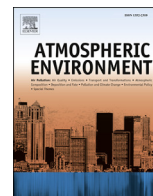




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Response of the summertime ground-level ozone trend in the Chicago area to emission controls and temperature changes, 2005–2013



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HIGHLIGHTS

- O₃ in Chicago did not decline during 2005–2013, despite reductions in NO_x emissions.
- Since 2008/2009, O₃ formation has become more sensitive to VOC emissions.
- Concentrations of reactive VOCs increased significantly after 2008/2009.
- Meteorological conditions explain about 53% of the O₃ variance.

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ABSTRACT

Despite strenuous efforts to reduce the emissions of ozone precursors such as nitrogen oxides (NO_x), concentrations of ground-level ozone (O₃) still often exceed the National Ambient Air Quality Standard in U.S. cities in summertime, including Chicago. Furthermore, studies have projected a future increase in O₃ formation due to global climate change. This study examines the response of summertime O₃ to emission controls and temperature change in the Chicago area from 2005 to 2013 by employing observations of O₃, O₃ precursors, and meteorological variables. We find that meteorology explains about 53% of the O₃ variance in Chicago. O₃ mixing ratios over Chicago are found to show no clear decline over the 2005–2013 period. The summertime ground-level O₃ trend consists of a decrease of 0.08 ppb/year between 2005 and 2009 and an increase of 1.49 ppb/year between 2009 and 2013. Emissions of NO_x and concentrations of NO₂ have been decreasing steadily from 2005 to 2013 in the Chicago area. Concentrations of volatile organic compounds (VOCs) in Chicago, however, have more than doubled since 2009, even though emission inventories suggest that VOC emissions have decreased. We believe that O₃ production in Chicago became more sensitive to VOCs starting in 2008/2009 and may have switched from being NO_x-limited to VOC-limited. The warmer climate since 2008 has also contributed to the increasing ozone trend in the Chicago area. Increased attention should be paid to improving the quantification of VOC sources, enhancing the monitoring of reactive VOC concentrations, and designing VOC mitigation measures.

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1. Introduction

Despite strenuous efforts over a period of almost 25 years since the passage of the U.S. Clean Air Act Amendments (CAAA) of 1990, large areas of the U.S., particularly urban areas, continue to

experience elevated summertime ozone (O₃) concentrations. These high concentrations aggravate asthma and other respiratory conditions and may lead to premature death, especially of people with pre-existing heart and lung disease. Because of these effects, the costs for medication, doctor visits, emergency department visits, and hospital admissions add to the economic burden of U.S. cities and their residents. Sensitive vegetation can also be harmed by elevated O₃ levels. In addition, O₃ plays a critical role in

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photochemical reactions that control the lifetimes of other air pollutants. Regulatory initiatives by the U.S. Environmental Protection Agency (U.S. EPA), in concert with state and tribal agencies, have driven down emissions of the O₃ precursors nitrogen oxides (NO_x) and volatile organic compounds (VOC), and yet summertime O₃ concentrations have not shown a corresponding downward trend in many locations. Why is this? And what is the prognosis for air quality improvement in a world of increasingly limited and expensive emission controls, a growing population, and a warming climate? This study examines the experience in Chicago over the period 2005–2013.

The National Ambient Air Quality Standards (NAAQS) for O₃ were codified in their current form in 1997 as an 8-h concentration of 0.08 parts per million (ppm) or 80 parts per billion (ppb)—rounded to 84 parts per billion (ppb) for compliance purposes—defined as the annual fourth-highest daily maximum value, averaged over three years. In 2008, the level was reduced to 75 ppb. These values applied to both primary (for the protection of public health) and secondary (for the protection of public welfare) standards. At present, as part of its mandatory five-year review, U.S. EPA is considering revising the standard again, down to somewhere in

the range of 60–70 ppb. In 2012, U.S. EPA made final designations on compliance with the 2008 O₃ standard. The greater Chicago area—consisting of eight Illinois (IL) counties (two of them partial), two northwest Indiana (IN) counties, and one southeast Wisconsin (WI) county (partial)—was designated to be in marginal non-attainment, based on monitoring data, state recommendations, and related technical information.

In order to reduce O₃ concentrations nationwide and to achieve compliance with the NAAQS, several initiatives were triggered by the 1990 CAAA with the aim of reducing emissions of O₃ precursors. Because NO_x is an important precursor of O₃, efforts were made to restrict NO_x emissions from on-road vehicles and fossil-fuel-burning power plants. Vehicle NO_x emissions declined nationwide due to implementation of the requirements of the 1990 CAAA, especially after the more-stringent Tier 2 standards were phased-in between 2004 and 2009 (Dallmann and Harley, 2010; McDonald and Gentner, 2013). The State Implementation Plan (SIP) Call was issued in 1998 with the objective of cutting NO_x emissions so that summertime O₃ levels would be lowered (<http://www.epa.gov/airmarkets/progsregs/nox/noxsipcall.html>). Furthermore, the Clean Air Interstate Rule (CAIR) was introduced in 2005 for 27

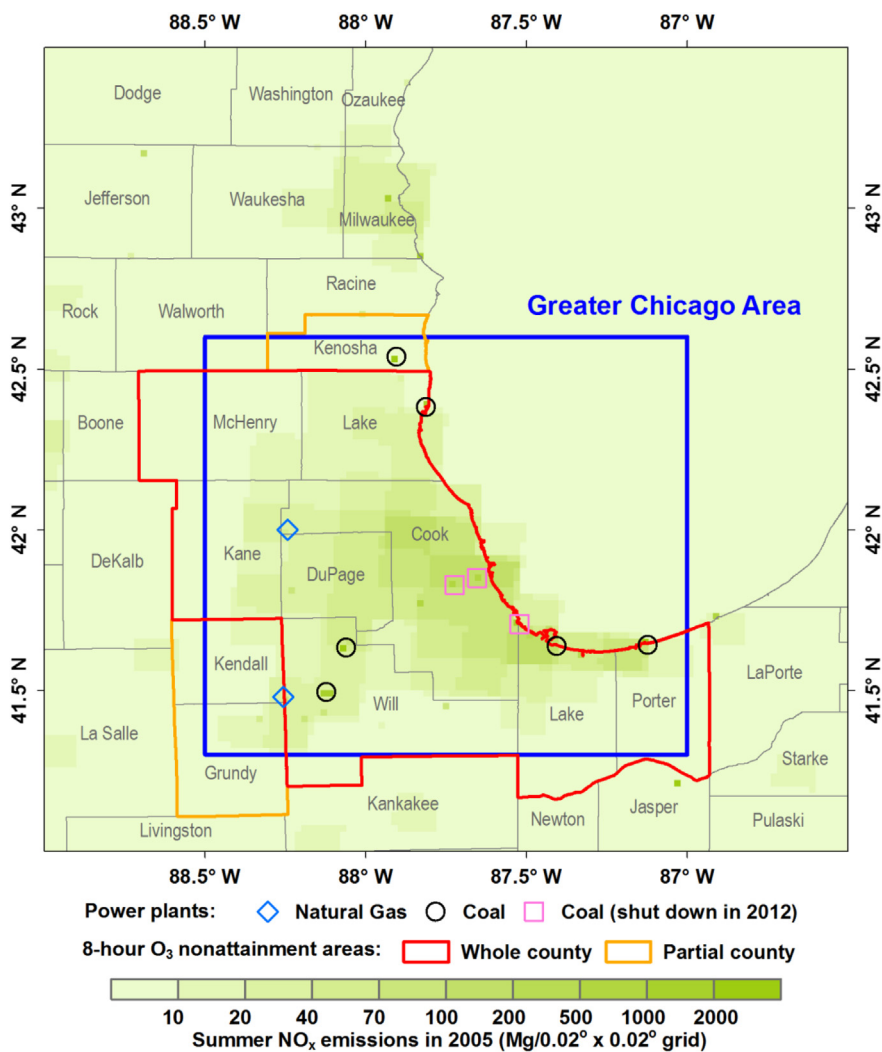


Fig. 1. Summertime NO_x emissions in 2005 in Chicago and surrounding regions from Xing et al. (2013) at 0.02° × 0.02° resolution. The greater Chicago area is enclosed by the blue box. The red line encloses whole 8-h O₃-nonattainment counties; partial O₃-nonattainment counties are enclosed by orange lines. Blue diamonds mark the locations of large natural-gas-burning power plants, black circles are large coal-burning power plants, and pink squares are the three coal-burning power plants that were shut in 2012. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

eastern states, including IL, to further reduce NO_x emissions from coal-fired power plants (<http://www.epa.gov/cair/>). As we show in this paper, these regulatory initiatives did cause a downward trend in NO_x emissions in the greater Chicago area during the study period, 2005–2013; and this was reinforced by the closure of three aging coal-fired power plants in 2012: the Fisk Generating Station and the Crawford Generating Station in Chicago and the State Line Generating Plant in Hammond, IN, on the border between IL and IN (locations shown in Fig. 1). Yet there has been no perceptible downward trend in O₃ during the period. The purpose of this study is to develop an understanding of (a) how O₃ concentrations have changed since 2005 in light of the emission reductions that have occurred, (b) how temperature and other meteorological factors are related to the O₃ changes, and (c) what the implications are for O₃ levels in the future.

2. Data and methods

The greater Chicago area is defined for the purposes of this study as the area between 41.3°N and 42.6°N latitude, and between 87.0°W and 88.5°W longitude, as shown in Fig. 1. It includes the western suburban areas of Chicago in IL and parts of northwest IN and southeast WI. Counties designated as nonattainment for the 8-h O₃ standard are outlined in red (whole county) and orange (partial county) (in web version). Fig. 1 also shows the intensity of summertime (May to August) NO_x emissions (in Mg per 0.02° × 0.02° grid) in 2005, according to a recent U.S. emission inventory (Xing et al., 2013). The area comprising urban Chicago showed high NO_x emission rates in 2005 because of its high energy consumption and extensive road transportation. Coal-burning and natural-gas-burning power plants can be seen in Fig. 1 as large point sources of NO_x, and the eleven largest units in the greater Chicago area are highlighted with symbols.

This study analyzes the trends of summertime O₃ concentrations in the greater Chicago area for the period 2005–2013. We focus on the summer months from May to August when elevated O₃ concentration events are most likely to occur. The variations in ground-level O₃ concentration are compared with variations in NO₂ and CO concentrations, because of the strong atmospheric chemistry linkages among the three species. Monitored air quality data are obtained from U.S. EPA data archives (<http://www.epa.gov/airquality/airdata/index.html>): daily maximum 8-h O₃ mixing ratio, daily maximum 1-h NO₂ mixing ratio, and daily maximum 8-h CO mixing ratio. There were 23 O₃ monitoring sites that operated in the greater Chicago area in the period 2005–2013. Nineteen of them operated continuously throughout the nine-year period: 10 in Cook County, IL; four spread across the suburban IL counties of DuPage, Kane, Lake, and McHenry; and five in Lake County, IN, and Porter County, IN. The correlation coefficients of the daily 8-h maximum O₃ mixing ratios between any two sites were calculated and found to range between 0.71 and 0.94, with the lower values occurring among sites that are the furthest apart in a north-south direction. This indicates good correlation in the temporal variability among O₃ concentrations at different sites. The spatial homogeneity of the data among different sites was also examined by calculating the coefficient of divergence (COD), as described in Yadav and Turner (2014). The COD values between any two sites were found to range between 0.04 and 0.13; low COD values (less than 0.20) are associated with spatial homogeneity while high COD values indicate spatial heterogeneity. The high correlation coefficients and low COD values both indicate that O₃ is homogeneous within the study area—consistent with the regional nature of ozone formation—and that observations made at a central site are representative of the entire greater Chicago area. We also use NO₂ and CO observations in the area. There were six NO₂ monitoring

sites in Cook County, IL, and one in Lake County, IN; there were five CO monitoring sites in Cook County, IL, and one in Lake County, IN.

We also examine changes in the tropospheric columns of O₃ and NO₂ in the Chicago area from 2005 to 2013 based on satellite observations. The Ozone Monitoring Instrument (OMI) on NASA's Aura satellite is able to provide daily global observations of tropospheric NO₂ and O₃ from 2004 to present with an equator crossing time of 1:45 p.m. (Levelt et al., 2006; Ziemke et al., 2006). Studies have shown that OMI NO₂ data can be used to assess emissions from power plants in the U.S. and in the world (Lu and Streets, 2012; Streets et al., 2013; Duncan et al., 2013). We use monthly average tropospheric mean O₃ mixing ratios from the Data Service of NASA's Atmospheric Chemistry and Dynamics Laboratory (<http://acd-ext.gsfc.nasa.gov/>) and NO₂ vertical column data from the Derivation of OMI tropospheric NO₂ (DOMINO) product of the Royal Netherlands Meteorological Institute (KNMI) (Boersma et al., 2011).

The NO_x emission data used in this study are from the 1990–2010 historical emissions inventory for the U.S. developed by Xing et al. (2013), which were spatially allocated by them to 12 km × 12 km using the SMOKE model. We reprocessed their gridded inventory for the greater Chicago area to 0.02° × 0.02° resolution for the summer months of 2005–2013, to be consistent with the spatial resolution of our OMI NO₂ data. The inventory of Xing et al. (2013) was developed by U.S. EPA to be consistent with the triennial National Emission Inventory (NEI), constrained by U.S. EPA AP-42 emission factors, and built upon activity data from the State Energy Data System (SEDS).

This study evaluates the relationship between daily maximum O₃ concentration and daily surface meteorological conditions by using a linear regression model. The following meteorological variables are considered: daily maximum temperature, daily average dew point temperature, daily minimum relative humidity, and wind speed and direction. The meteorological data are

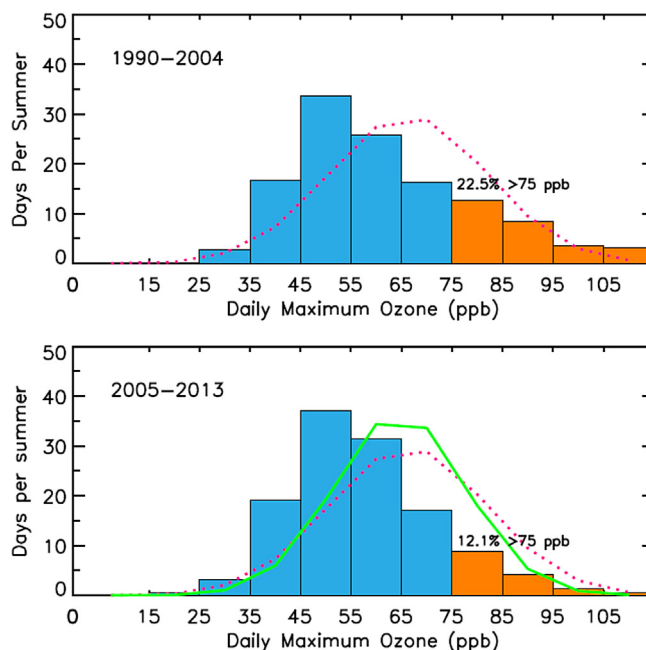


Fig. 2. Average frequency of summertime daily maximum O₃ mixing ratios in the greater Chicago area, as defined in Fig. 1, for the time periods of 1990–2004 (top) and 2005–2013 (bottom). The orange bars show values in excess of the current standard of 75 ppb. The pink dotted line is the Gaussian fit for the 1990–2004 period and the green solid line is the Gaussian fit for 2005–2013. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

collected for the O'Hare Airport station (41.98°N, 87.90°W) from the Midwestern Regional Climate Center (<http://mrcc.isws.illinois.edu/CLIMATE/>).

3. Results

In this section we present trends in measured ground-level concentrations of O₃, NO₂, and CO in the greater Chicago area during the study period, trends in O₃ and NO₂ column amounts observed from space, and trends in the emissions of the key O₃ precursors NO_x and VOC. We also relate the trends in measured ground-level O₃ concentrations to simultaneous measurements of meteorological variables at the same sites.

3.1. Trends in O₃ concentrations

In order to assess progress made by implementation after about 2005 of the first set of NO_x emission limitations prescribed by the 1990 CAAA and subsequent regulations like CAIR, we first compared O₃ concentrations in the 2005–2013 period with the prior 1990–2004 period by calculating the average number of days per summer when maximum daily O₃ mixing ratios fell within certain ranges. The maximum daily O₃ mixing ratio was determined by selecting the highest value among the daily maximum 8-h O₃ concentrations at all the available O₃ monitoring sites within the greater Chicago area, according to the U.S. EPA data archives. The results are shown in Fig. 2. Gaussian fits of the distributions for the two time periods show that the concentration distribution did not change much. The center value of the Gaussian fit is shifted downward by only 1.7 ppb from 56.3 ppb in 1990–2004 to 54.6 ppb in 2005–2013. The Gaussian fit for the period 2005–2013 has a smaller spread than that for 1990–2004, with a reduction in both low and high O₃ concentration tails, but the reduction in the high-end tail is more significant. It shows that high O₃ episodes (>75 ppb) occurred on average 22.5% of the summertime days in the greater Chicago area during the period 1990–2004. This was reduced to 12.1% of days during 2005–2013, suggestive of partial effectiveness of emission controls at limiting high O₃ episodes. However, it is of concern that O₃ concentrations still often exceeded the current standard of 75 ppb during 2005–2013 and occasionally exceeded 100 ppb. It is important to understand why only limited improvement in O₃ concentrations has occurred since 2005, despite all the efforts to reduce emissions, as this has important implications for the ability of Chicago to ever achieve attainment, particularly in light of potential future tightening of the O₃ standard. From this point on, our study focuses on the summers from 2005 to 2013.

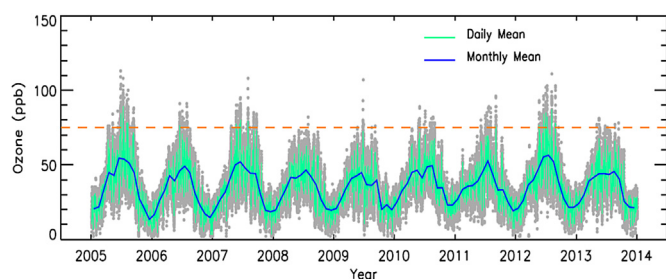


Fig. 3. Observed ground-level O₃ concentrations in the greater Chicago area in the period 2005–2013. The gray dots represent the daily 8-h O₃ maximum values observed at the 19 monitoring sites in the region; the green line shows the mean values of daily 8-h O₃ maxima at all these sites; and the blue line is the monthly mean. The orange dashed line shows the 75-ppb O₃ standard. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3 shows the complete time record of measured O₃ concentrations across all 19 monitoring sites that have a continuous record in the greater Chicago area for the time period 2005–2013. The data show no obvious trend in daily maxima, daily means, or monthly means. Nor is there any apparent systematic reduction in the number of days of exceedances of the current 75 ppb standard over the nine-year period or of days with very high exceedances (>100 ppb, say). There is significant interannual variability, however, with several years showing sustained high O₃ concentrations (2005, 2007, and 2012, for example) and a few years in which 75 ppb was barely exceeded on any days (2008 and 2013).

A clearer view of the trend in O₃ concentrations in the greater Chicago area can be obtained by calculating an average O₃ mixing ratio from the entire U.S. EPA monitoring data set for each summer in the period (Fig. 4). The resulting trend shows that the average summertime ground-level O₃ concentration decreased from 2005 to 2009 by 10.6 ppb (21% of the 2005 value). However, this decline was followed by an increase of 12.7 ppb (31.7% of the 2009 value) between 2009 and 2012, followed by a decrease in 2013. We then examined the trend of tropospheric column O₃ in the greater Chicago area using the monthly-mean tropospheric O₃ mean volume mixing ratios from OMI satellite observations (http://acd-ext.gsfc.nasa.gov/Data_services/cloud_slice/new_data.html). The results are also shown in Fig. 4. The trend in ground-level O₃ measurements is similar, but not identical, to OMI satellite observations of the tropospheric column O₃ over Chicago during the same period. OMI shows a decreasing trend (16.9%) from 2005 to 2011, followed by increases in both 2012 and 2013. The main difference between the two datasets is the contrasting changes between 2012 and 2013.

3.2. Trends in concentrations of O₃-related species

In order to explain the observed O₃ concentration changes, we also gathered and analyzed ground-level concentrations of NO₂ and CO—the two criteria air pollutants that are linked with O₃ formation and destruction in the atmosphere. Note that, although VOCs are also important in ozone photochemistry, they are not criteria air pollutants and are not routinely measured in the same U.S. EPA monitoring network. Selected VOC species are measured as hazardous pollutants (HAPs) in a different and smaller network. Results for several VOC species are discussed later this section.

Using U.S. EPA's surface measurements, we calculated the summertime average CO and NO₂ mixing ratios. The results are plotted in Fig. 5 in comparison to O₃. The O₃ data are the same as in Fig. 4, except that we have added the best-fit linear trend line through the entire time period, as well as two sub-trends to

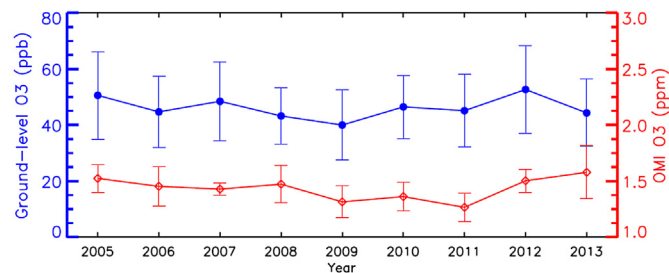


Fig. 4. The summertime O₃ trend in the greater Chicago area during 2005–2013. The blue dot line represents the summertime average ground-level daily 8-h maximum O₃ mixing ratio averaged over the 19 U.S. EPA monitoring sites. The red diamond line represents the summertime average tropospheric column O₃ mixing ratios observed by OMI. The bars are the one-standard-deviations from the respective mean values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

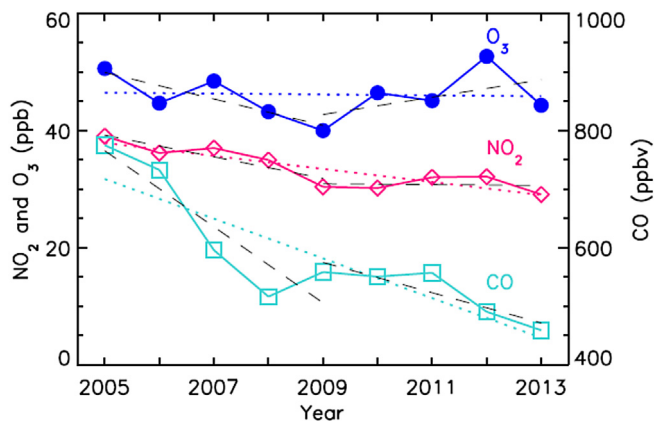


Fig. 5. Trends of average summertime (May to August) O_3 , NO_2 , and CO concentrations in the greater Chicago area from 2005 to 2013. The blue circles represent the average daily maximum 8-h O_3 mixing ratios; the pink diamonds are the average daily maximum 1-h NO_2 mixing ratios; and the light blue squares represent the average daily maximum 8-h CO mixing ratios. The dotted lines are the best-fit linear trend lines for 2005–2013 and the dashed lines are the sub-trend lines for 2005–2009 and 2009–2013. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

represent the periods of apparent decline (2005–2009) and increase (2009–2013). According to the slopes of the linear-fit lines for the different periods, summertime average O_3 mixing ratios demonstrated an insignificant overall decline at 0.08 ± 0.54 ppb per year from 2005 to 2013; they decreased at 2.27 ± 0.80 ppb per year from 2005 to 2009 and increased at 1.49 ± 1.44 ppb per year from 2009 to 2013. Summertime average NO_2 and CO mixing ratios decreased by 29% at 1.11 ± 0.23 ppb per year and by 41% at 33.90 ± 7.11 ppb per year, respectively, between 2005 and 2013. The NO_2 trend can be divided into two sub-trends with a significant decline (-1.85 ± 0.50 ppb per year) during the period 2005–2009, followed by a slower decline (-0.07 ± 0.47 ppb per year) from 2009 to 2013. The CO trend can also be divided into two sub-trends, showing a rapid decline (-64.95 ± 16.79 ppb per year) from 2005 to 2009, followed by a slower decline (-25.89 ± 7.36 ppb per year) from 2009 to 2013. Overall, we see certain similarities and differences in the trends of the three species: CO decreasing significantly, NO_2 decreasing slowly, and O_3 essentially flat, with an apparent break in all three trend lines in the years 2008/2009.

In light of the relatively sparse distribution of NO_2 monitors in the study region (only seven in the entire region, six of them in

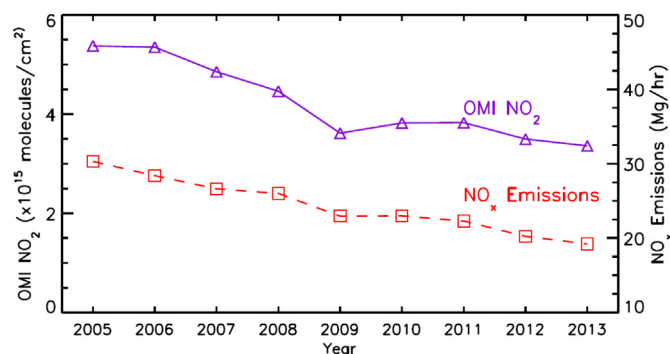


Fig. 6. Trends in summertime (May to August) tropospheric NO_2 vertical columns from OMI observations using the KNMI DOMINO v2.0 retrieval (purple triangles), and summertime NO_x emissions (red squares) from Xing et al. (2013), both for the greater Chicago area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Cook County, IL) and the importance of NO_x in the formation of O_3 , we developed further information on NO_x trends by examining satellite NO_2 column information from OMI. We used the OMI tropospheric NO_2 vertical columns during the period 2005–2013 from the level-2 product of the DOMINO v2.0 retrievals developed at the Royal Netherlands Meteorological Institute (KNMI) (Boersma et al., 2011). Only summertime data (i.e., May to August) were used, because the short NO_x lifetime in summer makes the relationship between emissions and satellite observations more robust than in the other seasons (e.g., Zhang et al., 2007). Daily pixel retrievals were filtered to remove data affected by row anomalies (RA) and data with large solar zenith angle ($>80^\circ$), relatively high cloud radiance fraction (>0.5), or large surface albedo (>0.3). Pixels at the swath edges (five pixels on each side) were also excluded to limit the across-track pixel width to ~ 65 km. Finally, all the valid pixels were oversampled (see, e.g., de Foy et al., 2009) on a $2 \text{ km} \times 2 \text{ km}$ grid for the greater Chicago area to yield the detailed spatial distribution of NO_2 for each year.

The OMI NO_2 vertical column trend (Fig. 6) shows a similar quantitative decline over the study period: 34% between 2005 and 2013, compared with 29% for the ground-level measurements of NO_2 mixing ratios, as described above. This OMI trend for Chicago is also similar to the average reduction of 32% in the OMI column NO_2 from 2005 to 2011 observed over 47 cities across the U.S. (Russell et al., 2012). In addition, we find that the OMI NO_2 trend shape is similar to the ground-level NO_2 concentration trend shape. It exhibits a clear break point in 2009, just like the concentration trend, with the slope of the decline significantly lower after 2009 than before 2009.

Fig. 6 also shows the NO_x emission trend for the same region from Xing et al. (2013). For emissions, the magnitude of the decrease is consistent (35% between 2005 and 2013). The recession in 2009 is also noticeable in the NO_x emissions in the greater Chicago area (about 12% reduction from 2008 to 2009). Further analysis on the emission inventories suggests that this reduction in 2009 is associated with decreased energy consumption in electric generating units, non-road activities (such as inland shipping), and on-road transportation (such as associated vehicle miles traveled for trucks), which was reduced by 33%, 14%, and 11%, respectively, from 2008 to 2009. The NO_x emissions leveled off from 2009 to 2010 due to economic recovery and they continued to decrease after 2010 due to tighter regulations.

The decline in NO_x emissions reflects a combination of reductions in point- and mobile-source NO_x emissions. Point-source NO_x emissions in the state of IL as a whole are reported to have dropped by 35% between 2008 and 2012 (IL EPA, 2013), with a major decline occurring between 2009 and 2010 that is attributed to the power sector (emissions of 121 kt/year in 2009 and 74 kt/year in 2010). This is not reflected in either the inventory or the OMI data over the greater Chicago area and likely is the result of actions at IL power plants far from Chicago (emissions controls or plant closures). The three local power plants did not close until 2012. Changes in transportation emissions are likely to have influenced emission trends in the greater Chicago area the most. Due to the growth in heavy-duty truck traffic and in diesel sales in and around urban areas like Chicago, the importance of NO_x emissions from heavy-duty trucks grew dramatically in the 1960s and 1970s. U.S. EPA began to tighten heavy-duty truck emission standards in the 1980s. Through a requirement to control NO_x emissions using exhaust-gas recirculation, the standard was lowered by about 63% from 10.7 g/bhp-hr in 1985 to 4.0 g/bhp-hr in 2003 (<http://www.epa.gov/otaq/standards/heavy-duty/hdci-exhaust.htm>). An even greater reduction in NO_x emissions subsequently became possible through development of selective catalytic reduction technology, and U.S. EPA promulgated increasingly tighter standards such that

by 2013 the standard had been reduced by a further 95%, down to 0.2 g/bhp-hr. Nationally, it has been shown that these standards began to yield a significant decrease in truck emissions after 2007 (McDonald et al., 2012).

Based on the National Emission Inventory (NEI) data provided by the U.S. EPA that are available every three years since 2002 (<http://www.epa.gov/ttn/chieff/eiinformation.html>), annual total anthropogenic VOC and CO emissions from the counties in the greater Chicago area were calculated for 2005, 2008, and 2011. The results are shown in Fig. 7. Similar to the NO_x emission trend, VOC emissions and CO emissions decreased 21% and 34%, respectively, from 2005 to 2011 in the study area. Most of the anthropogenic VOC emission reductions were obtained from modifications in the use of organic solvents and in industrial processes. Large VOC emission reductions had also been achieved prior to our study period. Early attempts to implement a cap-and-trade approach to VOC reductions in the Chicago area were not without their flaws, yet through a combination of emission controls and facility closings IL state emissions had been reduced by almost 70% between 1981 and 2003 (Kosobud et al., 2008). It should be noted, however, that the changes shown in Fig. 7 are not strictly “trends”, because NEI assumptions and methods change each time a new emission inventory is assembled.

Because VOC emissions are uncertain, yet their role in O₃ chemistry is so important, we need to examine trends in VOC concentrations in Chicago. As VOCs are not criteria air pollutants, they are monitored as hazardous air pollutants (HAPs) through the National Air Toxics Trend Station (NATTS) Network. Measurements of selected VOC species are available at http://aqsd1.epa.gov/aqswb/aqstmp/airdata/download_files.html. We collected measurements of the five most abundant VOC compounds (benzene, toluene, formaldehyde, acetaldehyde, and acrolein) at two EPA monitoring sites in Cook County, IL: the Northbrook site that is coded 17-031-4201 and the Schiller Park site coded 17-031-3103. VOC concentrations were generally measured once every 6 day at these two sites. Fig. 8 shows that average summertime concentrations of these VOC compounds, except for acrolein, decreased slightly from 2005 to 2008 and then they all increased from 2009 to 2012. Average concentrations of the three most abundant VOC compounds, formaldehyde, acetaldehyde, and acrolein, have more than doubled since 2009. The average concentration of 1,3-butadiene (not shown in Fig. 8), although not as abundant as the five aforementioned VOC species, increased sevenfold from

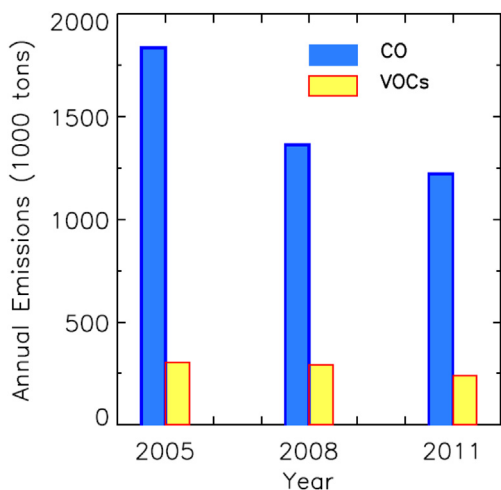


Fig. 7. Annual total emissions of CO and VOCs in the greater Chicago area based on the EPA National Emission Inventory data for 2005, 2008, and 2011.

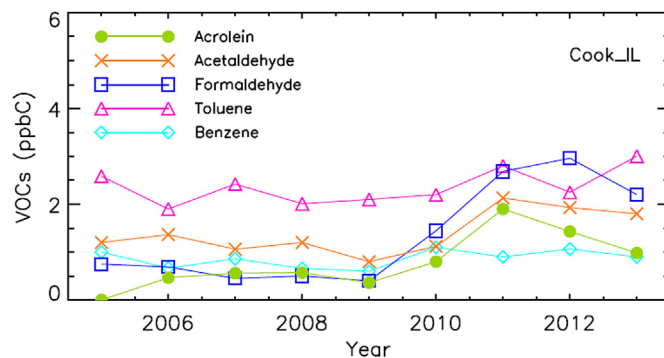


Fig. 8. Trends in average summertime (May to August) concentrations of the five most abundant VOC species in Cook County, IL, from 2005 to 2013.

0.02 ppb C in 2005–2008 to 0.17 ppb C in 2009–2012 (IL EPA, 2013).

Among these VOC compounds, formaldehyde (HCHO) is most directly linked to O₃ formation and is worthy of closer study. Fortunately, there are satellite observations of global tropospheric HCHO columns, though they cannot be easily tied to anthropogenic emissions. Based on OMI monthly mean tropospheric HCHO column data (<http://h2co.aeronomie.be/>), we calculated the average summertime tropospheric HCHO column values in the greater Chicago area from 2005 to 2013. They showed confirmatory trends: a slow 14.7% decreasing trend from 2005 to 2009 followed by an increasing trend from 2009 to 2011 (Fig. 9). The presence of greater amounts of formaldehyde indicates greater photochemical production of ozone in the troposphere.

3.3. Relationship of O₃ concentrations to meteorological conditions

The effect of meteorological conditions, particularly temperature, on the formation of ground-level O₃ has been well documented (see Cox and Chu, 1996; Jacob and Winner, 2009; for a summary of previous work on this topic). This study used meteorological data at the O'Hare Airport station (41.98°N, 87.90°W): daily maximum temperatures, daily average dew point temperature, daily minimum relative humidity, and wind speed and direction. They were compared with ozone observations at the site in downtown Chicago that is coded 17-031-4002 at (41.86°N, 87.75°W). Results are shown in Fig. 10 and Fig. 11. We have also examined the relationship of O₃ concentrations to meteorological conditions at the other ozone monitoring sites. The results are similar to what are shown in Figs. 10 and 11.

Fig. 10 shows that summertime O₃ in Chicago is positively correlated with daily temperature. The maximum daily

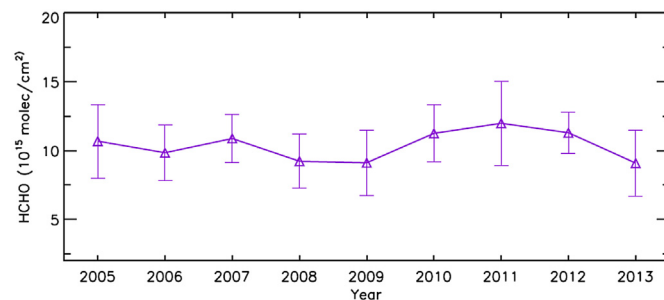


Fig. 9. The summertime average tropospheric formaldehyde trend in the greater Chicago area during 2005–2013 observed by OMI. The bars are the one-standard-deviations from the respective mean values.

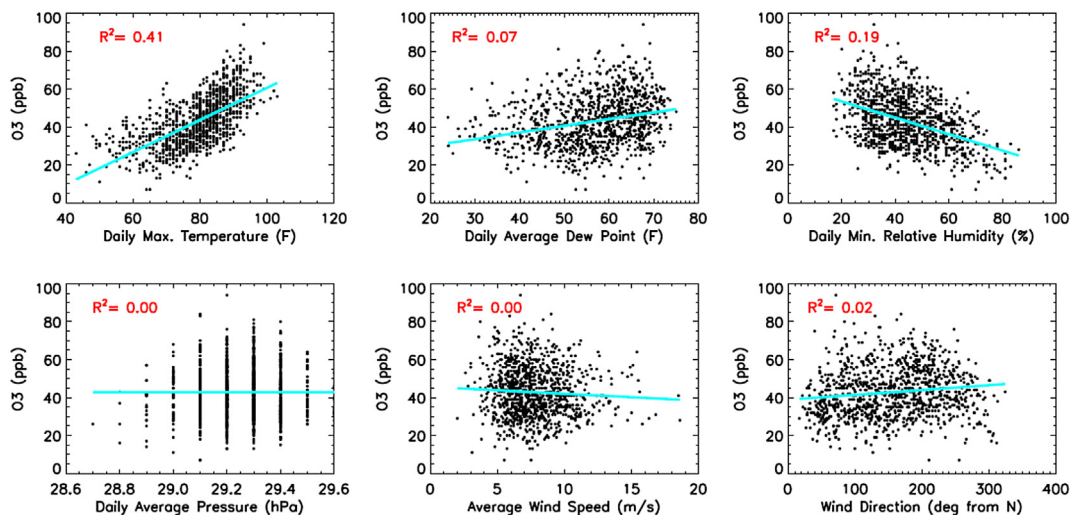


Fig. 10. Scatterplots of summertime O₃ concentration with respect to six meteorological variables at a single monitoring site in downtown Chicago during the period 2005–2013.

temperature is shown to be the most important variable, and it explains 41% of the variance of daily 8-h maximum O₃ concentrations in Chicago. Although O₃ is shown to be negatively correlated with relative humidity, this is mainly because relative humidity decreases with increasing air temperature; therefore, relative humidity should not be considered as an independent variable. There is a weak positive correlation between O₃ and dew point temperature, which reflects the actual water vapor content in the atmosphere. There is no significant correlation between O₃ concentration and pressure and wind variables. If measured O₃ concentrations are regressed against all the meteorological variables included in Fig. 10, then the resulting correlation in Fig. 11 shows that meteorology can explain 53% of the variance in O₃ concentrations in Chicago. The regression shows best agreement for mid-range concentration values (30–50 ppb); the linear-fitted O₃ values tend to be underestimated for both high and low concentration values. Bloomfield et al. (1996) suggested the use of a polynomial regression between O₃ and temperature. We tested a third-order polynomial regression model to fit O₃ with temperature, and it increased the R^2 value to 0.46 from the linear-fit R^2 value of 0.41. We concluded that a linear-fit model was adequate for this study.

The R^2 value between observed O₃ concentrations and the estimated O₃ concentrations based on meteorological variability is 0.53 in this study, which is in agreement with other work. The R^2 value was previously shown to be in the range of 0.56–0.80 for 39

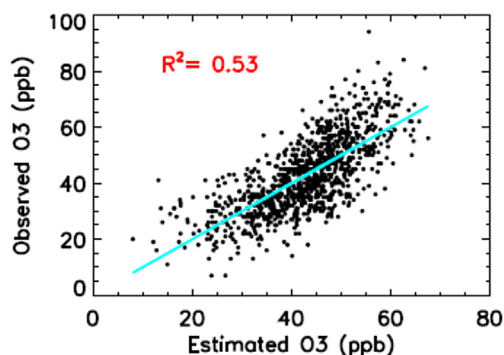


Fig. 11. Correlation of O₃ observations with estimated O₃ concentrations derived from the linear regression model that includes meteorological variables.

eastern U.S. urban areas (Camalier et al., 2007), and in the range of 0.50–0.80 (average 0.70) for 74 areas across the eastern U.S. (Davis et al., 2011).

It is shown in Fig. 10 that among all meteorological variables temperature has the strongest relationship to O₃, which is consistent with the findings of Bloomfield et al. (1996) and Camalier et al. (2007). In further support of the observed relationship between O₃ concentration and temperature, it is interesting to note that the years that had an elevated number of high O₃ days in Chicago were also the years that had the highest number of hot days (when the daily average temperature was warmer than 90 °F). Fig. 12 shows this relationship over the study period, 2005–2013.

3.4. Relationship of O₃ to NO₂

By employing all the measurements of summertime ground-level O₃ and NO₂ in the greater Chicago area, we used a quadratic regression model to fit O₃ with NO₂ for 2005–2008 and 2009–2013. The results are shown in Fig. 13. It shows that the mean

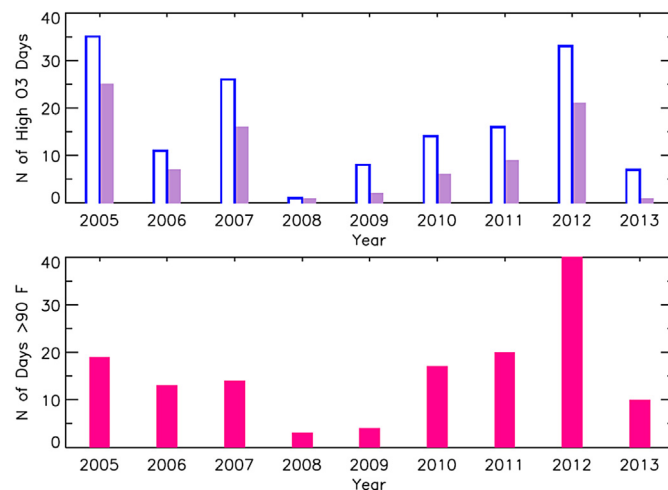


Fig. 12. High O₃ concentration days (upper): blue unfilled bars are the number of days that exceeded 75 ppb, and purple filled bars are the number of days that exceeded 80 ppb. Hot days (lower): the number of days that were warmer than 90 °F in Chicago, according to observations at O'Hare Airport. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

daily maximum O₃ concentration increased with increasing mean daily maximum NO₂ concentrations from 2005 to 2008, throughout the concentration range shown. However, from 2009 to 2013, O₃ decreased with increasing NO₂ for NO₂ concentration values greater than 26 ppb. This figure also shows that when NO₂ concentrations were less than 20 ppb, the mean daily maximum ozone mixing ratios were higher in 2009–2013 than in 2005–2008 for the same NO₂ mixing ratio value. This figure demonstrates that during 2009–2013 decreasing NO₂ was associated with higher O₃ mixing ratios in the Chicago area than during 2005–2008. According to the statistical analysis parameters for the O₃–NO₂ relationship listed in Table 1, the quadratic relationship of O₃ with NO₂ was statistically significant ($p = 0.002$, which was <0.05) during 2009–2013, but insignificant ($p = 0.107$) during 2005–2008. In fact, the O₃–NO₂ relationship was linear ($p = 0.000$) between 2005 and 2008, indicating that O₃ was sensitive to NO₂ and restricting NO₂ emissions resulted in lower O₃ mixing ratios. However, O₃ had become insensitive to NO₂ changes after 2009, as indicated by the quadratic relationship of O₃ to NO₂ between 2009 and 2013.

We then repeated the above analysis for higher O₃ (≥ 75 ppb) and lower O₃ (< 75 ppb) conditions. See Fig. 14. In the 2005–2008 period, O₃ increased with increasing NO₂ in both lower O₃ and higher O₃ conditions through the entire NO₂ range. However, in the 2009–2013 period, O₃ had a quadratic relationship ($p < 0.05$) with NO₂ at lower O₃ concentrations, and O₃ decreased with increasing NO₂ at NO₂ concentrations greater than 30 ppb; and for higher O₃ conditions (≥ 75 ppb) there was a slight decline in O₃ concentrations with increasing NO₂ throughout the NO₂ concentration range, although with high uncertainties ($R^2 = 0.001$).

Taken together, these results show that O₃ became insensitive to NO₂ during 2009–2013, especially for high ozone concentration (> 75 ppb) conditions. Due to lack of VOC observational data, we are unable to do similar analysis between O₃ and VOCs, although Fig. 8 showed that the average summertime concentrations of the five most abundant VOC species have increase significantly since 2009. We therefore conclude that it is highly likely that summertime O₃ in the Chicago area has switched from NO_x-limited to VOC-limited since 2009.

4. Discussion and conclusions

In light of the trends of steadily declining emissions of NO_x and probable but uncertain declines in CO and anthropogenic VOCs

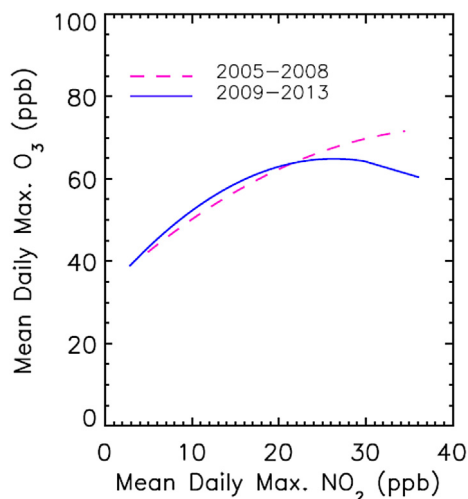


Fig. 13. O₃–NO₂ relationships in the Chicago area during 2005–2008 and 2009–2013 using measurements from all sites in the area in summer months from May to August.

(Figs. 6 and 7), confirmed by satellite in the case of NO_x, it is necessary to look elsewhere for the cause of the disparate trends in ground-level monitored concentrations shown in Fig. 5. While NO₂ and CO concentrations have declined steadily, consistent with the emission trends, there is no clear decline in O₃ concentrations over the nine-year period. In fact, the summertime O₃ trend consists of a decline of 21% between 2005 and 2009 and an increase of 11% between 2009 and 2013 in the ground-level O₃ mixing ratio, which is confirmed by OMI satellite observations that show a decline of 14% between 2005 and 2009 and an increase of 20% between 2009 and 2013 in the average tropospheric column O₃ mixing ratio. Observed surface concentrations of the most abundant VOC compounds in the Chicago area have increased significantly (more than doubled) since 2009. OMI satellite observations of tropospheric column HCHO also increased 31% from 2009 to 2011. We conclude that NO_x emission reductions since 2008/2009 have not yielded commensurate reductions in O₃ concentrations. Ozone production in the greater Chicago area—at least in the city of Chicago itself—seems to have become insensitive to NO_x starting in 2008/2009 and may have switched from being NO_x-limited to VOC-limited at this time.

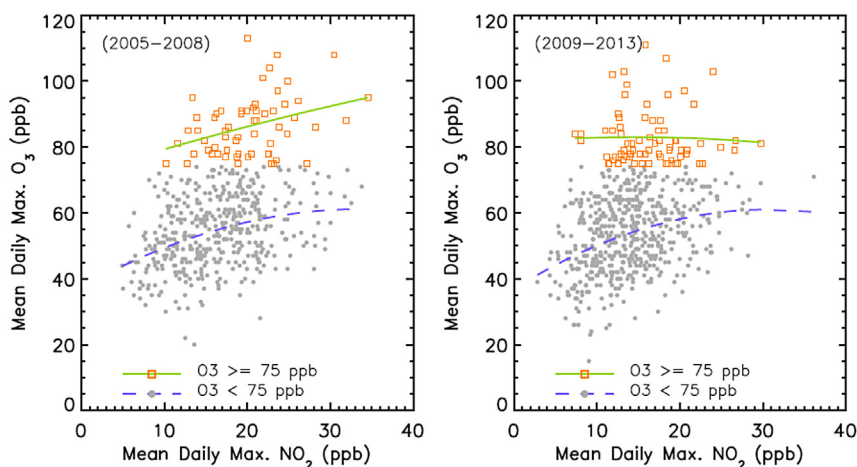
There have been several earlier indications in literature studies that Chicago may be approaching a condition of VOC-limited O₃ production. Early modeling work by Milford et al. (1994) had shown that Chicago, under stable summertime mixing conditions, had high NO_y concentrations, showed a typical increase in the ratio of reactive organic gases (ROG) to NO_x in a plume from 6:1 to 10:1 during the course of a day, and sustained an ROG-sensitive region that extended 300 km downwind of the urban area. U.S. EPA benefits analysis with the CMAQ model showed negative benefits for reducing mobile source NO_x emissions in Chicago (projected results for 2015), attributed to a VOC-limited situation, where additional NO_x reductions in NO_x-rich urban areas lessen the titration of O₃ and lead to more O₃ formation (Fann et al., 2009).

An interesting recent study in Brazil may have relevance to the Chicago situation. Salvo and Geiger (2014) have shown the effects of a shift from ethanol to gasoline in urban São Paulo, Brazil. During the period 2009–2011, there were large price fluctuations for ethanol and gasoline that resulted in a major shift from ethanol to gasoline in bio-fuel vehicles. O₃ concentrations fell by about 20% as a result, while concentrations of NO₂ and CO rose by about 26% and 18%, respectively. The authors attribute this to the fact that O₃ production in São Paulo is hydrocarbon-limited, and increasing the share of ethanol in the fuel mix affected the production of O₃ and the relative shares of NO_x and CO. Inverting the conclusions of the São Paulo study could imply that an increase in VOC emissions in the Chicago area has led to higher O₃ levels and lower NO₂ and CO levels. It may even be related to the increased use of ethanol in fuels in Chicago, though any increase of reactive VOCs would have a similar effect. Unfortunately, confirmation is hampered by lack of detailed information about speciated local emissions of VOCs.

A switch from NO_x-limited conditions to VOC-limited conditions could be revealed by examination of weekday/weekend O₃ trends. Blanchard and Tanenbaum (2005) found that local O₃ production in the Chicago area did not decline on weekends even though there were large local reductions in O₃ precursors due to less commuter activity. The implication was that there was greater O₃ production per NO_x molecule on weekends than on weekdays. It was also observed that O₃ levels in São Paulo tend to increase on weekends and NO and CO levels decrease, when road traffic congestion is less (Salvo and Geiger, 2014). A similar situation has been observed for Mexico City (Stephens et al., 2008). We therefore reconstructed the trends in Fig. 5, separating weekday and weekend observations (Fig. 15).

Table 1Statistical analysis parameters for the O₃–NO₂ relationship using the quadratic regression model: $y = b_0 + b_1x + b_2x^2$, in which y is O₃ and x is NO₂.

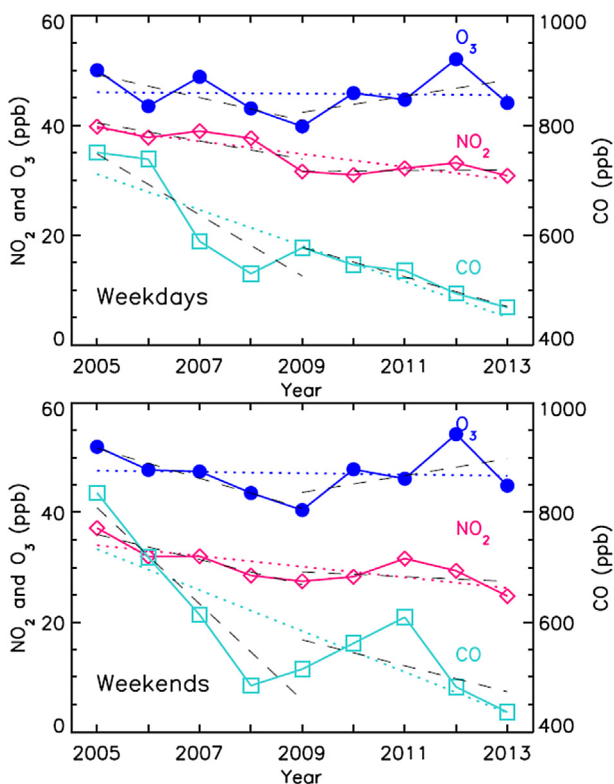
	2005–2008			2009–2013		
	All O ₃ range	O ₃ < 75 ppb	O ₃ ≥ 75 ppb	All O ₃ range	O ₃ < 75 ppb	O ₃ ≥ 75 ppb
b_0	33.27 ± 4.57	37.38 ± 3.51	71.73 ± 14.33	32.15 ± 3.74	36.95 ± 2.98	81.52 ± 11.27
b_1	1.93 ± 0.53	1.41 ± 0.42	0.80 ± 1.36	2.48 ± 0.49	1.57 ± 0.40	0.21 ± 1.31
b_2	–0.024 ± 0.015	–0.021 ± 0.012	–0.004 ± 0.032	–0.047 ± 0.015	–0.026 ± 0.012	–0.007 ± 0.036
p	0.107	0.076	0.912	0.002	0.041	0.848

**Fig. 14.** Observed summertime O₃–NO₂ relationships in the Chicago area for O₃ < 75 ppb and O₃ > 75 ppb conditions during 2005–2008 (left) and 2009–2013 (right).

The weekday/weekend differences in the trends of the three species are supportive of a switch to VOC-limited conditions since 2008/2009. Immediately apparent is that O₃ concentrations in the last five years were not lower on weekends compared to weekdays,

even though NO_x emissions on weekends would have been much less. Since 2008/2009 there is little difference between the two data sets for O₃. Indeed, concentrations of NO_x and CO were generally lower on weekends than on weekdays, especially towards the end of the period—by about 5 ppb for NO₂ and 20 ppb for CO, consistent with fewer emissions on weekends. The trend lines over the five-year period from 2009 to 2013 have slopes of +1.49, –0.07, –25.89 ppb per year for O₃, NO₂, and CO, respectively, again suggesting that O₃ in Chicago has become less sensitive to NO_x emissions and has transitioned to a VOC-limited situation. Table 2 summarizes the slopes of the various trend lines studied.

While surface concentrations of the most abundant VOC compounds, including HCHO, have increased significantly since 2009 (Fig. 8), the U.S. EPA estimated emissions of VOCs in the NEI, which are available only every three years, show a decrease from 2008 to 2011. Local emission estimates, on the other hand, appear to be incomplete and to focus only on point sources. All these VOC inventories only include anthropogenic sources of VOCs. Biogenic VOC emissions are poorly known but they can be significant sources of VOCs. As a result, neither local nor federal EPA emissions data are presently adequate to identify trends in total VOCs, the speciation of VOCs, and the trends in reactive VOC species. Our

**Fig. 15.** Same as Fig. 5, but for weekdays (top) and weekends (bottom).**Table 2**Slopes of the linear fits of O₃, NO₂, and CO mixing ratio trends in ppb/year.

		2005 to 2013	2005 to 2009	2009 to 2013
O ₃	Both	–0.08 ± 0.54	–2.27 ± 0.80	+1.49 ± 1.44
	Weekdays	–0.06 ± 0.53	–2.09 ± 0.99	+1.47 ± 1.37
	Weekends	–0.12 ± 0.57	–2.73 ± 0.32	+1.53 ± 1.61
NO ₂	Both	–1.11 ± 0.23	–1.85 ± 0.50	–0.07 ± 0.47
	Weekdays	–1.17 ± 0.26	–1.65 ± 0.70	+0.07 ± 0.35
	Weekends	–0.97 ± 0.32	–2.28 ± 0.43	–0.43 ± 0.89
CO	Both	–33.90 ± 7.11	–64.95 ± 16.79	–25.89 ± 7.36
	Weekdays	–32.56 ± 6.22	–55.61 ± 17.98	–26.91 ± 2.37
	Weekends	–37.30 ± 10.56	–87.59 ± 16.39	–23.63 ± 20.51

investigations suggest that VOC emissions in Chicago may be underestimated, as has been found for other urban areas, for example in Houston, Texas (Ryerson et al., 2003), but that remains to be confirmed.

In addition to concerns that O₃ attainment may be difficult to achieve even under a stable climate, forecasting has suggested that climate change will cause an increase in mean and maximum O₃ concentrations in the Chicago area because of warmer temperatures. In a study of the effects of future climate change on Chicago, surface O₃ concentrations were projected to increase by as much as 8.7 ppb in the Chicago area under climate change scenarios out to 2100 (Lin et al., 2010); Holloway et al. (2008) projected an increase in summertime mean O₃ mixing ratios of 6–17 ppb by 2100. Nationwide, forecasts of the effect of climate change on O₃ out to 2050 suggest an increase of about 8 ppb in the 95th percentile for summertime daily 8-h maximum O₃ concentrations (Pfister et al., 2014). The potential problems facing U.S. cities under a changing future climate are complex. Civerolo et al. (2007) studied the likely effects of increased urbanization of New York City and consequent emission increases out to 2056. Near-surface temperatures increased by 0.6 °C, due to the heat-island effect, and the water-vapor mixing ratio decreased significantly. The effects on O₃ concentrations were complex, with 8-h maximum concentrations increasing by more than 6 ppb in places, with high spatial variability.

A warmer climate in U.S. cities will also have an effect on energy demand, which in turn is likely to increase local emissions. Energy requirements for summertime cooling will increase everywhere (Hadley et al., 2006), and the potential synergistic increases in power-plant NO_x emissions and O₃ concentrations in the eastern U.S. have been investigated (He et al., 2013). Therefore, in addition to emission controls, energy conservation measures are likely to be necessary to prevent O₃ increases and hopefully to aid in reduction of O₃ levels. Of all major world cities, Chicago has among the highest per capita energy consumption and per capita greenhouse-gas emissions, as well as a high number of heating degree days, driven by its interior continental climate (Kennedy et al., 2014). The situational profile of Chicago suggests that a low-carbon strategy could emphasize building-integrated photovoltaics (Kennedy et al., 2014). Chicago has also taken the initiative to promote the use of green roofs. Several hundred such roofs are presently in place, covering a reported 20–30 ha in total. It has been estimated that this vegetation has removed about 870 kg/year of O₃ through dry deposition (Yang et al., 2008). If all roofs in Chicago were similarly covered, it is estimated that the total O₃ removal could be in the region of 1000 tonnes/year. Careful planning is needed in the introduction of urban green spaces, however, because biogenic VOC emissions from some types of vegetation can increase significantly under hot conditions, sometimes increasing isoprene emissions and the formation of O₃. This has been shown to be a potential issue in rapidly developing urban areas of China (Ren et al., 2014). It is predicted that future ground-level ozone will be more sensitive to biogenic VOC emission changes than to climate change alone (Lin et al., 2007).

In conclusion, we have demonstrated that, despite effective emission control measures for O₃ precursors, there has been no noticeable reduction in O₃ concentrations in the greater Chicago area during the period 2005–2013. Summertime meteorological conditions mainly drive the formation of O₃, with an R² value of 0.53 between O₃ concentrations and meteorological conditions, particularly temperature. The evidence also suggests that in about 2008/2009 O₃ formation in Chicago transitioned from being NO_x-limited to VOC-limited. Further NO_x emission reductions without reductions in emissions of key reactive VOCs could exacerbate the O₃ situation. Under future conditions of higher temperatures, O₃

can only increase under constant emissions. All this evidence suggests that it will be very difficult to achieve the current 8-h O₃ standard of 75 ppb in Chicago, let alone a tighter standard of 60–70 ppb that might be on the horizon. We recommend that increased attention be paid to better quantification and speciation of the emissions of reactive VOCs from both stationary and mobile sources in the Chicago area, followed up by aggressive emission control measures. In the same vein, attention needs to be paid to local and regional biogenic VOC emissions and how they are changing in the changing urban and suburban landscape.

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