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Spatial and Temporal Variations of $PM_{2.5}$ in North Carolina

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ABSTRACT

Studies have indicated that the adverse effects on human health and the decrease in visibility caused by fine particulate matter ($PM_{2.5}$) exhibit spatial heterogeneity. Moreover, the environmental effects produced by different chemical compositions of $PM_{2.5}$ vary on a regional scale. Therefore, understanding the spatiotemporal variations and chemical compositions of $PM_{2.5}$ is necessary for assessing the regional impacts. Secondary inorganic $PM_{2.5}$ ($iPM_{2.5}$) is formed through chemical reactions between the base gas NH_3 and acidic gas pollutants (e.g., NO_2 or SO_2). The major components of $iPM_{2.5}$ include NH_4^+, SO_4^{2-}, and NO_3^-. To fully comprehend the regional impacts of $PM_{2.5}$, this research quantifies the spatiotemporal variations of $iPM_{2.5}$ with the aim of evaluating the contributions from $iPM_{2.5}$ to $PM_{2.5}$ in North Carolina (NC). The concentrations (at 34 sites) and chemical components (at 7 sites) of $PM_{2.5}$ from 2005 to 2014 were extracted from the EPA's AirData, with the highest concentrations measured in the urban areas of central NC. Notably, $PM_{2.5}$ concentrations have been significantly reduced over the past 10 years, with a concurrent decreasing trend in $iPM_{2.5}$. Seasonal variation analysis indicates that $PM_{2.5}$ concentrations were higher in summer and lower in winter; however, significant variation occurred only between 2005 and 2011. Although $iPM_{2.5}$ formed the largest mass fraction of $PM_{2.5}$ for 2005–2011, organic carbon matter (OCM) contributed the dominant share for 2012–2014. Significant seasonal variations in the $iPM_{2.5}$ mass fractions were also observed, with NO_3^- and SO_4^{2-} exhibiting inverse variations. This study links the ambient $PM_{2.5}$ to various sources by revealing the spatiotemporal variations of $PM_{2.5}$ and their associated chemical compositions in NC, thereby enabling the development of effective control and mitigation strategies.

Keywords: Chemical compositions; Inorganic $PM_{2.5}$; Spatiotemporal variations.

INTRODUCTION

By definition, $PM_{2.5}$ represents particulate matter (PM) with aerodynamic equivalent diameter ≤ 2.5 μm. As a criteria air pollutant in the United States (U.S.), it has gained intensive attention due to its adverse health effects, special role in visibility degradation, and the potential impact on climate (Boucher, 2000; Dominici *et al.*, 2006; Haywood and Pope *et al.*, 2009; Pui *et al.*, 2014). Franklin *et al.* (2007) studied the relationship between $PM_{2.5}$ and mortality across the U.S. with a conclusion that elevated $PM_{2.5}$ mass concentration can lead to the increase in mortality; the responses to $PM_{2.5}$ exposures may differ for people of different ages and genders in different areas of the U.S. Dominici *et al.* (2006) estimated the health risk of $PM_{2.5}$ exposures and discovered that cardiovascular risks were increased by $PM_{2.5}$ short-term exposures with higher risk in the eastern U.S. Moreover, research has indicated that standalone $PM_{2.5}$ mass concentration is inadequate to vigorously explain the health effects of $PM_{2.5}$; detailed information of $PM_{2.5}$ chemical compositions is needed to establish a relationship between human health and $PM_{2.5}$ exposures (Franklin *et al.*, 2008). In addition to spatially varied adverse effects on human health, a visibility research conducted by Malm *et al.* (1994) indicated that sulfate (SO_4^{2-}) and organic materials were more effective in reducing the visibility across the U.S. than the other components of $PM_{2.5}$. In the eastern U.S., SO_4^{2-} is the dominant component to contribute to light extinction. Similar investigations performed by Brewer and Adlhoch (2005) and Brewer and Moore (2009) suggested that ammonium sulfate ($(NH_4)_2SO_4$) and organic carbon matter (OCM) were the dominant contributors to light extinction in the southeastern U.S.; however, wildfires and windblown dust dominated in light extinction in the western U.S.

In ambient air, large spatiotemporal variations exist in mass concentration and chemical compositions of $PM_{2.5}$, caused by spatiotemporal variations of emission sources, formation and deposition processes, meteorological conditions, and atmospheric fate and transport (Martuzevicius *et al.*, 2004; Seinfeld and Pandis, 2006; Bell *et al.*, 2007; Wang-Li, 2015). The regional impacts of $PM_{2.5}$ may vary

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due to such spatiotemporal variations. Hu *et al.* (2014) used satellite-retrieved aerosol optical depth (AOD) data to estimate the spatiotemporal variations of $PM_{2.5}$ mass concentrations in the southeastern U.S. in 2001–2010; the results indicated that urban areas and major highways can display higher $PM_{2.5}$ concentrations than rural or mountain areas. In addition, around 20% reduction in $PM_{2.5}$ concentrations has been achieved over the past 10 years in the southeastern U.S. Previous research on the spatiotemporal variations of $PM_{2.5}$ mass and chemical compositions in the U.S. has indicated that $PM_{2.5}$ mass concentrations had higher values in the eastern U.S. and California and lower values in the central and northwestern regions of the nation. Moreover, $PM_{2.5}$ chemical components such as SO_4^{2-} and nitrate (NO_3^-) exhibited inverse seasonal variation patterns in eastern and western coast areas of U.S. (Bell *et al.*, 2007). In addition, Hasheminassab *et al.* (2014) identified the main contributors to the $PM_{2.5}$ to be secondary inorganic $PM_{2.5}$ ($iPM_{2.5}$) in California. Another study performed in Cincinnati metropolitan area found that major components of $PM_{2.5}$ can be identified as organic carbon (OC) followed by SO_4^{2-}, elemental carbon (EC), crustal elements and trace metals (Martuzevicius *et al.*, 2004). Similar research conducted by Saunders *et al.* (2015) in the northeastern U.S. identified two main $PM_{2.5}$ pollutants: OC and $(NH_4)_2SO_4$. Goetz *et al.* (2008) analyzed the major compositions of $PM_{2.5}$ in eastern NC from 2001 to 2004 at sites representing urban and rural sites; the results indicated that OC, SO_4^{2-}, ammonium (NH_4^+), NO_3^- and EC were the major contributors to $PM_{2.5}$ mass; SO_4^{2-} and NH_4^+ tended to be slightly higher in the rural site. Previous research has discovered that different areas exhibited different $PM_{2.5}$ chemical characteristics such that the regional impact of $PM_{2.5}$ may differ correspondingly.

The chemical compositions of $PM_{2.5}$ include ions (e.g., NH_4^+, SO_4^{2-}, and NO_3^-), OC, EC, elements (e.g., crustal materials) and other unknown components (Malm *et al.*, 1994; Frank, 2006). The $iPM_{2.5}$ is defined as the ion components, including NH_4^+, SO_4^{2-}, and NO_3^-, in this paper. Different compositions of $PM_{2.5}$ can be linked to different emission sources and formation processes (Abdeen *et al.*, 2014). As a subset of total $PM_{2.5}$, $iPM_{2.5}$ is formed through the partitioning of gas-phase NH_3 and particle-phase NH_4^+. The formation of secondary $iPM_{2.5}$ can be characterized by the reactions between precursor gases such as ammonia (NH_3), nitric acid (HNO_3) and sulfuric acid (H_2SO_4). While H_2SO_4 and HNO_3 are mainly transformed from the primary pollutants, SO_2 and NO_x (NO_x = NO + NO_2), through photochemical reactions, NH_3 is directly emitted from emission sources such as agricultural operations (Seinfeld and Pandis, 2006). Because secondary $iPM_{2.5}$ constitutes a significant part of total $PM_{2.5}$ (Sawant *et al.*, 2004; Katzman *et al.*, 2010; Philip *et al.*, 2014), it is important to establish a holistic understanding of the spatiotemporal variations of secondary $iPM_{2.5}$ such that the regional impact of $PM_{2.5}$ may be fully understood.

Aneja *et al.* (2003) investigated the relationship between NH_3 emissions from agricultural sources and ambient NH_4^+ concentrations in the southeastern U.S. with spatiotemporally varied NH_3 emissions and NH_4^+ concentrations data. This research indicated that higher NH_3 emissions led to higher NH_4^+ at the given location. Other research discovered that in the rural areas of North Carolina (NC), ambient NH_3 concentration was high, sometime reaching up to 45.87 ppb (34.80 μg m^{-3}); ambient air was dominated by NH_3-rich conditions in those rural areas due to high NH_3 emissions from agricultural operations (Robarge *et al.*, 2002; Walker *et al.*, 2000b). Walker *et al.* (2004) compared the secondary $iPM_{2.5}$ concentrations at three sites located in NC Coastal Plain region with different NH_3 emission densities, and reported that NH_3 emitted from agricultural sources posed large influences on $iPM_{2.5}$ concentrations; higher total NH_3 emissions led to higher $iPM_{2.5}$ concentrations in rural areas. Furthermore, Walker *et al.* (2006) performed another study and reported a two-year average concentration of secondary $iPM_{2.5}$ from 1999 to 2000 to be 8.0 ± 5.84 μg m^{-3} at an agricultural site in the southeastern area of NC; among the measured various $iPM_{2.5}$ chemical components, SO_4^{2-}, NO_3^-, and NH_4^+ were the most dominant components.

As a complex mixture, various chemical components of $PM_{2.5}$ contribute to total $PM_{2.5}$ mass differently. The reduction of any specific chemical component may have different effects on the reduction of $PM_{2.5}$ mass. The in-depth understanding of spatial and temporal variations of $PM_{2.5}$ characteristics is the foundation to study regional impact of $PM_{2.5}$ and to develop effective control strategies of $PM_{2.5}$; more research is necessary to quantitatively characterize $PM_{2.5}$ mass and chemical compositions in spatial and temporal scales. This research was to quantitatively assess the variations of $PM_{2.5}$ and its associated chemical compositions in spatial and temporal scales in NC to advance our understanding of spatial and temporal variations of $PM_{2.5}$ in the region.

METHODS

$PM_{2.5}$ Monitoring Stations in North Carolina

Investigation of $PM_{2.5}$ spatial and temporal variations started with identification of the EPA's $PM_{2.5}$ monitoring stations in NC and obtaining $PM_{2.5}$ data for each given station. Under the State and Local Air Monitoring Stations (SLAMS) for criteria pollutants (EPA, 2016a), $PM_{2.5}$ mass concentrations were routinely monitored at 34 stations in NC from 2005 to 2014. In addition, under the EPA's Chemical Speciation Network (CSN) (EPA, 2016b), $PM_{2.5}$ chemical speciation samples were taken and analyzed at 7 stations, where $PM_{2.5}$ mass measurements were concurrently taken. Fig. 1 shows the spatial distribution of these monitoring stations in the state. While the $PM_{2.5}$ mass concentration monitoring stations were evenly distributed across the whole state, most of the $PM_{2.5}$ chemical speciation monitoring stations were located in central areas of the state. Based on the topography of NC, the whole state can be divided into three geographic areas: mountains in the west, the Piedmont in the center, and the Coastal Plain in the east (NC SOS, 2018).

Under the SLAMS, $PM_{2.5}$ concentration measurements were taken once every day using either Federal Reference

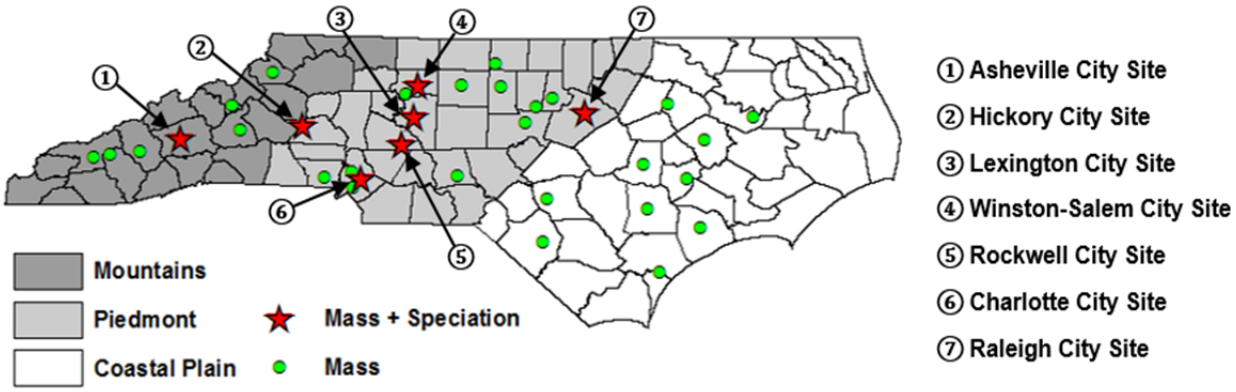

Fig. 1. $PM_{2.5}$ mass and chemical component measurement stations across North Carolina.

Method (FRM) or Federal Equivalent Method (FEM). Under the CSN, $PM_{2.5}$ chemical speciation samples were taken once every six days using the chemical speciation samplers that had three filter types with Teflon for mass concentration and elemental analyses, nylon for ion analyses, and quartz for OC and EC analyses.

Data Acquisition

To investigate the temporal and spatial variations, the 10 years (2005–2014) of $PM_{2.5}$ concentrations and chemical speciation data for all the monitoring sites in Fig. 1 were extracted from EPA's AirData (EPA, 2016c). For analysis of seasonal variations, dataset was grouped into four seasons with spring in March, April and May; summer in June, July and August; fall in September, October and November; and winter in December, January, and February.

Data Adjustment

Organic carbon measurements reported in EPA's AirData database should be adjusted to derive total mass of organic compounds. According to Turpin and Lim, (2001), Weber *et al.* (2003), Frank (2006), El-Zanan *et al.* (2009), and Dillner *et al.* (2012), the adjusted organic carbon matter (OCM) may be calculated using Eq. (1):

$$OCM = 1.4 \times (OC_m - OC_b) \quad (1)$$

where OCM = organic carbon matter; OC_m = measured organic carbon; OC_b = field blank organic carbon. In this research, the adjusted OCM concentrations were used to check the mass closure of $PM_{2.5}$ chemical speciation.

In an effort to understand the contribution of each chemical component to the total $PM_{2.5}$ mass concentration, chemical speciation data were used to construct $PM_{2.5}$ chemical speciation distribution pie chart, also named the mass closure. In this $PM_{2.5}$ mass closure analysis, percentage of each chemical component was calculated using Eq. (2). For valid data selection, only those days having simultaneous measurements of $PM_{2.5}$ mass and chemical components were used to construct $PM_{2.5}$ mass closure. In addition, it was discovered in many cases, the sum of individual chemical component masses exceeded the measured $PM_{2.5}$ mass. This may be due to some artifacts such as adsorption of organics, inappropriate estimation of OCM, the loss of ammonium nitrate, water existing in the samples, and measurement errors (Andrews *et al.*, 2000; Frank, 2006; Watson *et al.*, 2008; Chow *et al.*, 2015). To conduct mass closure analysis, when measured $PM_{2.5}$ mass concentration was less than the sum of individual chemical compositions masses, those data were excluded.

$$P_i = (C_i/C_m) \times 100 \quad (2)$$

where P_i = percentage of the chemical component i to the total $PM_{2.5}$ mass concentration, C_i = measured or adjusted concentration of the chemical composition i, C_m = measured $PM_{2.5}$ mass concentration from Teflon filter.

In the period of 2004–2009, the $PM_{2.5}$ chemical speciation dataset included SO_4^{2-}, NO_3^-, NH_4^+, Na^+ and K^+, OC/EC, and 48 elements, whereas for the years of 2010–2014 the $PM_{2.5}$ chemical speciation dataset included SO_4^{2-}, NO_3^-, NH_4^+, Na^+ and K^+, OC/EC, and 33 elements. Since each element only accounted for very small portion of total $PM_{2.5}$ mass concentration, the individual elements were grouped into one category to construct the mass closure. In addition, since S has been taken into account in SO_4^{2-} measurements, and Na^+ and K^+ have been taken into account in Na and K elemental measurements, S element, Na^+, and K^+ were excluded to avoid double counting when analyzing the mass closure.

Statistical Analysis and Map Development

The relationship between $PM_{2.5}$ mass concentration and $PM_{2.5}$ chemical compositions were characterized by Spearman correlation coefficient (R). In addition, Tukey test and Mann-Kendall trend test were performed to characterize the general change trend of the dataset in spatial and temporal scales under 0.05 significance level. The dataset in this research may not follow normal distribution; therefore, parametric test such as Tukey test may lack power to interpret the change trend of the data. The distribution of the data was examined as well. All the statistical tests were conducted using R software. To visually illustrate spatial variations, maps reporting $PM_{2.5}$ monitoring stations and associated $PM_{2.5}$ concentrations over time were developed using ArcMap 10.4.

RESULTS AND DISCUSSION

Spatial and Temporal Variations of $PM_{2.5}$ Concentration in North Carolina

The $PM_{2.5}$ concentrations measured by the FRM samplers from 2005 to 2014 were used to detect the spatiotemporal variations. For illustration purpose, Fig. 2 shows the annual average $PM_{2.5}$ concentrations at each site for 2005, 2008, 2012 and 2014. Based on continued research and updated scientific evidence on the adverse effects of $PM_{2.5}$, the $PM_{2.5}$ National Ambient Air Quality Standards (NAAQS) have been revised two times in the past 10 years. The $PM_{2.5}$ 24-hour average concentration was strengthened from 65 μg m^{-3} to 35 μg m^{-3} in 2006; in addition, the primary $PM_{2.5}$ annual average concentration threshold was strengthened from 15 μg m^{-3} to 12 μg m^{-3} in 2012. Selection of these years was to reflect the $PM_{2.5}$ regulation changes through the time (EPA, 2018).

In general, the annual average $PM_{2.5}$ concentrations were higher in central urban NC, the Piedmont areas, while the other areas exhibited lower annual average $PM_{2.5}$ concentrations. Specifically, large cities in central NC such as Charlotte and Lexington exhibited higher annual average $PM_{2.5}$ concentrations for the past 10 years, while lower $PM_{2.5}$ concentrations always occurred in western mountain areas and eastern Coastal Plain areas. The observation of such spatial variations in annual average $PM_{2.5}$ concentrations in NC was consistent with the finding of Hu *et al.* (2014). The spatial pattern of $PM_{2.5}$ concentrations may be attributed to the spatial heterogeneity of emission sources because major emission sources of primary $PM_{2.5}$ and precursor gases of secondary $iPM_{2.5}$ such as NO_x and SO_2 were mainly located in urban areas. More specifically, airport operations, foundries, food processing plants and steel mills were located in Charlotte (see Fig. 1), while glass plants and furniture manufacturing plants were located in Lexington. Among these emission sources, airport operations, steel mills, and glass plants can emit primary $PM_{2.5}$, NO_x

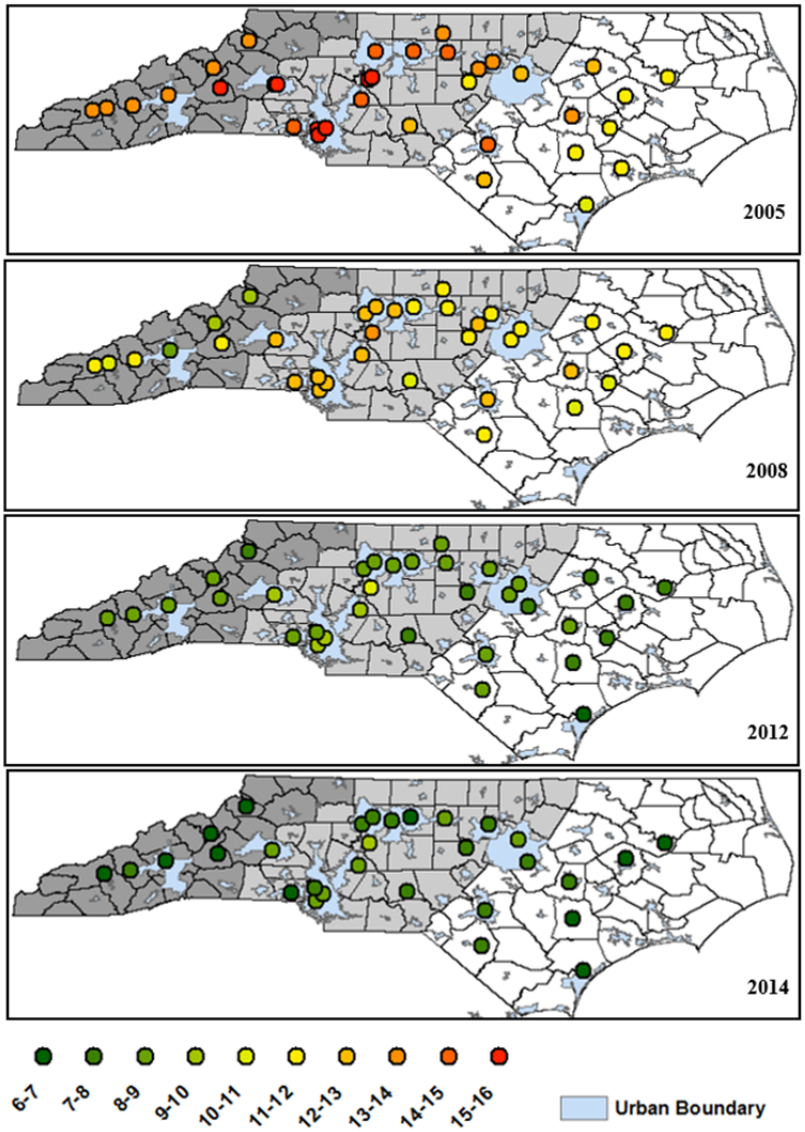

Fig. 2. Spatial and temporal variations of annual average $PM_{2.5}$ concentrations (μg m^{-3}) in NC.

and SO_2 at the same time (NEI, 2008). In addition, the topography might also affect atmospheric airflow dynamics and transport of $PM_{2.5}$. As reported by Chow *et al.* (2006), high elevation may prevent the transport of $PM_{2.5}$ toward mountain areas. The air mass blowing from coastal areas is cleaner than the inland. Various air pollutions may be picked up during the movement of air mass toward Piedmont area (central NC). If the air mass was trapped and circulated within the central NC, this may result in higher $PM_{2.5}$ mass concentrations. Whichever direction the wind may come from, the monitoring sites in the mountain areas may not be exposed to the air mass laden with higher $PM_{2.5}$ concentrations.

As for temporal variation, Mann-Kendall trend test indicates that the annual average $PM_{2.5}$ concentrations were significantly decreased from 2005 to 2014 at all the monitoring sites; annual average reduction of $PM_{2.5}$ concentrations ranged from 0.51 μg m^{-3} in the city of Raleigh to 0.86 μg m^{-3} in the city of Hickory. In 2005, there were 9 sites having annual average $PM_{2.5}$ mass concentration greater than 15 μg m^{-3}, the annual concentration threshold under the NAAQS back then; on the other hand, in 2014, all the sites had the annual concentrations below the latest NAAQS threshold of 12 μg m^{-3}. The temporal reduction of $PM_{2.5}$ mass concentration from 2005 to 2014 was reflective of the implementation of NAAQS. Under the Clean Air Act (CAA) and Clean Air Act Amendment (CAAA), each state has to develop effective reduction plans of six criteria pollutants known as the SIPs for nonattainment areas to meet NAAQS (EPA, 2016d). In 2002, NC Clean Smokestacks Act was passed to regulate the NO_x and SO_2 emissions from coal-burning power plant facilities and set the reduction plan of 77% in NO_x by 2009 and 73% in SO_2 by 2013. The utilization of control devices such as scrubbers and low-NO_x burners have guaranteed the compliance of the act (NCDAQ, 2014). The annual average $PM_{2.5}$ concentrations were significantly decreased to be below 14 μg m^{-3} in 2008 and 11 μg m^{-3} in 2009 across the whole state. The significant reduction of annual average $PM_{2.5}$ concentrations was also reflective of EPA's Clean Air Interstate Rule (CAIR), which was implemented in 2009. As requested by the rule, NC had to control both ozone and $PM_{2.5}$ pollutants, and electric generating units (EGUs) were required to control both NO_x and SO_2 emissions (EPA, 2016e). Moreover, as the replacement of CAIR, the implementation of Cross-State Air Pollution Rule (CSAPR) in 2012 further guaranteed the reduction of $PM_{2.5}$ concentrations, measures such as the lower S coal and improved pollution control equipment in power plants helped reduce the emissions of both SO_2 and NO_x (EPA, 2016f). Consequently, the annual average $PM_{2.5}$ concentrations became below 10 μg m^{-3} in 2014 across the state.

To further investigate the reduction trend of $PM_{2.5}$ concentrations in NC, higher temporal resolution datasets (monthly average $PM_{2.5}$ concentrations) were analyzed. Results at 4 representative sites are shown in Fig. 3.

The monthly average $PM_{2.5}$ concentrations at these 7 sites exhibited reduction trend from 2005 to 2014 as well. In addition, a seasonal variation of $PM_{2.5}$ concentrations can also be observed from the above plots. Furthermore, the 10 years can be divided into 3 consecutive periods based upon the reduction trend of $PM_{2.5}$ concentrations: 2005–2007, 2008–2011, and 2012–2014. The seasonal variations of $PM_{2.5}$ mass concentrations in these 3 periods are summarized in Table 1.

As can be seen from Table 1, in general, $PM_{2.5}$ concentrations were significantly higher in summer and lower in winter at 7 monitoring sites; however, the Tukey test indicated that this seasonal trend was only significant in 2005–2007 and 2008–2011, while no significant seasonal variation can be observed in 2012–2014 at 6 out of 7 sites. The seasonal variations were only significant at sites in the city of Winston-Salem in 2012–2014 period. This may be due to the aforementioned implementation of CSAPR in 2012 and effective emission control on NO_x and SO_2 continued in 2012 in NC. Thus, NO_x and SO_2 were less available in all four seasons compared with the emission conditions before 2012; less seasonal variations of various chemical components of $PM_{2.5}$ combined with opposite seasonal variations of OCM and SO_4^{2-} salts led to insignificant variations of $PM_{2.5}$ in 2012–2014.

Spatial and Temporal Variations of the iPM$_{2.5}$ Chemical Compositions

The variations of $PM_{2.5}$ concentrations may result from the variations in various $PM_{2.5}$ chemical compositions; therefore, spatiotemporal variations of $PM_{2.5}$ chemical compositions were analyzed and compared with the $PM_{2.5}$ concentration change trend at each location. Fig. 4 shows the analyses results of major i$PM_{2.5}$ composition changes over time at 7 urban sites located in the cities of Asheville, Hickory, Lexington, Winston-Salem, Rockwell, Charlotte, and Raleigh (see the map in Fig. 1). All the $PM_{2.5}$ mass concentrations were measured by the non-FRM samplers.

In general, there is no significant difference among 7 $PM_{2.5}$ chemical speciation monitoring sites for each of the 3 major i$PM_{2.5}$ chemical components, SO_4^{2-}, NH_4^+ and NO_3^-. The exceptions were that SO_4^{2-} concentrations in Lexington were significantly higher than in Raleigh in 2006, and NH_4^+ concentrations in Lexington were significantly higher than in Asheville in 2008 and 2009. Asheville was located in western mountain areas while Raleigh was located on the border of Piedmont and Coastal Plain areas (see Fig. 1); therefore, the impact of topography may explain the spatial variations of SO_4^{2-} and NH_4^+ in these years. Similar spatial distribution of the three major i$PM_{2.5}$ chemical compositions at 7 urban sites may indicate the similarity of the atmospheric chemistry background at the 7 monitoring sites, as all of them are located in urban areas. In rural areas, large NH_3 emissions from agricultural operations have resulted in NH_3-rich conditions in ambient air (Saylor *et al.*, 2010; Walker *et al.*, 2000a, b); therefore, atmospheric chemistry background in rural areas was different from those in urban areas. Some spatial variations of i$PM_{2.5}$ chemical compositions may be expected between urban and rural areas; further research is needed to establish holistic understanding of the spatial variations in the future.

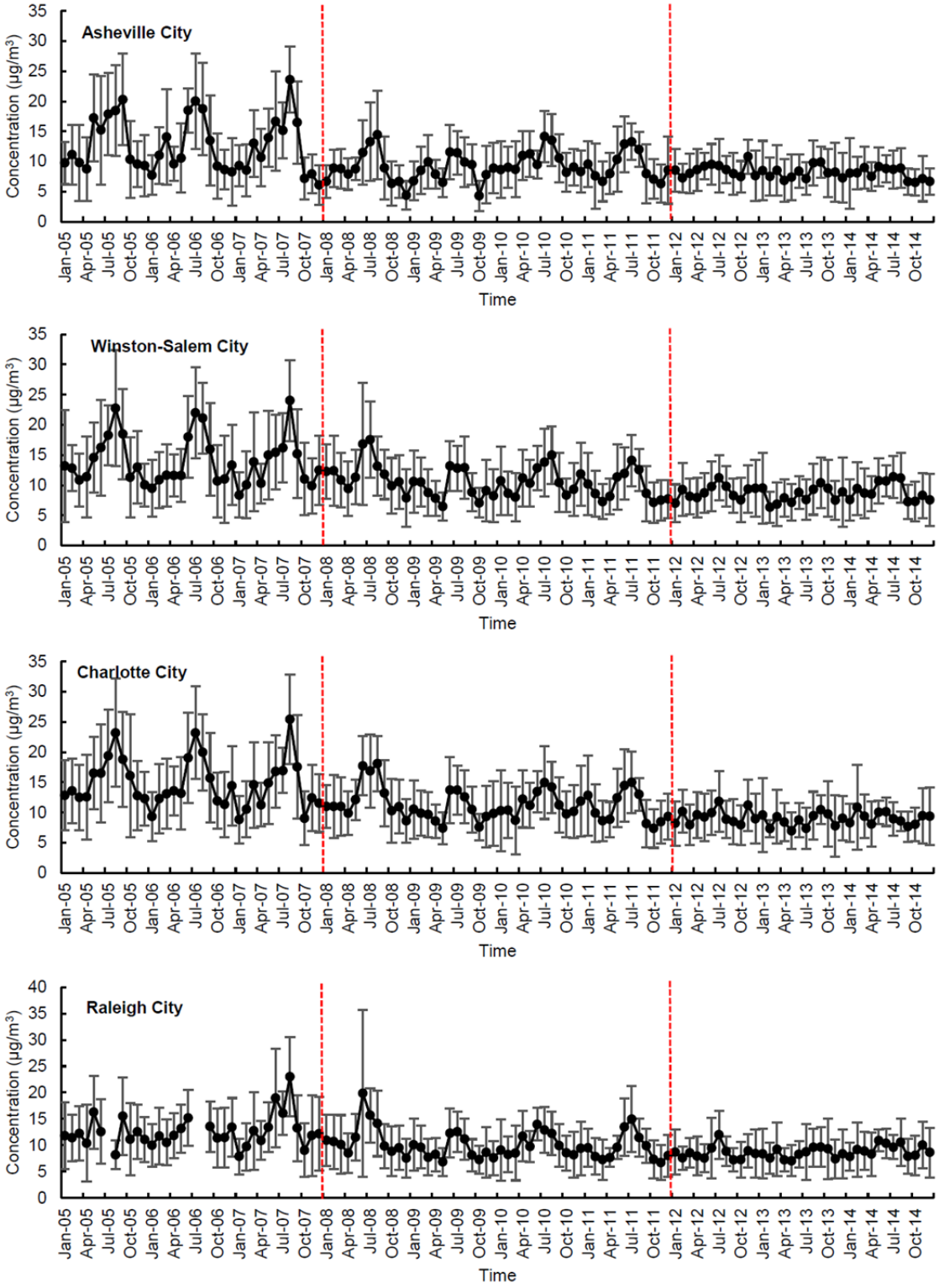

Fig. 3. Temporal variations of monthly average $PM_{2.5}$ concentrations at 4 representative sites.

Significant reduction trend in SO_4^{2-}, NO_3^-, and NH_4^+ concentrations from 2005 to 2014 occurred at all 7 monitoring sites, which is consistent with the reduction trend of total $PM_{2.5}$ concentrations. More specifically, the annual average $PM_{2.5}$ level at the largest city in NC, Charlotte, decreased from 18.21 ± 8.10 μg m^{-3} in 2005 to 9.12 ± 3.59 μg m^{-3} in 2014 and the SO_4^{2-}, NH_4^+ and NO_3^- concentrations also decreased significantly at this location from 6.42 ± 3.71 μg m^{-3} to 1.71 ± 0.76 μg m^{-3}, from 2.16 ± 1.18 μg m^{-3} to 0.50 ± 0.34 μg m^{-3}, and from 0.88 ± 0.96 μg m^{-3} to 0.62 ± 0.75 μg m^{-3}, respectively. Quantitatively, at Charlotte site, a 9.09 μg m^{-3} annual average $PM_{2.5}$ mass

Table 1. Seasonal variations of $PM_{2.5}$ concentrations in 3 monitoring periods.

Sites	Periods	Winter	Spring	Summer	Fall
Asheville City	2005–2007	8.99 ± 4.35	11.94 ± 6.11	18.63 ± 7.12	11.56 ± 6.78
	2008–2011	7.96 ± 3.97	8.74 ± 3.72	12.28 ± 4.65	7.69 ± 3.91
	2012–2014	7.73 ± 3.76	8.24 ± 3.31	8.80 ± 3.10	8.13 ± 3.45
Hickory City	2005–2007	12.23 ± 6.05	13.88 ± 7.09	20.37 ± 7.10	13.58 ± 6.90
	2008–2011	11.59 ± 5.99	10.21 ± 4.47	13.43 ± 5.08	9.84 ± 4.57
	2012–2014	9.25 ± 4.22	8.95 ± 3.77	9.00 ± 2.92	9.11 ± 4.12
Lexington City	2005–2007	12.77 ± 5.68	13.72 ± 5.76	20.30 ± 8.05	14.03 ± 6.67
	2008–2011	11.62 ± 5.45	10.32 ± 4.41	14.47 ± 4.79	10.57 ± 4.55
	2012–2014	10.41 ± 4.93	9.27 ± 3.65	9.90 ± 3.30	9.66 ± 4.36
Winston-Salem City	2005–2007	11.05 ± 5.71	12.39 ± 5.87	19.51 ± 7.47	12.97 ± 7.03
	2008–2011	9.92 ± 4.87	9.22 ± 4.24	13.89 ± 5.52	8.97 ± 4.17
	2012–2014	8.31 ± 4.49	8.22 ± 3.43	9.94 ± 3.72	8.40 ± 3.76
Rockwell City	2005–2007	11.07 ± 4.97	13.28 ± 5.77	19.14 ± 7.32	12.75 ± 6.18
	2008–2011	10.67 ± 4.85	10.05 ± 4.00	13.63 ± 4.58	9.96 ± 4.44
	2012–2014	9.08 ± 4.24	8.77 ± 3.54	9.57 ± 3.22	8.89 ± 4.04
Charlotte City	2005–2007	11.70 ± 5.35	13.61 ± 5.99	20.16 ± 7.70	13.85 ± 7.34
	2008–2011	10.42 ± 5.03	10.02 ± 4.23	14.74 ± 5.10	9.76 ± 4.49
	2012–2014	9.12 ± 4.26	8.70 ± 3.48	9.30 ± 3.40	8.98 ± 3.96
Raleigh City	2005–2007	10.97 ± 5.18	12.38 ± 5.80	17.75 ± 7.87	12.07 ± 6.32
	2008–2011	9.15 ± 4.55	9.15 ± 4.25	13.85 ± 6.96	8.69 ± 3.98
	2012–2014	8.31 ± 4.01	8.29 ± 3.40	9.69 ± 3.92	8.42 ± 3.81

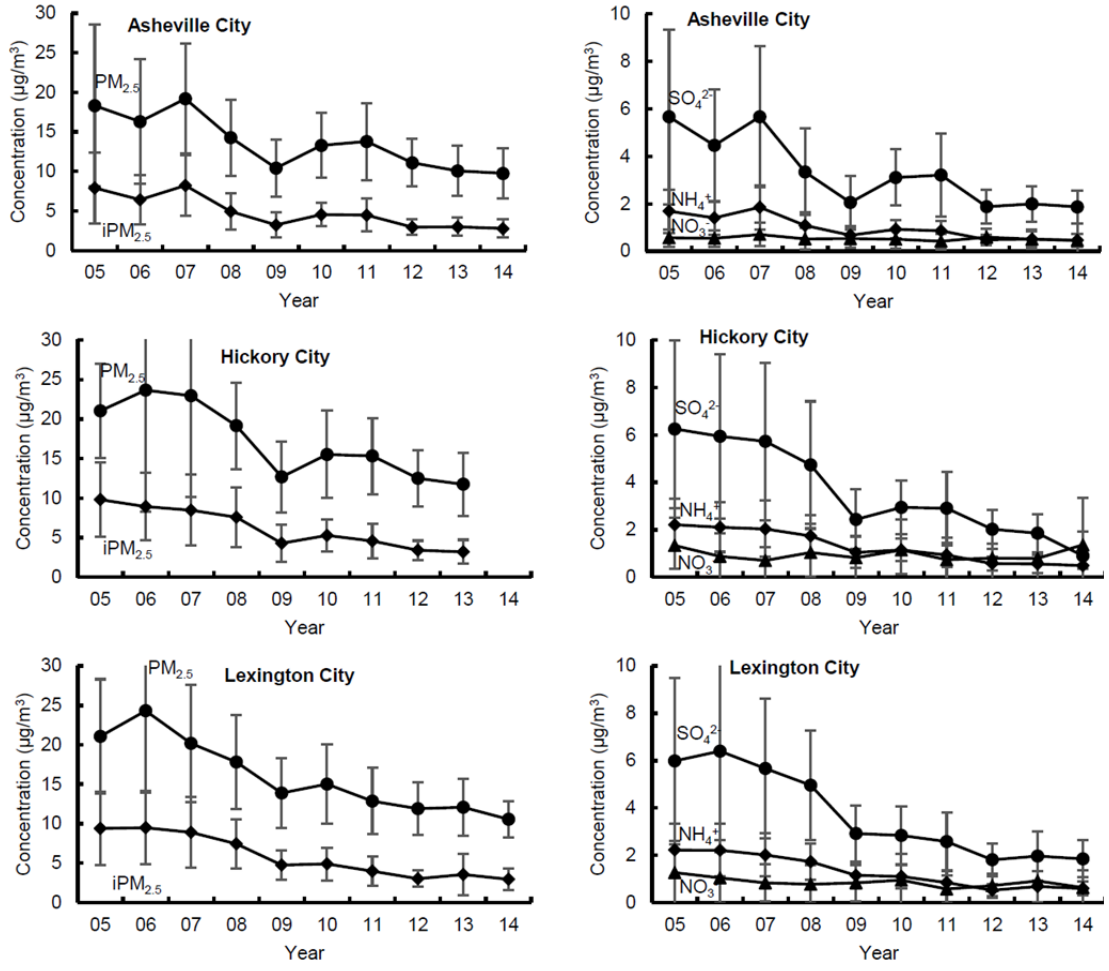

Fig. 4. Temporal variations of annual average concentrations of $PM_{2.5}$ and $iPM_{2.5}$ chemical compositions at 7 urban sites ($iPM_{2.5} = NH_4^+ + SO_4^{2-} + NO_3^-$).

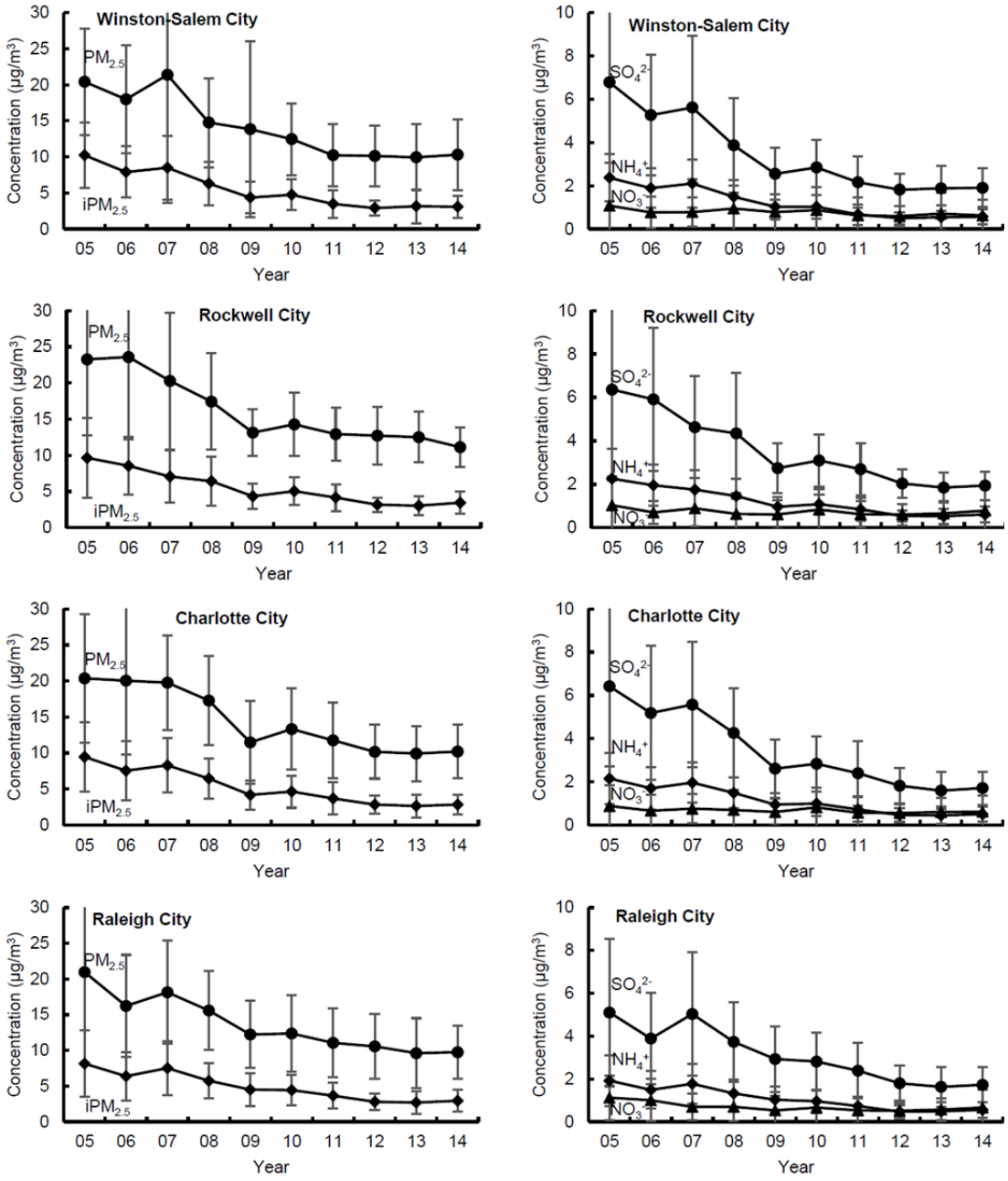

Fig. 4. (*continued*).

concentration reduction was achieved from 2005 to 2014; at the same time, 4.71 μg m^{-3}, 1.66 μg m^{-3}, and 0.26 μg m^{-3} annual average concentration reduction were achieved for SO_4^{2-}, NH_4^+, and NO_3^-, respectively. Together, $iPM_{2.5}$ contributed to around 73% of the $PM_{2.5}$ mass concentration reduction. The similar reduction trend of $iPM_{2.5}$ was observed at the other monitoring sites as well. Annual average OCM concentration was reduced from 5.63 ± 2.57 μg m^{-3} in 2005 to 3.63 ± 1.89 μg m^{-3} in 2014 at Charlotte site. The OCM contributed to 22% of the reduction in $PM_{2.5}$ mass concentration. The exceptions were Asheville, Hickory, and Rockwell; the OCM concentrations did not exhibit a significant reduction trend over the past 10 years. Concurrent variations of $PM_{2.5}$ mass and $iPM_{2.5}$ chemical compositions provided evidence of important contribution of $iPM_{2.5}$ to the reduction of total $PM_{2.5}$ mass in NC.

Trends in Extrema of $PM_{2.5}$ and its Chemical Component Concentrations

The trends in extrema of $PM_{2.5}$ mass and its chemical component concentrations at one of the seven sites (Charlotte) are shown in Fig. 5.

As can be seen from Fig. 5, the temporal variation in the distribution of $PM_{2.5}$ mass and its chemical component concentrations occurred in the three consecutive periods. Fewer high concentrations can be observed in the period of 2012 to 2014 in Charlotte. The 98th percentile of $PM_{2.5}$ mass concentration in 2012–2014 was about 18.6 μg m^{-3},

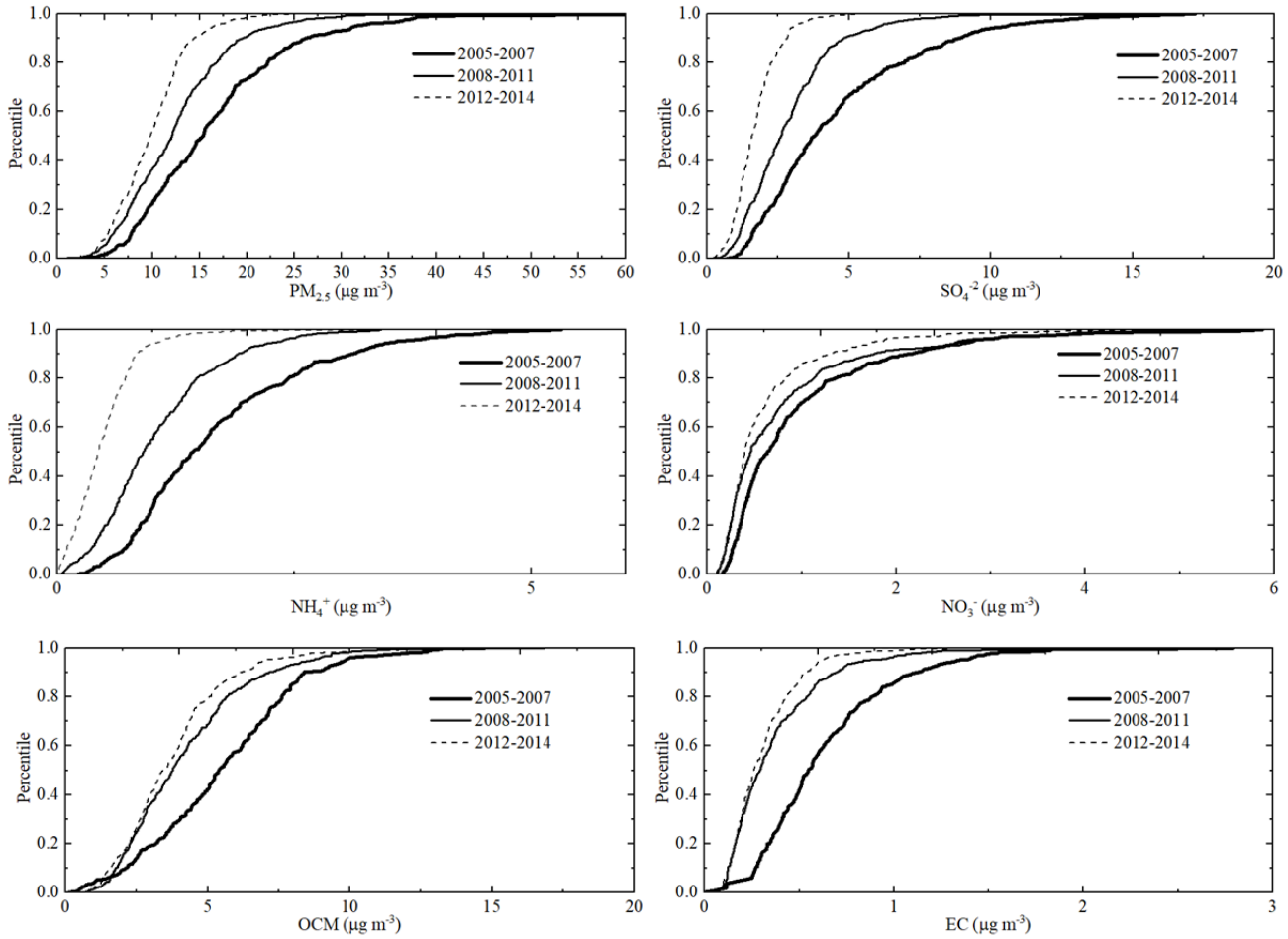

Fig. 5. Statistical distributions of daily concentrations of $PM_{2.5}$, SO_4^{2-}, NH_4^+, NO_3^-, OCM, EC at Charlotte site.

which was less than the primary and secondary 24-hr $PM_{2.5}$ NAAQS (35 μg m^{-3}). The temporal changes in various chemical components caused the temporal change in the distribution of $PM_{2.5}$ mass concentrations. The reduction of high $PM_{2.5}$ concentrations was the important evidence of air quality improvement in North Carolina over the past 10 years.

Correlations between $PM_{2.5}$ and Secondary $iPM_{2.5}$ Component Concentrations

To better understand the contribution of $iPM_{2.5}$ components to the total $PM_{2.5}$ mass, the correlations between $PM_{2.5}$ total mass and $iPM_{2.5}$ chemical components were analyzed and are shown in Table 2. The analyses include yearly and seasonal correlations to account for the impact of ambient conditions in four seasons.

As can be seen from Table 2, at 7 monitoring sites of NC, NH_4^+ and SO_4^{2-} were strongly correlated with $PM_{2.5}$ mass concentration ($R > 0.58$); however, the correlation between NO_3^- and $PM_{2.5}$ mass concentration varied in 4 seasons with stronger correlation in winter than in summer, spring and fall. The observation was consistent with the research performed by Bell *et al.* (2007), in which NH_4^+, SO_4^{2-}, and NO_3^- were determined to be 3 significant components of $PM_{2.5}$, exhibiting stronger correlation with total $PM_{2.5}$ mass. Stronger correlation of $PM_{2.5}$ mass concentration with NH_4^+ and SO_4^{2-} indicated the day-to-day covariation, while the fluctuated correlation between $PM_{2.5}$ and NO_3^- can be attributed to the semi-volatile characteristic of NH_4NO_3 (Olszyna *et al.*, 2005).

Evaluation of $PM_{2.5}$ Mass Closure

Analysis of the mass fraction of each chemical component may help to understand the individual chemical components' contributions to the total $PM_{2.5}$ concentrations. Fig. 6 shows the resultant mass distribution charts of the analysis at 4 selected monitoring locations, separated by the three periods.

The OCM was the dominant component of $PM_{2.5}$ in the 3 periods at 7 monitoring sites, especially in 2012–2014 accounting for 34.4–37.0% of total $PM_{2.5}$. Of the total $PM_{2.5}$ at seven monitoring sites, the three major $iPM_{2.5}$ components together accounted for 34.1–45.9% from 2005 to 2007, 34.8–39.1% from 2008 to 2011, and 28.3–30.9% from 2012 to 2014. Among the three major $iPM_{2.5}$ chemical components, SO_4^{2-} was the dominant contributor to the total $PM_{2.5}$ mass. The mass fraction of SO_4^{2-} exhibited a significant reduction trend in the 3 periods. Contribution of NH_4^+ to total $PM_{2.5}$ mass was also significantly reduced, while no significant reduction trend can be observed for

Table 2. Correlation of secondary $iPM_{2.5}$ chemical compositions with $PM_{2.5}$ total mass at the 7 sites of NC.

Monitoring Sites	Chemical Species	Yearly	Winter	Spring	Summer	Fall
Asheville City	NH_4^+	0.74	0.72	0.60	0.87	0.75
	SO_4^{2-}	0.78	0.64	0.65	0.88	0.76
	NO_3^-	**0.26**	0.65	**0.38**	**0.46**	**0.49**
Hickory City	NH_4^+	0.81	0.80	0.75	0.88	0.83
	SO_4^{2-}	0.75	0.68	0.72	0.89	0.77
	NO_3^-	**0.37**	0.82	**0.38**	**0.43**	0.57
Lexington City	NH_4^+	0.76	0.73	0.70	0.85	0.79
	SO_4^{2-}	0.73	0.64	0.73	0.86	0.74
	NO_3^-	**0.39**	0.81	**0.43**	**0.45**	0.63
Winston-Salem City	NH_4^+	0.79	0.83	0.71	0.87	0.83
	SO_4^{2-}	0.81	0.77	0.77	0.89	0.79
	NO_3^-	**0.30**	0.82	**0.42**	**0.28**	0.57
Charlotte City	NH_4^+	0.77	0.72	0.74	0.88	0.75
	SO_4^{2-}	0.77	0.62	0.78	0.89	0.73
	NO_3^-	**0.28**	0.74	**0.45**	**0.40**	**0.45**
Rockwell City	NH_4^+	0.77	0.79	0.71	0.87	0.78
	SO_4^{2-}	0.77	0.68	0.74	0.88	0.75
	NO_3^-	**0.32**	0.80	**0.40**	**0.39**	0.61
Raleigh City	NH_4^+	0.73	0.68	0.73	0.84	0.77
	SO_4^{2-}	0.74	0.58	0.77	0.86	0.74
	NO_3^-	**0.30**	0.73	**0.50**	**0.30**	**0.48**

All the values were calculated as Spearman correlation coefficient (R). $R \leq 0.5$ were marked bold.

the mass fraction of NO_3^-. The contribution of unidentified components ("other") to total $PM_{2.5}$ mass was actually increased throughout the whole periods. The increase of unidentified component mass fraction may be caused by the inappropriate estimation of OCM through the OCM/OC ratio of 1.4; this conversion ratio may be higher in the later period (Blanchard *et al.*, 2013). The relative contributions of various chemical components to the total $PM_{2.5}$ mass resulted from different emission sources and atmospheric physiochemical processes. As mentioned above, in the past 10 years, several regulations such as CAIR and CSAPR have been promulgated to reduce the emissions of SO_2 and NO_x in eastern U.S. to control the pollution of $PM_{2.5}$; the reduction of the mass fraction of the secondary $iPM_{2.5}$ proved the effectiveness of all these regulation and control policies.

In addition, seasonal variation analysis indicates that NO_3^- contribution to the total $PM_{2.5}$ had a significant seasonal pattern with higher fraction in winter and lower fraction in summer, while the mass fraction of SO_4^{2-} exhibited an inverse seasonal pattern with higher fraction in summer and lower fraction in winter. No significant seasonal variations can be observed for the mass fraction of NH_4^+. This can be justified by the semi-volatile characteristic of NH_4NO_3. Low temperature (T) and high relative humidity (RH) in winter favored the formation of NH_4NO_3 (Olszyna *et al.*, 2005). However, in contrast to NO_3^- salts, SO_4^{2-} salts had very low vapor pressure; therefore, most of the $(NH_4)_2SO_4$ stayed in particle phase even in summer. H_2SO_4 was transformed from SO_2 through photochemical reactions; more intense solar radiation in summer facilitated the formation of H_2SO_4 leading to more formation of $(NH_4)_2SO_4$ (Seinfeld and Pandis, 2006).

No significant spatial variations of 3 major $iPM_{2.5}$ chemical components were observed at the 7 monitoring sites. This may be due to similar chemistry background of atmosphere at these 7 sites. However, high NH_3 emissions from agricultural sources in rural areas may pose greater influence on the chemical compositions of $PM_{2.5}$; the relative contributions of $iPM_{2.5}$ to $PM_{2.5}$ mass may vary correspondingly. The monitoring data in rural areas are scarce in NC; future research is needed to fill this data gap so that analysis may be conducted for agricultural areas, where the highest base precursor gas (NH_3) concentrations occurred. At the 7 sites in NC, the 3 major $iPM_{2.5}$ components accounted for the largest portion of $PM_{2.5}$ mass in 2005–2011. However, in 2012–2014, OCM accounted for the largest portion of $PM_{2.5}$ mass. The reduction trend of $PM_{2.5}$ chemical components was consistent with finding of the research performed by Saylor *et al.* (2015) in other locations in southeastern U.S.

CONCLUSIONS

The variations of $PM_{2.5}$ mass concentrations in North Carolina from 2005 to 2014, measured at the EPA's monitoring sites, were found to be statistically significant on spatial and temporal scales, with the highest values recorded in the urban areas of central NC. A significantly decreasing trend in $PM_{2.5}$ levels was also observed across the state during this period. Temporal variations in the $iPM_{2.5}$ were consistent with this trend, exhibiting a concurrent reduction in concentration and thereby indicating the critical contribution of secondary $iPM_{2.5}$ to the total $PM_{2.5}$ mass. Although the $PM_{2.5}$ concentrations displayed a significant seasonal variation, with higher

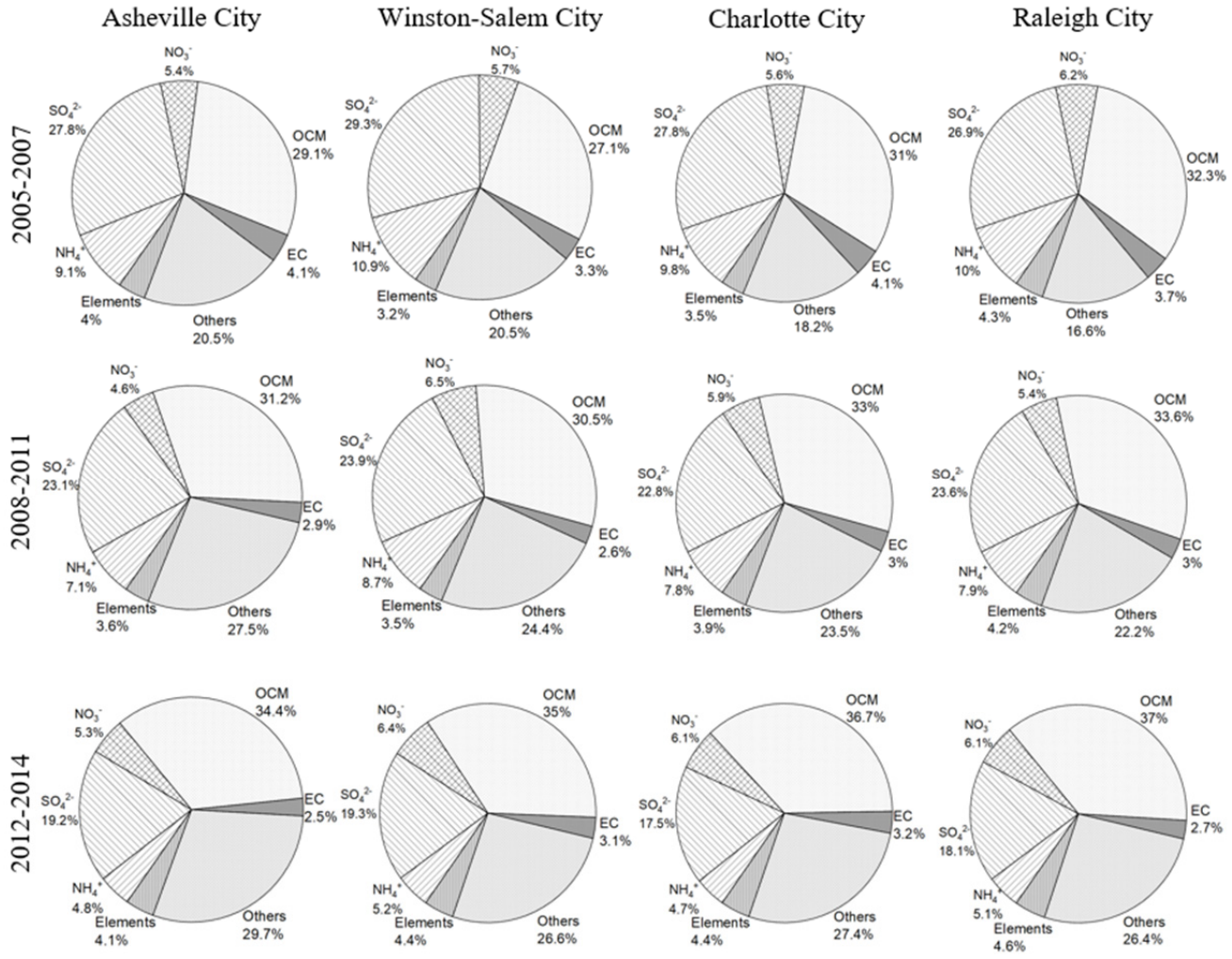

Fig. 6. Mass distributions of $PM_{2.5}$ chemical compositions at 4 representative monitoring sites.

concentrations in summer and lower concentrations in winter, respectively, between 2005 and 2011, this variation was insignificant between 2012 and 2014 at 6 of the 7 chemical speciation monitoring sites. Furthermore, $iPM_{2.5}$ composed the largest mass fraction of the $PM_{2.5}$ for 2005–2011, but organic carbon matter (OCM) was the dominant component for 2012–2014. The $iPM_{2.5}$ mass fractions also displayed significant seasonal variations, with NO_3^- and SO_4^{2-} exhibiting inverse variations. The results of this study improve our holistic understanding of $PM_{2.5}$ and $iPM_{2.5}$ on a regional scale.

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