



Long Term Trends in New York: PM_{2.5} Mass and Particle Components

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ABSTRACT

Measurements of PM_{2.5} mass and particle components over a 14–15 year period are used to explore trends at urban and rural locations across New York State. Such data are used to determine compliance with national ambient air quality standards (NAAQS), as well as track the effectiveness of reductions in source pollutant emissions. Since 2000 annual mean PM_{2.5} mass shows a downward trend with decreases of 4–7 $\mu\text{g m}^{-3}$ in urban areas versus 3–4 $\mu\text{g m}^{-3}$ for rural background sites. Much of this change can be attributed to particle sulfate (SO₄) and nitrate (NO₃) which showed annual decreases of 2–3 $\mu\text{g m}^{-3}$ and 0.5–1.0 $\mu\text{g m}^{-3}$, respectively. Determining accurate trends for the carbonaceous particle material is challenging due to the changes in the carbon sampling and analysis methods which impact the measurements. Analysis of the data indicate some decreases in particle elemental carbon (EC) but little change in the organic carbon fraction (OC). Significant improvements in air quality are observed since 2000, when New York City metropolitan area exceeded the 1997 annual PM_{2.5} standard of 15 $\mu\text{g m}^{-3}$, to the present conditions where it meets the current standard of 12 $\mu\text{g m}^{-3}$. Further improvements in air quality may benefit from controls on carbonaceous material which is currently the major component of PM_{2.5}.

Keywords: PM_{2.5} mass; Long term trends; Particle species; Major ions; Air monitoring.

INTRODUCTION

As a consequence of the various studies (for example Dockery *et al.*, 1993; Pope *et al.*, 1995) linking outdoor exposure to particulate matter (PM) with adverse health effects, the Environmental Protection Agency (EPA) promulgated National Ambient Air Quality Standards (NAAQS) for PM mass in 1997 (<http://www3.epa.gov/ttn/naaqs/criteria.html>). An annual average standard of 15 $\mu\text{g m}^{-3}$ and a 24 h standard (based on the 98th percentile of observed 24 h values) of 65 $\mu\text{g m}^{-3}$ were established for PM_{2.5} (particles with an aerodynamic diameter at or below 2.5 microns). Both standards were applied to a 3 consecutive year period. Subsequent reviews led to a lowering of the 24h PM_{2.5} NAAQS to 35 $\mu\text{g m}^{-3}$ in 2006 and the annual primary to 12 $\mu\text{g m}^{-3}$ in 2012. In the late 1990's a national PM_{2.5} monitoring network was established to monitor spatial and temporal variability in PM_{2.5} mass for compliance with the standard. Subsequently, the PM_{2.5} Chemical Speciation Network (CSN) was designed to monitor spatial and temporal

patterns in the particle chemical components useful for emission control implementation and provide data in support of health based research.

Generally, the major components of PM_{2.5} particles in the US include SO₄, NO₃, ammonium (NH₄) and carbonaceous material (USEPA, 2012). The crustal or soil material proportion is small although it can be important in arid locations. In the northeastern US, particle SO₄ and associated NH₄ as well as carbonaceous material are the dominant components with particle NO₃ being important in urban areas particularly during colder periods (Tolocka *et al.*, 2001; Schwab *et al.*, 2004).

Over the past few decades large reductions in air pollutants have occurred throughout the US (USEPA, 2012) as a result of various emission controls (USEPA, 2014). These include the Clean Air Act (CAA) and Clean Air Act Amendments (CAAA), NO_x State Implementation Plan (SIP) Call, Clean Air Interstate Rule (CAIR) and Tier 2 light duty vehicle standards and lower fuel S rule as well as improved vehicle technology. The recent downturn in the economy around 2008–2009 and consequent reduced energy consumption may also have resulted in lower emissions. A recent review (Lurmann *et al.*, 2015) reported reductions in ambient air pollutants over a 20 yr period in Southern California. Blanchard *et al.* (2013) found major improvements in air quality since 1999 in the southeastern US. Reductions

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in PM_{2.5} mass and major components have also been observed at locations in Europe (Cusack *et al.*, 2012). Decreases in PM_{2.5} mass have been noted in selected New York urban centers over the period 1999–2007 (Buckley and Mitchell, 2011). With a view to gaining insight into major source categories Schwab *et al.* (2004) analyzed PM chemical components measurements from various New York sites over a 2 year period. In this study, we evaluate trends in PM_{2.5} mass and major components using an extensive dataset covering an approximate 14–15 year period. This dataset is also used to explore urban-rural differences as well as seasonal patterns. Such datasets are important in evaluating the effectiveness of existing emission controls and for future regulations.

METHODS

Site Description

A list of the sites used for this analysis along with their locations are shown in Table 1 and Fig. S1. In the New York City (NYC) area PM_{2.5} mass is measured across the 5 boroughs; Manhattan, Bronx, Brooklyn, Queens, and Staten Island. Data from a total of 11 sites in NYC, listed in Table 1, are included in the analysis of PM_{2.5} mass. Outside of NYC measurements from 3 urban sites; Buffalo (BUFF), Rochester (ROCH) and Albany (ALB) and two rural sites; Pinnacle State Park (PSP) and Whiteface Mountain (WFM) are also used. PSP is a rural site located near the village of Addison (line of sight approx. 310 km northwest of NYC) within 12 km of the border with Pennsylvania (Schwab *et al.*, 2009). The site is at an elevation of 500 m and impacted by pollutants transported from the southwest across the region. WFM is located approximately 410 km north of NYC in the village of Wilmington, at an elevation of 600 m on the side of Whiteface Mountain. This configuration of sites provides a representation of measurements across

urban as well as urban-rural contrasts. PM_{2.5} components measured at seven of the sites MAN, IS52, QUEENS, ROCH, BUFF, PSP and WFM are also included in the analysis. The MAN site operated from two nearby (line of sight distance under 1 km) locations, Canal Street up to March 2007 and Division Street thereafter. Since species measurements at the New York Botanical Gardens (NYBG) ceased in December 2005 and measurements at ALB only commenced in August 2007 particle species data from these two sites were deemed not suitable for this long term analysis.

Sampling Instruments

PM_{2.5} mass samples were collected based on the Federal Reference Method (FRM) from midnight to midnight generally on a 1 in 3 day schedule with the following exceptions. At QUEENS the 1 in 3 day schedule switched to daily sample collection in May, 2001. Sample collection at the IS52 and PSP sites was on a daily schedule up to 2010 but switched to a 1 in 3 day thereafter. WFM sampling was also setup on a daily schedule but switched to a 1 in 6 day collection in 2007. Both ALB and BUFF sites switched to daily sampling from 2007 to 2011 but reverted back to a 1 in 3 day schedule in 2012.

The FRM employed the Partisol Plus Sequential Air Sampler, Model 2025, Thermo Scientific, Franklin, MA for PM_{2.5} mass sampling. A summary of sampler details is provided in Table 2. The sampler employs a PM₁₀ size-selective inlet followed by a Well Impactor Ninety-Six (WINS) impactor with a 2.5 μm cut-point. Air flow is volumetrically controlled at 16.7 LPM and particles are collected on a 47 mm Teflon filter housed in a cassette. A supply chamber which stores filters prior to sampling is maintained to within 5°C of ambient using a continuous air ventilation system. Unused filters automatically move across under pneumatic pressure to the sample chamber for sampling

Table 1. Summary details of ambient monitoring sites.

Site Name	Location	Site ID	FRM start date	Speciation start date
IS45	Manhattan	36-061-0079	1/2000	
PS19	Manhattan	36-061-0128	10/2001	
PS59	Manhattan	36-061-0056	7/1999	
Canal St. / Division St. (MAN)	Manhattan	36-0610-0062	7/1999–3/2007	8/2002–3/2007 ^a
		36-061-0134	3/2007	3/2007
Morrissania (MORR)	Bronx	36-005-0080	7/1999	
New York Botanical Gardens (NYBG)	Bronx	36-005-0083/0133	7/1999	2/2000–12/2005 ^b
IS52	Bronx	36-005-0110	9/1999	11/2000
Queens College (QUEENS)	Queens	36-081-0124	1/2001	3/2001
JHS 126	Brooklyn	36-047-0076	1/2001	
Susan Wagner (SWAG)	Staten Island	36-085-0067	7/1999	
Port Richmond (PRICH)	Staten Island	36-085-0055	12/1999	
Buffalo (BUFF)	Weiss St.	36-029-0005	7/1999	1/2002
Rochester (ROCH)	Yarmouth Rd.	36-055-1007	8/1999	1/2001
Albany (ALB)	South Pearl St.	36-001-0005	7/1999	8/2007 ^c
Pinnacle State Park (PSP)	Addison	36-101-0003	8/1999	2/2001
Whiteface Mountain (WFM)	Wilmington	36-031-0003	7/1999	5/2001

^a Canal Street sampling end date and Division street start date. ^b NYBG speciation sampling end date. ^c Speciation data for ALB and NYBG not included for long term analysis.

Table 2. Summary details of Sampling Instruments.

Sampler	Inlet type	Sharpness $\sqrt{(D_{16}/D_{84})}$	Flow rate L min ⁻¹	Filter diameter mm	Modules
FRM	^a WINS	1.18	16.7	47	T
R&P2300	impactor	1.18	16.7 10	47	^b 3 modules T, N, Q
MetOne	cyclone	1.24 ^c	6.7	47	^b 3 modules T, N, Q
URG-3000N	cyclone	1.20	22	25	Quartz

^a Well Impactor Ninety-Six;

^b T = Teflon, N = Nylon, Q = Quartz;

^c Peters *et al.* (2001).

while the already sampled filter moves into a storage chamber. This facilitates unattended sample collection over holiday and weekend periods. Blank filters were collected by installing a filter into the chamber with no flow through the filter over the 24 h period. Ambient meteorological and filter parameter data are recorded for each sample. Sampled filters are shipped to RTI International, Durham, North Carolina for analysis. Mean 24h PM_{2.5} mass measurements for blank filters in 2012–2013 was 8.02 µg filter⁻¹ with a 2 sigma of 1.06 µg corresponding to 0.33 ± 0.04 µg m⁻³.

PM_{2.5} chemical speciation sample collection was based on a 1 in 3 day schedule except for BUFF which used a 1 in 6 day schedule. Collection at WFM switched to a 1 in 6 day schedule in 2006. Measurements were made using either a Rupprecht & Patashnick Co., Inc. Partisol Speciation Sampler model 2300, Albany, NY (hereafter R&P2300) or a Met One Instruments Spiral Aerosol Speciation Sampler, Grants Pass, OR (hereafter MetOne). A summary of instrument parameters is listed in Table 2 and detailed descriptions are provided elsewhere (Solomon *et al.*, 2003). The R&P2300 contained three individual sample modules with greased impactor PM_{2.5} size selective inlets (Demokritou *et al.*, 2001). A Teflon filter module operated at 16.7 LPM was used for PM_{2.5} mass and element analysis by gravimetric and X-ray Fluorescence, respectively. Nylon and quartz filter modules which operated at 10 LPM were used to sample for major ions and carbonaceous particle material, respectively. The MetOne sampler also had three individual modules but the flow through each channel was 6.7 LPM. A sharp cut cyclone (SCC 2.141, BGI Incorporated, Waltham, MA) provided the 2.5 µm cut-point. Blank filter measurements were obtained by placing a filter into the sampler for the 24h period with no flow through the filter. Filters were shipped to RTI for analysis. Mean blank measurements for major ions (analyzed by ion chromatography) typically varied from 0.02–0.06 µg m⁻³ for SO₄ and NO₃ and were below 0.02 µg m⁻³ for NH₄. Quartz filters were analyzed based on the NIOSH 5040 method (Peterson and Richards, 2002) using Thermal Optical Transmission (TOT). Typical mean blank measurement for OC of 1.0 µg m⁻³ was subtracted from the raw OC mass measurements. No correction was applied to the EC fraction as the blanks were below the detection limit.

A change to the CSN sampling and analysis methods of carbonaceous particles (Rice, 2006) led to the introduction of a URG-3000N Sequential Particulate Speciation System

(URG, Chapel Hill, NC) in 2007. A cyclone (Air and Industrial Hygiene Laboratory, Berkeley, CA) operated at 22 LPM (volumetrically controlled) provided the PM_{2.5} size cut. The sampler used a pair of 25 mm Pallflex Tissue quartz filters placed back to back and is based on that used in the IMPROVE (Interagency Monitoring of Protected Visual Environments) network. The use of the second filter was to provide a measurement of the active adsorptive material. In addition blank filters were also collected. Mean blank measurements for OC ranging from 0.10–0.20 µg m⁻³ were subtracted from the reported OC mass concentrations. Quartz filters were analyzed using the IMPROVE_A temperature protocol (Chow *et al.*, 2007) at Desert Research Institute, Reno, NV. Dual mode detectors provided for analysis using both transmission (TOT) and reflectance (TOR).

RESULTS AND DISCUSSION

PM_{2.5} Mass

Annual mean PM_{2.5} mass concentrations are shown for the NYC and various sites across the state since 2000 in Figs. 1(a) and 1(b), respectively. A summary of the data is presented in Table 3 along with 95% confidence intervals. Concentrations reflect population density being highest in NYC and BUFF followed by ALB and ROCH with the rural PSP and WFM sites the lowest. Across the NYC metropolitan area the highest levels are in Manhattan, followed by Bronx then Brooklyn, Queens and Staten Island in that order. A consistent decline in the annual mean PM_{2.5} mass is observed throughout the region since 2000. Mann-Kendall trend tests shows these are significant at the 95% confidence interval. For example in the NYC metropolitan area annual mean PM_{2.5} mass ranged from 12.4–18.5 µg m⁻³ in 2000 versus 8–11 µg m⁻³ in 2014 which is a drop of 4–7 µg m⁻³ equivalent to a 30–40% decrease. Thus PM_{2.5} mass in NYC which exceeded the 1997 annual standard of 15 µg m⁻³ at several sites in 2000, has dropped below the current NAAQS of 12 µg m⁻³ in recent years. Similar decreases are observed for upstate urban sites of BUFF (6 µg m⁻³) and ALB (5 µg m⁻³) with ROCH slightly less (~4 µg m⁻³). The corresponding reduction at the rural PSP and WFM sites is 2–3 µg m⁻³ equivalent to a change of 25–30%. Likewise, the 98th percentile PM_{2.5} mass has decreased (significant at the 95% interval) although with considerable year to year variations, Fig. 2. In NYC

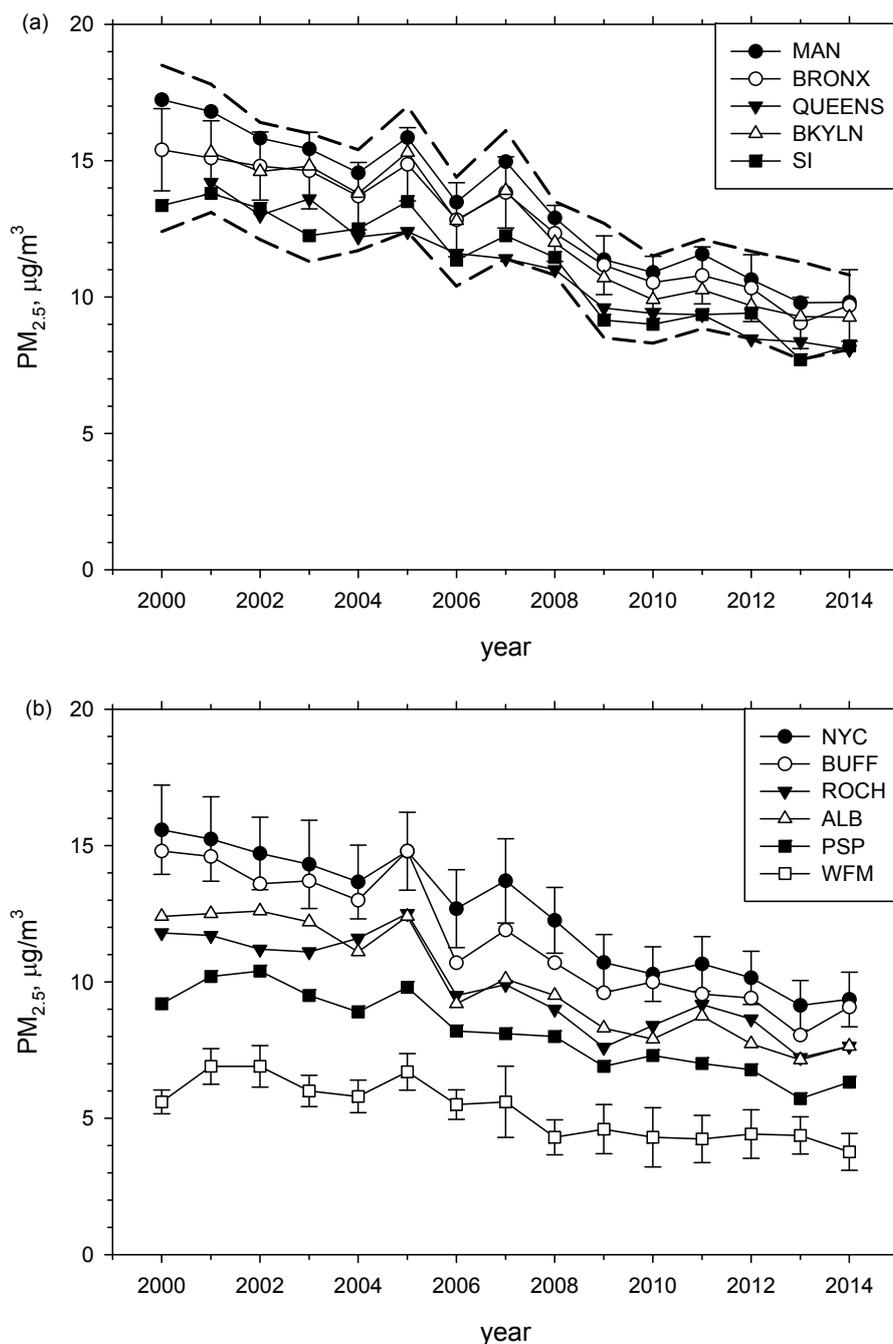


Fig. 1. Annual mean PM_{2.5} mass for (a) NYC boroughs and (b) across NY state. In panel (a) MAN, BRONX and SI refer to the means across the Manhattan, Bronx and Staten Island sites, respectively and BKLYN refers to Brooklyn. The dashed lines in (a) show the range across individual NYC sites. The error bars represent 95% confidence limits on (a) BRONX data and (b) the NYC and WFM data.

and BUFF the 98th percentile PM_{2.5} mass has decreased by 15–20 $\mu\text{g m}^{-3}$ compared to 9–14 $\mu\text{g m}^{-3}$ for upstate urban centers, ALB and ROCH versus 5–10 $\mu\text{g m}^{-3}$ at the rural locations. In 2000–2001 the 98th percentile PM_{2.5} mass was approximately 35–40 $\mu\text{g m}^{-3}$ in NYC and BUFF, 30–35 $\mu\text{g m}^{-3}$ for ROCH and ALB versus 20–30 $\mu\text{g m}^{-3}$ for the two rural sites. The highest daily values across the state were observed on July 7, 2002 when the Eastern US was impacted by smoke from wildfires in Quebec, Canada

(DeBell *et al.*, 2004). On that day PM_{2.5} mass for the NYC area ranged from 75–85 $\mu\text{g m}^{-3}$ versus 50–75 $\mu\text{g m}^{-3}$ in ALB and 40–50 $\mu\text{g m}^{-3}$ in the western part of the state. This event increased the annual mean PM_{2.5} mass by approximately 0.5 $\mu\text{g m}^{-3}$ for 2002. Although the 98th percentile annual PM_{2.5} mass values were high across the state in 2002, they were not unusually high in NYC and in fact 2003 was slightly higher. Further details of the forest fire event are discussed in the supplemental section.

Table 3. Summary of annual PM_{2.5} mass mean concentrations in $\mu\text{g m}^{-3}$ at various sites.

Year	NYC	BUFF	ROCH	ALB	PSP	WFM
2000	15.6 (18.5–12.4) ^a	14.8 ± 1.5 ^b	11.8 ± 1.2	12.4 ± 1.4	9.2 ± 0.7	5.6 ± 0.4
2001	15.2 (17.8–13.1)	14.6 ± 1.7	11.7 ± 1.6	12.5 ± 1.8	10.2 ± 0.8	6.9 ± 0.7
2002	14.7 (16.4–12.1)	13.6 ± 1.6	11.2 ± 1.3	12.6 ± 3.7	10.4 ± 0.8	6.9 ± 0.8
2003	14.3 (16.0–11.3)	13.7 ± 1.6	11.1 ± 1.3	12.2 ± 1.7	9.5 ± 0.7	6.0 ± 0.6
2004	13.7 (15.4–11.7)	13.0 ± 1.5	11.6 ± 2.8	11.1 ± 1.4	8.9 ± 0.8	5.8 ± 0.6
2005	14.8 (17.0–12.4)	14.8 ± 1.7	12.5 ± 1.6	12.4 ± 1.5	9.8 ± 0.8	6.7 ± 0.6
2006	12.7 (14.4–10.4)	10.7 ± 1.3	9.50 ± 1.1	9.2 ± 1.6	8.2 ± 0.6	5.5 ± 0.6
2007	13.7 (16.1–11.4)	11.9 ± 0.9	9.90 ± 1.4	10.1 ± 0.8	8.1 ± 0.6	5.6 ± 1.3
2008	12.3 (13.5–10.8)	10.7 ± 0.6	9.00 ± 1.1	9.5 ± 0.6	8.0 ± 0.6	4.3 ± 0.6
2009	10.7 (12.7–8.5)	9.6 ± 0.5	7.60 ± 0.8	8.3 ± 0.6	6.9 ± 0.4	4.6 ± 0.9
2010	10.3 (11.5–8.3)	10.0 ± 0.7	8.40 ± 1.1	7.9 ± 0.6	7.3 ± 0.6	4.3 ± 1.1
2011	10.7 (12.2–8.8)	9.6 ± 0.6	9.17 ± 1.2	8.7 ± 0.6	7.0 ± 0.9	4.2 ± 0.9
2012	10.2 (11.7–8.5)	9.4 ± 0.9	8.64 ± 1.0	7.7 ± 0.8	6.8 ± 0.7	4.4 ± 0.9
2013	9.1 (11.3–7.7)	8.1 ± 0.8	7.22 ± 0.8	7.1 ± 0.9	5.7 ± 0.7	4.4 ± 0.7
2014	9.3 (10.8–8.1)	9.1 ± 1.0	7.64 ± 0.9	7.6 ± 0.8	6.3 ± 0.8	3.8 ± 0.7

^a The values in parenthesis for NYC shows the range across the metropolitan sites. The values ^b for other sites are the 95% confidence intervals.

Seasonal Patterns

In order to compare seasonal patterns over the time period mean seasonal PM_{2.5} mass concentrations were calculated for combined calendar years 2000–2001 versus 2012–2013, shown in Fig. 3. Seasonal data for 2000–2001, Fig. 3(a), show highest NYC mean concentration in winter (Dec, Jan, Feb) of 17.6 $\mu\text{g m}^{-3}$ followed closely by summer (Jun, Jul, Aug) 16.6 $\mu\text{g m}^{-3}$ then autumn (Sep, Oct, Nov) 15.0 $\mu\text{g m}^{-3}$ with the lowest in spring (Mar, Apr, May) of 13.3 $\mu\text{g m}^{-3}$, representing a seasonal amplitude of 4 $\mu\text{g m}^{-3}$. Corresponding seasonal variations in upstate urban centers, ROCH and ALB are similar although at ROCH both winter and summer have equivalent concentrations as well as spring and autumn. BUFF shows highest seasonal concentrations in summer and lowest in autumn, however the seasonal amplitude is the same. These seasonal differences, except for winter and spring at ALB, are not significant within the 95% confidence limits. At the rural sites of PSP and WFM seasonal concentrations for 2000–2001 show summer is significantly higher than the other seasons with a 5.5 $\mu\text{g m}^{-3}$ and a 3.3 $\mu\text{g m}^{-3}$ variation (between summer and winter) at the two sites, respectively. The similarity in summer PM_{2.5} mass at PSP and NYC and upstate urban centers is also reflected in the seasonal SO₄ concentrations, one of the major components of PM_{2.5} (discussed below). In addition another major component, OC, is also similarly elevated in summer. This can result in an extensive pollution event across the Northeastern US lasting over a day or more. Secondary species are regional in nature which leads to high spatial homogeneity (Turner and Allen, 2008). By 2012–2013 mean seasonal PM_{2.5} mass has decreased by 3.4–7.5 $\mu\text{g m}^{-3}$ across NYC, and upstate urban centers versus 2–5 $\mu\text{g m}^{-3}$ and 1.3–2.3 $\mu\text{g m}^{-3}$ at the rural PSP and WFM sites, respectively. Seasonal data for 2012–2013 shows summer PM_{2.5} mass is significantly higher than other seasons except in NYC and ALB. NYC seasonal PM_{2.5} differences are not significant and at ALB only spring is significantly lower than winter and summer.

PM_{2.5} Particle Species

(i) Major Ions

Annual mean SO₄, NO₃ and NH₄ for the PM_{2.5} CSN sites are shown in Figs. 4(a), 4(b), 4(c), respectively. A major difference between annual SO₄ and PM_{2.5} mass is the similarity in PM_{2.5} SO₄ concentrations across the state with the exception of WFM which is significantly lower by about 2 $\mu\text{g m}^{-3}$. In fact, SO₄ is highly correlated across all sites with coefficients of determination, R², varying from 0.89 to 0.98. Concentrations at the rural PSP site are within 0.5 $\mu\text{g m}^{-3}$ of those at the urban NYC and BUFF sites. ROCH appears on the lower edge of the group, just outside the 95% confidence interval of the QUEENS data. Similar observations were reported by Dutkiewicz *et al.* (2004) and Schwab *et al.* (2004). Highest SO₄ was associated with air mass transport through the Ohio River Valley and Great Lakes Basin, regions of high SO₂ emissions (Dutkiewicz *et al.*, 2004). This reflects the regional nature of particle SO₄ with its major precursor emission source from Electric Generating Utilities (EGUs) lying towards the south and west of the state. Over the 10 yr period between 2002–2003 and 2012–2013 SO₂ emissions have been cut by about 65–70%, Fig. S2(a), compared to decreases in SO₄ of 50–64% observed across NY state. WFM being furthest from the emissions sources shows the least decrease of 50%. There is a linear relationship between SO₂ emissions and ambient SO₄ with coefficients of determination above 0.89 for all sites. However, there is not quite a 1:1 proportional response in SO₄ to the SO₂ emissions reductions as previously observed in the Southeastern US (Blanchard *et al.*, 2013). A change in the rate of SO₄ decrease is evident around 2005–2007, with a general levelling off in concentrations in recent years. The same pattern is observed in EGU SO₂ emissions as it took time for CAAA controls to be adopted. Elemental selenium (Se) which is associated with coal combustion in the northeastern US (Dutkiewicz *et al.*, 2006) also shows a similar decrease around 2006 (see below). Therefore, we attribute the decreases in SO₄ to the CAAA

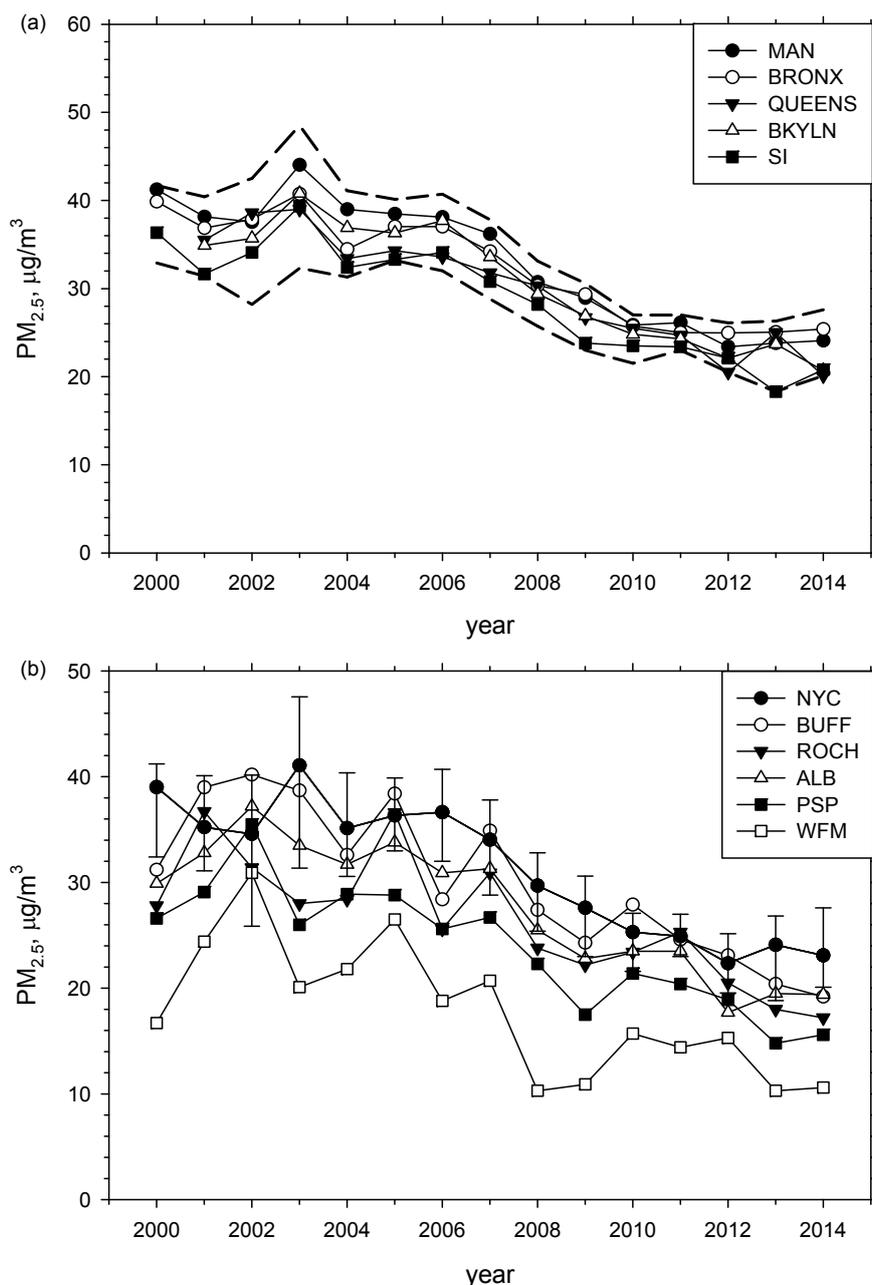


Fig. 2. Annual 98 percentile PM_{2.5} mass for (a) NYC boroughs and (b) across NY State. In panel (a) MAN, BRONX and SI refer to the means across the Manhattan, Bronx and Staten Island sites, respectively and BKLYN refers to Brooklyn. The dashed lines in (a) and error bars in (b) represent the range across individual NYC sites.

and CAIR which targeted EGU emissions. Annual mean NO₃ data are shown in Fig. 4(b). The data appear as three distinct groups with highest concentrations at urban sites then PSP approximately $1 \mu\text{g m}^{-3}$ lower and WFM the lowest of all. Concentrations across the urban sites vary by $0.5\text{--}0.8 \mu\text{g m}^{-3}$ bordered by MAN on the top and ROCH on the lower edge. A downward trend is observed with urban concentrations reduced by $1.0\text{--}1.6 \mu\text{g m}^{-3}$ over the 10 yr period 2002–2003 to 2012–2013, or 40–50%. Smaller concentration reductions of $0.3\text{--}0.6 \mu\text{g m}^{-3}$ are observed at the rural sites of PSP and WFM but the percentage differences are similar (40–50%). NO_x (precursor to NO₃)

emissions are more widely distributed among various source sectors compared to SO₂ which is dominated by EGUs. Transportation accounts for the bulk of the NO_x emissions, Fig. S2(b), with highway traffic amounting to approximately 40%, and off-road vehicles accounting for 20%. Emissions from EGUs account for less than 20% of the NO_x emissions. Between 2002–2003 and 2012–2013 total NO_x emissions have been cut by 42% or 4.2 \% yr^{-1} which is similar to reduction rates for particle NO₃ from 3.7 to 5.1 \% yr^{-1} across NY State. Emission controls for SO₂ on EGUs also reduced NO_x. In addition, the NO_x SIP call in 2004 required further NO_x reductions on EGUs and major combustion sources.

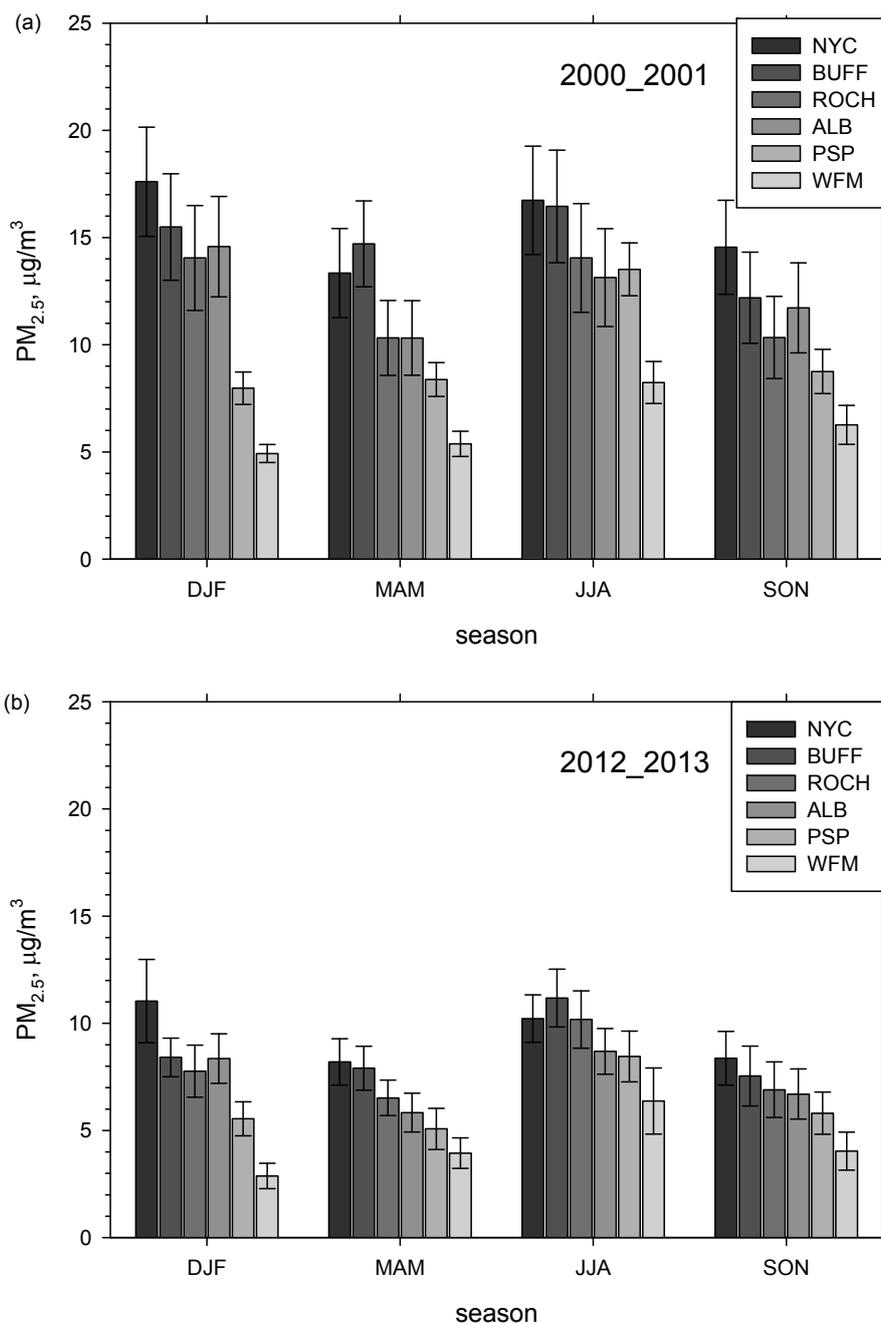


Fig. 3. Mean seasonal $PM_{2.5}$ mass during (a) 2000–2001 and (b) 2012–2013. DJF represents months Dec, Jan and Feb. The error bars show the 95% confidence intervals.

The National Low Emission Vehicle (NLEV) program in 2000 and Tier 2 Vehicle controls led to reductions in tailpipe emissions including NO_x . Therefore, the reductions in ambient particle NO_3 are attributed to the combined impact of the above controls on stack and vehicle emissions. NH_4 data, Fig. 4(c), also are generally clustered with urban sites showing the highest concentrations. PSP is intermediate between ROCH and WFM, the latter exhibiting the lowest concentrations. All sites show a downward trend (as for SO_4) with two distinct rates of decrease, most noticeable in the urban data. A small or negligible decrease is observed from 2001 to 2007 (less than 10% in NYC and 15% or less

at other sites) with a more rapid change between 2007 and 2012 (55–60% decrease). Concentrations appear relatively uniform from 2012 onwards. Since ambient particle NH_4 is associated with SO_4 and NO_3 the reductions are attributed to the combined emissions controls on SO_2 and NO_x mentioned above.

Seasonal Patterns

Enhanced photochemical activity (higher solar flux and extended daylight hours compared to other seasons) leads to higher SO_2 to SO_4 conversion during summer months throughout the region (Rattigan et al., 2006). In addition

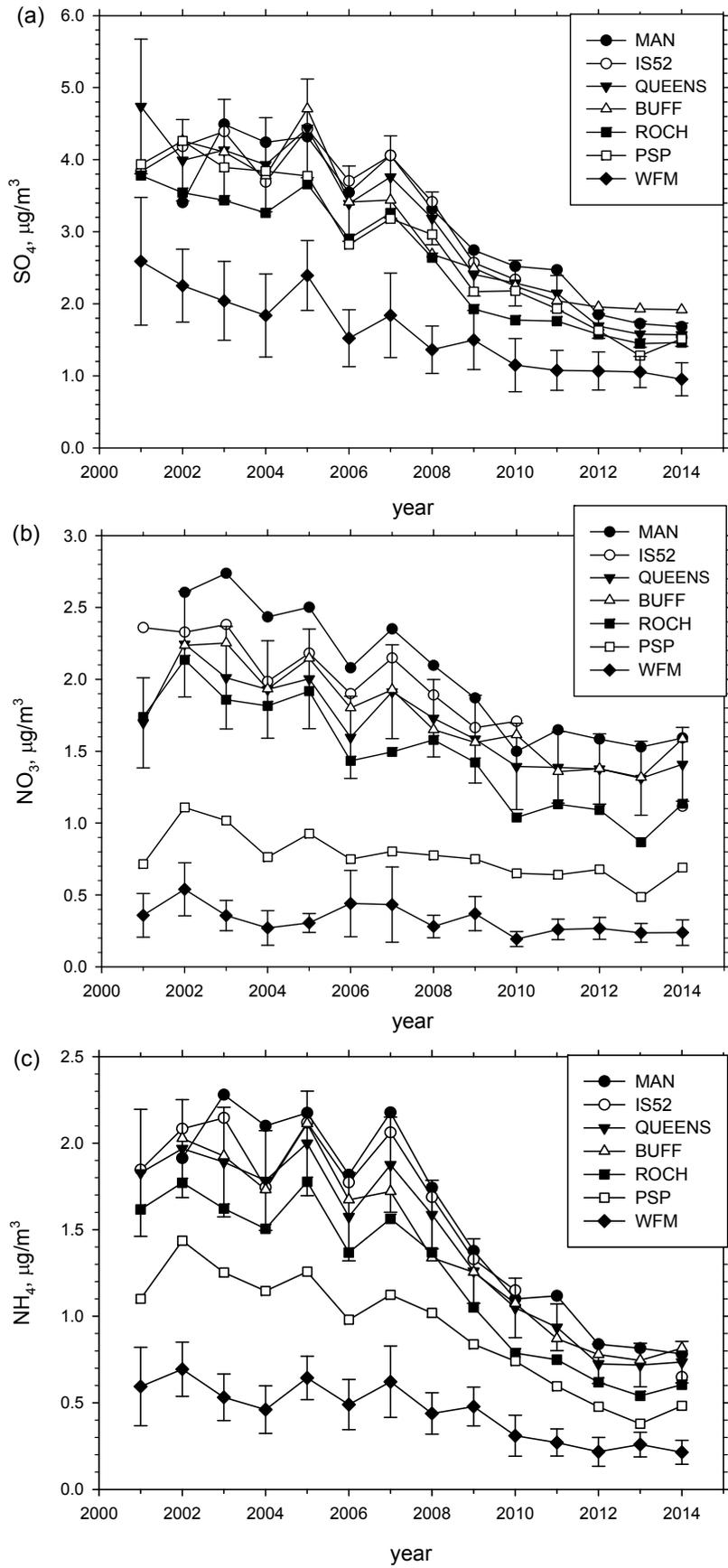


Fig. 4. Annual mean concentrations of (a) SO_4 , (b) NO_3 and (c) NH_4 at sites in New York. Error bars represent the 95% confidence intervals on QUEENS and WFM data.

air mass transport during summer is frequently from the southwest or west and through high SO₂ emitting areas (Dutkiewicz *et al.*, 2004). Photochemical conversion along the route results in high SO₄ in downwind states including New York. Mean seasonal SO₄ for combined years 2002–2003 show highest concentrations (significant at all sites except WFM) during summer by a factor of 2–2.5 compared to other seasons, Fig. S3(a). Minimum concentrations are typically observed in winter and autumn. Due to the large reductions in the precursor SO₂ (65–70%) a substantial decrease in summer SO₄ (produced within or transported to New York) is observed by 2012–2013. For example, summer SO₄ is reduced by approximately a factor of 3–3.5 at the NYC, BUFF and PSP sites with ROCH and WFM summer SO₄ a factor of 2.5 lower compared to 2002–2003, Fig. S3(b). At all sites the summer/winter SO₄ amplitude is damped in 2012–2013 compared to 2002–2003. At NYC sites winter and summer SO₄ are similar in 2012–2013 whereas other sites still show higher summer SO₄ by factor of 30–60% compared to winter. However, at all sites seasonal SO₄ differences in 2012–2013 are not significant within the 95% confidence intervals. Using back trajectories Dutkiewicz *et al.* (2004) estimated that during Oct–Mar approximately 39–44% of SO₄ is transported versus 48–65% during Apr–Oct at QUEENS. At the rural locations of WFM and PSP approximately 49% and 60% of the SO₄ is transported during Oct–Mar versus 72 and 62% during Apr–Oct, respectively. Therefore, in NYC there is a higher local contribution of SO₄ during winter months compared to summer which tends to offset the summer SO₄ increase. Dutkiewicz *et al.* (2004) defined “local” as equivalent to 6 h of air mass transport or within 160 km of QUEENS. Within NYC urban area we attribute a proportion of the winter SO₄ to residential oil combustion used for space and water heating as reflected in the higher winter elemental nickel (Ni) concentrations shown in Fig. S10. On the other hand particle NO₃ arises via nitrogen oxides with large emissions from roadway vehicles particularly high traffic density metropolitan areas. Particle NO₃ in the northeastern US shows elevated concentrations from Nov to May (Wittig *et al.*, 2004; Rattigan *et al.*, 2006) because the partitioning between NO₃ and its precursors, HNO₃ and NH₃, favors particle NO₃ during colder temperatures (Seinfeld and Pandis, 1998). Fig. S4 shows NO₃ seasonal pattern with highest concentrations during winter and lowest in summer. Winter concentrations are significantly higher compared to summer (but not different compared to other seasons). Highest NO₃ is observed at the urban locations with mean winter values of 3.1–4.2 μg m⁻³, during 2002–2003, Fig S4(a). Although MAN shows highest concentrations among the urban sites the intraurban differences for a given season are not significant. Winter NO₃ is a factor of 2 to 5 lower (significant) at the rural locations of PSP and WFM. These urban-rural NO₃ differences also contribute to the spatial differences observed in PM_{2.5} mass in Fig. 3. By 2012–2013 NO₃ has decreased by approximately 37–50% across all sites. Concentration changes ranged from 0.5–1.7 μg m⁻³ at urban and 0.1–0.9 μg m⁻³ at rural sites, Fig. S4(b). NO₃ is likely dominated by local production but even if some NO₃ is transported

from other locations, the amount of particle NO₃ will still be determined by the partitioning which depends on ambient temperature and relative humidity. When emissions of NO_x were lowered this led to a uniform drop in the amount of NO₃ throughout the year. Since it is ambient temperature which drives the seasonal NO₃ pattern, the same seasonal pattern is retained following the NO_x reductions. Seasonal patterns for NH₄ in 2002–2003 show highest concentration during summer, Fig. S5(a), although not significant. Urban areas show lowest values are in autumn with a summer/autumn amplitude from 30% to a factor of 2. At the rural location of PSP, autumn and winter have similar minimum values of around 1 μg m⁻³ whereas at WFM autumn, spring and winter are all around 0.60 μg m⁻³ with a slight summer max of 0.80 μg m⁻³. The higher summer values reflects more the seasonal pattern of SO₄ rather than NO₃ since NH₄ preferentially associates with SO₄ first, then providing there is sufficient NH₃ available it also associates with NO₃ (Seinfeld and Pandis, 1998). By 2012–2013 the seasonal pattern has switched from a summer high to a winter max, Fig. S5(b), at all sites except for WFM where all seasons are similar. The winter/summer amplitude in 2012–2013 is approximately a factor of two at NYC sites and 40–60% at BUFF, ROCH and PSP. Thus, as a consequence of the substantial reductions in SO₂ and particle SO₄ the seasonal pattern of NH₄ reflects that of NO₃ in 2012–2013 rather than SO₄.

(ii) Carbonaceous Material

Trends in PM_{2.5} carbon, Fig. 5, are less evident and the interpretation of the data is hampered due to the change in sampling and analysis methods in 2007. This impacted the organic carbon fraction the most as the fraction is sensitive to both ambient conditions and measurement methods including sampling schedule, filter face velocity and shipment and transport conditions (Dillner *et al.*, 2009; Rattigan *et al.*, 2011). The impact on EC is less pronounced. In order to provide a consistent trend the more recent URG-3000N carbon OC and EC data were scaled to match those of the older CSN method using collocated measurements at the IS52 and PSP sites (Rattigan *et al.*, 2011). Additional data became available since then including collocated data from QUEENS which were included in the analysis. The scaling factor for OC was approximately a 1.5 multiplier to the URG-3000N OC (by TOR analysis) to match the older CSN OC and a small downward scaling factor of 5–8% for the EC fraction. In addition collocated measurements from other carbon samplers were also analyzed for trends.

The annual mean EC concentrations in Fig. 5(a) show a large site to site variability with close to an order of magnitude range in concentrations between the highest urban areas of the Bronx and Manhattan to the lowest at the rural WFM location. Annual mean concentrations are similar for IS52 and MAN varying from 1.1 to 1.4 μg m⁻³ with uniform concentrations up to 2007–2008 and concentrations declining thereafter. This is more evident in the continuous MAN data record where 2014 is significantly lower by 30% compared to the 2007–2008 data. IMPROVE measurements at IS52, which sampled on the same day as the CSN, indicate

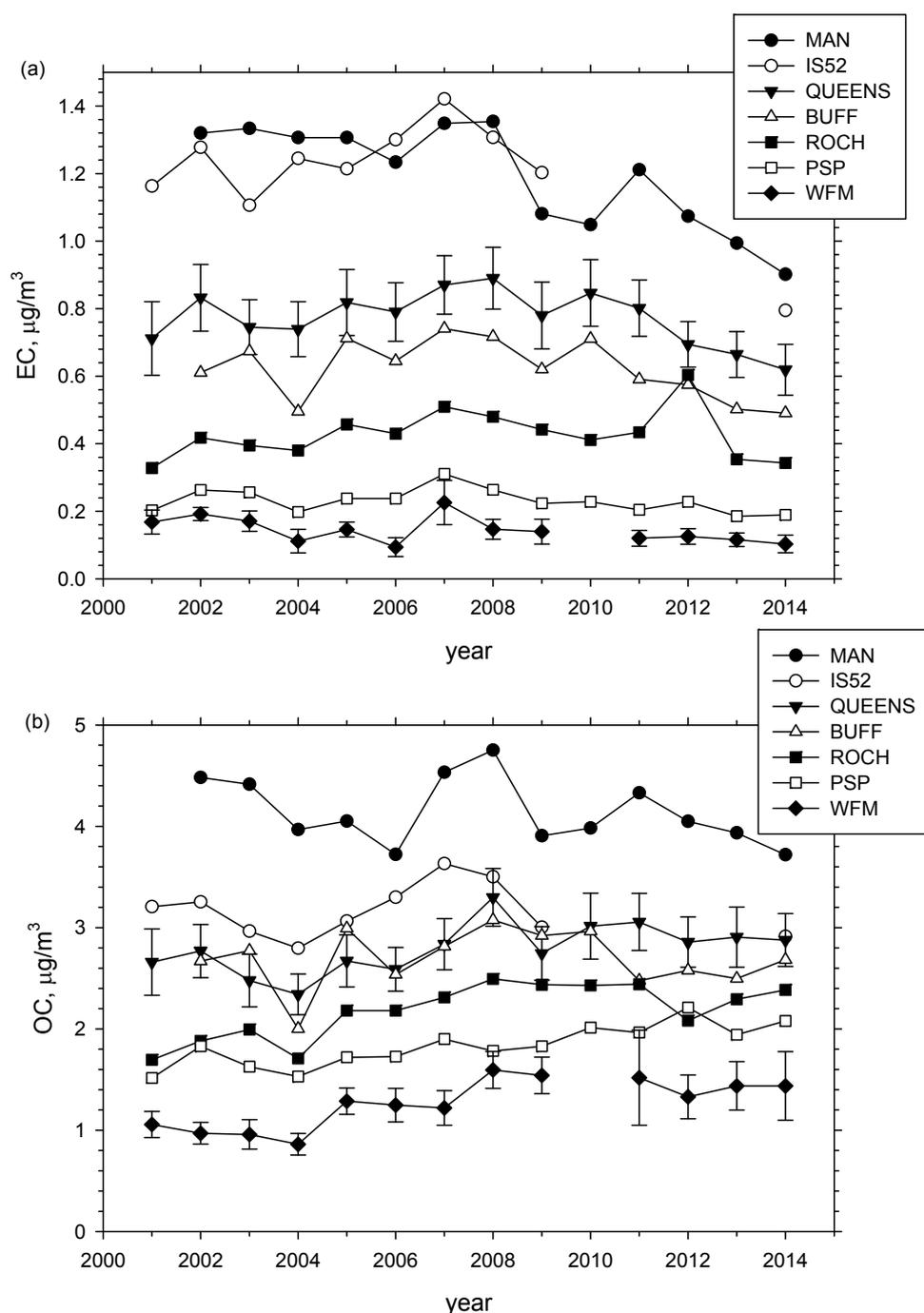


Fig. 5. Annual mean concentrations of (a) EC and (b) OC at sites in New York. Gaps in the data are due to instrumental problems (WFM) or no site sampling (IS52). OC was adjusted for the adsorption artifact based on respective site field blank data. Error bars show 95% confidence intervals on QUEENS and WFM data.

relatively uniform concentrations between 2005 and 2007 with a 15% drop between 2007 and 2009, Fig. S6(a). Note 2010 IS52 data is not an entire calendar year. Annual mean EC at QUEENS and BUFF are 30–40% lower than at MAN and IS52 but show similar patterns (except 2004 BUFF data are unusually low) with little evidence of a trend up to 2007–2008. Concentrations subsequently decrease with 2014 EC data 30–35% lower compared to 2007–2008 (consistent with the change observed at MAN). These

downward changes are attributed to the implementation of cleaner fuels (lower S content of heavy duty vehicle diesel fuel) and the use of alternative and cleaner residential heating fuels (number 2 versus number 6) in New York City (Environmental Defense Fund, Dec 2009). A target date of July 1, 2015 was set for complete phase out of Number 6 residual oil in NYC. The downturn in the economy leading to reductions in industrial production and fewer vehicle miles travelled (USEPA, 2012) may also be a contributing

factor to lower levels after 2007. EC at ROCH appears to increase slightly by $0.2 \mu\text{g m}^{-3}$ between 2001 and 2007 followed by a moderate decline up to 2010 (approximate 20% decrease). However, 2011 and 2012 show higher concentrations, 2012 being elevated by approximately $0.2 \mu\text{g m}^{-3}$ compared to 2010. An atypical coloration was noted in the 2011–2012 ROCH carbon filters which is believed to have caused an interference in the determination of EC and OC fractions (but did not impact total carbon) at this location. Apart from these 2 years the ROCH trend is similar to that at other urban sites. At PSP EC varied between 0.20 and $0.26 \mu\text{g m}^{-3}$ with little indication of a trend at least up to 2006. EC in 2007 appears somewhat elevated attributed to 2 days when concentrations (2.1 and $1.5 \mu\text{g m}^{-3}$, respectively) were more than a factor of 5 above the annual mean. Subsequently, EC appears to decline with concentrations 30% lower in 2012–2013. A change in the sampler occurred in 2009 (URG-3000N replaced the MetOne). In addition the analysis methods also changed to the IMPROVE_A method (Chow *et al.*, 2007). The trend in the IMPROVE EC data at PSP is somewhat different compared to the CSN with IMPROVE showing uniform concentrations of 0.33 – $0.40 \mu\text{g m}^{-3}$ between 2001 and 2007, Fig. S6(b). Subsequently, IMPROVE EC shows a drop of approximately 30% between 2007 and 2010 consistent with EC patterns observed at the above urban sites. At WFM although there is an indication of an initial downward trend up to 2006, EC in 2007 like at PSP appears elevated. The high 2007 data at WFM was attributed to 5 days when EC was unusually high, 0.65 – $0.9 \mu\text{g m}^{-3}$, compared to the annual mean of around $0.2 \mu\text{g m}^{-3}$. Furthermore, there were 2 additional days with concentrations of approximately $0.5 \mu\text{g m}^{-3}$. After 2007 EC at WFM also decreases similar to other locations, but like PSP a change in the sampling and analysis methods occurred in 2009. In addition, since EC at WFM (and PSP) is at or near the detection limit the interpretation of EC trends at these rural locations should be viewed with caution.

OC annual mean data in Fig. 5(b) also show an urban-rural contrast with concentrations at MAN a factor of 3–4 higher than the remote WFM location. OC concentrations in descending order are highest at MAN with IS52 approximately $1 \mu\text{g m}^{-3}$ lower, then QUEENS and BUFF $0.5 \mu\text{g m}^{-3}$ lower with ROCH approximately $0.5 \mu\text{g m}^{-3}$ lower still. OC at PSP is lower than ROCH and WFM is the lowest of all the sites. There is no consistent trend in the annual OC long term record. OC at MAN shows an initial decrease up to 2006 (18% drop) but 2007 and 2008 appear somewhat elevated and subsequent OC varying between 3.9 to $4.3 \mu\text{g m}^{-3}$ from 2009 to 2014. The change in sampling methods which occurred part way through 2007 and missing samples during June to August in 2009 and March to June 2010 may have impacted the annual mean values for those years. Nevertheless, QUEENS OC and a shorter record at the IS52 site are also similarly uniform and there is an indication that 2007 OC is also elevated at IS52. BUFF OC is very similar to QUEENS except that 2004 BUFF OC is unusually low (30% lower than 2003 and 2005) and concentrations drop by 18% after 2010. Annual

OC at ROCH, PSP and WFM shows a slight upward trend at least until 2008 at ROCH and WFM with the trend at PSP being upward throughout.

Seasonal patterns for EC and OC are shown in Figs. S7 and S8, respectively. Mean seasonal EC for combined years 2002–2003 are shown in Fig. S7(a). At urban sites the seasonal EC differences are approximately 10–15% and not significant. At the rural sites EC seasonal differences are approximately 30% but only spring is significantly higher compared to autumn. Small seasonal differences are also observed for 2012–2013, Fig. S7(b), which are mainly not significant in NYC, except for QUEENS spring EC being lower than winter. At BUFF and ROCH, summer EC tends to be higher than winter but it is barely significant. EC in 2012–2013 at the rural sites is higher in summer and autumn but not significant. At the large urban centers EC is dominated by local primary emissions which appear reasonably consistent throughout the year or show a slight winter maximum. At rural locations there are few if any major sources of EC and the sites are impacted more by transported pollutants (and occasional vegetative burning episodes) thus leading to different seasonal patterns and significantly lower EC. The seasonal pattern for OC for both time periods shows a consistent summer maximum at all locations (as observed previously, Schwab *et al.*, 2004) most noticeable at ROCH, BUFF and the rural locations of PSP and WFM where it is significantly higher compared to other seasons, Fig. S8. Among the NYC sites QUEENS summer OC is significantly higher than spring and autumn but not winter and at MAN only 2012–2013 summer is significantly higher than other seasons. The summer OC maximum is attributed to enhanced secondary organic aerosol production and is most noticeable at less polluted sites which are impacted less by local primary emissions. Enhanced emissions in winter from space heating sources lead to increased production of primary OC (and EC) thus leading to a lower seasonal contrast in OC at the larger urban NYC locations.

(iii) Selected Elements

Se shows some similarities with SO_4 in that concentrations are relatively similar at all sites across the state ranging from 1 – 1.6 ng m^{-3} except WFM which is a factor of 2–3 lower, Fig. 6. A downward trend is also observed but the pattern is somewhat different to SO_4 . The largest change occurs around 2006, where a factor of 3 decrease is observed across the state (WFM showing a somewhat smaller decrease, factor of 2) between 2006 and 2008. Since Se is associated with coal combustion sources outside the region (Dutkiewicz *et al.*, 2006) this change is attributed to the emission reductions on EGU's and large combustion sources through the CAAA and NO_x SIP call. After 2008 concentrations are relatively flat and are uniform across all sites with a range of 0.2 – 0.5 ng m^{-3} , WFM being on the lower edge. The fact that Se concentrations at PSP are similar to urban areas also indicates that the major source emissions are from outside the state. Since Se is produced from direct emissions it is not influenced by photochemistry and therefore has a different seasonal pattern to secondary species like

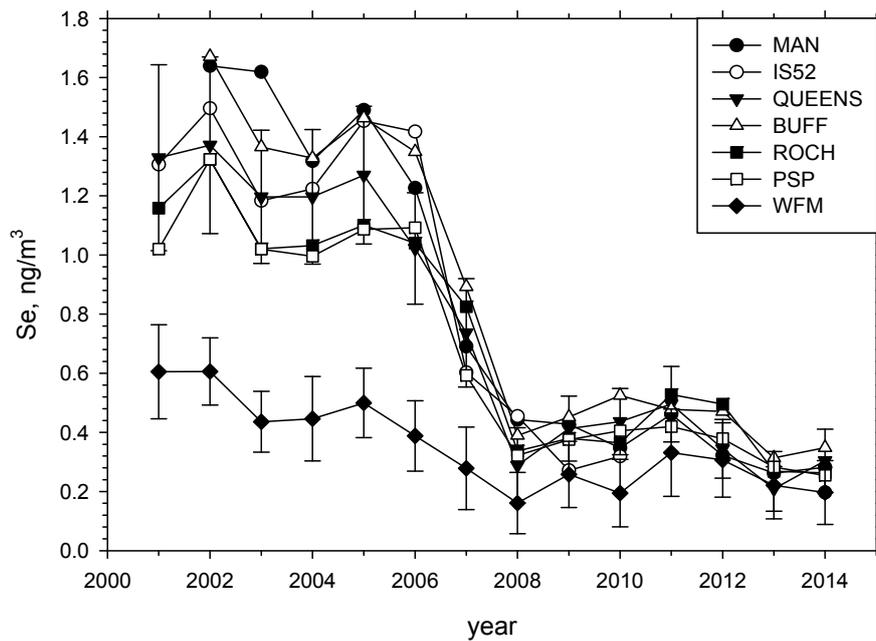


Fig. 6. Annual mean PM_{2.5} Se concentrations at sites in New York. Error bars show 95% confidence intervals on QUEENS and WFM data.

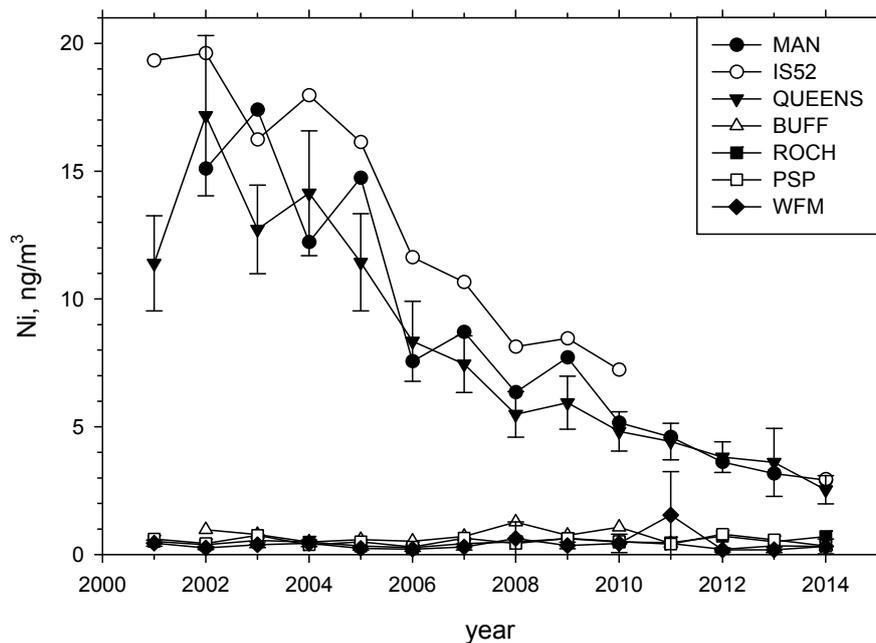


Fig. 7. Annual mean PM_{2.5} Ni concentrations at sites in New York. Error bars show the 95% confidence intervals on QUEENS and WFM data.

SO₄. There is however an indication of a winter source, likely from space heating sources such as oil, (Graham, 2010) in the 2002–2003 data as shown in the slightly higher (although not significant) winter concentrations at all sites except MAN in Fig. S9. By 2012–2013 concentrations are frequently near the detection limit and seasonal differences may not be meaningful.

Ni is characterized by showing elevated concentrations only in the NYC area with values below or at detection limits

elsewhere, Fig. 7. In 2001–2003 annual mean Ni ranged from around 15–20 ng m⁻³ in NYC but a steady decline is observed since with concentrations reaching 3 ng m⁻³ by 2013 (factor of 5–6 decrease). A strong seasonal gradient is observed, Fig. S10, with higher concentrations (more than a factor of 2 between winter and summer) during colder months consistent with the major sources being residential heating oil combustion used for space and water heating (Lippmann, 2009). In addition the ratio of Ni to Co of around 12–14

(Rattigan *et al.*, 2013) is typical of fuel oils used in the Northeastern states (Graham, 2010). The very low Ni concentrations observed at sites outside NYC is due to the predominant use of natural gas and wood rather than oil for domestic heating in these areas. A switch to alternative type heating fuel oils (NYC required the phase out of number 6 heating oil by July 1, 2015) or natural gas which have lower Ni emissions is largely responsible for the extensive Ni reductions observed in NYC.

Other Locations

In addition to the reductions in PM_{2.5} mass and components reported here reductions in gas phase species, SO₂, NO₂ and CO have also occurred (Civerolo *et al.*, Manuscript in Preparation). Reductions in air pollutants reported here are generally consistent with that observed throughout the US (USEPA, 2012). For example the US annual mean PM_{2.5} mass has shown a 24% decrease over the period 2001–2010 whereas the 98th percentile 24h PM_{2.5} mass has decreased by 28%. More recent data show a 34% decrease in the annual and daily mean PM_{2.5} mass from 2000 to 2013. Corresponding decreases in the annual PM_{2.5} mass reported above were 30–40% at urban New York sites and 25–30% at rural locations whereas, the 98th percentile PM_{2.5} mass decreased by 40–50%. The national emission inventories trends (USEPA, 2014) reported decreases of 68% and 42% over the period 2000–2013, for SO₂ and NO_x, respectively. An analysis of PM_{2.5} mass data from various New York sites over the period 1999 to 2007 by Buckley and Mitchell (2011) also showed downward trends. Long term measurements of particle SO₄ across the US (Hand *et al.*, 2012) also show decreasing trends. Average PM_{2.5} mass decreased by 13 to 54% at various sites in southern California over the period 1994–2011 (Lurmann *et al.*, 2015). However, further improvements in air quality are required as the Los Angeles area still lies outside the NAAQS for PM_{2.5}. Decreasing trends in PM_{2.5} and various components have been observed across European locations (Cusack *et al.*, 2012). These trends were attributed to pollution abatement strategies, downturn in the economy (which had a greater impact in Europe compared to the US) and unusual meteorological conditions. Ambient measurements in the southeastern US (Blanchard *et al.*, 2013) show reductions in PM_{2.5} of around 4.5 μg m⁻³ and SO₄ of 2.3 μg m⁻³ from 1999 to 2010 which is similar to that reported here. Controls on EGU and vehicle emissions is largely responsible for these decreases. However, Blanchard *et al.* (2013) also report large reductions in carbonaceous species, OM (2.2 μg m⁻³) which is not observed in New York. An analysis of trends in PM_{2.5} OC and EC across the US (Hand *et al.*, 2013) found the largest downward trends in the western US with generally small or insignificant changes at eastern US locations. Thus, it seems that trends in PM_{2.5} carbonaceous particles are more variable and less homogeneous compared to the inorganic species which show a consistent downward trend throughout the US. The impact of the reductions on the percentage contribution to PM_{2.5} mass can be seen in Fig. 8 which shows annual mean data from QUEENS. Here a multiplier of 1.6 for converting OC to organic mass was used (Bae *et al.*,

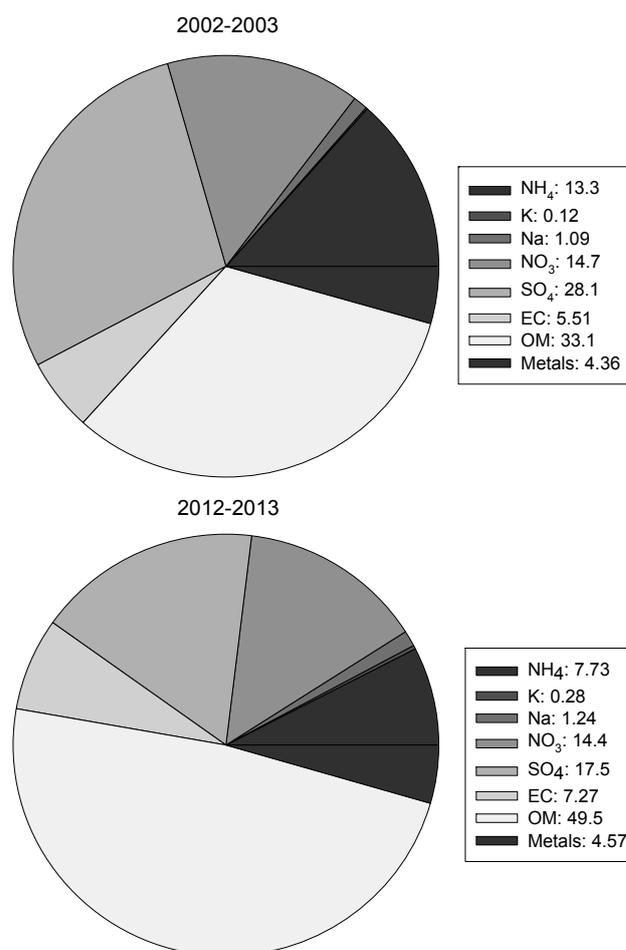


Fig. 8. Species percentage composition of PM_{2.5} in 2002–2003 versus 2012–2013 at QUEENS.

2006). Metals was calculated as the sum of soil components (coarse metal oxides) and remaining trace elements. Percentages are relative to total PM_{2.5} mass on the CSN speciation sample filter. Sum of species is within ± 5–10% of total mass. Uncertainties in total PM_{2.5} mass and species measurements and the OC multiplier can account for the differences. In 2002–2003 the combined contribution from particle SO₄, NO₃ and NH₄ was approximately 60%, whereas the organic mass contribution was 30%. By 2012–2013 a substantial change in the proportions are observed, with the major ion species amounting to 40% compared to approximately 45–50% for organic mass. These percentages vary somewhat from year to year, but the impact is essentially the same. Thus, in recent years the carbonaceous (OM and EC) fraction is the dominant component amounting to approximately 50–60% of the total PM_{2.5} mass. Therefore, targeting carbonaceous species emissions may be required in order to achieve additional air quality improvements, particularly since trends in inorganic species mass concentrations have levelled off in recent years.

CONCLUSIONS

Analysis of an approximate 15 yr period of PM_{2.5} mass

and major chemical component measurement data in New York has shown a downward trend for PM_{2.5} mass and most major species (except organic carbon) since 2000. For example the reductions amount to a 30–40% decrease in annual mean PM_{2.5} mass since 2000. Large reductions are also observed for the major ion particle species; SO₄, NO₃ and NH₄ and selected metals, Se and Ni. These trends are mainly attributed to emissions reductions under the CAAA, NO_x SIP call and CAIR which targeted Electric Generating Utilities and large combustion facilities. The introduction of improved vehicle technology and cleaner fuels (transport and residential heating) also lowered NO₃ and Ni levels. A decrease in EC after 2007 of approximately 30% is also attributed to lower vehicle emissions. These changes have led to large improvements in ambient air quality particularly, in the New York City region, which in 2000 was out of compliance of the NAAQS annual PM_{2.5} 15 µg m⁻³ standard, to the present day conditions where it is within the newer 12 µg m⁻³ standard. However, the downward trend is less evident for carbonaceous particle species, particularly the OC fraction which is currently the dominant component of PM_{2.5} mass. Therefore, future improvements in air quality may benefit from targeting this species.

ACKNOWLEDGMENT

This work was supported by the NYSDEC and the New York State Energy Research & Development Authority (NYSERDA), and was only made possible because of the efforts of many NYSDEC site operators over the years.

DISCLAIMER

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

SUPPLEMENTARY MATERIALS

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

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Received for review, May 14, 2015

Revised, September 30, 2015

Accepted, October 12, 2015