et al., 2015; Xu et al., 2017). AMONI also correlate positively to ozone over the
9 high-altitude west. This is because a negative ONI anomaly (La Niña-like) means a decrease in
10 lower-tropospheric transport of ozone-poor air from the Eastern Pacific (Xu et al., 2017) and a
11 more meandering subtropical jet and strengthened ozone transport from the stratosphere that
12 compensates for weakened transport from Asia (Lin et al., 2015). AMONI correlates negatively
13 to ozone over southern California, likely reflecting reduced temperature there associated with a
14 positive AMONI (negative ONI) anomaly (Fig. 8b, c).

15 Figure 6a-c shows that the de-trended annual nighttime ozone anomaly corresponds weakly to the
16 three climate indices, with statistically insignificant correlations at 0.15–0.34 (P-value = 0.39–
17 0.78). Figure 7 also shows that AMONI is statistically significantly correlated to the de-trended
18 nighttime ozone only in a few grid cells. We also found statistically insignificant de-trended
19 correlations between the nighttime ozone and other climate indices such as the Pacific Decadal
20 Oscillation ($R = 0.06$), the Arctic Oscillation ($R = -0.05$), and the North Atlantic Oscillation ($R =$
21 -0.29). A possible reason for weaker correlations between climate indices and the nighttime
22 ozone anomaly (compared to the daytime and daily anomalies) is the distinct chemistry at night
23 (i.e., titration by nitrogen), compared to the daytime photochemistry. As the vertical mixing
24 weakens at night, the chemical process becomes more localized and may be less sensitive to
25 large-scale climate variability.

26 Table 4 further shows the seasonal and regional differences in the correlation between de-trended
27 AMONI and de-trended ozone. Over the eastern US, the correlations for daytime ozone reach
28 0.72 in summer and 0.74 in fall. The correlations for nighttime ozone are also relatively large
29 (0.55–0.60) due to influences by “residual” ozone transitioned from the daytime (see Sect. 5.2 for
30 diurnal cycle of model-observation correlations). The correlations are very weak (0.06–0.18) in
31 winter and spring for both daytime and nighttime ozone. Over the western US, the correlations do
32 not exceed 0.50 in all seasons for daytime, nighttime and daily mean ozone, smaller than those
33 over the eastern US. This is likely due to compensating effects on different transport and
34 chemical processes. For example, a positive AMONI are associated with enhanced ozone
35 production (due to enhanced temperature and reduced precipitation in the context of a positive
36 AMO), weakened trans-pacific ozone transport from Asia (due to a negative ONI with a La Niña
37 pattern), and strengthened STE. Nonetheless, the correlations for the western US are higher in
38 winter and spring (0.37–0.50) than in summer and fall (0.19–0.27). Overall, Table 4 and Fig. 7
39 suggest that the AMONI-associated large-scale climate variability (AMO and ENSO) affects the

1 warm season eastern US ozone (likely via chemical processes) and cold season western US ozone
2 (likely via dynamic transport processes).

3 **5. Effects of emissions and climate variability on ozone revealed by GEOS-Chem** 4 **simulations**

5 We further used GEOS-Chem simulations to investigate the distinctive effects of interannual
6 climate variability and anthropogenic emissions on the US daytime and nighttime ozone.

7 We investigated the simulated US ozone changes and driving factors from 2004 through 2012, in
8 which years assimilated meteorological data are available to drive model simulations. Figure 9
9 shows that the measured annual ozone trends over 2004–2012 (Fig. 9d-f) are stronger than but
10 spatially consistent with the trends over 1990–2014. For the US annual mean, the growth rates
11 over 2004–2012 are 0.43 ppb/yr for the nighttime ozone and 0.14 ppb/yr for the daytime ozone,
12 about twice the growth rates over 1990–2014. The diurnal cycle of US annual ozone trends over
13 2004–2012 is similar to the cycle for the 1990–2014 trends (red solid versus black solid line in
14 Fig. 3), although with a stronger diurnal range (maximum – minimum).

15 We note here that the stronger trend in annual ozone over 2004–2012 is partly due to the choice
16 of beginning and end years (Bacer et al., 2016). For example, the growth rates over 2005–2011
17 are 0.31 ppb/yr for the nighttime mean, 0.13 ppb/yr for the daytime mean, and 0.23 ppb/yr for the
18 daily mean ozone (Table 2), consistent but smaller than the trends over 2004–2012. As an
19 extreme case, the growth rates between 2002 (with a local ozone maximum) and 2014 (with a
20 local minimum) are only 0.13 ppb/yr (P-value < 0.05) for nighttime ozone, 0.05 ppb/yr for
21 daytime ozone, and 0.08 ppb/yr for daily mean ozone. For seasonal ozone, the trend differences
22 between 2004–2012 and 1990–2014 are generally similar to the differences for annual ozone
23 (Table 2). A possible reason for the stronger ozone trend in the recent decade is that
24 anthropogenic emissions of NO_x decline much more rapidly (Fig. 4b) over 2004–2012 (at a rate
25 of 4.1%/yr relative to 2004) than over 1990–2014 (2.1%/yr relative to 1990). Also, a heat wave
26 swept much of the US in 2012, partly contributing to the high value in that year.

27 **5.1 Evaluation of modeled ozone in the “Control” simulation**

28 Figure 10 compare the spatial distributions of modeled (the “Control” simulation) and observed
29 2004–2012 average daily, daytime and nighttime mean ozone over the US. The “Control”
30 simulation overestimates the observed ozone, especially over the eastern US, a common problem
31 in chemical transport models (Fiore et al., 2009; Lin et al., 2008; Stevenson et al., 2006; Yan et al.,
32 2016; Young et al., 2013). Model biases are about 8.8 ppb, 6.3 ppb and 10.4 ppb for the daily,
33 daytime and nighttime mean ozone, respectively, averaged over the US.

34 The solid yellow line in Fig. 11 shows that the “Control” simulation captures the diurnal variation
35 of the observed ozone trends (red line), although with a slight systematic underestimate. The
36 model produces significant growth in the nighttime mean ozone (0.31 ppb/yr), modest growth in

1 the daily mean ozone (0.22 ppb/yr), and statistically insignificant growth in the daytime ozone
2 (0.14 ppb/yr), weaker than but consistent with the observed trends (0.19–0.43 ppb/yr). Table 5
3 further shows that the “Control” simulation reproduces the observed interannual and seasonal
4 variability of ozone. The model-observation correlations (0.82–0.91, P-value < 0.01) are
5 statistically significant for the US annual/seasonal average daily, daytime and nighttime mean
6 ozone, no matter whether the ozone data are de-trended. The last column of Fig. 10 also shows
7 that the “Control” simulation captures the observed interannual variability of annual ozone in
8 most model grid cells, with statistically significant correlation coefficients.

9 A sensitivity simulation was conducted to test the effect of anthropogenic NMVOC emission
10 changes not included in the “Control” simulation. In the sensitivity simulation, we scaled the
11 NMVOC emissions to the years of 2004 and 2012 based on the EDGARv4.3.2 database which
12 provides the emission time series (1970–2012). Emissions of NMVOC were scaled according to
13 emissions over five regions (China, rest of Asia, the US, Europe and rest of world). Other
14 emissions are the same with the “Control” simulation.

15 In this sensitivity simulation, the modeled change in annual mean ozone from 2004 to 2012 is 1.7
16 ppb (equivalent to 0.21 ppb/yr) averaged over the US, with local ozone changes ranging from
17 -1.9 to 8.1 ppb across the selected 124 grid cells. This magnitude of ozone change is consistent
18 with the “Control” simulation results with the modeled ozone trend at 0.22 ppb/yr during 2004–
19 2012 (Table 5). For the urban sites, the mean ozone change in the sensitivity simulation (2.1 ppb,
20 or 0.26 ppb/yr) is also close to the “Control” simulation (0.28 ppb/yr). These results suggest that
21 changes in anthropogenic NMVOC emissions have not led to a systemic ozone trend across the
22 US on top of the effect of NO_x emission changes, consistent with the results in Simon et al.
23 (2015).

24 **5.2 Effects of anthropogenic emissions versus climate variability revealed by perturbation** 25 **simulations**

26 The second simulation (named **fixed emis** in Fig.11) tests the sole sensitivity of ozone to
27 interannual climate variability, by fixing global anthropogenic emissions at the 2004 levels. As
28 such, both the decline in US emissions and the growth in Asian emissions are excluded. Table 5
29 shows that with fixed emissions, the modeled annual daytime and daily mean ozone are still
30 highly correlated to the observed counterparts (R = 0.61–0.83, P-value < 0.01). By comparison,
31 the model-observation correlation becomes statistically insignificant for the annual nighttime
32 ozone. The modeled US annual ozone trends are not statistically significant (0.05–0.07 ppb/yr)
33 for daily mean, daytime and nighttime ozone. The short dashed yellow line in Fig. 11 also shows
34 statistically insignificant ozone trends at individual hours when anthropogenic emissions are
35 fixed.

36 For the second simulation, results for seasonal ozone are in line with those for annual ozone
37 (Table 5). Among the seasons, the model nighttime ozone is best correlated with the observations

1 in summer, whereas the correlation coefficients (0.44–0.48) are much still lower than those for
2 daytime (0.77–0.83) and daily mean (0.72–0.79) ozone. The summertime daytime ozone growth
3 rate increases from -0.05 ppb/yr in the “Control” case to 0.03 ppb/yr, with a sign of change
4 opposite to other seasons. This reflects the importance of controlling anthropogenic emissions to
5 reducing summertime daytime ozone (Bloomer et al., 2009; Cooper et al., 2012; Simon et al.,
6 2015; Sather and Cavender, 2016; Lin et al., 2017). [As discussed in Sect. 3, the summertime
7 daytime decline here is weaker than previous results for peak ozone because we included the
8 morning and late afternoon hours that exhibit ozone growth.] For other seasons, the ozone growth
9 rates decrease drastically from the “Control” to the second case. This reflects “penalty” of
10 reducing NO_x (Jhun et al., 2015), which is consistent with previous findings that the 5th
11 percentile of peak ozone (normally occurring in cold seasons) over the eastern US has increased
12 due to weakened NO_x titration (Gao et al., 2013; Clifton et al., 2014., Simon et al., 2015; Lin et
13 al., 2017).

14 The third sensitivity simulation fixes the US anthropogenic emissions at the 2004 levels while
15 allowing emissions in other regions and meteorology to vary interannually (Table 5). The
16 resulting ozone growth rates and model-observation correlations resemble the second case,
17 suggesting that reductions in the US NO_x emissions and ozone titration are the dominant driver of
18 modeled all-season nighttime ozone growth and summertime daytime ozone reduction over
19 2004–2012. For the US annual ozone, the effects of decreasing US emissions are approximately
20 0.15 ppb/yr for daily mean ozone, 0.08 ppb/yr for daytime mean ozone and 0.22 ppb/yr for
21 nighttime mean ozone, based on the difference between the third and the “Control” simulation.
22 The annual ozone growth rates are slightly higher (by 0.01–0.02 ppb/yr) than the second case
23 because of rising Asian emissions simulated in the third case but not in the second case.
24 Seasonally, the increase from the second to the third case is greatest in spring (0.11–0.14 ppb/yr
25 versus 0.06–0.07 ppb/yr, Table 5). The contribution of rising Asian emissions to the springtime
26 US ozone growth, especially over the western US, were also found by previous studies (Fiore et
27 al., 2009; Huang et al., 2013; Lin et al., 2015; Verstraeten et al., 2014; Lin et al., 2017).

28 The fourth simulation (named **fixed met** in Fig.11) fixes meteorological data in 2004 but allows
29 global anthropogenic emissions to vary interannually. The resulting trends of annual ozone are
30 close to the trends in the “Control” simulation across the individual hours (long dashed yellow
31 versus solid yellow line in Fig. 11). Table 5 shows that the trend in annual nighttime mean ozone
32 is still notable, at 0.26 ppb/yr (P-value < 0.01) compared to 0.31 ppb/yr in the “Control”
33 simulation. This confirms that the nighttime growth is driven by reduced NO_x emissions and
34 weakened ozone titration. The model-observation correlation for the annual nighttime ozone is
35 0.71 (P-value < 0.01) and 0.31 (P-value = 0.43) before and after de-trending, respectively. The
36 correlations for the annual daytime ozone are much weaker than the second simulation no matter
37 whether the ozone data are de-trended (0.39–0.41 versus 0.76–0.81), suggesting the dominant
38 effect of interannual climate variability on the ozone in this part of the day. For season ozone,
39 changes from the “Control” to the fourth case are generally similar to those for annual ozone
40 (Table 5).

1 For each hour of the day, the two shaded areas in Fig. 11 broadly separate the contribution of
2 anthropogenic emissions (dark grey shade) to the 2004–2012 annual ozone changes from the
3 contribution of interannual climate variability (light grey shade). The contributions are calculated
4 as $C_{anth} = R_{anth}^2 / (R_{anth}^2 + R_{clim}^2)$ and $C_{clim} = 1 - C_{anth}$, where R_{anth} is the correlation between
5 observed and modeled annual mean ozone (at a particular hour) with fixed model meteorology
6 and R_{clim} the observation-model correlation with fixed global anthropogenic emissions. Figure
7 11 shows that the emission contribution dominates in the nighttime hours (relatively constant at
8 about 70%), with a reduction in the morning hours, an increase in the late afternoon hours, and a
9 minimum value (at 10%) around 15:00.

10 Overall, the modeling results indicate that for the interannual variation of US mean ozone over
11 2004–2012, climate variability and anthropogenic emissions are the main drivers of the historical
12 daytime ozone variability and nighttime ozone trend, respectively. The rising Asian emissions
13 contribute to the US annual mean ozone trends (0.01–0.02 ppb/yr for daily mean, daytime and
14 nighttime ozone) much less than the contributions from the US anthropogenic emission changes
15 (0.08–0.22 ppb/yr) and climate variability (0.05–0.07 ppb/yr).

16 **6. Concluding Remark**

17 This work shows that reductions in the US anthropogenic emissions have effectively lowered the
18 summertime daytime ozone from 1990 to 2014, consistent with previous studies on afternoon or
19 MDA8 ozone. On an annual mean basis, the daytime ozone have continued to increase.
20 Furthermore, the great sensitivity of the annual average daytime ozone to interannual climate
21 variability increases the difficulty in projecting future ozone air quality (Jacob and Winner,
22 2009;Rieder et al., 2015). The daily mean and particularly the nighttime ozone have experienced
23 substantial growth, due to weakened titration by NO_x . This likely implies potential growth in
24 health risk from long-term exposure of enhanced low- and medium-level ozone (Jerrett et al.,
25 2009;Bell et al., 2006;Peng et al., 2013). As the extent of outdoor activities differs notably at
26 different times of day, the overall effect of ozone trends at individual hours on public health
27 warrants further research. Nonetheless, pollution mitigation strategies might consider to address
28 ozone changes at different times of the day and not only during peak hours.

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34 NOAA/ESRL (<http://www.esrl.noaa.gov/psd/data/timeseries/AMO/>), and the ONI index from the
35 NOAA Climate Prediction Center
36 (http://www.cpc.noaa.gov/products/analysis_monitoring/ensostuff/ensoyears.shtml).

1

2 **Reference**

3 Auvray, M., and Bey, I.: Long-range transport to Europe: Seasonal variations and implications for the European
4 ozone budget, *Journal of Geophysical Research-Atmospheres*, 110, 10.1029/2004jd005503, 2005.

5 Bell, M. L., Peng, R. D., and Dominici, F.: The exposure-response curve for ozone and risk of mortality and the
6 adequacy of current ozone regulations, *Environmental Health Perspectives*, 114, 532-536, 10.1289/ehp.8816, 2006.

7 Bloomer, B. J., Stehr, J. W., Piety, C. A., Salawitch, R. J., and Dickerson, R. R.: Observed relationships of ozone air
8 pollution with temperature and emissions, *Geophysical Research Letters*, 36, 10.1029/2009gl037308, 2009.

9 Brauer, M., Freedman, G., Frostad, J., van Donkelaar, A., Martin, R. V., Dentener, F., van Dingenen, R., Estep, K.,
10 Amini, H., Apte, J. S., Balakrishnan, K., Barregard, L., Broday, D., Feigin, V., Ghosh, S., Hopke, P. K., Knibbs, L. D.,
11 Kokubo, Y., Liu, Y., Ma, S. F., Morawska, L., Sangrador, J. L. T., Shaddick, G., Anderson, H. R., Vos, T., Forouzanfar, M.
12 H., Burnett, R. T., and Cohen, A.: Ambient Air Pollution Exposure Estimation for the Global Burden of Disease 2013,
13 *Environmental Science & Technology*, 50, 79-88, 10.1021/acs.est.5b03709, 2016.

14 Cooper, O. R., Gao, R.-S., Tarasick, D., Leblanc, T., and Sweeney, C.: Long-term ozone trends at rural ozone
15 monitoring sites across the United States, 1990-2010, *Journal of Geophysical Research-Atmospheres*, 117,
16 10.1029/2012jd018261, 2012.

17 Fiore, A. M., Dentener, F. J., Wild, O., Cuvelier, C., Schultz, M. G., Hess, P., Textor, C., Schulz, M., Doherty, R. M.,
18 Horowitz, L. W., MacKenzie, I. A., Sanderson, M. G., Shindell, D. T., Stevenson, D. S., Szopa, S., Van Dingenen, R.,
19 Zeng, G., Atherton, C., Bergmann, D., Bey, I., Carmichael, G., Collins, W. J., Duncan, B. N., Faluvegi, G., Folberth, G.,
20 Gauss, M., Gong, S., Hauglustaine, D., Holloway, T., Isaksen, I. S. A., Jacob, D. J., Jonson, J. E., Kaminski, J. W.,
21 Keating, T. J., Lupu, A., Marmer, E., Montanaro, V., Park, R. J., Pitari, G., Pringle, K. J., Pyle, J. A., Schroeder, S.,
22 Vivanco, M. G., Wind, P., Wojcik, G., Wu, S., and Zuber, A.: Multimodel estimates of intercontinental
23 source-receptor relationships for ozone pollution, *Journal of Geophysical Research-Atmospheres*, 114,
24 10.1029/2008jd010816, 2009.

25 Forouzanfar, M. H., et al., Global, regional, and national comparative risk assessment of 79 behavioural,
26 environmental and occupational, and metabolic risks or clusters of risks in 188 countries, 1990-2013: a systematic
27 analysis for the Global Burden of Disease Study 2013, *Lancet*, 386, 2287-2323, 10.1016/s0140-6736(15)00128-2,
28 2015.

29 Forouzanfar, M. H., et al., Global, regional, and national comparative risk assessment of 79 behavioural,
30 environmental and occupational, and metabolic risks or clusters of risks, 1990-2015: a systematic analysis for the
31 Global Burden of Disease Study 2015, *Lancet*, 388, 1659-1724, 2016.

32 Fu, T.-M., Zheng, Y., Paulot, F., Mao, J., and Yantosca, R. M.: Positive but variable sensitivity of August surface ozone
33 to large-scale warming in the southeast United States, *Nature Climate Change*, 5, 454-458, 10.1038/nclimate2567,
34 2015.

35 Guenther, A.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and
36 Aerosols from Nature) (vol 6, pg 3181, 2006), *Atmospheric Chemistry and Physics*, 7, 4327-4327, 2007.

37 Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of
38 Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for
39 modeling biogenic emissions, *Geoscientific Model Development*, 5, 1471-1492, 10.5194/gmd-5-1471-2012, 2012.

40 Hu, L., Millet, D. B., Baasandorj, M., Griffis, T. J., Travis, K. R., Tessum, C. W., Marshall, J. D., Reinhart, W. F.,
41 Mikoviny, T., Muller, M., Wisthaler, A., Graus, M., Warneke, C., and de Gouw, J.: Emissions of C-6-C-8 aromatic
42 compounds in the United States: Constraints from tall tower and aircraft measurements, *Journal of Geophysical
43 Research-Atmospheres*, 120, 826-842, 10.1002/2014jd022627, 2015.

44 Hu, Q., Feng, S., and Oglesby, R. J.: Variations in North American Summer Precipitation Driven by the Atlantic
45 Multidecadal Oscillation, *Journal of Climate*, 24, 5555-5570, 10.1175/2011jcli4060.1, 2011.

46 Hudman, R. C., Moore, N. E., Mebust, A. K., Martin, R. V., Russell, A. R., Valin, L. C., and Cohen, R. C.: Steps towards
47 a mechanistic model of global soil nitric oxide emissions: implementation and space based-constraints,

1 Atmospheric Chemistry and Physics, 12, 7779-7795, 10.5194/acp-12-7779-2012, 2012.

2 Jacob, D. J., and Winner, D. A.: Effect of climate change on air quality, *Atmospheric Environment*, 43, 51-63,
3 10.1016/j.atmosenv.2008.09.051, 2009.

4 Jerrett, M., Burnett, R. T., Pope, C. A., Ito, K., Thurston, G., Krewski, D., Shi, Y. L., Calle, E., and Thun, M.: Long-Term
5 Ozone Exposure and Mortality, *New England Journal of Medicine*, 360, 1085-1095, 10.1056/NEJMoa0803894, 2009.

6 Jhun, I., Coull, B. A., Zanobetti, A., and Koutrakis, P.: The impact of nitrogen oxides concentration decreases on
7 ozone trends in the USA, *Air Quality Atmosphere and Health*, 8, 283-292, 10.1007/s11869-014-0279-2, 2015.

8 Kuhns, H., Etyemezian, V., Green, M., Hendrickson, K., McGown, M., Barton, K., and Pitchford, M.: Vehicle-based
9 road dust emission measurement - Part II: Effect of precipitation, wintertime road sanding, and street sweepers on
10 inferred PM10 emission potentials from paved and unpaved roads, *Atmospheric Environment*, 37, 4573-4582,
11 10.1016/s1352-2310(03)00529-6, 2003.

12 Lefohn, A. S., Shadwick, D., and Oltmans, S. J.: Characterizing changes in surface ozone levels in metropolitan and
13 rural areas in the United States for 1980-2008 and 1994-2008, *Atmospheric Environment*, 44, 5199-5210,
14 10.1016/j.atmosenv.2010.08.049, 2010.

15 Lim, S. S., et al., A comparative risk assessment of burden of disease and injury attributable to 67 risk factors and
16 risk factor clusters in 21 regions, 1990-2010: a systematic analysis for the Global Burden of Disease Study 2010,
17 *Lancet*, 380, 2224-2260, 2012.

18 Lin, J. T., Youn, D., Liang, X. Z., and Wuebbles, D. J.: Global model simulation of summertime US ozone diurnal cycle
19 and its sensitivity to PBL mixing, spatial resolution, and emissions, *Atmospheric Environment*, 42, 8470-8483,
20 10.1016/j.atmosenv.2008.08.012, 2008.

21 Lin, J.-T., Wuebbles, D. J., and Liang, X. Z.: Effects of intercontinental transport on surface ozone over the United
22 States: Present and future assessment with a global model, *Geophysical Research Letters*, 35, L02805,
23 doi:10.1029/2007gl031415, 2008.

24 Lin, J. T., and McElroy, M. B.: Impacts of boundary layer mixing on pollutant vertical profiles in the lower
25 troposphere: Implications to satellite remote sensing, *Atmospheric Environment*, 44, 1726-1739,
26 10.1016/j.atmosenv.2010.02.009, 2010.

27 Lin, J. T., Liu, M. Y., Xin, J. Y., Boersma, K. F., Spurr, R., Martin, R., and Zhang, Q.: Influence of aerosols and surface
28 reflectance on satellite NO2 retrieval: seasonal and spatial characteristics and implications for NOx emission
29 constraints, *Atmospheric Chemistry and Physics*, 15, 11217-11241, 10.5194/acp-15-11217-2015, 2015.

30 Lin, M., Horowitz, L. W., Oltmans, S. J., Fiore, A. M., and Fan, S.: Tropospheric ozone trends at Mauna Loa
31 Observatory tied to decadal climate variability, *Nature Geoscience*, 7, 136-143, 10.1038/ngeo2066, 2014.

32 Lin, M. Y., Fiore, A. M., Horowitz, L. W., Langford, A. O., Oltmans, S. J., Tarasick, D., and Rieder, H. E.: Climate
33 variability modulates western US ozone air quality in spring via deep stratospheric intrusions, *Nature*
34 *Communications*, 6, 10.1038/ncomms8105, 2015.

35 Mao, J. Q., Paulot, F., Jacob, D. J., Cohen, R. C., Crounse, J. D., Wennberg, P. O., Keller, C. A., Hudman, R. C., Barkley,
36 M. P., and Horowitz, L. W.: Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene
37 chemistry, *Journal of Geophysical Research-Atmospheres*, 118, 11256-11268, 10.1002/jgrd.50817, 2013.

38 McLinden, C. A., Olsen, S. C., Hannegan, B., Wild, O., Prather, M. J., and Sundet, J.: Stratospheric ozone in 3-D
39 models: A simple chemistry and the cross-tropopause flux, *Journal of Geophysical Research-Atmospheres*, 105,
40 14653-14665, 10.1029/2000jd900124, 2000.

41 Murray, L. T., Jacob, D. J., Logan, J. A., Hudman, R. C., and Koshak, W. J.: Optimized regional and interannual
42 variability of lightning in a global chemical transport model constrained by LIS/OTD satellite data, *Journal of*
43 *Geophysical Research-Atmospheres*, 117, 10.1029/2012jd017934, 2012.

44 Murray, L. T., Logan, J. A., and Jacob, D. J.: Interannual variability in tropical tropospheric ozone and OH: The role of
45 lightning, *Journal of Geophysical Research-Atmospheres*, 118, 11468-11480, 10.1002/jgrd.50857, 2013.

46 Oglesby, R., Feng, S., Hu, Q., and Rowe, C.: The role of the Atlantic Multidecadal Oscillation on medieval drought in
47 North America: Synthesizing results from proxy data and climate models, *Global and Planetary Change*, 84-85,

1 56-65, 10.1016/j.gloplacha.2011.07.005, 2012.

2 Peng, R. D., Samoli, E., Pham, L., Dominici, F., Touloumi, G., Ramsay, T., Burnett, R. T., Krewski, D., Le Tertre, A.,
3 Cohen, A., Atkinson, R. W., Anderson, H. R., Katsouyanni, K., and Samet, J. M.: Acute effects of ambient ozone on
4 mortality in Europe and North America: results from the APHENA study, *Air Quality Atmosphere and Health*, 6,
5 445-453, 10.1007/s11869-012-0180-9, 2013.

6 Price, C., and Rind, D.: A SIMPLE LIGHTNING PARAMETERIZATION FOR CALCULATING GLOBAL LIGHTNING
7 DISTRIBUTIONS, *Journal of Geophysical Research-Atmospheres*, 97, 9919-9933, 1992.

8 Rieder, H. E., Fiore, A. M., Horowitz, L. W., and Naik, V.: Projecting policy-relevant metrics for high summertime
9 ozone pollution events over the eastern United States due to climate and emission changes during the 21st century,
10 *Journal of Geophysical Research-Atmospheres*, 120, 784-800, 10.1002/2014jd022303, 2015.

11 Shen, L., Mickley, L. J., and Tai, A. P. K.: Influence of synoptic patterns on surface ozone variability over the eastern
12 United States from 1980 to 2012, *Atmospheric Chemistry and Physics*, 15, 10925-10938,
13 10.5194/acp-15-10925-2015, 2015.

14 Rienecker, M. M., et al., The GEOS-5 Data Assimilation System— Documentation of Versions 5.0.1, 5.1.0, and 5.2.0.
15 Technical Report Series on Global Modeling and Data Assimilation, Vol. 27, 2008, pp. 118.

16 Simon, H., Reff, A., Wells, B., Xing, J., and Frank, N.: Ozone Trends Across the United States over a Period of
17 Decreasing NO_x and VOC Emissions, *Environmental Science & Technology*, 49, 186-195, 10.1021/es504514z, 2015.

18 Stevenson, D. S., Dentener, F. J., Schultz, M. G., Ellingsen, K., van Noije, T. P. C., Wild, O., Zeng, G., Amann, M.,
19 Atherton, C. S., Bell, N., Bergmann, D. J., Bey, I., Butler, T., Cofala, J., Collins, W. J., Derwent, R. G., Doherty, R. M.,
20 Drevet, J., Eskes, H. J., Fiore, A. M., Gauss, M., Hauglustaine, D. A., Horowitz, L. W., Isaksen, I. S. A., Krol, M. C.,
21 Lamarque, J. F., Lawrence, M. G., Montanaro, V., Muller, J. F., Pitari, G., Prather, M. J., Pyle, J. A., Rast, S., Rodriguez,
22 J. M., Sanderson, M. G., Savage, N. H., Shindell, D. T., Strahan, S. E., Sudo, K., and Szopa, S.: Multimodel ensemble
23 simulations of present-day and near-future tropospheric ozone, *Journal of Geophysical Research-Atmospheres*, 111,
24 10.1029/2005jd006338, 2006.

25 Strode, S. A., Rodriguez, J. M., Logan, J. A., Cooper, O. R., Witte, J. C., Lamsal, L. N., Damon, M., Van Aartsen, B.,
26 Steenrod, S. D., and Strahan, S. E.: Trends and variability in surface ozone over the United States, *Journal of*
27 *Geophysical Research-Atmospheres*, 120, 9020-9042, 10.1002/2014jd022784, 2015.

28 van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., Morton, D. C., DeFries, R. S.,
29 Jin, Y., and van Leeuwen, T. T.: Global fire emissions and the contribution of deforestation, savanna, forest,
30 agricultural, and peat fires (1997-2009), *Atmospheric Chemistry and Physics*, 10, 11707-11735,
31 10.5194/acp-10-11707-2010, 2010.

32 van Donkelaar, A., Martin, R. V., Leaitch, W. R., Macdonald, A. M., Walker, T. W., Streets, D. G., Zhang, Q., Dunlea, E.
33 J., Jimenez, J. L., Dibb, J. E., Huey, L. G., Weber, R., and Andreae, M. O.: Analysis of aircraft and satellite
34 measurements from the Intercontinental Chemical Transport Experiment (INTEX-B) to quantify long-range
35 transport of East Asian sulfur to Canada, *Atmospheric Chemistry and Physics*, 8, 2999-3014, 2008.

36 Vinken, G. C. M., Boersma, K. F., Maasackers, J. D., Adon, M., and Martin, R. V.: Worldwide biogenic soil NO_x
37 emissions inferred from OMI NO₂ observations, *Atmospheric Chemistry and Physics*, 14, 10363-10381,
38 10.5194/acp-14-10363-2014, 2014.

39 Yan, Y., Lin, J., Chen, J., and Hu, L.: Improved simulation of tropospheric ozone by a global-multi-regional two-way
40 coupling model system, *Atmospheric Chemistry and Physics*, 16, 2381-2400, 10.5194/acp-16-2381-2016, 2016.

41 Yan, Y. Y., Lin, J. T., Kuang, Y., Yang, D., and Zhang, L.: Tropospheric carbon monoxide over the Pacific during HIPPO:
42 two-way coupled simulation of GEOS-Chem and its multiple nested models, *Atmospheric Chemistry and Physics*, 14,
43 12649-12663, 10.5194/acp-14-12649-2014, 2014.

44 Yang, C. X., Yang, H. B., Guo, S., Wang, Z. S., Xu, X. H., Duan, X. L., and Kan, H. D.: Alternative ozone metrics and
45 daily mortality in Suzhou: The China Air Pollution and Health Effects Study (CAPES), *Science of the Total*
46 *Environment*, 426, 83-89, 10.1016/j.scitotenv.2012.03.036, 2012.

47 Young, P. J., Archibald, A. T., Bowman, K. W., Lamarque, J. F., Naik, V., Stevenson, D. S., Tilmes, S., Voulgarakis, A.,

1 Wild, O., Bergmann, D., Cameron-Smith, P., Cionni, I., Collins, W. J., Dalsoren, S. B., Doherty, R. M., Eyring, V.,
2 Faluvegi, G., Horowitz, L. W., Josse, B., Lee, Y. H., MacKenzie, I. A., Nagashima, T., Plummer, D. A., Righi, M.,
3 Rumbold, S. T., Skeie, R. B., Shindell, D. T., Strode, S. A., Sudo, K., Szopa, S., and Zeng, G.: Pre-industrial to end 21st
4 century projections of tropospheric ozone from the Atmospheric Chemistry and Climate Model Intercomparison
5 Project (ACCMIP), *Atmospheric Chemistry and Physics*, 13, 2063-2090, 10.5194/acp-13-2063-2013, 2013.

6 Zhang, Q., Streets, D. G., Carmichael, G. R., He, K. B., Huo, H., Kannari, A., Klimont, Z., Park, I. S., Reddy, S., Fu, J. S.,
7 Chen, D., Duan, L., Lei, Y., Wang, L. T., and Yao, Z. L.: Asian emissions in 2006 for the NASA INTEX-B mission,
8 *Atmospheric Chemistry and Physics*, 9, 5131-5153, 2009.

9 Zhang, Y. Z., and Wang, Y. H.: Climate-driven ground-level ozone extreme in the fall over the Southeast United
10 States, *Proceedings of the National Academy of Sciences of the United States of America*, 113, 10025-10030,
11 10.1073/pnas.1602563113, 2016.

12 Lin, M. Y., Horowitz, L. W., Payton, R., Fiore, A. M., and Tonnesen, G.: US surface ozone trends and extremes from
13 1980 to 2014: quantifying the roles of rising Asian emissions, domestic controls, wildfires, and climate, *Atmospheric
14 Chemistry and Physics*, 17, 2943-2970, 10.5194/acp-17-2943-2017, 2017.

15 Lu, X., Zhang, L., Yue, X., Zhang, J. C., Jaffe, D. A., Stohl, A., Zhao, Y. H., and Shao, J. Y.: Wildfire influences on the
16 variability and trend of summer surface ozone in the mountainous western United States, *Atmospheric Chemistry
17 and Physics*, 16, 14687-14702, 10.5194/acp-16-14687-2016, 2016.

18 Reddy, P. J., and Pfister, G. G.: Meteorological factors contributing to the interannual variability of midsummer
19 surface ozone in Colorado, Utah, and other western US states, *Journal of Geophysical Research-Atmospheres*, 121,
20 2434-2456, 10.1002/2015jd023840, 2016.

21 Sather, M. E., and Cavender, K.: Trends analyses of 30 years of ambient 8 hour ozone and precursor monitoring
22 data in the South Central US: progress and challenges, *Environmental Science-Processes & Impacts*, 18, 819-831,
23 10.1039/c6em00210b, 2016.

24 Verstraeten, W. W., Neu, J. L., Williams, J. E., Bowman, K. W., Worden, J. R., and Boersma, K. F.: Rapid increases in
25 tropo- spheric ozone production and export from China, *Nat. Geosci.*, 8, 690-695, doi:10.1038/Ngeo2493, 2015.

26 Seager, R. and Hoerling, M.: Atmosphere and Ocean Origins of North American Droughts, *J. Climate*, 27, 4581-4606,
27 doi:10.1175/Jcli-D-13-00329.1, 2014.

28 Huang, H. C., Lin, J.-T., Tao, Z. N., Choi, H., Patten, K., Kunkel, K., Xu, M., Zhu, J. H., Liang, X. Z., Williams, A., Caughey,
29 M., Wuebbles, D. J., and Wang, J. L.: Impacts of long-range transport of global pollutants and precursor gases on US
30 air quality under future climatic conditions, *Journal of Geophysical Research-Atmospheres*, 113, D19307,
31 doi:10.1029/2007jd009469, 2008.

32 Huang, M., Carmichael, G. R., Chai, T., Pierce, R. B., Oltmans, S. J., Jaffe, D. A., Bowman, K. W., Kaduwela, A., Cai, C.,
33 Spak, S. N., Weinheimer, A. J., Huey, L. G., and Diskin, G. S.: Impacts of transported background pollutants on
34 summertime western US air quality: model evaluation, sensitivity analysis and data assim- ilation, *Atmos. Chem.
35 Phys.*, 13, 359-391, doi:10.5194/acp-13- 359-2013, 2013.

36 Gao, Y., Fu, J. S., Drake, J. B., Lamarque, J.-F., and Liu, Y.: The impact of emission and climate change on ozone in
37 the United States under representative concentration pathways (RCPs), *Atmos. Chem. Phys.*, 13, 9607-9621,
38 doi:10.5194/acp-13-9607- 2013, 2013.

39 Clifton, O. E., Fiore, A. M., Correa, G., Horowitz, L. W., and Naik, V.: Twenty-first century reversal of the surface
40 ozone seasonal cycle over the northeastern United States, *Geophys. Res. Lett.*, 41, 7343-7350,
41 doi:10.1002/2014gl061378, 2014.

42 Xu, L., J.-Y. Yu, J. L. Schnell, and M. J. Prather: The seasonality and geographic dependence of ENSO impacts on U.S.
43 surface ozone variability, *Geophys. Res. Lett.*, 44, 3420-3428, doi:10.1002/2017GL073044, 2017.

44 Shen, L. and L. J. Mickley: Influence of large-scale climate patterns on summertime U.S. ozone: A seasonal
45 predictive model for air quality management, *Proc. Natl. Acad. Sci. U.S.A.*, 114(10), 2491-2496, 2017.

46 Colette, A., Granier, C., Hodnebrog, O., Jakobs, H., Maurizi, A., Nyiri, A., Bessagnet, B., D'Angiola, A., D'Isidoro, M.,
47 Gauss, M., Meleux, F., Memmesheimer, M., Mieville, A., Rouil, L., Russo, F., Solberg, S., Stordal, F., and Tampieri, F.:
48 Air quality trends in Europe over the past decade: a first multi- model assessment, *Atmospheric Chemistry and
49 Physics*, 11, 11657-11678, 10.5194/acp-11-11657-2011, 2011.

50 Wilson, R. C., Fleming, Z. L., Monks, P. S., Clain, G., Henne, S., Konovalov, I. B., Szopa, S., and Menut, L.: Have
51 primary emission reduction measures reduced ozone across Europe? An analysis of European rural background
52 ozone trends 1996-2005, *Atmospheric Chemistry and Physics*, 12, 437-454, 10.5194/acp-12-437-2012, 2012.

1 Guerreiro, C. B. B., Foltescu, V., and de Leeuw, F.: Air quality status and trends in Europe, *Atmospheric Environment*,
2 98, 376-384, 10.1016/j.atmosenv.2014.09.017, 2014.

3 Bjercknes, J.: ATMOSPHERIC TELECONNECTIONS FROM EQUATORIAL PACIFIC, *Monthly Weather Review*, 97, 163-&,
4 10.1175/1520-0493(1969)097<0163:atftpe>2.3.co;2, 1969.

5 Delworth, T. L., and Mann, M. E.: Observed and simulated multidecadal variability in the Northern Hemisphere,
6 *Climate Dynamics*, 16, 661-676, 10.1007/s003820000075, 2000.

7 Enfield, D. B.: EL-NINO, PAST AND PRESENT, *Reviews of Geophysics*, 27, 159-187, 10.1029/RG027i001p00159, 1989.

8 Enfield, D. B., Mestas-Nunez, A. M., and Trimble, P. J.: The Atlantic multidecadal oscillation and its relation to
9 rainfall and river flows in the continental US, *Geophysical Research Letters*, 28, 2077-2080, 10.1029/2000gl012745,
10 2001.

11 Fiore, A., Naik, V., and Leibensperger, E.: Air Quality and Climate Connections (vol 65, pg 645, 2015), *Journal of the*
12 *Air & Waste Management Association*, 65, 1159-1159, 10.1080/10962247.2015.1059177, 2015.

13 Johannessen, O. M., Bengtsson, L., Miles, M. W., Kuzmina, S. I., Semenov, V. A., Alekseev, G. V., Nagurnyi, A. P.,
14 Zakharov, V. F., Bobylev, L. P., Pettersson, L. H., Hasselmann, K., and Cattle, H. P.: Arctic climate change: observed
15 and modelled temperature and sea-ice variability (vol 56A, pg 328, 2004), *Tellus Series a-Dynamic Meteorology and*
16 *Oceanography*, 56, 559-560, 10.1111/j.1600-0870.2004.00092.x, 2004.

17 Kunkel, K. E., Huang, H. C., Liang, X. Z., Lin, J. T., Wuebbles, D., Tao, Z., Williams, A., Caughey, M., Zhu, J., and
18 Hayhoe, K.: Sensitivity of future ozone concentrations in the northeast USA to regional climate change, *Mitigation*
19 *and Adaptation Strategies for Global Change*, 13, 597-606, 10.1007/s11027-007-9137-y, 2008.

20 Liang, Y.-C., Yu, J.-Y., Lo, M.-H., and Wang, C.: The changing influence of El Nino on the Great Plains low-level jet,
21 *Atmospheric Science Letters*, 16, 512-517, 10.1002/asl.590, 2015.

22 McCabe, G. J., Palecki, M. A., and Betancourt, J. L.: Pacific and Atlantic Ocean influences on multidecadal drought
23 frequency in the United States, *Proceedings of the National Academy of Sciences of the United States of America*,
24 101, 4136-4141, 10.1073/pnas.0306738101, 2004.

25 Olsen, M. A., Wargan, K., and Pawson, S.: Tropospheric column ozone response to ENSO in GEOS-5 assimilation of
26 OMI and MLS ozone data, *Atmospheric Chemistry and Physics*, 16, 7091-7103, 10.5194/acp-16-7091-2016, 2016.

27 Ropelewski, C. F., and Halpert, M. S.: NORTH-AMERICAN PRECIPITATION AND TEMPERATURE PATTERNS
28 ASSOCIATED WITH THE ELNINO SOUTHERN OSCILLATION (ENSO), *Monthly Weather Review*, 114, 2352-2362,
29 10.1175/1520-0493(1986)114<2352:napatp>2.0.co;2, 1986.

30 Sutton, R. T., and Hodson, D. L. R.: Climate response to basin-scale warming and cooling of the North Atlantic Ocean,
31 *Journal of Climate*, 20, 891-907, 10.1175/jcli4038.1, 2007.

32 Tanimoto, H.: Increase in springtime tropospheric ozone at a mountainous site in Japan for the period 1998-2006,
33 *Atmospheric Environment*, 43, 1358-1363, 10.1016/j.atmosenv.2008.12.006, 2009.

34 Wang, T., Wei, X. L., Ding, A. J., Poon, C. N., Lam, K. S., Li, Y. S., Chan, L. Y., and Anson, M.: Increasing surface ozone
35 concentrations in the background atmosphere of Southern China, 1994-2007, *Atmospheric Chemistry and Physics*,
36 9, 6217-6227, 2009.

37 Xu, X., Lin, W., Wang, T., Yan, P., Tang, J., Meng, Z., and Wang, Y.: Long-term trend of surface ozone at a regional
38 background station in eastern China 1991-2006: enhanced variability, *Atmospheric Chemistry and Physics*, 8,
39 2595-2607, 2008.

40 Yu, J.-Y., Zou, Y., Kim, S. T., and Lee, T.: The changing impact of El Nino on US winter temperatures, *Geophysical*
41 *Research Letters*, 39, 10.1029/2012gl052483, 2012.

42 Yu, J.-Y., and Zou, Y.: The enhanced drying effect of Central-Pacific El Nino on US winter, *Environmental Research*
43 *Letters*, 8, 10.1088/1748-9326/8/1/014019, 2013.

44 Sicard, P., De Marco, A., Troussier, F., Renou, C., Vas, N., and Paoletti, E.: Decrease in surface ozone concentrations
45 at Mediterranean remote sites and increase in the cities, *Atmospheric Environment*, 79, 705-715,
46 10.1016/j.atmosenv.2013.07.042, 2013.

47 Sun, L., Xue, L., Wang, T., Gao, J., Ding, A., Cooper, O. R., Lin, M., Xu, P., Wang, Z., Wang, X., Wen, L., Zhu, Y., Chen,
48 T., Yang, L., Wang, Y., Chen, J., and Wang, W.: Significant increase of summertime ozone at Mount Tai in Central
49 Eastern China, *Atmospheric Chemistry and Physics*, 16, 10637-10650, 10.5194/acp-16-10637-2016, 2016.

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1 Table 1. Trends and correlations in observed US average ozone during 1990–2014 calculated
 2 based on different data selection criteria ¹.

Data selection criteria	Ozone trend (ppb/yr) and correlation								
	Daily			Daytime			Nighttime		
	Trend (ppb/yr)	Corr. ⁷	De-trended Corr. ⁸	Trend (ppb/yr)	Corr. ⁷	De-trended Corr. ⁸	Trend (ppb/yr)	Corr. ⁷	De-trended Corr. ⁸
Default ²	0.16**			0.09*			0.21**		
Default_strict ³	0.15**	0.94**	0.94**	0.08*	0.93**	0.94**	0.21**	0.95**	0.93**
Data-continuity ⁴	0.17**	0.88**	0.87**	0.09*	0.87**	0.87**	0.24**	0.88**	0.86**
Data-coverage ⁵	0.14**	0.86**	0.85**	0.06*	0.83**	0.85**	0.22**	0.87**	0.84**
Cooper et al. ⁶	0.15**	0.88**	0.87**	0.06*	0.85**	0.87**	0.23**	0.89**	0.87**

- 3 1. ** P-value < 0.01, * P-value < 0.05 under an *F*-test for trends and a one-sided *T*-test for
 4 correlation.
 5 2. based on data in the 124 grid cells, our default choice.
 6 3. similar to a, but based on data in the 100 grid cells that include at least three sites.
 7 4. based on data in the 94 grid cells covering the sites with valid data in at least three years for
 8 every five years.
 9 5. based on 70 sites with more than 75% of hourly data available in all years.
 10 6. based on 82 sites passing criteria similar to those adopted by Cooper et al.(Cooper et al.,
 11 2012).
 12 7. Correlation between the US annual ozone time series in a sensitivity case and the time series
 13 in the default case.
 14 8. Similar to 7 but for de-trended ozone.
 15

1
 2 Table 2. Observed trends for seasonal and annual ozone over the eastern (25 °–50 °N, 65 °–100 °W)
 3 and western (25 °–50 °N, 100 °–125 °W) United States during various time periods ¹.

	MAM	JJA	SON	DJF	Annual
Daily mean ozone trend (ppb/yr)					
1990–2014 US	0.21 ^{**}	0.02	0.14 ^{**}	0.13 ^{**}	0.16 ^{**}
1990–2014 Eastern US	0.19 ^{**}	-0.03	0.12 ^{**}	0.12 ^{**}	0.12 ^{**}
1990–2014 Western US	0.25 ^{**}	0.12 ^{**}	0.16 ^{**}	0.16 ^{**}	0.20 ^{**}
2004–2012 US	0.34 ^{**}	0.16 ^{**}	0.29 ^{**}	0.27 ^{**}	0.30 ^{**}
2005–2011 US	0.27 ^{**}	0.09 [*]	0.20 ^{**}	0.21 ^{**}	0.23 ^{**}
2002–2014 US	0.12 ^{**}	0.04	0.07 [*]	0.06	0.08 [*]
Daytime mean ozone trend (ppb/yr)					
1990–2014 US	0.17 ^{**}	-0.08 [*]	0.09 [*]	0.12 ^{**}	0.09 [*]
1990–2014 Eastern US	0.15 ^{**}	-0.11 [*]	0.07 [*]	0.11 [*]	0.06
1990–2014 Western US	0.21 ^{**}	0.03	0.10 [*]	0.15 ^{**}	0.13 ^{**}
2004–2012 US	0.26 ^{**}	-0.03	0.20 ^{**}	0.24 ^{**}	0.19 ^{**}
2005–2011 US	0.21 ^{**}	-0.04	0.14 ^{**}	0.16 ^{**}	0.13 ^{**}
2002–2014 US	0.09 [*]	0.03	0.05	0.06	0.05
Nighttime mean ozone trend (ppb/yr)					
1990–2014 US	0.26 ^{**}	0.13 ^{**}	0.19 ^{**}	0.14 ^{**}	0.21 ^{**}
1990–2014 Eastern US	0.24 ^{**}	0.05	0.16 ^{**}	0.13 ^{**}	0.18 ^{**}
1990–2014 Western US	0.30 ^{**}	0.20 ^{**}	0.23 ^{**}	0.17 ^{**}	0.25 ^{**}
2004–2012 US	0.46 ^{**}	0.35 ^{**}	0.40 ^{**}	0.30 ^{**}	0.43 ^{**}
2005–2011 US	0.35 ^{**}	0.24 ^{**}	0.28 ^{**}	0.25 ^{**}	0.31 ^{**}
2002–2014 US	0.16 ^{**}	0.06	0.11 [*]	0.07 [*]	0.13 ^{**}

4 1. ** P-value < 0.01. * P-value < 0.05 under an *F*-test.

5

1 Table 3. Observed trends for the 5th, 50th and 95th percentiles of ozone over the rural, suburban
 2 and urban areas during 1990–2014 ¹.

	Rural	Suburban	Urban
Daily mean ozone trend (ppb/yr)			
5 th	0.25 ^{**}	0.25 ^{**}	0.24 ^{**}
50 th	0.11 [*]	0.15 ^{**}	0.21 ^{**}
95 th	0.06	0.04	0.08 [*]
Daytime mean ozone trend (ppb/yr)			
5 th	0.29 ^{**}	0.29 ^{**}	0.28 ^{**}
50 th	0.02	0.10 [*]	0.19 ^{**}
95 th	-0.13 ^{**}	-0.21 ^{**}	-0.15 ^{**}
Nighttime mean ozone trend (ppb/yr)			
5 th	0.21 ^{**}	0.21 ^{**}	0.19 ^{**}
50 th	0.19 ^{**}	0.20 ^{**}	0.22 ^{**}
95 th	0.22 ^{**}	0.24 ^{**}	0.27 ^{**}

3 1. ^{**} P-value < 0.01. ^{*} P-value < 0.05 under an *F*-test.

4

1 Table 4. Correlations (R) between de-trended time series of AMONI index and de-trended daily
 2 mean ozone, daytime mean ozone and nighttime mean ozone in different seasons and regions ¹.

		MAM	JJA	SON	DJF	Annual
US	Daily	0.25	0.58*	0.67**	0.22	0.62**
	Daytime	0.19	0.67**	0.70**	0.23	0.71**
	Nighttime	0.29	0.51*	0.59*	0.21	0.33
Eastern US	Daily	0.11	0.66**	0.68**	0.06	0.68**
	Daytime	0.11	0.72**	0.74**	0.18	0.73**
	Nighttime	0.07	0.55*	0.60**	0.09	0.38
Western US	Daily	0.48*	0.27	0.22	0.44*	0.45*
	Daytime	0.38	0.25	0.19	0.37	0.34
	Nighttime	0.50*	0.27	0.24	0.46*	0.46*

3 1.** for P-value < 0.01 and * for P-value < 0.05 under a one-side *T*-test

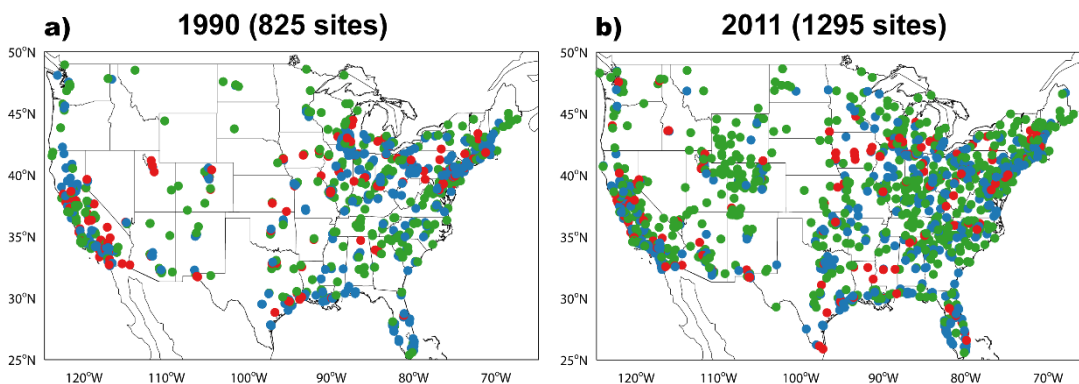
1 Table 5. Interannual variability of observed and modeled ozone during 2004–2012 and their
 2 correlation¹.

	Observation	Model				
		Control	Fixed anthropogenic emissions	global	Fixed anthropogenic emissions	US Fixed meteorology
Annual daily mean ozone						
Trend (ppb/yr)	0.30**	0.22**	0.06	0.07	0.18**	
Correlation		0.86**	0.64**	0.65**	0.52*	
De-trended correlation ²		0.89**	0.61**	0.63**	0.31	
Annual daytime mean ozone						
Trend (ppb/yr)	0.19**	0.14	0.05	0.06	0.10	
Correlation		0.88**	0.76**	0.78**	0.41*	
De-trended correlation ²		0.90**	0.81**	0.82**	0.39	
Annual nighttime mean ozone						
Trend (ppb/yr)	0.43**	0.31**	0.07	0.09	0.26**	
Correlation		0.86**	0.39	0.37	0.71**	
De-trended correlation ²		0.88**	0.24	0.28	0.31	
Spring daily mean ozone						
Trend (ppb/yr)	0.34**	0.25**	0.07	0.12	0.15**	
Correlation		0.84**	0.62**	0.67**	0.61**	
De-trended correlation ²		0.87**	0.65**	0.69**	0.42	
Spring daytime mean ozone						
Trend (ppb/yr)	0.26**	0.19**	0.06	0.11	0.09	
Correlation		0.89**	0.73**	0.76**	0.52*	
De-trended correlation ²		0.90**	0.78**	0.77**	0.38	
Spring nighttime mean ozone						
Trend (ppb/yr)	0.46**	0.32**	0.07	0.14	0.20**	
Correlation		0.83**	0.41*	0.49*	0.69**	
De-trended correlation ²		0.85**	0.33	0.36	0.34	
Summer daily mean ozone						
Trend (ppb/yr)	0.16*	0.09	0.04	0.03	0.06	
Correlation		0.88**	0.72**	0.77**	0.50*	
De-trended correlation ²		0.89**	0.79**	0.79**	0.28	
Summer daytime mean ozone						
Trend (ppb/yr)	-0.03	-0.05	0.03	0.02	-0.07	
Correlation		0.89**	0.77**	0.77**	0.48*	
De-trended correlation ²		0.91**	0.83**	0.81**	0.35	
Summer nighttime mean ozone						
Trend (ppb/yr)	0.35**	0.24**	0.05	0.05	0.18*	
Correlation		0.86**	0.48*	0.46*	0.58*	
De-trended correlation ²		0.88**	0.44*	0.48*	0.40	
Fall daily mean ozone						
Trend (ppb/yr)	0.29**	0.22**	0.06	0.06	0.19**	
Correlation		0.85**	0.67**	0.66**	0.56*	
De-trended correlation ²		0.87**	0.65**	0.67**	0.32	
Fall daytime mean ozone						
Trend (ppb/yr)	0.20**	0.13	0.05	0.06	0.11	
Correlation		0.86**	0.69**	0.68**	0.49*	
De-trended correlation ²		0.87**	0.72**	0.71**	0.34	
Fall nighttime mean ozone						
Trend (ppb/yr)	0.40**	0.29**	0.07	0.07	0.26**	
Correlation		0.84**	0.36	0.37	0.67**	
De-trended correlation ²		0.87**	0.29	0.33	0.36	
Winter daily mean ozone						
Trend (ppb/yr)	0.27**	0.21**	0.05	0.07	0.19**	
Correlation		0.83**	0.61**	0.63**	0.61**	
De-trended correlation ²		0.84**	0.63**	0.64**	0.33	
Winter daytime mean ozone						
Trend (ppb/yr)	0.24**	0.17*	0.04	0.05	0.12	
Correlation		0.85**	0.68**	0.67**	0.54*	
De-trended correlation ²		0.86**	0.72**	0.73**	0.32	
Winter nighttime mean ozone						

Trend (ppb/yr)	0.30**	0.24**	0.05	0.08	0.25**
Correlation		0.82**	0.31	0.35	0.72**
De-trended correlation ²		0.84**	0.23	0.26	0.29

- 1 1. ** P-value < 0.01, * P-value < 0.05 under an *F*-test for trends and a one-sided *T*-test for
- 2 correlation.
- 3 2. Model and observation data are de-trended prior to correlation calculations.

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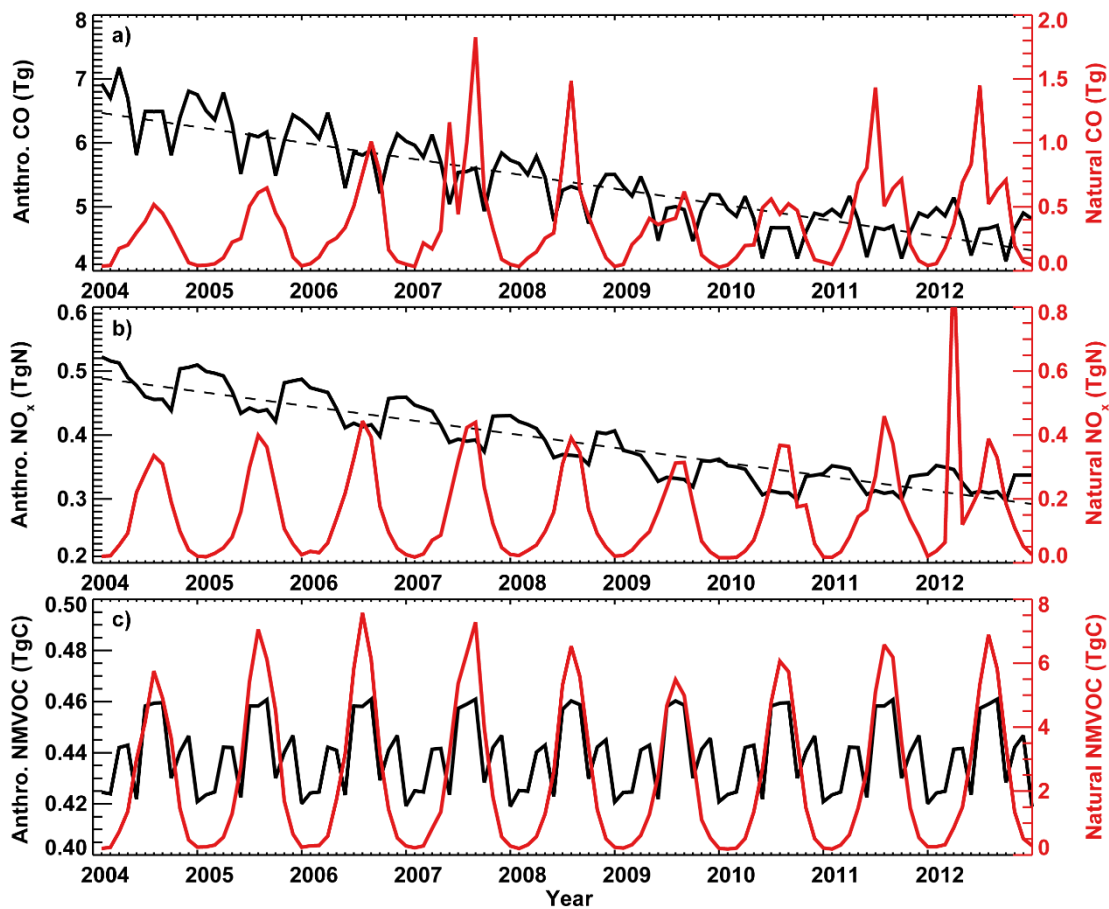


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9 Figure 1. AQS ozone site distributions in 1990 (with the fewest sites) and 2011 (with the most
10 sites). Rural, suburban and urban sites are shown in green, blue and red, respectively.

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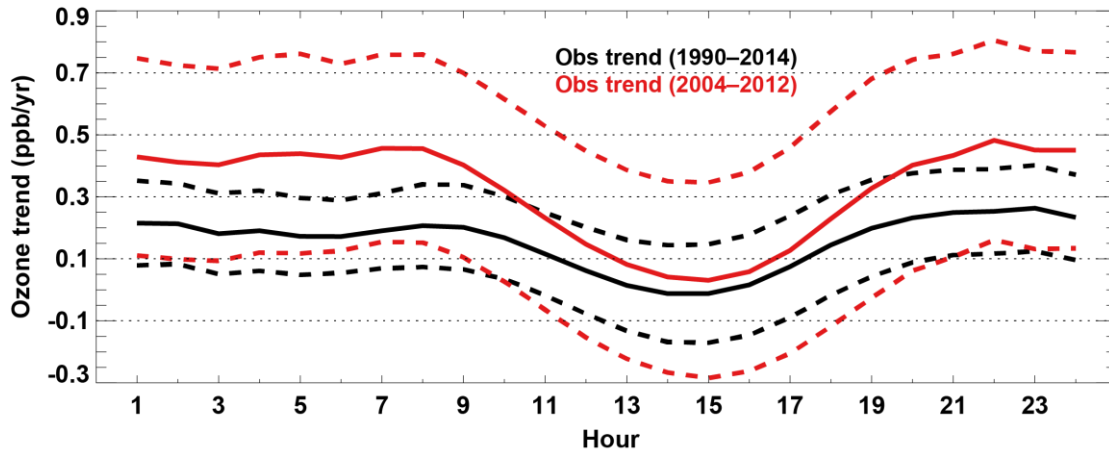
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 2 Figure 2. Monthly anthropogenic (fossil + biofuel, black lines) and natural (red lines) emissions
 3 of ozone precursors over the US used in GEOS-Chem. Natural NO_x emissions include biomass
 4 burning, lightning, and soil (including fertilizer) sources. Natural CO emissions are from biomass
 5 burning and oxidization of monoterpenes. Natural NMVOC emissions are from biomass burning
 6 and biogenic sources.

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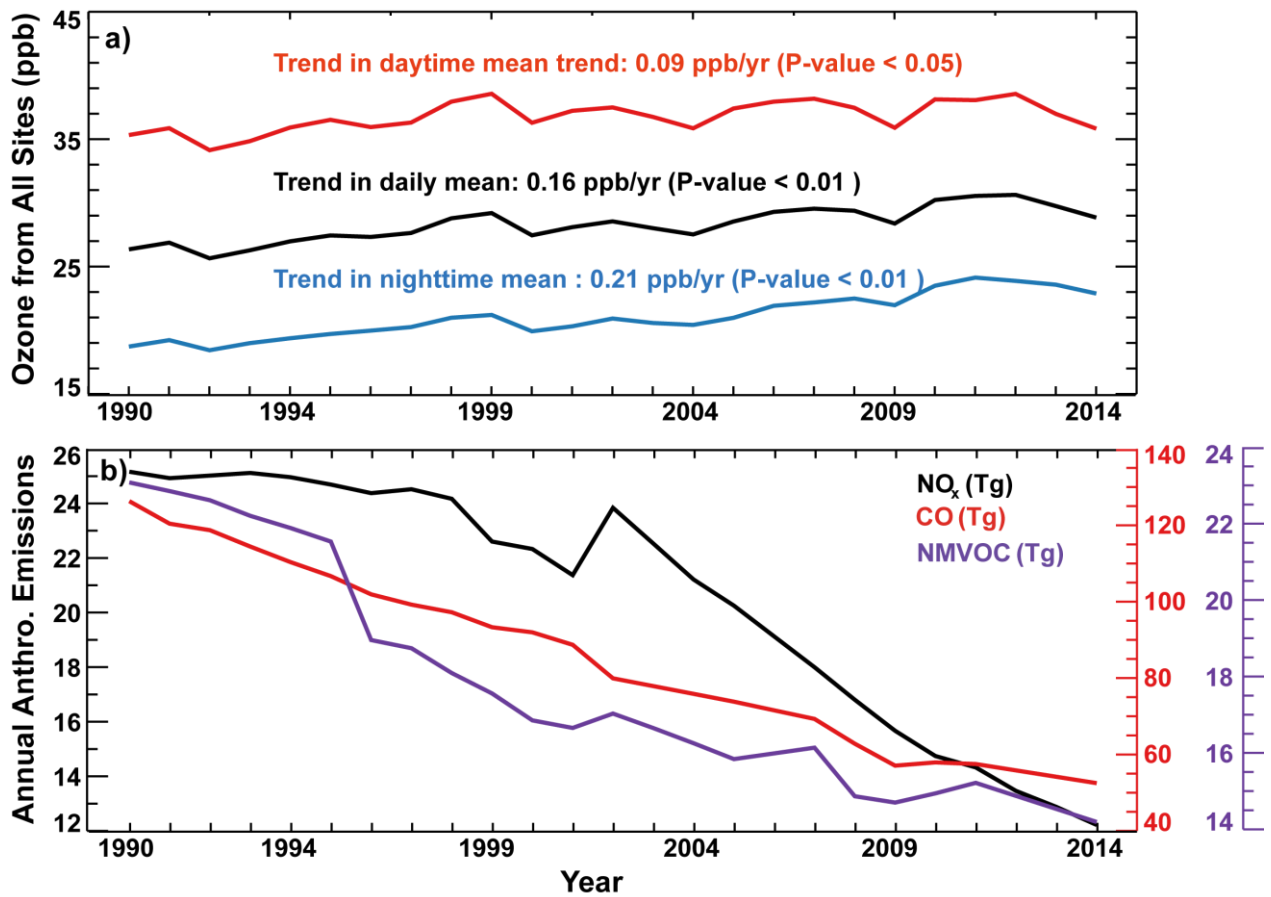
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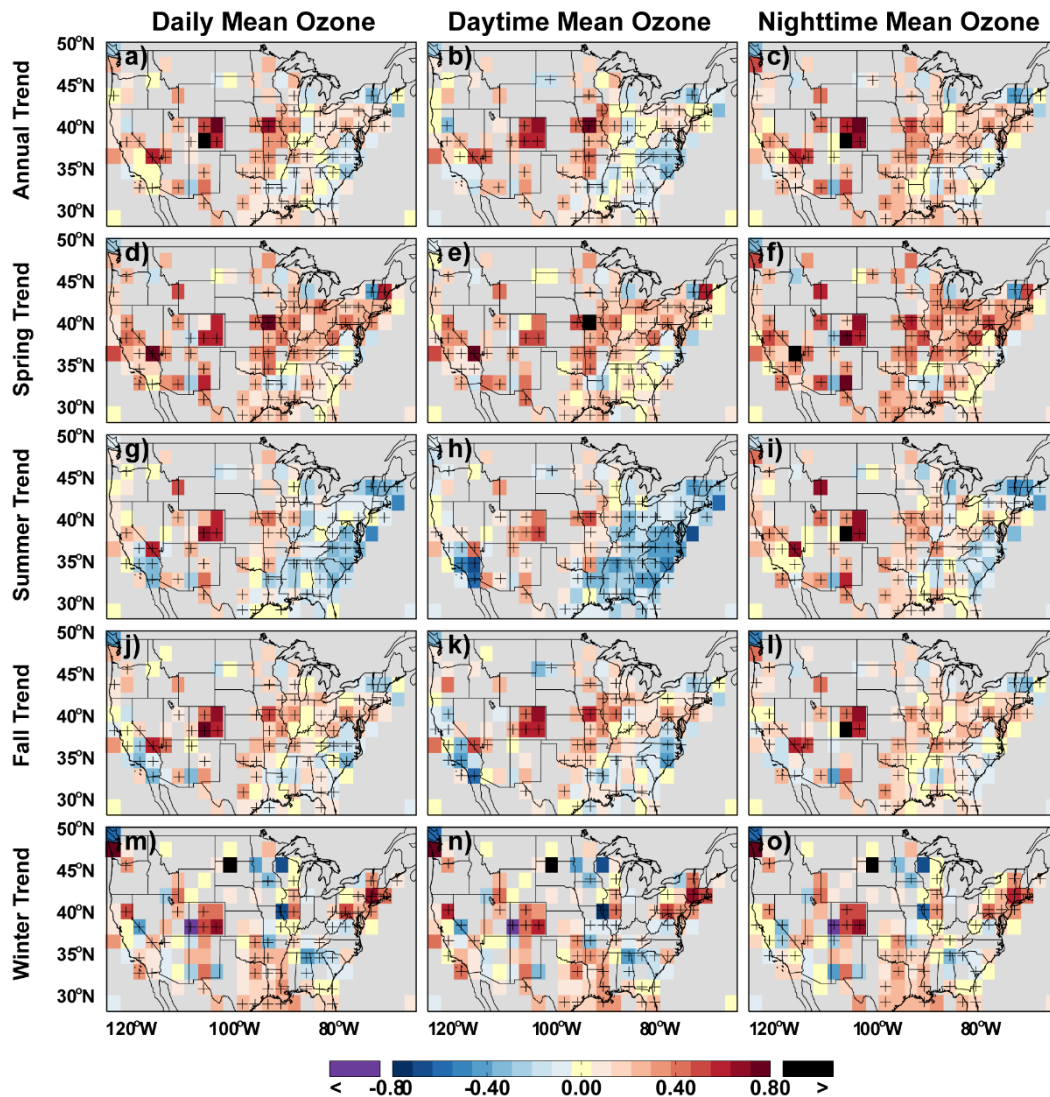
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3 Figure 3. Trends in the observed surface ozone over the US, calculated based on data in the
4 selected 124 grid cells. The black line shows the 1990–2014 trend in the US annual mean ozone
5 for each hour of the day (local standard time), the red line depicts the observed trend over 2004–
6 2012, and the dashed lines indicate their deviations.

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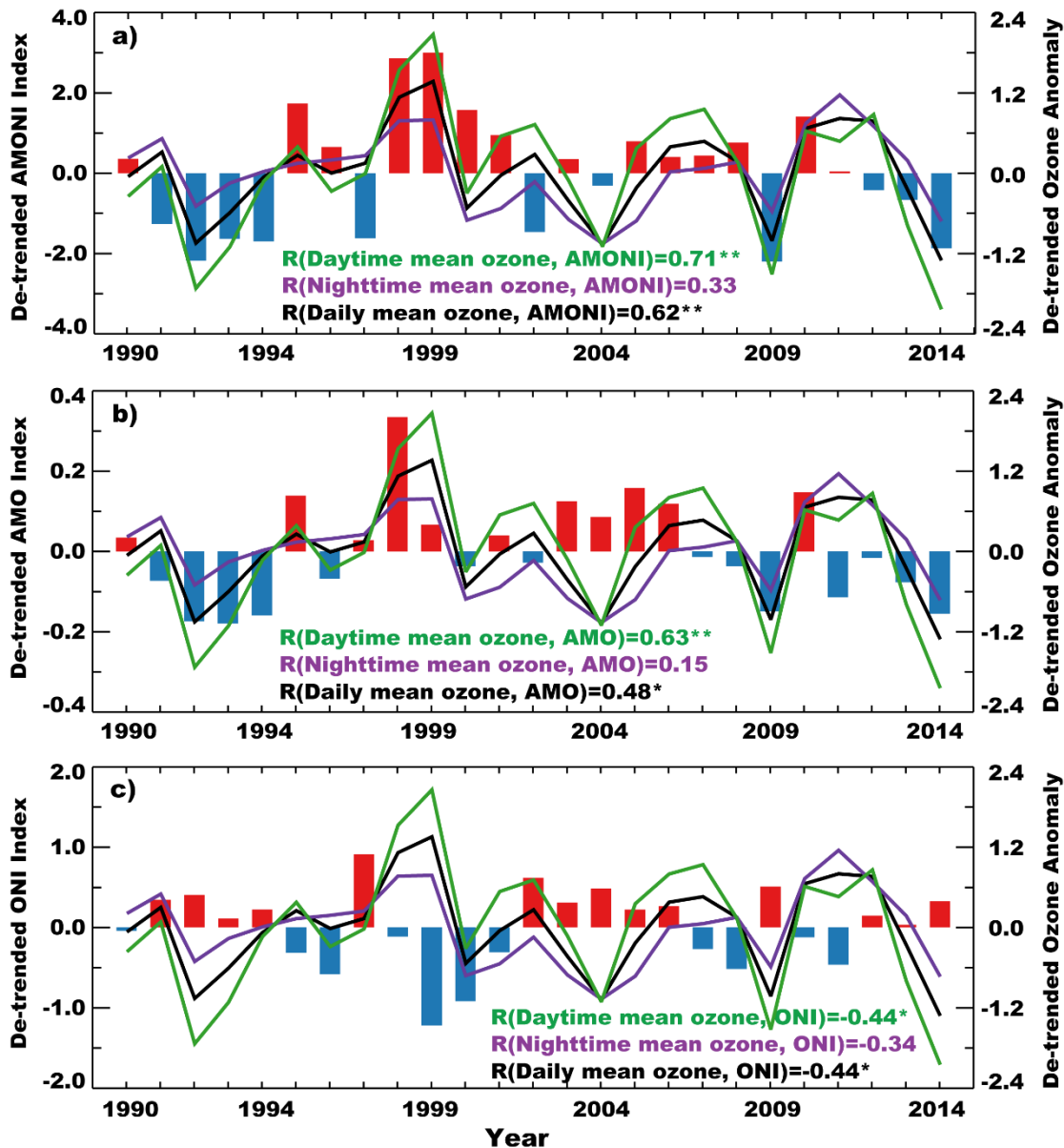


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 2 Figure 4. Long-term trends in the observed surface ozone and anthropogenic precursor emissions
 3 over the US during 1990–2014. (a) The ozone trend averaged over the 124 gridd cells. (b) The
 4 US annual anthropogenic (fossil + biofuel) emissions of NO_x (black line), CO (red line), and
 5 NMVOC (purple line) from the National Emissions Inventory
 6 (<http://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data>).



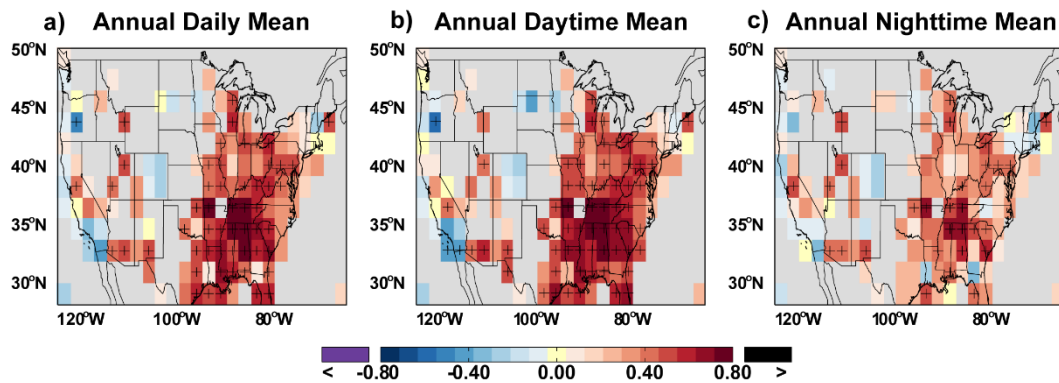
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 2 Figure 5. Trends over 1990–2014 in annual and seasonal daily mean, daytime mean, and
 3 nighttime mean ozone observations in the selected 124 grid cells. Trends are statistically
 4 significant (P -value < 0.05 under a F -test) in grid cells overlaid with '+'. The grid cells in grey
 5 have no data.

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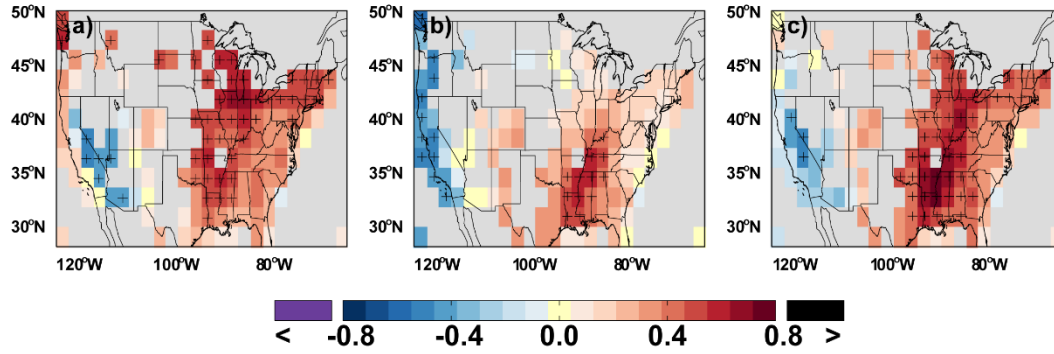


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2 Figure 6. De-trended anomaly time series of climate indices and observed US mean ozone. The
3 anomalies of annual mean daily mean ozone (black lines), daytime mean ozone (green lines) and
4 nighttime mean ozone (purple lines) are plotted with the annual AMONI index (a), with the
5 annual AMO index (b), and with the annual ONI index (c). Red and blue bars indicate positive
6 and negative anomalies of climate indices, respectively. Also shown are correlations between
7 ozone and individual indices (** for P-value < 0.01 and * for P-value < 0.05 under a one-side
8 T-test).

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 2 Figure 7. Correlation in interannual variability over 1990–2014 between the annual AMONI
 3 index and the annual average daily mean ozone (a), daytime mean ozone (b), and nighttime mean
 4 ozone (c). All data are de-trended prior to correlation calculations. Correlations are statistically
 5 significant (P-value < 0.05 under a one-sided *T*-test) in grid cells overlaid with '+'. The grid cells
 6 in grey have no AQS data.

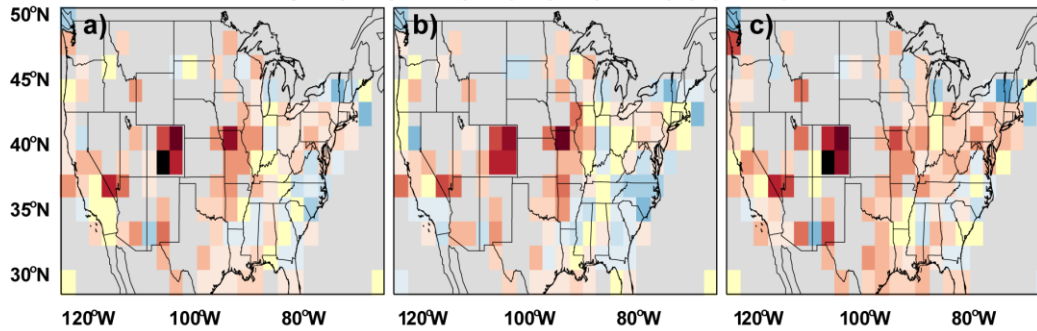


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 2 Figure 8. Correlation for interannual variability over 1990–2010 between the annual AMO (a),
 3 ONI (b), and AMONI (c) anomalies and the annual average daily mean 2-meter air temperature
 4 from MERRA. Correlations are statistically significant (P-value < 0.05 under a one-sided *T*-test)
 5 in grid cells overlaid with '+'. MERRA temperature data are available through 2010, and are
 6 sampled based on valid daily mean ozone data. MERRA data are used here (in place of GEOS-5)
 7 to include years prior to 2004. All data are de-trended prior to correlation calculations. The grid
 8 cells in grey have no AQS data.

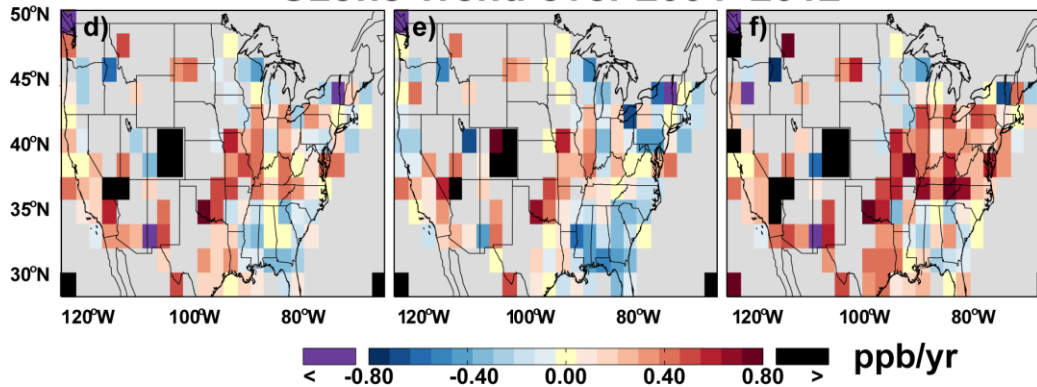
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Ozone Trend over 1990–2014

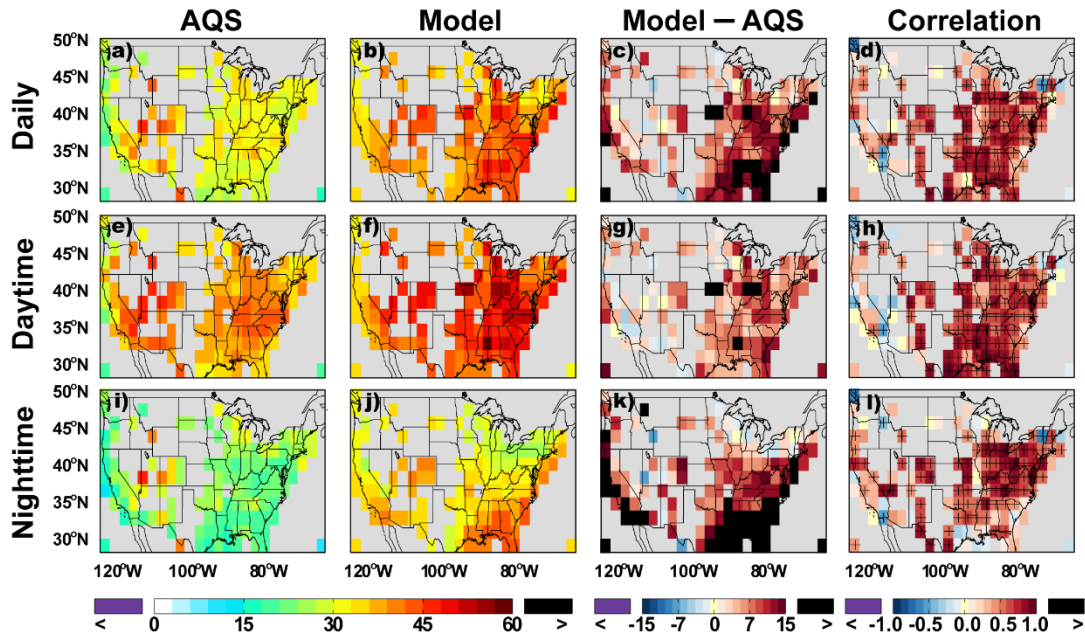


Ozone Trend over 2004–2012



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2 Figure 9. Trends in AQS annual ozone over different time periods. (a-c) Trends (ppb/yr) over
3 1990–2014 in daily mean ozone (a), daytime mean ozone (b), and nighttime mean ozone (c). (d-f)
4 Similar to (a-c) but for trends over 2004–2012. Panels (a-c) are the same as Fig. 5a-c. The grid
5 cells in grey have no data.

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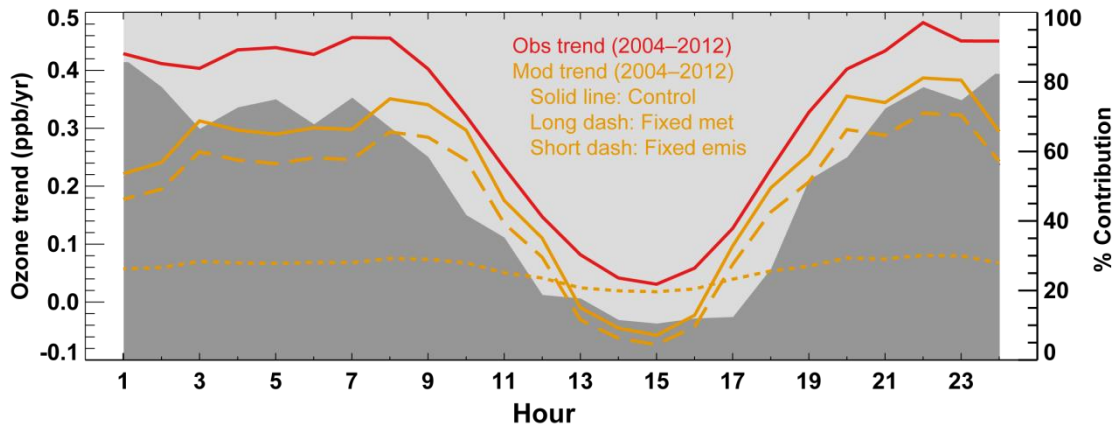


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 2 Figure 10. Observed and modeled 2004–2012 average daily, daytime and nighttime mean ozone
 3 (ppb) over the US, as well as model biases (ppb) against and interannual correlation to the
 4 observations. Grid cells with statistically significant correlation coefficients are highlighted by
 5 ‘+’. The grid cells in grey have no AQS data.

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4 Figure 11. Trends in the modeled surface ozone over the US at different times of day. The yellow
5 lines depict the trends in three model simulations (control, fixed meteorology, and fixed global
6 anthropogenic emissions). The two shaded areas indicate the individual contributions of
7 interannual climate variability (light grey shade) and global anthropogenic emissions (dark grey
8 shade) to the simulated 2004–2012 ozone changes.

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