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Changes in ambient air pollutants in New York State from 2005 to 2019: Effects of policy implementations and economic and technological changes

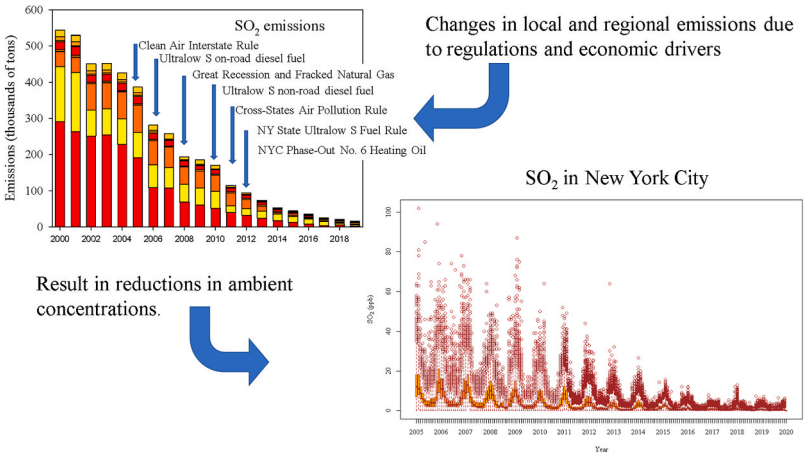
Yunle Chen [a], David Q. Rich [a,b,c], Mauro Masiol [d], Philip K. Hopke [a,e,*]

[a] Department of Public Health Sciences, University of Rochester School of Medicine and Dentistry, Rochester, NY, 14642, USA
[b] Department of Environmental Medicine, University of Rochester School of Medicine and Dentistry, Rochester, NY, 14642, USA
[c] Department of Medicine, University of Rochester School of Medicine and Dentistry, Rochester, NY, 14642, USA
[d] Dipartimento di Scienze Ambientali Informatica e Statistica, Università Ca' Foscari Venezia, Venezia, Italy
[e] Institute for a Sustainable Environment, Clarkson University, Potsdam, NY, 13699, USA

HIGHLIGHTS

- Concentrations trends of criteria pollutants measured across New York were assessed.
- Multiple trend analyses were applied to assess regulatory and economic drivers.
- SO_2 declined the most as a result of the closure of coal fired power plants.
- NO_2, CO, and $PM_{2.5}$ declined at lower rates.
- Ozone increased at most monitoring sites indicating that they are VOC-limited.

GRAPHICAL ABSTRACT



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ABSTRACT

Over the past 20 years, a number of regulatory efforts have been applied to improve air quality in the United States and specifically in New York State. These measures generally focused on mobile emissions through emissions controls and improved fuel quality, and controls on electricity generation to reduce emissions from older, uncontrolled electricity generation units (EGUs). In addition, economic drivers such as the major recession in 2007–2009 and the change in the relative costs of natural gas and coal also drove changes in the mixture of EGU technologies. To assess the effects of these changes and to define the baseline for future changes as the economy further decarbonizes through renewable electricity generation and electric vehicles, the concentrations of all pollutants measured at all regulatory monitoring sites in New York State were assessed for their trends. Trends were examined using seasonal-trend decomposition with local regression smoothing (STL), Mann-Kendall trend analysis with the Theil-Sen nonparametric slope estimation, and piecewise regression analysis to identify

* Corresponding author. Department of Public Health Sciences, University of Rochester School of Medicine and Dentistry, Rochester, NY, 14642, USA.
E-mail address: phopke@clarkson.edu (P.K. Hopke).

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breakpoints in the slopes of the time series data. The concentrations of primary gaseous pollutants, CO, NO_2, and SO_2 have decreased substantially in step with the declining emissions. $PM_{2.5}$ has substantially declined largely due to the reductions in particulate sulfate. However, in recent years, the rate of decline has diminished due to relatively constant or increasing particulate nitrate and secondary organic aerosol. O_3 has also generally increased at the urban sites likely as a result of reduced NOx emissions, while it declined or remained constant at the rural sites. Thus, the promulgated regulations assisted by the economic drivers have improved air quality, but additional actions will be needed to further reduce urban O_3 and $PM_{2.5}$.

1. Introduction

It is now clear that air pollution is a major contributor to morbidity and mortality with the Global Burden of Disease (GBD, 2020) estimating that air pollution was the 4th highest risk factor for mortality and 4th and 3rd highest risk factors for disability-adjusted life-years (DALYs) in males and females, respectively. Within the total air pollution risks, between 5.7 and 7.2 million premature deaths in 2019 were caused by particulate air pollution alone (https://vizhub.healthdata.org/gbd-results/). The WHO (2021) recently revised down their health-based guidance levels for air pollutants with a recommendation of 5 and 15 $\mu g/m^3$ for annual and 24-h exposures, respectively. Thus, there are ongoing efforts to reduce air pollutant concentrations and improve public health.

During the past 3 decades, there have been many efforts to improve air quality in the United States through a variety of policy implementations that have focused on controlling emissions from various sources. Table 1 provides a summary of several major implemented actions. To assess the effectiveness of such regulatory efforts, it is useful to determine the changes in pollutant concentrations. However, other factors such as economic drivers can also induce changes in emissions and resulting concentrations. For example, the combination of the 2007–09 recession coupled with the advent of low-cost fracked natural gas, led to a substantial change in electricity generation from coal combustion to natural gas fired turbines.

Rattigan et al. (2016), Squizzato et al. (2018a) and Blanchard et al. (2019a,b) have analyzed air pollution concentrations across New York State to assess their concentration trends through 2014, 2016 and 2015, respectively. Rattigan et al. (2016) examined the trends over 2000 to 2014 in $PM_{2.5}$ mass and chemical constituent concentrations focused on sulfate, nitrate, organic and elemental carbon measured at 16 sites across New York State. Seven sites had speciation data for most of this period. One speciation site covered only 2000 to 2005 and a pair of sites (Canal Street and Division Street that are within 1 km of each other) were considered to provide a continuous data record. They found that most of the $PM_{2.5}$ decline was due to results in particulate sulfate and nitrate with some decreases in elemental carbon, but little or no change in organic carbon. They only made general attributions of the sulfate and nitrate decreases to the implementation of major regulations such as the NOx SIP call and the Clean Air Interstate Rule (CAIR) and reductions in elemental carbon after 2007 as a result of improved vehicle technology.

Squizzato et al. (2018a) examined seasonal patterns, diel cycles, spatial gradients, and trends in $PM_{2.5}$ and gaseous pollutants concentrations (NOx, SO_2, CO and O_3) monitored in New York State (NYS) from 2005 to 2016. Trends were primarily assessed using the Theil-Sen slope estimation coupled with the nonparametric Mann-Kendall analysis (Sen, 1968; Theil, 1992) to determine monotonic variations for those sites for which there were at least 9 years of data. Thus, details of the changes in concentrations during the study period could not be assessed since only a single linear fit was made. They did find that there were decreases clearly related to the economic indicators (e.g., the "Great Recession" of 2007–2009 recession and changes in the price of natural gas) and

Table 1
Major policy implementations and economic drivers that affected ambient air pollution concentrations.

Relevant Date(s)	Jurisdiction	Action
Electricity Generation		
1993–2012	National	The NOx SIP (State Implementation Plan) Call (1998) and the NOx Budget Trading Program (2003) as well as the Clean Air Interstate Rule/ Cross-State Air Pollution rules to reduce SO_2 and NOx emissions from coal-fired power plants.
2004	State	Renewable Portfolio Standard, approved by the New York State Public Service Commission, aimed to include a higher proportion of renewable energy sources in the state electricity generation mix leading to phase out of all coal-fired power plants in NYS.
2009–2014	Provincial	Electricity policy changes in Ontario beginning in 2009 to go "carbon-free." Started with half of the Nanticoke plant that was the largest SO2 in North America and shutting down the last of their coal-fired power plants in 2014.
2015	State	All but 1 coal-fired power plant in NYS have been closed. Remaining plant in Niagara County continued to run intermittently until 2020.
Building Space Heating		
2010–2016	City	Beginning in 2010, New York City began forcing a switch from No 6 oil to No 4 or 2 for large building heating. No. 6 use ended in 2016; No. 4 continued to be used until 2030.
July 2012	State	New York State required that all distillate fuels sold within the state for any purpose to be ultralow S including No. 2 oil used for home heating.
Motor Vehicles		
2004	National	Tier II Tailpipe Emissions and Fuel Quality Standards
2007	National	Begin change from port fuel injection (PFI) to gasoline direct injection (GDI) for improved fuel economy to meet CAFE standards;
2006 to 2010	National	On-road diesel fuel sold after October 1, 2006 (80%), was required to have ultralow S concentrations (<15 ppm) and all being ultralow S by 2010
2007/2010	National	Particle control traps (2007) and NOx control (2010) for new heavy-duty vehicles
2008	National	Revised Corporate Average Fuel Economy (CAFE) standards; Model years 2008–2011. Manufacturers introduce Gasoline Direct Injection (GDI) to replace Port Fuel Injection (PFI) to improve fuel efficiency.
2010–2013	National	Nonroad fuels required to be ultralow S by January 1, 2014
2011–2013	National	Reformulation of gasoline to reduce benzene content by January 1, 2014; Replaced with intermediate volatility organic compounds.
August 2012	National	North American Emission Control Area (NA-ECA) required marine fuels reduced to 1.0% sulfur.
January 2015	National	North American Emission Control Area (NA-ECA) required marine fuels reduced to 0.1% sulfur
January 2017	National	New light-duty vehicles must meet Tier 3 emission standards.
Economic Drivers		
December 2007–June 2009		The Great Recession after the bursting of the U.S. housing bubble and the global financial crisis.
2008–2009		Price of natural gas drops from $12.69/million BTU in June 2008 to $3.38/million BTU in June 2009

qualitative relationships between oxides of nitrogen species emissions and concentrations examined for individual monitoring sites. However, detailed analyses of each pollutant at each site for possible relationships with policy implementations were not conducted.

Blanchard et al. (2019a) primarily examined O_3 and NOx trends from 1995 to 2015. They show a strong relationship between changing regional NOx emissions and the ambient NOx and particulate nitrate concentrations averaged over multiple sites across the state. They also reported multiple site reductions in CO and volatile organic compounds (VOCs). They reported trends assessed using a general additive model regression for a variety of O_3 concentration parameters including peak daily 8-h O_3, O_3 associated with morning NO, morning NO_2, daily CO, daily maximum temperature, and mid-day RH and separated their analyses to all days, June to August, and December to February. All day and June to August trends were all negative except for morning NO and mid-day RH. However, the December to January results showed increases for peak daily 8-h O_3, the trends associated with morning NO and NO_2, daily maximum temperature, and mid-day RH. There were no associations of the trends with any of the actions that drove the changing emissions. Blanchard et al. (2019b) focused on $PM_{2.5}$ organic and elemental carbon constituents and the emission influences on their concentrations with a focus on the rural monitoring site of Pinnacle State Park in southwestern NY. They did relate multiple site sulfate concentrations with regional average SO_2 emissions.

In a more limited scope study, Pititanggon et al. (2021) only quantified the long-term changes in local and regional source contributions to $PM_{2.5}$ in New York City from 2002 to 2018. They also examined trends in the major particulate species. A major focus of this work was assigning fractional contributions of local and regional sources using the Community MultiScale Air Quality (CMAQ) model to bound the amounts of regional transport of secondary aerosol and a land-use regression model to assess local contributions. They provided qualitative relationships of the observed reductions to various regional and local regulations.

The aim of the current study was to update the trend analyses through 2019 and adding breakpoint analysis to better associate the changes in concentrations with the policy implementations and economic and technological drivers to the extent possible for all pollutants at all sites individually across the state. However, most regulatory actions involved implementation over multiple years and many of the activities overlapped in time. Major economic events like the "Great Recession" of 2007–2009 also resulted in changed levels of activity as well as changes in production methods given the advent of low cost fracked natural gas that came extensively to market in 2008. Thus, multiple causalities were operating to change the local concentrations measured at each site and the effects of any single policy or economic change cannot be derived from data analyses.

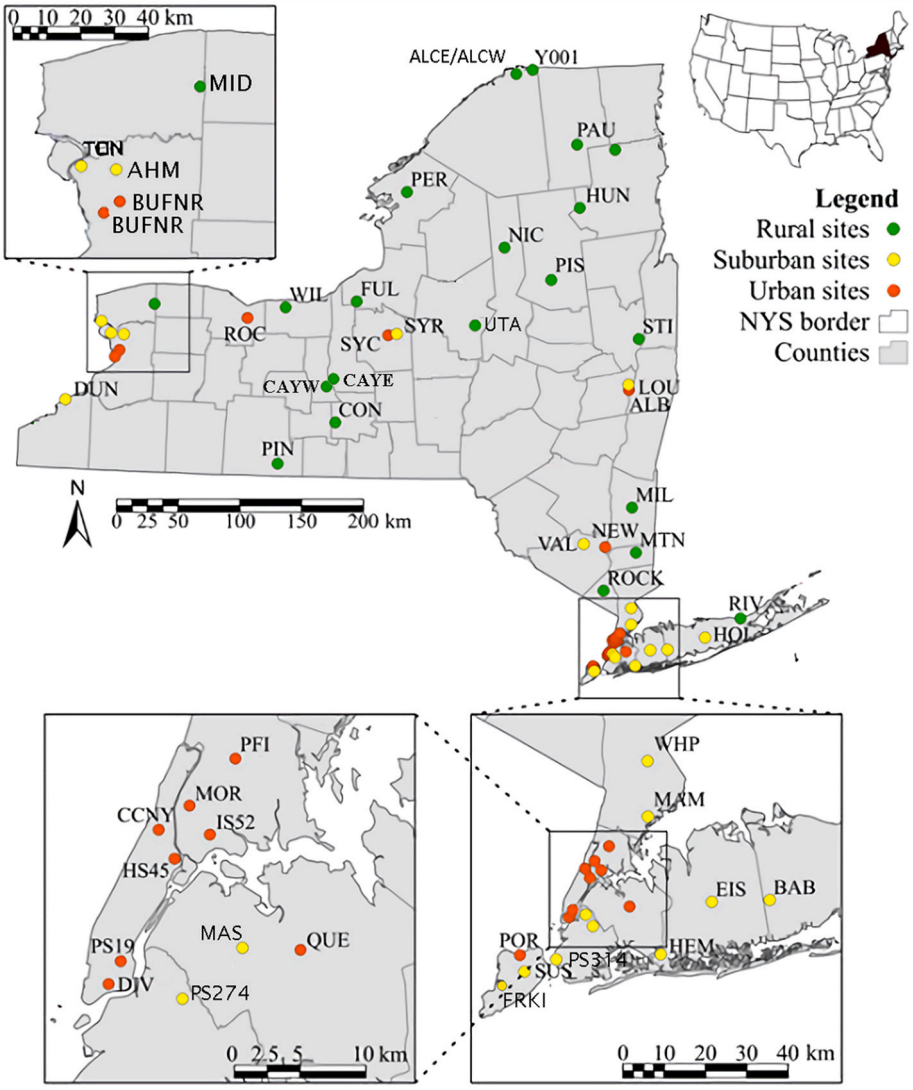

Fig. 1. View of New York State and the location of the air quality monitoring sites. Site denoted by ROC and QUE represent both the main site and the nearby Near Road site since they are too close to display separately.

2. Materials and methods

2.1. Study area

NYS is located in the northeastern United States. It is bordered by two Great Lakes and covers over 141,000 km^2 (max extension ~500 km along its N–S axis and ~520 km along its W-E axis) (Fig. 1). There are nine metropolitan statistical areas (MSAs) classified in NYS in 2020 (Census, 2020): (i) Albany-Schenectady (population 880,766); (ii) Buffalo-Cheektowaga (1,129,018); (iii) Elmira-Corning (84,115); (iv) Ithaca-Cortland (102,237); (v) New York City (NY-NJ-PA Metro Area, (19,261,570). (vi) Ogdensburg-Massena (108,352); (vii) Rochester-Batavia-Seneca Falls (1,071,784); (viii) Syracuse-Auburn (650,211) and (ix) Utica-Rome (290,812). These MSAs are shown in Fig. S1 in the supplemental information file.

2.2. Air quality data

Since the analyses reported by Squizzato et al. (2018a), the number of NYS monitoring sites has been reduced from 74 to 54 locations. Their locations are provided in Fig. 1. Not all pollutants are measured at every site. Details of the sites and the species measured are provided in Supplemental Material Table S1 including the abbreviations to designate the sites. The hourly concentrations of CO, NO_2, O_3, SO_2, and $PM_{2.5}$ were downloaded from the Federal Land Manager Environmental Database website (http://views.cira.colostate.edu/fed/QueryWizard/). These data are collected by this website from the U.S. Environmental Protection Agency's Air Quality System (AQS). Thus, these are the same data as can be downloaded directly from the AQS, but CIRA provides them in a much easier to use format.

2.3. Policy and economic drivers of emission changes

Although substantial progress in improving air quality had been made from 1970 to the early 2000s, it was clear that to protect public health, further reductions would be needed (e.g., Zhang et al., 2018; Croft et al., 2019; Hopke et al., 2019). Thus, a number of additional control initiatives were put into place. These actions were primarily aimed at electricity generating unit (EGUs) and motor vehicular emissions. These initiatives are summarized in Table 1.

An important set of regulations affected emissions from light-duty vehicles being sold in the US beginning in 2004 (USEPA, 2000). The classification of light-duty vehicles with respect to these regulations is given in Table S2. The required reductions in emissions and related implementation schedule are provided in Tables S3 and S4, respectively. Tier 3 regulations of emissions from vehicles affect vehicles sold after January 1, 2017 (USEPA, 2014) and were more stringent than the Tier 2 requirements. Some of the major changes involved the regulation of the sum of NMHC + oxygenated hydrocarbons (NMOG) and NOx emissions with the bins now named in terms of their NMHC + NOx limits in mg/mi (Tables S5 and S6). Bin 160 (NMOG + NOx = 160 mg/mi) is equivalent to Bin 5 in the Tier 2 regulations. These standards were also phased in with the fleet average NMOG + NOx emissions required to decline to 30 mg/mi (Bin 30 = Tier 2 Bin 2) by 2025. Gasoline vehicles now had to be tested for both exhaust and evaporative emissions using 10% ethanol fuel. In contrast to Tier 2 regulations, Tier 3 rules also provided for heavy-duty vehicular emissions such as heavy-duty pick-ups and vans. The definitions for LDVs, LDTs, and MDPVs were consistent with those for Tier 2 (Table S2).

Over the period of 2006–2014, there have been mandated improvements in fuel quality, primarily associated with the amount of sulfur in distillate fuels as well as changes in the formulation of gasoline to reduce the benzene content and the resulting exposure to a known carcinogen. Beginning in 2005, the Tier 2 rules required domestic gasoline refiners to produce fuel with an average sulfur (S) content under 30 ppm S, but with corporate averages of 90 ppm and a cap of any fuel of 300 ppm since refined gasoline is imported. By 2007, the requirements were 30 ppm with a maximum cap of 80 ppm. Tier 3 fuel standards require gasoline to not contain more than 10 ppm S on an annual average basis by January 1, 2017. Reformulation of gasoline was directed by the Mobile Source Air Toxics (MSAT) rules that aimed to reduce the benzene, 1,3-butadiene, formaldehyde, acetaldehyde, acrolein, and naphthalene concentrations (USEPA, 2007). The MSAT program began on January 1, 2011 and required the annual average benzene content in gasoline to be 0.62% with a maximum benzene content of 1.3% by July 1, 2012. To retain the combustion properties, toluene and intermediate volatility organic compounds have been used resulting in increased production of secondary organic aerosol (SOA) (Zhao et al., 2016).

For on-road diesel fuel, 80% of the fuel sold on October 1, 2006 had to have an ultralow S content (<15 ppm S) with 100% being ultralow S by January 1, 2010. Ultralow S fuel for non-road vehicles, locomotives, and marine diesel engines was phased in between 2007 and January 1, 2014. Additionally, New York required all distillate fuels sold within its jurisdiction to be ultralow S by July 1, 2012. Marine diesel emissions were regulated by the North American Emissions Control Area (NA-ECA) that required all marine vehicles to reduce the sulfur content of fuels used within U.S. and Canadian waters (200-mile limit) to 1% S as of July 1, 2012 and to 0.1% S as of January 1, 2015 (USEPA, 2010). Prior work in Canada demonstrated the effectiveness of the NA-ECA rules (Anastasopolos et al., 2021).

In addition to the regulatory actions, there were economic drivers that also led to changes in emissions. The 2007–2009 Great Recession involved a substantial reduction in economic activity in the United States and resulted in decreasing demand for electricity and the shutdown of many less efficient coal-fired power plants. There was also a decrease in the movement of goods via rail and truck. In this same period, fracked natural gas came into the market drastically reducing the cost of natural gas. Thus, as the recession came to an end and the demand for electricity began to rebound, it became more economical to build natural gas fired turbine/combined cycle generation units (Squizzato et al., 2018a). Since 2008, there has been a continuing decline in the use of coal and concomitantly increased use of natural gas for EGU operation.

2.4. Emission trends

The regulations have resulted in estimated reductions in the emissions of the criteria pollutants (USEPA, 2022). EPA provides these estimates for the country as a whole and for individual states with the emissions characterized by source type: fuel combustion - electric utilities; fuel combustion – industrial, fuel combustion - other; chemical & allied product manufacturing; metals processing; petroleum and related industries; other industrial processes; solvent utilization; storage and transport; waste disposal and recycling; highway vehicles, off-highway, miscellaneous, wildfires; and prescribed fires. Fig. 2 presents the emission trends for CO, NO_2, SO_2, and primary $PM_{2.5}$ from 2005 to 2019 (USEPA, 2022). However, the vast majority of $PM_{2.5}$ mass is secondary in nature (sulfate, nitrate, ammonium, secondary organic aerosol). Their trends depend on both changes in emissions of their precursor species (SO_2, NOx, NH_3, and VOCs) and in rates of atmospheric oxidative processes so that the trends in their formation rates can only be modeled using chemical transport models. Such modeling is beyond the scope of the current work. Similarly, O_3 is a secondary species whose formation depends on NO_2 and oxidizable VOCs and the resulting atmospheric chemistry.

2.5. Trend analysis

The trend analyses were performed in the same way they were done by Masiol et al. (2014, 2018, 2019) in R (R Project for Statistical Computing, https://www.r-project.org/). Three different approaches

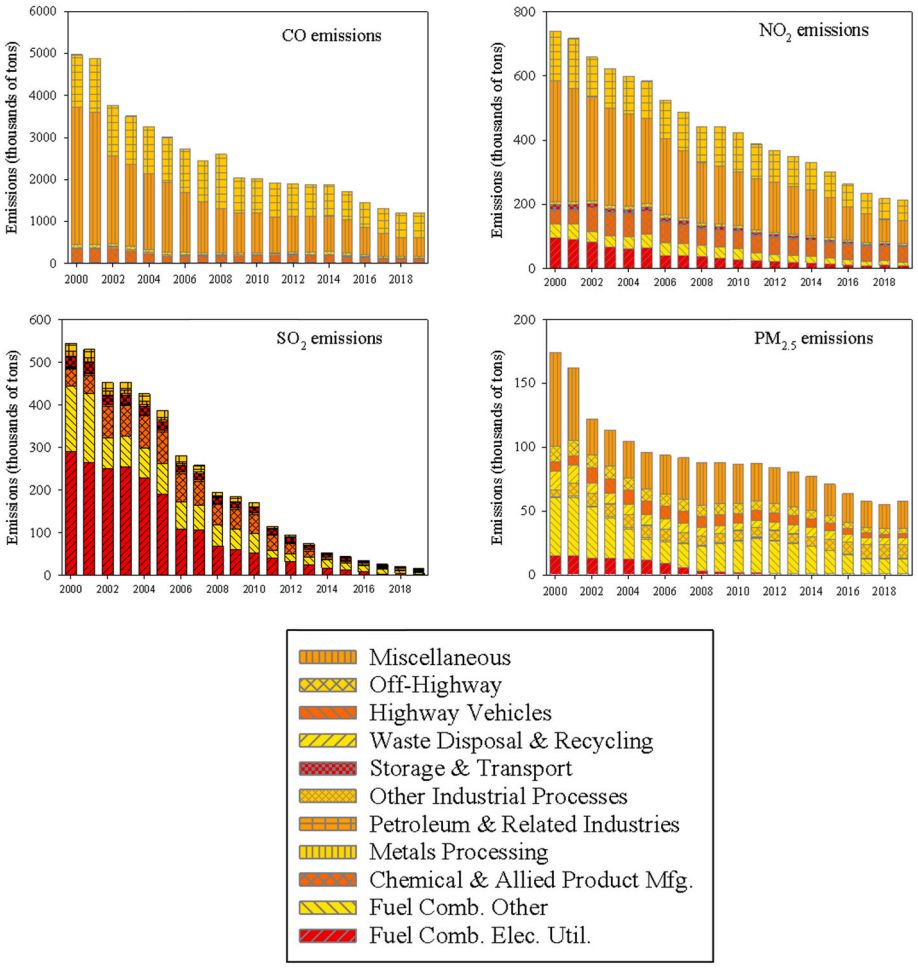

Fig. 2. Annual Emissions of CO, NO_2, SO_2, and primary $PM_{2.5}$ in New York State.

have been applied to assess the changes in concentrations over time. Monthly average values were calculated for each month where ≥75% of the possibly measured data were available. The seasonal-trend decomposition time series approach that is based on "Loess" (STL) (Cleveland et al., 1990) was used to explore the trend shapes and their seasonal variations. In the STL procedure, the data were resolved into three separate time series: seasonal variations, trends in the values, and the residuals after the subtraction of these two time series from the original data. Local regression smoothing (LOESS) was applied to provide smoothly varying estimates for the time series. STL cannot deal with missing data. Thus, a seasonal Kalman filter (Zeileis and Grothendieck, 2005) was applied to interpolate the missing values. For the IS52 site, there was a significant multiple year gap in monitoring. In this case, the STL analysis was applied separately to the two separate time series. For a number of sites, measurements were only made during the "ozone" season and thus, STL analyses could not be done due to the missing data. These environmental data were found to not be normally distributed (Shapiro-Wilk test at $p \leq 0.05$) and thus, the robust mode was applied in the STL analyses. Bootstrapping was applied to provide 95% confidence intervals for the trend and seasonality values.

To assess monotonic trends over the whole 2005 to 2019 interval, Mann-Kendall trend analysis (Mann, 1945; Kendall, 1975) with the Theil-Sen nonparametric slope estimation (Theil, 1950; Sen, 1968) was also performed using the 'openair' package in R (Carslaw and Ropkins, 2012). However, it can only examine overall linear trends so it cannot examine changes in slope that might occur due to implementation of control strategies or economic changes. To examine the possibility of "breakpoints" in the time series, the "segmented" package (Muggeo, 2003; 2008) was applied. It iteratively explores potential changes in slope based on estimated starting points. Bootstrapping (Wood, 2001) was again applied to provide standard error estimates for the slopes and the breakpoint locations.

3. Results and discussion

Summary statistics for the measured ambient concentrations of CO, NO_2, O_3, SO_2, and $PM_{2.5}$ at each site are presented in Tables S8–S12, respectively.

3.1. CO

The results for the trend analyses of the CO data at the 10 sites at which it is measured are provided in Table S12. The plots showing these results are shown in Figs. S2–S10. The BUFNR results were not plotted given the short interval for which data were available and a non-significant slope. Near the end of 2010, NYS DEC replaced the existing monitors with more sensitive units and that period appeared as breakpoints at a number of the sites.

The overall reductions as provided by the Thiel-Sen slopes range from decreases of 3.66% per yr at the urban PFI site in New York City to a rise of 0.11% per year at the rural PIN site. Other than for the site with the largest decrease in CO (54.9% over the 15 years of this study), the site-by-site results do not agree well with the state-wide decrease in estimated emissions of 60.5% since the reductions at the other sites were all substantially lower.

Reductions in the CO concentrations were observed up to 2010 at the

urban sites although there was a rise followed by a decline at ALB. The rate of decline was smaller in the period from 2010 to 2019. There would have been an increasing fraction of Tier 2 vehicles in the on-road light duty fleet as Tier 2 standards were phased-in between 2004 and 2009. A partial implementation began in 2004 with the full implementation occurring by the end of 2007. The primary focus of this standard was on NOx emissions, but it also included mandated reductions in CO and non-methane hydrocarbon emissions (Table S3). The slower reductions after 2010 would be consistent with fewer older vehicles being rotated out of the fleet for new lower emitting vehicles once the Tier 2 regulations were fully implemented (Table S4). This trend continued from 2017 to 2019 suggesting a low impact of Tier 3 vehicles entering the fleet even though those vehicles had to meet more stringent emissions standards (Table S5). However, the standards were more focused on NOx emissions than CO.

Another source of CO would be recreational wood combustion. Many people outside of the cores of the large cities burn wood in fireplaces and wood stoves in the late fall to early spring, particularly on weekends (Wang et al., 2012a,b). There have been no efforts to control these emissions other than the imposition by US EPA of emission standards and testing in 2015 with requirements to only sell new stoves that meet these standards by 2020. Thus, the limited changes in CO in the later part of the study period may be due to lack of controls on residential wood combustion.

There was a sharp increase at PIN from 03/2015–04/2018 and a decrease from 05/2018 to the end of 2019. Squizzato et al. (2018b) had previously suggested that the high concentration of diesel $PM_{2.5}$ observed at PIN was likely due to extensive fracking for natural gas in nearby northern Pennsylvania (see their Fig. S65). Inquiries of the site operator did not provide information about any known activity near the site that would have led to increase CO concentrations.

3.2. NO_2

There were only 8 sites where NO_2 measurements were made. The plots are shown in Figs. S11–S18 and the numerical results are provided in Table S13. Only 3 sites had data from 2005 to 1 from 2007. Others started from 2010 (ROC) to 2017 (QUE NR). For the longer time series sites, the trends were similar to those seen for CO. Thus, again the changes in NO_2 were likely driven by the turnover in the light duty vehicle fleet to those that met the Tier 2 standards and in part, from the introduction of NOx controls on new heavy-duty diesel vehicles sold after January 1, 2010. Other than ROC, all of the sites showed similar Thiel-Sen slopes ranging from −1.79% per yr to −5.53% per yr. Using an average slop of −3.2%/yr yields an overall reduction of 48% while the estimated emissions reduction over this period was 66.4%. Thus, the observed reductions were more consistent with the emissions estimates than was found for CO. The piecewise analyses had inconsistent breakpoints suggesting that the impact of the controls on heavy-duty vehicles had a limited effect on ambient NOx concentrations. However, given the substantial NOx emissions from gasoline vehicles and other sources (Fig. 2) primarily building heating, a limited effect of the 2010 NOx controls could be expected.

There is a difference between the near road sites (BUFNR, QUENR, and ROCNR). BUFNR shows a small decrease (−0.39 ppb yr^{-1}) from 2017 to 2019. ROCNR had a larger decline (−0.94 ppb yr^{-1}) while QUENR experienced a large decline (−1.30 ppb yr^{-1}) until October 2018, but then a rise of 0.97 ppb yr^{-1} until the end of 2019. Comparing these near-road sites to the companion sites, both Buffalo sites declined. However, ROC increased, ROCNR decreased while QUE decreased and QUENR increased. The reasons for these differences are not obvious.

3.3. SO_2

The trend analysis results for SO_2 measured at 21 sites are provided in Table S14 with the plots shown in Figs. S18–S36. There are several pairs of sites to explore the impact of specific sources. ALCE and ALCW are located east and west of the two aluminum smelters in Massena, New York. CAYE and CAYW are placed to examine the emissions from an electric generating plant on the eastern lake shore. As might be expected given the focus on the reduction in sulfur in liquid fuels, there are generally declining trends across most of the sites. In the 2008 to 2016 period, there was a substantial shift in electricity generation from coal-fired power plants including grandfathered plants with no controls to new gas turbine combined cycle plants that must meet new point source pollution standards. As described by Squizzato et al. (2018a), the 2008 recession reduced the demand for electricity. Then the low cost of fracked natural gas changed the relative prices of generating electricity by coal or natural gas. Thus, as the economy rebounded, the share of natural gas generation increased with a more rapid trend in New York compared to the rest of the country. In addition, New York State adopted rules to force the shutdown of coal fired power plants within its jurisdiction by the end of 2020, but most plants terminated operations sooner. The reduction in coal fired generation can be seen in Fig. S38.

Many building in New York City (NYC) were heated by burning No. 6 (residual oil) or No. 4 (mixture of No. 2 and No. 6) oils. After 2011, no new permits for No. 6 oil were approved. Only No. 4 or cleaner oils could be burned beginning in 2015. No. 4 oil could contain 1500 ppm S (Kheirbek et al., 2014), but from the substantial reductions of SO_2 concentrations across NYC as seen in the graphic abstract, the combined requirements implemented by NYS and NYC have substantially reduced local emissions.

The Thiel-Sen slopes across all sites were large and negative ranging from −2.12%/yr to −18.9%/yr. However, again there was a change in monitors to more sensitive units near the end of 2010 that may have perturbed the analyses. In one case (PIS), there was a clear discontinuity in the time series with a very sharp drop suggesting uncertainty about the early period data.

There are several locations (BUF, DUN, and TON) where there were short periods of increasing or constant concentrations following the end of the 2008 recession and increasing economic activity. These sites are all relatively close to major interstate highways with substantial heavy-duty truck traffic. However, there were no similar increases at urban sites like QUE that is also near a major highway. There were typically larger decreases in the 2005 to 2012 period than in the remaining period suggesting that there was a strong effect of the combination of lower fuel S concentrations and the switch from coal-fired power plants to natural gas-fired turbines.

3.4. O_3

O_3 is formed in the atmosphere through the photolysis of NO_2 and reaction of the resulting O atom with an O_2 molecule. However, in the absence of reactive hydrocarbon compounds, the O_3 concentration is governed by the photochemical steady state (Leighton, 1961; Seinfeld and Pandis, 2016) in which the reverse reaction of O_3 with NO restores a molecule of NO_2. O_3 concentrations rise due to the conversion of NO to NO_2 without the consumption of an O_3 through reaction with an oxidant formed by the oxidation of an organic molecule to form a peroxy radical (COO·). Detailed mechanisms of COO· formation and its reaction with NO are provided by Seinfeld and Pandis (2016). Thus, emissions of NO, NO_2, and oxidizable VOCs contribute to the O_3 concentrations. However, there are two regimes depending on the relative concentrations of NO and reactive hydrocarbons. In the VOC-limited regime, reduce NO can lead to increased O_3 by reducing the titration back to NO_2 (Seinfeld and Pandis, 2016).

The trend analysis results for the 30 sites at which O_3 is monitored are presented in Table S15. Although the regulatory variable in the United States is the daily maximum 8-h O_3 concentration, these analyses were performed on all of the hourly data averaged up to monthly values to calculate the trends. The associated trend plots are shown in Figs. S39–S68. There is a distinct difference between the rural and urban

sites. For the rural sites, the Thiel-Sen slopes ranged from 0 to −0.46% per yr. These results suggest that the rural areas are primarily NOx (NO + NO_2) limited areas such that the reduced emissions (Fig. 2) resulted in somewhat lower O_3 concentrations. However, the urban and suburban sites generally had positive Thiel-Sen slopes ranging from 0.11 to 5.15% per yr suggesting that the higher population areas are commonly in the VOC-limited regime. Anthropogenic VOC emissions declined (Fig. S69), but there have been changes in their composition due to the reformulation of gasoline. The increased emissions of intermediate volatility organic compounds (IVOCs) from mobile sources (Zhao et al., 2015, 2016) contribute to O_3 formation as well as leading to increased SOA more than the benzene that they replaced. As such, it will require large reductions in urban NOx to substantially reduce the ambient O_3 concentrations. Similar results were observed in most locations around the world during COVID-19 lockdowns that resulted in substantially reduced traffic and NOx concentrations (e.g., Amouei Torkmahalleh et al., 2021).

3.5. $PM_{2.5}$

$PM_{2.5}$ is a combination of primary emissions and secondary particulate mass formation. The bulk of $PM_{2.5}$ is secondary in the form of secondary inorganic aerosol (SIA, ammonium sulfate + ammonium nitrate) and SOA. Thus, the substantial reductions in SO_2 and NO_2 emissions (Fig. 2) have contributed to the previously observed reductions in $PM_{2.5}$ concentrations as well as the reductions in particulate sulfate, nitrate, and primary organic carbon (Squizzato et al., 2018b). However, Squizzato et al. (2018b) reported that secondary organic carbon (SOC) declined between the periods of 2005–2007 and 2008–2013, but increased or remained constant from 2008 to 2013 to 2014–2016 at all 8 Chemical Speciation Network sites in NYS.

There are 30 sites at which $PM_{2.5}$ is measured including sites that still use the Federal Reference Method (FRM) filter collection method while most sites use continuous monitors. For most of the study period, the Federal Equivalent Method (FEM) Filter Dynamic Measurement System Tapered Element Oscillating Microbalance (FDMS-TEOM) monitors were employed at many of the sites. Details of the sampling systems are provided by Rattigan et al. (2016). In 2017, most of the FDMS-TEOM units were replaced with Teledyne Advanced Pollution Instrumentation Model T640 p.m. Mass Monitor that is also an FEM monitor. For consistency, we only used data from sites having continuous monitors operating across the study period.

The results of the trend analyses are summarized in Table S16 with the individual site plots provided in Figs. S70–S99. For those sites having data for the all or most of study period (not shaded lines), the overall Thiel-Sen slopes are uniformly negative ranging from −1.97%/yr for the QUE site to −6.85%/yr at MOR. For the sites where $PM_{2.5}$ monitoring started after October 2014, a mixture of positive and negative slopes were obtained. At the urban IS52 site in the Bronx where there was a multiple year gap from 2010 to 2014 in monitoring due to construction, there was a −5.24%/yr decline in the early period, but a 4.16%/yr rise in the second period. For multiple urban/suburban sites (ALB, EIS, NEW, PS314, QUE, ROC, and SYR), the slopes become positive after breakpoints that occurred between 2016 and 2018 while at others (BUF, GDI, HOL, IS74, IS143, MOR, PS274, RICPO, TONII, WHF), the magnitude of the negative slope was much lower than before the breakpoint.

The near-road sites (BUFNR, QUENR, and ROCNR) show overall negative Thiel-Sen slopes, but different breakpoint behavior. BUFNR showed no breakpoint so there was a continuous −3.6%/yr decline since October 2014 when the site was established. ROCNR was similar with a smaller slope of −1.74%/r. QUENR operated starting in April 2017 and had a declining trend until July 2018 when a small increasing slope followed. The number of registered vehicles remained relatively constant in each of the years from 2016 to 2019 although traffic volumes generally increased. The trend in engine technology from port fuel injection (PFI) to gasoline direct injection (GDI) began to flatten around 2016 with about 50% of light duty vehicles using each technology.

To further explore the trends in $PM_{2.5}$ concentrations, the time series of the major constituents (sulfate, nitrate, organic and elemental carbon) measured at the Chemical Speciation Network sites (Solomon et al., 2014) were explored. Previously, Squizzato et al. (2018b) found that in the 2014–2016 period compared to the previous period (2008–2014), secondary organic carbon increased, nitrate either remained constant or rose while elemental carbon, primary organic carbon and sulfate declined. These trends can be seen in Figs. S100–S102 for sulfate, nitrate, and elemental carbon measured at the 3 New York City sites (IS52, MAN, QUE) and Rochester (ROC) as an example of upstate small city sites. Fig. S103 provide the organic carbon plots for these 4 sites. The trend analyses are presented in Tables S17–S20.

It can be seen that there were very large decreases in sulfate concentrations resulting from a combination of reduced sulfur in liquid fuels and the switch in electricity generation from coal to natural gas (Fig. S38). The NYC switch in building heating from No. 6 oil to No. 4 or No. 2 oils also had a substantial impact on local $PM_{2.5}$ emissions (Kheirbek et al., 2014). However, it can be seen that nitrate and organic carbon do not decline in the most recent years (post 2015), and in a number of cases, they increase although generally not back to the 2005 to 2009 values. For nitrate to remain relatively constant or show increases is unexpected given the decreases in NO_2 described above. The formation of ammonium nitrate (NH_4NO_3) depends on the concentrations of both HNO_3 and NH_3. If NO_2 is decreasing, then to have the nitrate concentration to stay constant or even increasing suggests there are increasing concentrations of NH_3. Hopke and Querol (2022) recently suggested that NH_3 is likely increasing particularly in urban areas because of increased NH_3 emissions from motor vehicles. Zhou et al. (2019) reported NH_3 monitoring in QUE and ROC showed diel patterns strongly suggesting that its major source were motor vehicular traffic. Reche et al. (2022) reported an increasing trend in NH_3 at a heavily trafficked site in Barcelona during the period of 2011–2020 compared to weaker or no trends at urban background or rural sites. Increasingly stringent requirements for NOx emissions reductions from both gasoline and diesel vehicles likely resulted in higher NH_3 emissions. For example, Li et al. (2020) reported increasing NH_3 emissions from light-duty vehicles in China. Song et al. (2015) reported that there was likely increased NH_3 slip from selective catalytic reduction systems (SCR) used to control NOx emissions from diesel vehicles. Abualqumboz et al. (2022) reported ammonia emissions from light duty vehicles by EPA Tier based on laboratory and on-road measurements. They found that newer vehicles (Tier 2 and 3) had lower NH_3 emissions than earlier systems particularly the National Low Emission Vehicle (model years from 2001 to 2003). However, Preble et al. (2019) showed increasing NH_3 emissions from heavy duty diesel (HDD) vehicles particularly after 2015 when there was likely a sufficient penetration of post-2010 HDDs with SCRs that have NH_3 slip. Another source of additional NH3 arises from the reduction in sulfate concentrations since sulfate binds NH3 irreversably (Vasilakos et al., 2018). Thus, nitrate represents a larger fraction of the $PM_{2.5}$ mass.

In terms of the organic carbon trends, Rich et al. (2019) suggested that the increased secondary organic carbon was also related to the increase in light-duty gasoline vehicular emissions of IVOCs (Zhao et al., 2016) because of the increasing fraction of GDI vehicles in the light-duty vehicle fleet. Rich et al. (2019) reported that the extracted gasoline vehicular source contributions to the $PM_{2.5}$ mass values were highly correlated with the SOC concentrations through 2016. Zhao et al. (2018) reported that Tier 3 vehicles that began entering the market in January 2017 produced less SOA and thus, part of the effect of the light duty vehicles contributions to $PM_{2.5}$ by supporting increased SOA formation will likely decline as the Tier 3 vehicles replace older cars in the light-duty fleet. However, the issue of NH_3 emissions would still support particulate nitrate formation unless control technologies are modified.

4. Conclusions

Given the observed trends in all the gaseous pollutants except ozone, the promulgated regulations in combination with the economic drivers such as the 2007–09 recession and the reduced cost of fracked natural gas had the desired effect of improving air quality. $PM_{2.5}$ also substantially declined largely due to the reductions in particulate sulfate. However, there were unintended consequences of changing light-duty engine technology to improve fuel economy and both light- and heavy-duty vehicle control technologies to reduce NOx emissions that have led to constant or increasing concentrations of particulate nitrate and organic carbon. The reductions in NOx and the changes in the composition of urban VOCs from the reformulation of gasoline likely led to the general increase in urban O_3 across the state while the rural sites showed decreasing trends. The Tier 3 regulations that required further reductions in NOx emissions and the resulting technology changes should produce less SOA and potentially reduced O_3. However, it does not appear that there has not yet been a sufficient penetration of Tier 3 vehicles into the on-road fleet to make a discernible change in the ambient concentrations. However, the replacement of older vehicles with Tier 3 vehicles may eventually lead to NOx and $PM_{2.5}$ decrements. However, the apparent increases in NH_3 from HDD vehicular NOx controls needs to be studied and likely will need to be reduced. The switch to electric vehicles would also reduce the gaseous emissions and the secondary $PM_{2.5}$ being formed from those emissions. However, there will still be mobile vehicular emissions of brake and tire wear. Thus, it is important to continue following the air pollutant trends into the future as further changes in both electricity generation and motor vehicle technology are expected to result in lower emissions, better air quality, and better public health.

CRediT authorship contribution statement

Yunle Chen: Formal analysis, Writing – review & editing. **David Q. Rich:** Conceptualization, Resources, Writing – review & editing. **Mauro Masiol:** Formal analysis, Writing – review & editing. **Philip K. Hopke:** Conceptualization, Formal analysis, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data is available from the US EPA

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Appendix A. Supplementary data

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