Changes in Gas-Phase Air Pollutants across New York State, USA

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ABSTRACT

Over the past several decades, the New York State Department of Environmental Conservation (NYSDEC) has monitored air quality in urban, suburban, and rural locations across the state. Such data are used to determine compliance with national ambient air quality standards (NAAQS), as well as track the effectiveness of pollutant emission controls. This paper summarizes the changes in gas-phase criteria and related pollutants on an annual, seasonal and diurnal basis across New York, USA. Annual average and peak concentrations of carbon monoxide (CO), nitrogen dioxide (NO2), and sulfur dioxide (SO2) have decreased by 50% or more since 1980 across New York, USA. Generally consistent with anthropogenic emissions reductions across different source sectors over the past 35 years. At the same time, annual average concentrations of the secondary pollutant ozone (O3) appear flat or are increasing even though peak daily 8-hour concentrations have declined. This pollutant will likely remain a challenging public health issue for the foreseeable future.

Keywords: Air pollution trends; Emissions trends; Criteria pollutants; Air monitoring; Air quality standards.

INTRODUCTION

The Clean Air Act (CAA) of 1970 and subsequent Amendments in 1990 required the United States Environmental Protection Agency (USEPA) to establish and review National Ambient Air Quality Standards (NAAQS) for pollutants considered harmful to human health and the environment. These “criteria” pollutants are carbon monoxide (CO), nitrogen dioxide (NO2), sulfur dioxide (SO2), ozone (O3), particulate matter, and lead (Pb). The New York State Department of Environmental Conservation (NYSDEC) has been the lead agency charged with ambient air monitoring of these and related pollutants in New York.

Since the 1980s, emissions control programs to address air quality concerns have largely focused on motor vehicle emissions and the power generation sector in the eastern US. Federal programs including the Acid Rain Program (ARP), Clean Air Interstate Rule (CAIR), Cross-State Air Pollution Rule (CSAPR), and NOx Budget Trading Program (NBP), as well as New York’s own State Acid Deposition Control Act (SADCA) and Acid Deposition Reduction Program (ADRP), have led to sharp declines in nitrogen oxides (NOx = nitric oxide (NO) + NO2) and SO2 emissions from the power sector. This in turn has led to significant reductions in acid deposition (e.g., Lynch et al., 2000; Butler et al., 2001), and improved air quality (e.g., Schwab et al., 2009; Buckley and Mitchell, 2011; Aleksic et al., 2013) and surface water quality (e.g., Driscoll et al., 2003; Waller et al., 2012) across New York and the northeastern US. Mobile source emissions of NOx and CO in the US have also declined substantially since the 1970s and 1980s with the phase-in of three-way catalytic converters, Federal fuel programs regulating both light-duty and heavy-duty diesel vehicles, more efficient internal combustion engines, and fleet turnover (e.g., Brandmeyer et al., 2003; McDonald et al., 2012; McDonald et al., 2013).

Owing to the range in pollutant concentrations across urban and regional scales, ambient measurements are required at different locations in order to track improvements in air quality. This paper builds upon recent studies by Buckley and Mitchell (2011) which reported trends in criteria pollutants in urban areas through 2007, and Schwab et al. (2009) which focused on air quality at a rural site. It is important to update those analyses since, as will be shown later, there have been substantial changes in air concentrations of these pollutants across New York even over the past 5–7 years. Here we focus on changes in gas-phase criteria and related pollutants over the past 35 years, in response to numerous emission control programs. We also examine seasonal and diurnal variations in these pollutants to help provide context for the long-term trends. We do not address Pb or fine particulate matter (PM2.5) in this paper, but changes in PM2.5 mass and major species are presented elsewhere (Rattigan et al., 2016).

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MEASUREMENT METHODS AND DATA ANALYSIS

The NYSDEC network currently consists of 54 air monitoring stations, with 22 in New York City and Long Island, and the remaining 32 in urban, suburban, and rural areas across the rest of the state (NYSDEC, 2016). The network is designed to provide pollutant information across different population density areas while also providing coverage representative of rural regions. Note that the number of sites can vary somewhat from one year to the next, as measurements commence, instruments move, or sites close for a variety of reasons. Although air monitoring equipment from different manufacturers has been installed at various times at these sites, the basic measurement methods for a given parameter are essentially consistent. Over the years equipment with enhanced data acquisition and higher levels of sensitivity have been introduced particularly as ambient concentrations have decreased. However, quality assurance and quality control (QA/QC) procedures have been carefully documented and observed for all instrumentation (USEPA, 2016a), providing confidence in the reliability and validity of these long-term measurements. Furthermore, our monitoring sites and procedures are periodically audited by the USEPA in order to provide consistency both within our network and with other locations throughout the US. Sulfur dioxide is measured using pulsed fluorescence analyzers; NO2 by catalytic conversion with heated molybdenum (Mo) followed by the chemiluminescent reaction with O3; CO with non-dispersive infrared absorption analyzers; and O3 with ultraviolet absorption analyzers since the mid-1980s. In addition to criteria gas pollutants, we examined available NO data from O3-chemiluminescent detectors across the state, and volatile organic compounds (VOC) data from the Photochemical Assessment Monitoring Station (PAMS) program in New York City. The PAMS compounds were measured using dual column thermal desorption gas chromatography coupled to a flame ionization detector.

Each of the criteria pollutants has one or more primary (human-health based) and secondary (welfare-based) NAAQS values, which are established and periodically reviewed and revised by the USEPA. In this paper we focus on annual average concentrations of these pollutants, as well as concentrations appropriate for the current primary NAAQS, which are based on relatively short-term (1-hour or 8-hour) peak concentrations to protect human health. The current NAAQS levels (USEPA, 2016b) are summarized in Table 1.

In each year from 1980 through 2014, we computed annual averages and NAAQS-relevant concentrations for each criteria pollutant at each site; only those sites with at least 75% valid data in a given year were included in this analysis. In order to compare how criteria pollutants are changing across New York, we examined the urban monitors by metropolitan area: the New York City (NYC) region, and other urban areas across upstate New York (Buffalo (BUF), Rochester (ROC), Syracuse (SYR), and Albany (ALB) metropolitan statistical areas). All of the air pollutant data from urban sites were obtained from the USEPA Air Quality System (AQS) database (USEPA, 2016c). In addition to the urban sites in New York we also examined the data from Pinnacle State Park (PSP), a rural site in the southwestern region of the state, downwind of pollution sources and urban areas in the US Midwest and Mid-Atlantic. Measurements at this site have been made through a long term collaborative effort between the NYSDEC and the State University of New York’s Atmospheric Sciences Research Center (SUNY ASRC; e.g., Rattigan et al., 2006; Schwab et al., 2009). The PSP site is one of two rural sites with long-term records of all four gas-phase criteria and related pollutants. Measurements from Whiteface Mountain, a remote elevated site in the Adirondack Mountain region of northern New York with a similar collaborative arrangement between NYSDEC and SUNY ASRC, are described elsewhere (e.g., Brandt et al., 2016). It should be noted that in contrast to NO2 monitors in urban locations, at PSP NO2 is measured via photolytic conversion to NO prior to the chemiluminescent reaction. Information on measurement methods and QA/QC of the PSP data are reported by Schwab et al. (2009). All of the PSP data are stored on a server at the SUNY ASRC and can be made available upon request.

To estimate how anthropogenic emissions and air concentrations of these criteria pollutants have changed, we use the nonparametric Mann-Kendall test for monotonic trends (e.g., Mann, 1945). We obtained annual, state-level, non-forest-fire emissions of CO, NOx, SO2, and VOC from two sources. While forest fires can certainly impact air quality, there does not appear to be a statistically significant trend in biomass burning emissions over North America since the late-1990s (see Supplementary Material); hence, in

Table 1. Summary of current primary national ambient air quality standards for gas-phase criteria pollutants, established by the USEPA (https://www.epa.gov/criteria-air-pollutants/naaqs-table).

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Averaging time</th>
<th>Level</th>
<th>Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1 hour</td>
<td>35 ppm</td>
<td>Not to be exceeded more than once per year</td>
</tr>
<tr>
<td></td>
<td>8 hour</td>
<td>9 ppm</td>
<td></td>
</tr>
<tr>
<td>NO2</td>
<td>1 hour</td>
<td>100 ppb</td>
<td>98th percentile of 1-hour daily maximum concentrations, averaged over 3 consecutive years</td>
</tr>
<tr>
<td></td>
<td>1 year</td>
<td>53 ppb</td>
<td>Annual mean</td>
</tr>
<tr>
<td>SO2</td>
<td>1 hour</td>
<td>75 ppb</td>
<td>99th percentile of 1-hour daily maximum concentrations, averaged over 3 consecutive years</td>
</tr>
<tr>
<td>O3</td>
<td>8 hour</td>
<td>0.070 ppm</td>
<td>Annual 4th highest daily maximum 8-hour concentration, averaged over 3 consecutive years</td>
</tr>
</tbody>
</table>
SO2 are dependent on changes in anthropogenic emissions, which have been tracked more consistently in time than biomass burning emissions. The first data source contains national annual emissions from the USEPA’s National Emissions Inventory (NEI; USEPA, 2016d), from 1980–2014 to cover the period of air quality data in New York. The second, covering the 1990–2010 period, was developed by Xing et al. (2013) from the NEI and other sources. We assumed that the Xing et al. (2013) emissions from the northeastern US as defined by Hand et al. (2012) – 21 states plus Washington, DC – would have the most direct impacts on air quality in New York. Although the first source of emissions data is less specific to the surrounding region impacting air quality in New York, a comparison (Fig. S1) shows there is a high degree of correlation between the national and regional emissions estimates. The NEI provides emissions estimates over the entire 35-year period of interest, allowing us to examine emissions and air quality in the 1980s as well as the most recent years; hence in this paper we present trends in nationwide anthropogenic emissions from the NEI in % yr\(^{-1}\), normalized by the median value during the 1980–2014 period. Trends in air concentrations of all gas-phase pollutants are also presented as % yr\(^{-1}\) over the same period.

**RESULTS AND DISCUSSION**

**Anthropogenic Emissions Changes**

Changes in ambient concentrations of CO, NO\(_2\), and SO\(_2\) are dependent on changes in anthropogenic emissions of these pollutants, and emissions of VOCs and NO\(_x\) are crucial to the formation of O\(_3\). The panels in Fig. 1 show the estimated annual US non-forest-fire emissions from 1980–2014. The broad source categories shown in these figures are fuel combustion (FC) from both electricity generating unit (EGU) and non-EGU sources; industrial processes (IP) including chemical, petroleum, and metals-related processing; transportation (TR) including on-road and off-road vehicles; and other/miscellaneous (MI) sources including agricultural activities and solvent use. It is generally accepted that there is more confidence in the emissions from the power generation sector of the NEI compared to other sectors, that emission estimation methodologies have changed over the years, and that new source categories can be added to emission inventories, making it difficult to quantitatively attribute changes in long-term air quality to changes in emissions (e.g., Xing et al., 2013; Hidy et al., 2014). However, in this paper, we assume that changes in anthropogenic emissions on a national level are generally reflective of changes in emissions in New York and surrounding states at least on an annual basis.

Fig. 1(a) shows that annual CO emissions in the US have declined from nearly 180 million short tons in 1980 to about 55 million short tons in 2014, at a rate of about –4 % yr\(^{-1}\) (p < 0.01). In 1980, the transportation sector accounted for approximately 90% of the total emissions, and by 2014 it accounted for about two-thirds of total emissions. Transportation-related CO emissions have declined by ~80% since 1980, similar to the findings of McDonald et al. (2013), who used a fuel-based approach to estimate changes in CO emissions from motor vehicles; the authors found that motor vehicle CO emissions have declined by ~80–90% from 1990–2010 in three large urban areas, including NYC. The introduction of three-way catalytic convertors, state-level inspection and maintenance programs, heavy-duty diesel controls, and more fuel efficient engines have led to substantial reductions in CO emissions from this sector. Such vehicle-related controls have also led to large declines in NO\(_x\) emissions over the same period (Fig. 1(b)). Motor vehicles account for ~55–60% of NO\(_x\) emissions over the entire period, and numerous emissions reductions programs to address regional haze, acid deposition, O\(_3\), and PM\(_{2.5}\) (e.g., ARP, CAIR, CSAPR, NBP) have also reduced NO\(_x\) emissions from the power sector. Emissions of NO\(_x\) over the 35-year period have decreased by a rate of about –2.5 % yr\(^{-1}\) (p < 0.01). While only small decreases were observed prior to 1998 (less than ~1 % yr\(^{-1}\)), the decreases between 1998 and 2014 are ~5.7 % yr\(^{-1}\). Some of the recent reductions in NO\(_x\) emissions may also be associated to the global recession of 2008/09. For example, Tong et al. (2015) found that ground-level measurements and satellite-based retrievals suggested larger reductions in NO\(_x\) from 2005–12 than did NEI-based emission estimates, which they attributed to reduced energy demand during the recession.

Emissions of SO\(_2\) have declined over this time period from about 26 million short tons to less than 5 million short tons (Fig. 1(c)), corresponding to a decrease of about –5 % yr\(^{-1}\) (p < 0.01). Much of the SO\(_2\) decline is associated with emissions reductions initiated through the 1990 CAA Amendments and ARP which targeted EGU and non-EGU fuel combustion, particularly large coal fired utilities. The use of low sulfur coals, the emission “Cap and Trade” program, and emission controls including flue gas desulfurization scrubbers have led to dramatic declines in SO\(_2\). In addition natural gas is replacing coal as the primary fuel at many facilities in the northeastern US, as the price of natural gas has diminished considerably in recent years (e.g., Lu et al., 2012). EGU and non-EGU sources still account for roughly 80% of the SO\(_2\) emissions nationwide. Levels of sulfur in home heating fuels are also declining. In addition, transportation-related SO\(_2\) emissions have declined with the phase-in of ultra-low sulfur diesel fuel starting in 2006, and more recent phase-in of lower sulfur content fuels for non-road, locomotive, and marine engines (USEPA, 2015). Finally, anthropogenic VOC emissions (Fig. 1(d)) have decreased by more than ~2 % yr\(^{-1}\) (p < 0.01). Industrial processes and mobile sources account for about 80–90% of VOC emissions nationwide.

**Ambient Annual Concentrations**

Figs. 2–5 show the time series of annual average concentrations for each criteria pollutant and the NAAQS-relevant concentrations, with the corresponding NAAQS levels shown as a solid line. Note the different scales for the rural PSP site in these figures. Table 2 lists the statistically significant (p < 0.05) trends in the annual averages and peak concentrations related to the primary NAAQS level of each criteria pollutant.
Fig. 1. Annual national-level emissions of (a) CO, (b) NO$_x$, (c) SO$_2$, and (d) VOC in selected years from 1980–2014 from the USEPA NEI. Emissions are displayed by broad source category: fuel combustion from EGU and non-EGU sources (FC; white), industrial processes (IP; light gray), transportation (TR; dark gray), and other/miscellaneous (MI; black).
CO Concentration Trends

Figs. 2(a)–2(c) display the time series of ambient CO from 1980 through 2014 at sites in New York. The panels in Figs. 2(a)–2(c) show the annual averages, second highest 1-hour concentrations, and second highest 8-hour concentrations (non-overlapping hours), respectively. In a given year, the median value and range across all monitors that had at least 75% complete data are displayed in the panels of Fig. 2, and the data are grouped by metropolitan area: NYC, BUF, ROC, SYR, and ALB, and the rural PSP site. There were occasional years where only measurements from a single air monitor in a given urban area was valid due to the data completeness criteria, and these years are denoted with a single symbol.

There is a large variation in absolute concentrations across New York State with the highest pollutant concentrations of several ppm in urban locations compared to hundreds of ppb at the rural PSP site. In the 1980s, the highest average CO levels of about 5 ppm were measured at sites in NYC most impacted by heavy motor vehicle traffic compared to 1.0–1.3 ppm at other urban sites. SYR was also elevated compared to other upstate urban sites from the 1980s to the mid-1990s. Thereafter, spatial differences across urban sites diminish with all urban sites converging by the mid-2000s. The differences across the various sites contrast locations dominated by extensive near-field emission sources (e.g., motor vehicle emissions) versus those influenced more by regional background levels or a small number of more distant sources.

It is evident that CO concentrations have declined substantially across New York, particularly at the urban locations where measurements extend back to 1980. Annual average concentrations of CO peaked at 1–5 ppm in NYC and 0.5–2 ppm in other urban areas in the mid- to late-1980s and began to decline through the 1990s. Currently, annual average CO concentrations at all urban sites are below 0.5 ppm, yet still elevated compared to the rural PSP site (0.1–0.2 ppm). The trend in annual average CO in NYC is about −6.1 % yr⁻¹, and −3.3 to −6.1 % yr⁻¹ in other urban areas, generally consistent with the declines in anthropogenic emissions of −4 % yr⁻¹ over this time period. Annual average concentrations have decreased at PSP by −2.4 % yr⁻¹. Blanchard et al. (2013) also observed similarly large variations in CO trends in the southeastern US, with lower rates of −1.2 to −2.2 % yr⁻¹ at non-urban sites compared to −5 to −7.2 % yr⁻¹ at urban sites. They reported that these differences existed even after adjusting for the continental background of 100 ppb. There was a fairly abrupt drop in CO at PSP from 2006 to 2007 which is not related to changes in measurement methodology, and we are currently looking into possible causes. It is unlikely due primarily to controls on vehicle emissions since this abrupt drop was not observed at urban sites, nor do we feel it is due to wildfires since trends in biomass burning over this time period do not appear to be statistically significant (see Supplementary Material).

Trends in the second highest 1-hour and 8-hour CO concentrations across all these sites are also significant. The highest hourly CO concentrations at PSP rarely exceed 0.2–0.3 ppm except when impacted by transport from upwind regions (e.g., Bae et al., 2011) or a sporadic source such as large-scale regional forest fires (e.g., Dutkiewicz et al., 2011). Similarly, there have been occasional single hour episodes at urban sites (e.g., 11.2 ppm at Queens, NYC in 2003) in recent years. However, since the early 1990s, the second highest 1-hour CO concentrations at all sites have been less than 15 ppm, well below the NAAQS level of 35 ppm. In addition, since 1996 the second highest 8-hour CO concentrations at each site have been below the NAAQS level of 9 ppm.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>NYC</th>
<th>BUF</th>
<th>ROC</th>
<th>SYR</th>
<th>ALB</th>
<th>PSP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO, 20th highest 8-hour concentration</td>
<td>1.0 % yr⁻¹</td>
<td>0.6 % yr⁻¹</td>
<td>N/S</td>
<td>N/S</td>
<td>N/S</td>
<td>N/S</td>
</tr>
<tr>
<td>CO, 1-hour daily max</td>
<td>−2.6 % yr⁻¹</td>
<td>−1.3 % yr⁻¹</td>
<td>N/S</td>
<td>N/S</td>
<td>N/S</td>
<td>−6.0 % yr⁻¹</td>
</tr>
<tr>
<td>CO, 1-hour max</td>
<td>−5.9 % yr⁻¹</td>
<td>−6.2 % yr⁻¹</td>
<td>−5.1 % yr⁻¹</td>
<td>−8.0 % yr⁻¹</td>
<td>−7.0 % yr⁻¹</td>
<td>−10.2 % yr⁻¹</td>
</tr>
<tr>
<td>CO, 2-hour max 8-hour</td>
<td>−6.3 % yr⁻¹</td>
<td>−4.6 % yr⁻¹</td>
<td>−4.4 % yr⁻¹</td>
<td>−7.1 % yr⁻¹</td>
<td>−4.6 % yr⁻¹</td>
<td>−2.7 % yr⁻¹</td>
</tr>
<tr>
<td>NO₂, annual average</td>
<td>−2.4 % yr⁻¹</td>
<td>−1.9 % yr⁻¹</td>
<td>N/S</td>
<td>N/S</td>
<td>N/S</td>
<td>−6.5 % yr⁻¹</td>
</tr>
<tr>
<td>NO₂, 1-hour daily max</td>
<td>−2.6 % yr⁻¹</td>
<td>−1.3 % yr⁻¹</td>
<td>N/S</td>
<td>N/S</td>
<td>N/S</td>
<td>−6.0 % yr⁻¹</td>
</tr>
<tr>
<td>SO₂, annual average</td>
<td>−5.9 % yr⁻¹</td>
<td>−6.2 % yr⁻¹</td>
<td>−5.1 % yr⁻¹</td>
<td>−8.0 % yr⁻¹</td>
<td>−7.0 % yr⁻¹</td>
<td>−10.2 % yr⁻¹</td>
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<tr>
<td>SO₂, 1-hour daily max</td>
<td>−5.7 % yr⁻¹</td>
<td>−6.2 % yr⁻¹</td>
<td>−4.1 % yr⁻¹</td>
<td>−6.5 % yr⁻¹</td>
<td>−7.0 % yr⁻¹</td>
<td>−6.3 % yr⁻¹</td>
</tr>
<tr>
<td>O₃, annual average</td>
<td>+1.0 % yr⁻¹</td>
<td>+0.6 % yr⁻¹</td>
<td>N/S</td>
<td>+0.5 % yr⁻¹</td>
<td>+1.1 % yr⁻¹</td>
<td>N/S</td>
</tr>
<tr>
<td>O₃, 4th highest 8-hour daily max</td>
<td>−1.1 % yr⁻¹</td>
<td>−0.7 % yr⁻¹</td>
<td>−0.9 % yr⁻¹</td>
<td>−1.0 % yr⁻¹</td>
<td>−0.8 % yr⁻¹</td>
<td>−1.3 % yr⁻¹</td>
</tr>
</tbody>
</table>

NO₂ Concentration Trends

Figs. 3(a)–3(b) display the time series of NO₂ concentrations from 1980 through 2014 across New York. Long-term measurements are only available in two urban areas, NYC and BUF, with some measurements at PSP since 1997. Fig. 3(a) shows the annual averages and Fig. 3(b) shows the 98th percentile of daily maximum 1-hour NO₂ concentrations. For most of the period, the highest average urban NO₂ concentrations were about an order of magnitude higher than PSP. Even within the NYC area prior to the late 2000s there was a substantial range in average NO₂ concentrations of about 15–25 ppb or nearly a factor of two. In decreasing order, the highest average NO₂ concentrations in NYC occur in the core urban borough of Manhattan followed by the other boroughs, with outlying counties having the lowest concentration. At BUF the variation between the two sites was approximately 4–7 ppb or 20–60%. Observed differences across these sites is attributed to variations in
Fig. 2. (a) Annual average, (b) second highest 1-hour concentrations, and (c) second highest 8-hour concentrations of CO, 1980–2014. Median values and ranges in concentration across all monitors with at least 75% valid data in a given year are displayed. Monitors are separated by metropolitan area: New York City (NYC), Buffalo (BUF), Rochester (ROC), Syracuse (SYR), Albany (ALB), and Pinnacle State Park (PSP). Note the different scale for the rural PSP site. The 1-hour NAAQS (35 ppm) and 8-hour NAAQS (9 ppm) are shown as solid lines in Figs. 2(b) and 2(c), respectively.

Decreases in annual average NO₂ concentrations have been most readily apparent since the 1990s in NYC, and since the 1980s in BUF (Fig. 3(a)). In the NYC area the annual average NO₂ concentrations have declined about \(-2.4 \% \text{ yr}^{-1}\) since 1980, but since 1990 the decline is \(-3.5 \% \text{ yr}^{-1}\); at BUF the decline in annual average NO₂ is about \(-1.9 \% \text{ yr}^{-1}\) since 1980, and about \(-2.0 \% \text{ yr}^{-1}\) since 1990. Currently, average urban NO₂ concentrations in NYC and BUF are > 50% lower than in the 1980s. This is consistent with the...
findings of Hidy and Blanchard (2015), who reported that NO$_2$ concentrations on a national average basis have decreased by ~60% between 1980 and 2013. Average NO$_2$ concentrations in NYC were about 20–25 ppb higher in NYC than BUF in the 1990s, whereas in more recent years the difference is about 10 ppb. The decreases in annual average NO$_2$ concentrations are consistent with decreases in NO$_x$ emissions over the past several decades. The average NO$_2$ concentrations at PSP are an order of magnitude or more lower than in urban areas, and are currently ~1 ppb or less. The NO$_2$ trend at the rural PSP site since 1997 is about ~6.5 % yr$^{-1}$. All sites in New York currently have annual average NO$_2$ concentrations well below the annual average NAAQS of 53 ppb.

The highest daily maximum NO$_2$ concentrations have also declined steadily across New York since the 1980s (Fig. 3(b)). Decreases in peak 1-hour NO$_2$ concentrations in NYC and BUF, the only regions with long-term NO$_2$ data, are statistically significant. The downward trend in daily maximum 1-hour NO$_2$ is most pronounced in the NYC metropolitan area since the late 1980s. Prior to the mid-1990s, the 98$^{th}$ percentile of daily maximum NO$_2$ concentrations in New York City often exceeded the NAAQS level of 100 ppb. In the past 15 years, only Amherst in the BUF area in 2007 has recorded a 98$^{th}$ percentile daily maximum value that exceeded 100 ppb. This was likely a localized or unusual event, since the daily maximum NO$_2$ on this day (April 25) at another urban site in BUF, ~13 km from the Amherst site, was only 47 ppb. Currently, 1-hour peak NO$_2$ concentrations in urban areas have been below 70 ppb, while at PSP the 1-hour peak NO$_2$ concentrations are now below 10 ppb.

**NO, NO$_x$, and VOC Concentration Trends**

It is also useful to examine trends in NO and NO$_x$ since they are interrelated with NO$_2$, and NO$_x$ NEI data emissions are available for comparison. However, hourly NO measurements have not been routinely recorded prior to 1990 by the NYSDEC, so NO data from the 1980s are very limited. Fig. S2(a) displays the time series of annual average NO in NYC, BUF, and PSP from 1990 onward, while Fig. S2(b) displays the time series of NO$_x$. As with NO$_2$, the highest NO and NO$_x$ levels are in NYC and lowest are at the rural PSP site. In the early 1990s NO varied

![Fig. 3.](image)
between ~30–80 ppb in NYC versus ~10–25 ppb in BUF, while NO levels ranged from ~70–120 ppb and ~25–45 ppb in these two regions, respectively. Over this period, annual average NO has decreased about –8.0 % yr\(^{-1}\) in NYC and –5.2% in BUF, while NO has decreased –5.3% yr\(^{-1}\) in NYC and –3.9 % yr\(^{-1}\) in BUF. At PSP, annual average NO levels have declined from ~0.4 ppb in the late 1990s to ~0.1 ppb currently (~6.2 % yr\(^{-1}\)), while average NO concentrations have dropped by a similar amount percentage-wise (~4 ppb to ~1 ppb; ~6.6 % yr\(^{-1}\)). Recall from the earlier discussion on NEI trends that NO emissions have decreased –5.7% yr\(^{-1}\) since 1998. Thus, downward trends in ambient NO, particularly in NYC, appear relatively consistent with emissions.

Although VOCs are not criteria pollutants and ambient monitoring data are extremely limited, they play a role in O\(_3\) formation, and it may be instructive to examine changes in ambient concentrations relative to changes in emissions as with the other pollutants. Fig. S3 displays the time series of summertime-only average concentrations of the sum of PAMS target compounds in NYC (New York Botanical Gardens, Bronx), which since 1996 has exhibited a decline of about –5 % yr\(^{-1}\). As mentioned earlier, VOC emissions have declined about –2 % yr\(^{-1}\) nationally since 1980, but since the mid-1990s the declines have been closer to –4.4 % yr\(^{-1}\), suggesting a qualitative agreement between emissions and ambient VOC concentrations in NYC.

**SO\(_2\) Concentration Trends**

Figs. 4(a)–4(b) display the time series of SO\(_2\) concentrations from 1980 through 2014 in New York. Fig. 4(a) shows the annual averages and Fig. 4(b) shows the 99\(^{th}\) percentile of daily maximum 1-hour SO\(_2\) concentrations. Through the 1980s, annual average concentrations of SO\(_2\) ranged from about 5–30 ppb across urban sites in New York; currently they are below 3 ppb. Annual average SO\(_2\) levels have generally been highest in NYC, followed by BUF and ROC in the western part of the state, then ALB and SYR, with PSP showing the lowest levels. In NYC highest levels are in Manhattan and Bronx associated with residual oil combustion in the many large apartment complexes characteristic of these boroughs (Clougherty et al., 2013), with lower concentrations in the remaining boroughs. Across the NYC region the annual average SO\(_2\) levels varied by ~10–15 ppb in the 1980s, and ~5–10 ppb in the 1990s and 2000s; in more recent years, these
differences have greatly diminished. The changes in the variation of SO2 across NYC are partly attributed to the introduction of cleaner heating fuel oils which also lead to widespread reductions in ambient nickel levels (Rattigan et al., 2016). Spatial variations across the BUF and ROC areas are less than NYC, typically 2–5 ppb and also less systematic. In general higher SO2 concentrations in the western part of the state are due to transport from upwind regions. These sources include coal-fired utilities in the Midwestern US as well as a number of smaller nearby utilities in western NY, including Kodak Park in the ROC area and Kintigh Generating Station in the BUF area. Annual average SO2 concentrations at PSP have been below 2 ppb over the past decade and lie towards the lower range of the urban areas. Trends in annual average SO2 concentrations are about −5.9 % yr−1 in NYC and −5.1 to −8.0 % yr−1 in other urban areas; the trend at PSP since 1997 is −10.2 % yr−1. These SO2 concentration trends are consistent with emission trends and those of Blanchard et al. (2013) who observed rates of −5.9 to −9.7 % yr−1 between 1999 and 2010 in the southeastern US. Fuel switching – less coal and more natural gas – in the energy generation sector, as well as the introduction of low-sulfur diesel and home heating fuels, have greatly reduced ambient SO2 levels across all areas of the state. Currently, annual average SO2 is below 2 ppb at all urban sites and below 0.5 ppb at PSP.

In the 1980s and into the 1990s, the annual 99th percentiles of daily maximum SO2 concentrations often exceeded the current NAAQS level of 75 ppb in New York City (Fig. 4(b)). These exceedances extended beyond the mid-2000s for the upstate urban sites. Until very recently, the highest annual average SO2 concentrations were more likely to occur in New York City, whereas the highest daily maximum SO2 concentrations were more likely to occur at the other urban sites. Although peak SO2 concentrations in NYC could exceed 100 ppb into the early 1990s, the highest annual 99th percentile concentrations, which could exceed 200 ppb, generally occurred at BUF area sites in the western part of the state, related to the relative proximity to coal-fired utilities. However, by the late 2000s peak SO2 concentrations were considerably lower than in previous years due to enforcement in emissions controls on these nearby coal-fired utilities, and currently all sites across New York have a 99th percentile daily maximum values well below the NAAQS level of 75 ppb.

O3 Concentration Trends

Figs. 5(a)–5(b) display the time series of O3 concentrations from 1980 through 2014 in New York. Fig. 5(a) shows the annual averages and Fig. 5(b) shows the fourth highest daily maximum 8-hour O3 concentrations. In contrast to other gas-phase pollutants, average O3 concentrations are typically higher at rural locations than those in urban areas where high NO emissions lead to O3 removal by titration (e.g., Chameides, 1978; Logan et al., 1981; and references within). In the NYC area, the highest average concentrations tend to occur upwind and downwind of the core urban center with the highest NOx emissions. Upstate urban concentrations are typically intermediate between the lowest NYC sites and the more rural PSP site. Fig. 5(a) shows that annual average O3 concentrations have been relatively flat, at least for PSP, but appear to have increased slightly since the late 1980s at urban locations. Trends in annual average O3 concentrations are +1.0 % yr−1 in NYC and between +0.5 and +1.1 % yr−1 at ALB, BUF, and SYR (the trend at ROC was not significant), while the trend is not statistically significant at PSP since 1997. The key to understanding these annual O3 trends lies in the seasonal and diurnal patterns, which will be discussed further in a later section. Maximum O3 concentrations are more likely to occur during the warmer months, when favorable meteorological conditions, enhanced photochemistry and availability of precursors are more conducive to O3 formation.

Daily maximum 8-hour O3 concentrations during the 1980s and into mid-2000s generally exceeded the NAAQS level of 70 ppb throughout the state, with a number of sites exceeding well over 100 ppb, particularly in NYC during the 1980s (Fig. 5(b)). Decreasing trends in the fourth highest daily maximum O3 concentrations are very similar at urban and rural sites in New York: −1.1 % yr−1 in NYC, −0.7 to −1.0 % yr−1 at other urban sites, and −1.3 % yr−1 at PSP since 1997. Although daily 8-hour maximum O3 levels have decreased by 20–30 ppb since the late 1980s as precursor emissions have declined, O3 decreases have been modest compared to the large reductions in primary pollutants. In 2014 for example, four sites in the NYC area had 4th highest daily 8-hr O3 maximum concentrations ≥ 70 ppb. Hence, it is likely that O3 will continue to be an air management problem for the foreseeable future.

In contrast to the other gas-phase criteria pollutants, O3 is dominated by secondary production, and O3 concentrations are controlled by highly non-linear and complex atmospheric chemical and physical processes. Emissions of NOx and VOCs can be transported from nearby or upwind source regions leading to O3 formation in New York. A recent study suggests that background O3 levels of ~30–45 ppb are expected to be transported into the state (Aleksic et al., 2011), making attainment even more difficult as the NAAQS has been lowered from 85 to 70 ppb.

Seasonal Variations

Primary and secondary pollutants can exhibit different seasonal variations. In addition seasonal patterns can vary over time and with location depending on seasonal energy demand and fuel usage across different areas. To examine how these patterns have changed over the past 35 years, Figs. 6–9 show the average seasonal variations in each criteria pollutant over four time periods: 1980–89, 1990–1999, 2000–09, and 2010–14. Here we define seasons as December–February (winter), March–May (spring), June–August (summer), and September–November (fall). Each panel displays the 10th–90th percentile value ranges (boxes) and median hourly value (filled circles) in each season, for each urban area and PSP. Note that air monitoring did not commence at PSP until the mid-1990s, therefore there are no data shown for the 1980s time period. Also not each parameter was measured in each urban area over the entire 35-year record.
Seasonal differences for CO vary depending on the location (Figs. 6(a)–6(f)). For example CO in NYC (Fig. 6(a)) does not exhibit a strong seasonal variation, but median CO concentrations have decreased from about 1.5 ppm to about 300 ppb since the 1980s. Wintertime CO in NYC in the 2010s is slightly elevated compared to other seasons. At other urban sites winter and fall are consistently elevated throughout the periods compared to other seasons. This is most evident during the 1980s and 1990s when the winter-summer amplitude ranged from 20% at BUF (Fig. 6(b)) to nearly a factor of two at SYR and ALB (Figs. 6(d) and 6(e)). Absolute seasonal differences at these sites ranged from a few 100 ppb to >1 ppm. Over the years seasonal differences have substantially diminished across all upstate urban sites. At PSP absolute seasonal differences are much smaller in relation to those at urban sites, but seasonal average CO concentrations have decreased about 50–70 ppb since the 1990s. Some of the highest hourly CO concentrations at PSP (Fig. 6(f)) occurred in the summer months of the 1990s, but on average there is a wintertime maximum at this rural site.

During the 1980s and 1990s NO₂ in NYC and BUF showed elevated summer or spring levels by about 10–25% compared to winter (Figs. 7(a)–7(b)). Substantial reductions in seasonal NO₂ concentrations at NYC are evident between the 1990s and 2000s. Note the very limited NO₂ data in ROC, SYR, and ALB (Figs. 7(c)–7(e)) do not allow for a comparison of seasonal changes in time. In the 1980s urban NO levels were considerably higher, leading to higher NO₂ concentrations in the summer when the NO-O₃ reaction is enhanced. The urban seasonal pattern has transitioned to a winter maximum during the 2010s, with summer concentrations about 40–70% lower than during the winter months. Large reductions in NO emissions and, hence, NO₂ formation via the NO–O₃ reaction, has led to lower secondary formation of NO₂ in the summer in urban areas. The NO₂ levels at the rural PSP location show a consistent winter maximum with summer levels lower by a factor of 4–5 (Fig. 7(f)).

The panels in Fig. 8 show that SO₂ has exhibited a clear winter maximum and summer minimum, and the amplitude of this seasonal variation has diminished substantially over the years. This seasonal pattern can be attributed to fuel combustion for space heating during the winter months, in combination with enhanced photochemical conversion to sulfate (SO₄) and higher planetary boundary layer heights.
(and hence dilution) during the summer months. As emissions of SO\(_2\) have declined dramatically since the 1980s, ambient concentrations have decreased during all seasons at urban sites and the rural PSP site. In the early 1980s, the

![Seasonal variation in CO concentrations in (a) NYC, (b) BUF, (c) ROC, (d) SYR, (e) ALB, and (f) PSP. The filled circles denote the median concentrations and the bars denote the 10th–90th percentile ranges in concentration across four time periods: 1980s (white bars), 1990s (light gray bars), 2000s (medium gray bars), and 2010s (dark gray bars). Note that monitoring data are not available in all regions for each time period.](image-url)
Fig. 7. Same as Fig. 6, except for NO₂.

median winter SO₂ concentrations were ~7–10 ppb or approximately a factor of 2–3 higher than median summer SO₂ concentrations at urban sites (Figs. 8(a)–8(e)), and in the 1990s they were > 3 ppb higher (about a factor of four) at PSP. Currently, the winter-summer differences in median SO₂ concentrations are ~1–2 ppb or less across the state.

Figs. 9(a)–9(f) display the seasonal variations of O₃ at urban sites across New York and PSP. The highest O₃ concentrations are generally observed in the warmer seasons, when meteorological conditions and photochemical
reactions tend to favor \( \text{O}_3 \) formation. Over the past 35 years, the highest summertime \( \text{O}_3 \) concentrations have declined across the state, in response to emissions reduction programs that have targeted precursors. During the 1980s and 1990s, there was a larger spread in \( \text{O}_3 \) concentrations during the summer months, across all urban areas (Figs. 9(a)–9(e)). There was also a clear wintertime \( \text{O}_3 \) minimum, when \( \text{NO}_2/\text{NO}_x \) concentrations were considerably higher, most

Fig. 8. Same as Fig. 6, except for \( \text{SO}_2 \).
evident in the NYC area. Currently, however, the highest \( \text{O}_3 \) concentrations can occur during either the spring or summer months. This is especially evident at sites outside of the NYC area (Figs. 9(b)–9(e)), particularly at PSP since the 1990s (Fig. 9(f)). At the same time, \( \text{O}_3 \) concentrations during the winter and fall seasons have increased across the state. This reduced amplitude in seasonal variation of \( \text{O}_3 \) has been occurring across many areas of the US (Simon)
likely due to reduced titration by NOx as emissions of this pollutant have decreased substantially. This change in the seasonal variation of O3 explains why annual average concentrations have either increased slightly or remained relatively flat over this period of time. In NYC, the wintertime 90th percentile has increased by >10 ppb since the early 1980s. Similarly, the wintertime 10th percentile in O3 at PSP and urban sites outside of NYC were ~0–1 ppb in the early 1980s, and are currently >10 ppb. In addition, the 10th percentile values across NYC during the spring months have also increased by ~10 ppb, whereas it has increased by ~15–20 ppb in other urban areas. As the O3 NAAQS is further lowered, it will be imperative to characterize background levels of O3 and the impacts of transport in order to meet air quality goals.

The photochemistry of O3, NO, and NO2 is tightly coupled, and, as will be discussed later, the diurnal variations in NO2 and O3 are generally anti-correlated. The sum of NO2 + O3 (Ox), an indicator of ambient oxidant levels and a more conserved quantity than NO2 or O3 individually, has been used in conjunction with NOx to examine local versus regional contributions to O3 in urban areas (e.g., Clapp and Jenkin, 2001). Fig. S4 displays the seasonal average Ox and NOx concentrations from monitoring stations in NYC and BUF (combined) from 1991–2014. Linear least-square regression equations in each season are also shown, although assuming that the O3–NO relationship is linear, especially at lower NOx concentrations, may oversimplify the actual processes. The slope of each seasonal line relates to local production of Ox, from direct emissions of NO2 as well as photochemical conversion. The slope is highest in the summer (0.35) when local oxidant production is most efficient, and lowest in the winter (0.09). The intercept (NOx = 0) reflects background O3 levels and also varies seasonally from ~31–34 ppb in fall and winter to ~42 ppb in both spring and summer. These latter variations are related to transport of O3 and precursors from other areas leading to elevated O3 locally. Characteristically, spring and summer experience region-wide photochemical events leading to elevated O3 and other pollutants being transported along the eastern US. Fig. S4 suggests that during the spring and summer months <30 ppb of O3 is produced locally in urban areas in New York on an average basis. In contrast to the urban sites where NOx concentrations are unlikely to actually reach zero, a rural site such as PSP, with very low ambient NOx concentrations on average, is even more influenced by regional transport of O3 and precursors. Therefore, despite the large decreases in precursor (NOx and VOC) emissions, from about ~3 to ~6 % yr−1, only moderate changes in O3 have occurred locally, similar to what has been observed in the southeastern US (Blanchard et al., 2013) and central California (Pusede and Cohen, 2012).

**Diurnal Variations**

While annual averages are used to assess long term trends in pollutant species, and daily maximum values are generally used to assess air quality standards and human health, it is often necessary to investigate if there are substantial changes to the seasonal or diurnal patterns related to more local emissions. For example CO and SO2 (not shown) have diurnal patterns similar to NO in urban areas such as NYC, reflecting the dominance of local primary emission sources. In contrast CO and SO2 at PSP show little diurnal variation due to the absence of local primary emission sources at this remote location. Since diurnal patterns can be particularly important for species like O3 and NOx which are inter-related and undergo substantial seasonal and diurnal changes, the focus here will be on these latter species.

The average diurnal pattern for NO, NO2 and O3 across the seasons during the 1990s, 2000s and 2010s are shown in Figs. 10–12 at representative sites with data from NYC (New York Botanical Gardens), BUF (Amherst), and PSP, respectively. At urban sites (Figs. 10 and 11) NO shows a characteristic early morning sharp peak between 6 and 9 am with a secondary broader peak in the evening. The morning peak amounts to a factor of 2–3 increase in concentrations and is attributed to fresh traffic emissions into the shallow planetary boundary layer (PBL) during the morning commute. Concentrations subsequently fall off with a minimum in the afternoon due to dilution and dispersion as wind speed increases and the PBL expands. In addition photochemical processes, such as titration by O3 lead to NO removal during daytime hours. The pattern is observed through all seasons but is most pronounced during winter and fall when primary pollutants are higher due to reduced photochemical removal pathways, and PBL depths and dispersion tend to be lower. Similar to NO2 and the other criteria pollutants, concentrations of NO in urban areas have declined substantially from the 1990s to present, with dramatic reductions during the morning hours. The NO levels at the rural PSP site (Fig. 12) are an order of magnitude or more lower than urban levels due to the lack of major emission sources such as motor vehicle traffic at this rural location. The NO concentrations at PSP are elevated during daytime hours due to photochemical production (photolysis of NO2) as well as mixing down from aloft as the PBL expands.

The NO2 diurnal pattern at urban sites also shows a morning peak generally coincident with that of NO but then concentrations drop quickly reaching a minimum in the early afternoon. This pattern indicates production from primary emission sources and PBL mixing similar to NO in the morning and evening hours, with photochemical conversion during daytime and subsequent production via NO reaction with O3. Concentrations of NO2 increase again later in the day due to increased emissions (e.g., motor vehicles), reduced photochemistry, and decreasing PBL depths, resulting in an evening to nighttime maximum which is higher than the morning peak. The NO2 levels at the rural PSP site are an order of magnitude lower than urban concentrations and are highest at nighttime with a characteristic decrease during daytime and a minimum around noon to early afternoon. This pattern reflects the absence of local primary NO2 sources while the daytime removal is consistent with its photolysis to NO.
Fig. 10. Average diurnal variations by season and decade at New York Botanical Gardens (NYC region): 1990s (solid line), 2000s (dotted line), and 2010s (broken line). From left to right the panels show winter, spring, summer, and fall. From top to bottom the panels show NO, NO₂, and O₃.
Fig. 11. Same as Fig. 10, except for Amherst (BUF region).
Fig. 12. Same as Fig. 10, except for PSP.
The diurnal pattern of O$_3$ is characterized by a noontime to early afternoon maximum with highest concentrations in summer, consistent with its formation from NO$_2$ photolysis (reflected in the NO$_2$ minimum). In general there is a larger diurnal variation in O$_3$ at urban sites, where local sources of NO$_x$ and other pollutants can lead to O$_3$ titration during the nighttime and early morning hours, resulting in generally lower daily or annual average concentrations than in non-urban areas. This is in contrast with more moderate diurnal variations in O$_3$ at a rural site like PSP, where NO$_x$ concentrations are substantially lower. During the summer months, afternoon peak O$_3$ concentrations in NYC are about a factor of four higher than nighttime minima, while at BUF they are a factor of 2–3 higher; at PSP, the difference is less than a factor of two. In contrast to both NO and NO$_2$ which have consistently decreased across all sites and all seasons in response to emission reductions, changes in O$_3$ can be positive or negative and vary with location, season and time of day. Since the 1990s winter O$_3$ has increased by about 5–10 ppb throughout the day at urban locations. At PSP the increase varies from 3–6 ppb, generally higher during the nighttime and early morning hours. During spring and fall O$_3$ at urban sites has also increased by about 3–10 ppb, but there had been little change at PSP during these seasons. Summer shows the most diverse changes across New York. In NYC the summer maximum has decreased slightly by 1–2 ppb, while values for the rest of the day have increased; the largest increase is at night (~10 ppb), due to lower NO concentrations and, therefore, less removal at night. At the Amherst site in BUF the maximum has decreased by 5 ppb while the minimum values have increased by an equal amount. Summer O$_3$ at PSP has decreased throughout the day by 1–7 ppb, the largest decreases occurring during the afternoon through nighttime hours. Therefore, complex and contrasting diurnal and seasonal O$_3$ patterns across urban and rural areas result in different annual trends.

SUMMARY

Air quality has improved substantially in New York State over the past three and a half decades, with changes in most criteria pollutant concentrations generally mirroring emissions reductions from the power generation and mobile source sectors. Anthropogenic emissions of SO$_2$, NO$_x$, and CO are estimated to be less than half of what they were in the early 1980s; this in turn has led to concomitant reductions in annual average and peak air concentrations of these pollutants across all areas of New York, especially urban locations. Currently, concentrations of CO, NO$_x$, and SO$_2$ are below their respective NAAQS levels, and the seasonal amplitudes and inter-regional concentration differences are considerably diminished in recent years compared to the 1980s and 1990s. Similarly, the diurnal amplitudes of NO and NO$_2$ have greatly diminished in response to anthropogenic emissions reductions. While summertime peak 8-hour O$_3$ concentrations are also lower now than they were 2–3 decades ago, the decreases are much more modest than those of precursor emissions. In addition, O$_3$ levels during the non-summer months and during nighttime hours appear to be increasing, especially in urban areas, but even in the winter months at a rural site like PSP. Thus attainment of the current O$_3$ NAAQS in both urban and rural locations will remain a management challenge for years to come.

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DISCLAIMER

Although this manuscript was reviewed internally, it does not necessarily reflect the views or policies of the participating organizations or funding agencies.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

REFERENCES


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